

Homogeneous Condensation—Freezing Nucleation Rate Measurements for Small Water Droplets in an Expansion Cloud Chamber

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ABSTRACT

Experimental data on ice nucleation, presented in an earlier paper, are analyzed to yield information about the homogeneous nucleation rate of ice from supercooled liquid and the heights of energy barriers to that nucleation. The experiment consisted of using an expansion cloud chamber to nucleate from the vapor a cloud of supercooled pure water drops and the observation of the fraction of drops which subsequently froze. The analysis employed standard classical homogeneous nucleation theory. The data are used to extract the first experimental measurement (albeit indirect) of the activation energy for the transfer of a water molecule across the liquid-ice interface at temperatures near -40°C . The results provide further evidence that the local liquid structure becomes more icelike as the temperature is lowered.

1. Introduction

The subject of ice nucleation in the atmosphere is of great practical and fundamental importance since supercooled clouds do commonly occur in nature and the interplay between supercooled drops and ice crystals strongly influences the release of snow, rain and hail. While supercooled droplets in natural clouds have been observed down to -35°C , suspended particulates in the atmosphere commonly initiate freezing at temperatures between -15 and -20°C . The heterogeneous mechanisms which are responsible for virtually all of the ice in nature are very complex processes which have not been satisfactorily explained. The homogeneous nucleation process, on the other hand, is a more fundamental and simpler phenomena that is more accessible to both laboratory experimentation and theoretical modeling. Its study can shed light on the microscopic properties of water and should serve as a valuable stepping stone toward the final goal of a better understanding of the more complex heterogeneous process.

The previous paper (Anderson *et al.*, 1980) dealt with an experimental study of the homogeneous condensation-freezing nucleation of small water droplets in an expansion cloud chamber. In that paper, the facility and experimental method were described, and data were presented and used to determine the threshold temperature for homogeneous ice nucleation and to show that the ice resulted from a two-step process: dropwise condensation followed by

freezing. The extraction of this information from the data was a rather simple task. A much more difficult task is the evaluation of homogeneous freezing nucleation rates and the determination of values for the nucleation energy barriers from the data. This evaluation is the subject of this paper.

The concept of the experiment is as follows. An expansion is used to carry a sample of moist gas through a desired temperature, pressure, and supersaturation versus time profile, and thereby create a supercooled cloud of freshly nucleated pure water drops. The transformation of the supercooled liquid cloud to a mixed ice and water particle cloud is then observed. The experiment is performed in such a way that observations of the resulting macroscopic cloud elements coupled with a suitable analysis gives information about the ice nucleation process. Thus, some of the results are model dependent. Vapor-to-liquid nucleation theory and drop growth theory are used to determine the volumes and temperatures of the drops. These processes have been extensively studied in this laboratory such that there is a high degree of confidence in the models used to represent them in this work. The experimental freezing data are fit to the freezing nucleation model. Then, assuming the validity of the standard theoretical expression for spontaneous nucleation freezing, the nucleation energy barrier is determined.

The analysis of the data makes use of classical nucleation theory. A weakness in the theory lies in the use of macroscopic thermodynamics and assumes that bulk values for complex parameters such as surface tension, ice density, or latent heat of melting can be used for the microscopic phases dealt with

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in nucleation theory. At present the most feasible method of overcoming these difficulties is to take a statistical mechanical approach that uses a molecular model to calculate the components of the partition function for the nucleation embryos (Plummer and Hale, 1972). While this approach offers good internal consistency, the carrying out of the calculations is hindered by many difficulties. Although attempts in this direction for ice nucleation have been made (Eadie, 1971; Hale and Plummer, 1974), a complete theory for homogeneous ice nucleation using the statistical mechanical/molecular approach is still lacking. In spite of its theoretical deficiencies the classical theory gives reasonable agreement with experiment and those preliminary results presently available from the molecular clathrate cluster theory (Pruppacher and Klett, 1978; Hale and Plummer, 1974).

2. Theory

a. Ice nucleation rate

The classical expression for the homogeneous nucleation rate of ice from supercooled liquid water at temperature T (K) is given by (Turnbull and Fisher, 1949; Dufour and Defay, 1963)

$$J_{LS} = n'v(4\sigma_{LS}/kT)^{1/2}(n_LkT/h) \times \exp(-\Delta g/kT) \exp(-\Delta G_{LS}^*/kT), \quad (1)$$

where n' is the number of water molecules in contact with unit area of the ice germ surface, v the volume of a water molecule in ice, σ_{LS} the interfacial free energy between water and ice, n_L the number of molecules per unit volume of liquid, k Boltzmann's constant, h Planck's constant, Δg the activation energy for the transfer of a water molecule across the ice-water boundary, and ΔG_{LS}^* the increase in free energy of the system when a critical size ice embryo is formed. This classical spontaneous rate of freezing is dependent only upon temperature and is not influenced by conditions peculiar to the expansion cloud chamber, e.g., the supersaturation of the vapor. ΔG_{LS}^* for a spherical ice embryo is given by (Hobbs, 1974)

$$\Delta G_{LS}^* = 16\pi\sigma_{LS}^3/[3(n_SkT \ln(P_L/P_S))^2], \quad (2)$$

where n_S is the number of molecules per unit volume of ice, and P_L and P_S are the saturated vapor pressures over plane surfaces of water and ice.

b. Droplet volume

J_{LS} denotes the number of liquid-to-solid nucleation events per unit time per unit volume of liquid. In order to correlate theory and experiment for ice nucleation in a cloud of supercooled drops, it is necessary to know the radius or volume of each drop at

the time of the ice nucleation event. Here we assume the functional validity of Eq. (1) and integrate it over the volume, temperature, time history of the supercooled drop population and compare the results with the observed ice particle population. The experimental feature which makes this experiment possible is the exceedingly short sensitive time (~ 0.01 s). The fast pulse technique developed in this laboratory makes it possible to observe nucleation phenomena which possess fairly high rates, which is the situation in this case. The time at which the liquid drops are nucleated from the vapor is determined from an empirical fit to a large body of homogeneous nucleation rate data which was obtained using exactly the same apparatus and immediately preceding the freezing experiments. These experiments extend into the thermodynamic region of interest, namely, the region near -40°C . Assuming that their radius is 10^{-7} cm (approximate radius for a critical sized water cluster of 50 molecules) at their birth, their condensational growth thereafter is described by diffusional droplet growth theory.

Both homogeneous and heterogeneous vapor-to-liquid nucleation were used to produce the drops in which spontaneous freezing took place. For the case of homogeneous nucleation the empirical expression (Miller *et al.*, 1976) used for the nucleation rate is

$$J_{VL} = S^2 \exp[328.12 - 5.5824T + 0.030365T^2 - 5.0319 \times 10^{-5}T^3 - (999.79 - 4.1008T + 3.0107 \times 10^{-3}T^2)/(\ln S)^2], \quad (3)$$

where J_{VL} is the nucleation rate (number $\text{cm}^{-3} \text{s}^{-1}$) and S the supersaturation ratio. This is virtually the only data available in the region of interest. T and S are well-known quantities throughout the expansion (Kassner and Schmitt, 1966). Virtually all of the nucleation (both vapor to liquid and liquid to solid) occurs in a span of 0.01 s near the maximum in S (minimum in T).² The record of T vs t is broken down into a number (≤ 44) of time increments. The number of drops nucleated during each time increment is given by J_{VL} multiplied by the length of the time increment. Of course, J_{VL} depends strongly on T and S which change with time so each drop family will in general have a different population or concentration. The size and temperature of all drops formed during a specific time increment are assumed to be and to remain the same, i.e., the droplet spectrum is represented by discrete families as is customary.

The heterogeneous cases studied, nucleation on ions and reevaporation nuclei, give rise to nearly

² Actually pressure P is the continuously recorded parameter in the experiment. T is calculated from the adiabatic law. Vapor depletion and the release of latent heat can be shown to be completely negligible during the 0.01 s during which the pulse of nucleation is taking place.

monodisperse clouds. The critical supersaturations needed to activate these nuclei are determined empirically by performing repeated expansions at different depths until the nucleation just occurs. This determines the critical supersaturation needed for the vapor to liquid nucleation. Then on the expansions used to study ice nucleation we assume all of the drop nucleation occurs at the point where the critical supersaturation is reached. The advantage of using heterogeneous nucleation lies in the fact that the expansion continues past the point at which vapor to liquid nucleation occurs giving the liquid drops a chance to grow larger. Again, the ice nucleation occurs at the bottom of the expansion where the minimum temperature is attained.³

The droplet growth model chosen for these calculations is discussed in detail by Carstens (1979). It is a reasonably simple and reliable theory of droplet growth which is valid over the range from 10^{-7} to 10^{-2} cm radius.

The equations describing growth by this model are given by

$$(a + l)(da/dt) = [S - S_{\text{sat}}(a)]\rho_{\text{eq}}(\infty) / (1/D + bL/K), \quad (4)$$

where

$$l = [(\lambda_v/\beta)/D + (\lambda_g/\alpha)bL/K] / (1/D + bL/K). \quad (5)$$

Here D is the diffusion coefficient of water vapor in air, K the thermal conductivity of the air-vapor mixture, L the latent heat of condensation, S the applied supersaturation ratio, $\rho_{\text{eq}}(\infty)$ the equilibrium vapor density far from the drop, b the slope ($\Delta\rho/\Delta T$) of the equilibrium vapor density versus temperature curve, λ_v and λ_g the approximate mean free paths referring to the vapor and air, α the thermal accommodation coefficient, β the condensation coefficient, a the drop radius, t time, and $S_{\text{sat}}(a)$ the equilibrium saturation.

The model has been compared to experimental droplet growth data taken in a similar expansion cloud chamber using Mie scattering from a laser beam to infer droplet growth rates in the range from one-half to ten micron radius.⁴ Consequently, this model should be most compatible with expansion cloud chamber experiments such as those presented here.

The application of present droplet growth models

has limitations of resolution brought about primarily by two factors. The first is the underlying inadequacy of droplet growth theory. Existing droplet growth routines do not accurately describe the actual processes which are taking place during growth. Hidy and Brock (1970) and Kelley and Sengers (1974) indicate that the accuracy of droplet growth calculations is especially questionable for the regions of kinetic growth where there has been no experimental determination. Unfortunately, it is just this growth regime which is fairly important to the analysis of the data in the present work. A comparison of independent theories which describe droplet growth throughout the same size range (one of which is the theory used in this investigation) reveals a discrepancy of as much as 12% (Smirnov, 1971). These results indicate that the ultimate level of droplet growth theory has not yet been attained.

The other factor which contributes to the uncertainty involved in the application of droplet growth routines is the lack of accurate information about the temperature dependence of the parameters which are essential to the theory throughout the range of interest here. Values of the condensation and accommodation coefficients of 0.022 and 1.0 are used in this analysis. These values were obtained from the comparison of theory and data performed by Carstens and Carter.⁴ Although these values are only verified for expansions from room temperature (final temperatures of $\sim 0^\circ\text{C}$), for lack of better information they are used here for expansions from pre-expansion temperatures as low as -15°C (final temperatures of $\sim -45^\circ\text{C}$). In the latter expansions, NaCl is dissolved in the water located in the base of the cloud chamber, reducing the freezing point as well as the vapor pressure of the solution (Anderson *et al.*, 1980). Numerical simulations were done with a condensation coefficient of 0.05 and the drop volumes changed (as compared to runs with condensation coefficient of 0.022) by at most a factor of 4 during the time when significant freezing nucleation occurred. This is well within the error limits shown on our results.

The chamber is operated in a short pulse mode (Kassner and Schmitt, 1966) which reduces the effects of depletion of vapor and release of latent heat by growing drops to negligible proportions during the period of time of interest—where the nucleation of liquid drops and the spontaneous freezing is occurring. See Fig. 1. Nucleation is concentrated in the short span of time at the bottom of the pressure well (top of supersaturation curve) and is over with before the drops grow large enough to affect their environment. Cloud-model calculations, using Carstens' (1979) droplet growth model, were performed to verify this for the worst case conditions (high drop concentration and low temperature) encountered in these experiments. The model results con-

³ Chamber operating conditions can be adjusted so that no new vapor to liquid homogeneous nucleation occurs at the lowest temperatures.

⁴ Carstens, J. C., and J. M. Carter, 1974: Current meteorological theory of drop growth by condensation and some comparisons with experiment. *Proc. Int. Coll. Drops and Bubbles*, Vol. 2, 529–552. [Available from J. C. Carstens, Graduate Center for Cloud Physics Research, University of Missouri–Rolla, Rolla, Missouri 65401.]

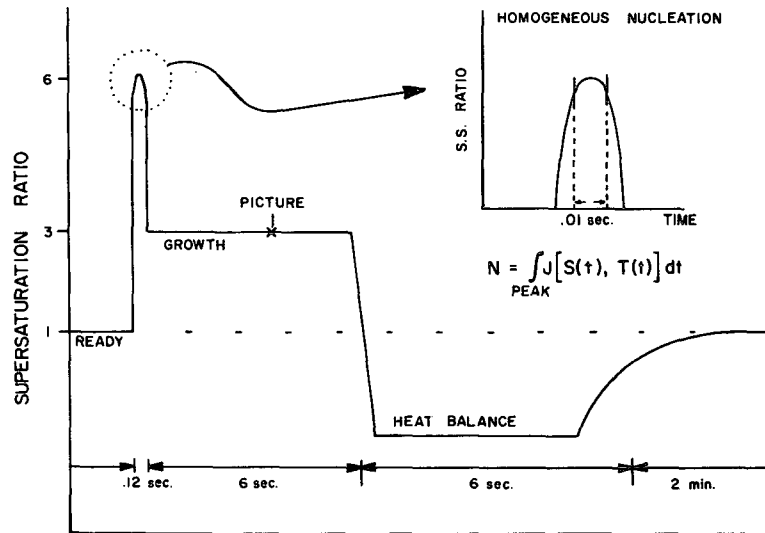


Fig. 1. Typical cloud chamber data cycle with fast supersaturation peak.

firmed that the growing drops have no significant effect on bulk conditions within the chamber.

The above droplet growth model yields the volume and temperature of each family of drops. The drops are always warmer than the ambient gas because of the release of the latent heat of condensation during growth. It should be noted that while Eq. (1) could be made to allow for a variation of the drop temperature between families of drops (by adding a subscript i to J_{LS} and using the appropriate temperature for each drop family), this refinement was deemed not necessary. Calculations show that the largest temperature variation which exists between the oldest and the youngest family for the present data is $\sim 0.01^\circ\text{C}$. Even with the extreme dependence of the freezing rate on temperature (see Fig. 2), this small temperature deviation was negligible. The temperature difference between the drops and the ambient gas was much larger, on the order of 0.1°C , and was accounted for in the calculations. Our resolution in determining the temperature of the gas from the adiabatic law was $\sim 0.1^\circ\text{C}$.

c. Functional form used for comparison of theory and experiment

The experimentally observed quantity, the number (N_f) of drops frozen at the end of the experiment, is given by (Anderson *et al.* 1980)

$$N_f = \int_0^t J_{VL}(t') \times \left\{ 1 - \exp \left[- \int_{t'}^t V(t', t'') J_{LS}(t'') dt'' \right] \right\} dt', \quad (6)$$

where $V(t', t'')$ denotes the volume at time t'' of a

liquid drop formed at time t' , and t denotes the time at which the data photograph is taken, i.e., the end of the experiment. The dependence on drop volume arises because J_{LS} represents a freezing nucleation rate per unit volume of liquid. When the cloud is broken down into discrete families of drops, this reduces to

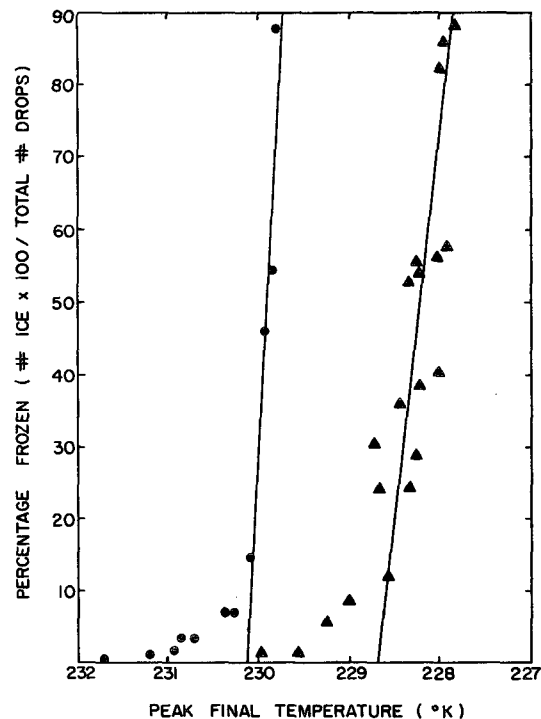


Fig. 2. Dependence of spontaneous freezing on final temperature for preexpansion temperature: (●) -9°C He, (▲) -12°C Ar.

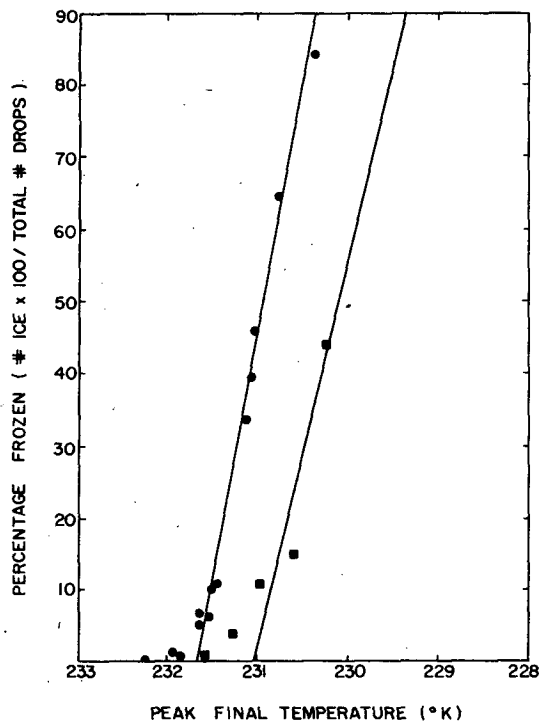


FIG. 3. Carrier gas dependence for spontaneous freezing of drops condensed by ions for a preexpansion temperature of -15°C : (●) He, (■) Ar.

$$N_f = \sum_i N_i \left\{ 1 - \exp \left[- \int_0^t V_i(t'') J_{LS}(t'') dt'' \right] \right\}, \quad (7)$$

where N_i denotes the number of drops nucleated in the i th family, and $V_i(t'')$ is the volume of a drop in the i th family at time t'' . The sum runs over all the drop families.

Eq. (7) is used to fit the experimental data. In J_{LS} [Eq. (1)] the energy barrier is assumed to be a linear function of temperature,

$$\Delta g + \Delta G_{LS}^* = x_1 + x_2 T, \quad (8)$$

and the x 's are adjusted to give the best least-squares fit.

3. Experimental data

Figs. 2, 3 and 4 (Anderson *et al.*, 1980) show the results for the fractional number of drops observed to have frozen⁵ in the course of the experiment (100

⁵ Note that in the case of cloud produced by homogeneous nucleation, both the homogeneous nucleation of new liquid droplets and the spontaneous freezing of somewhat older droplets is occurring simultaneously. Since the homogeneous nucleation rate for the formation of droplets is not quite as strong a function of T as is the spontaneous freezing process, the tail end of the expansion always produces some droplets which will appear as unfrozen. Moreover, these drops were too small and had less time to freeze.

$\times N_f / \sum_i N_i$) versus temperature for the cases of 1) homogeneous nucleation, and 2) nucleation on ions, and 3) reevaporation nuclei. Each data point represents one expansion, with empirically known time dependent values for T and S . Eq. (7) is fit to this data by adjusting the x 's in Eq. (8). The nonlinear least-squares minimization was accomplished through the use of the computer routine STEPIT (Chandler, 1965)⁶. The numerical integration used a value for dt of 10^{-3} s. This time increment was large enough to allow rapid evaluation of the integral in Eq. (7) and lead to only a tractable number of drop families for the homogeneous case, yet was small enough to produce a high degree of accuracy.

The resulting value of $\Delta G_{LS}^* + \Delta g$ obtained from the data are plotted in Fig. 5. Each short dashed line represents the range of values which reproduce the indicated data set. As expected, the collection of dashed lines do indicate a consistent tendency of $\Delta G_{LS}^* + \Delta g$, to decrease with decreasing temperature. The resulting least-squares fit to all of the data points produced the following linear fit to $\Delta G_{LS}^* + \Delta g$ (J):

$$\Delta G_{LS}^* + \Delta g = -1.739234 \times 10^{-18} + 8.1157 \times 10^{-21} T, \quad (9)$$

⁶ Chandler, J. P., 1965: STEPIT—Quantum Chemistry Program Exchange. Department of Chemistry, Indiana University, 47405.

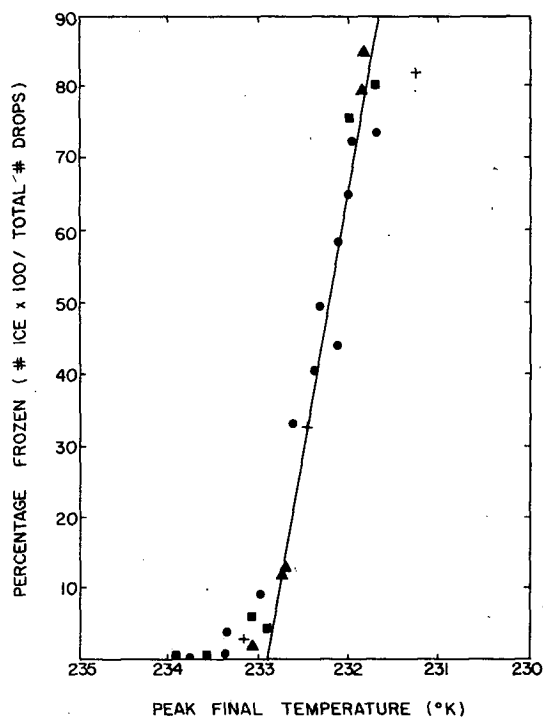


FIG. 4. The refreezing of reevaporation nuclei for a preexpansion temperature of -15°C in helium: (●) 2nd freezing, (■) 3rd freezing, (+) $+2^{\circ}\text{C}$ overcompression, (▲) minimum growth time.

where T is always in absolute temperature. This fit is plotted as the solid line in Fig. 5.

The scatter of the individual dashed lines about the solid line representing their accumulative least-squares fit can be attributed to uncertainty in the estimation of the droplet size at the instant of freezing. As previously discussed, droplet growth determinations are particularly inaccurate in the regime of kinetic growth where there has been no experimental verification.⁷ Unfortunately, for this analysis the size of the particles at the instant of freezing lies in the kinetic growth regime. On the other hand, working in this size regime has the advantage of keeping the probability that a given drop will freeze down to values which allow the apparatus to time resolve the process. Recall that J_{LS} is the freezing rate per unit volume of liquid. If the drop radius was ten times larger, the volume would be larger by a factor of 10^3 . At these temperatures all the drops would freeze and we would not be able to extract the nucleation rate.

The total uncertainty in the estimation of droplet volumes is due to inaccuracies in the theory and lack of information on growth parameters; further

⁷ The kinetic growth regime is generally assigned to the growth of droplets up to radii as large as 10 times the mean free path.

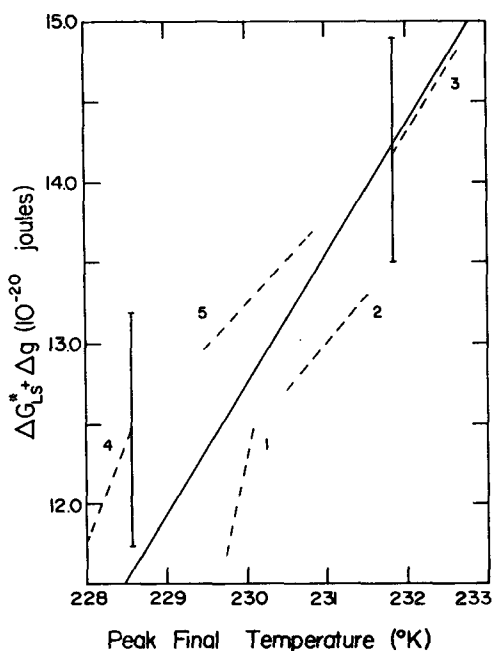


FIG. 5. Experimental determination of $\Delta G_{LS}^* + \Delta g$. The dashed lines are the values of each data set. The solid line is a least squares fit. The data sets are (1) -9°C (initial temperature before expansion) He and (4) -12°C Ar for homogeneously nucleated drops; (2) -15°C He and (5) -15°C Ar for drops formed on ions; and (3) -15°C He for drops formed on re-evaporation nuclei.

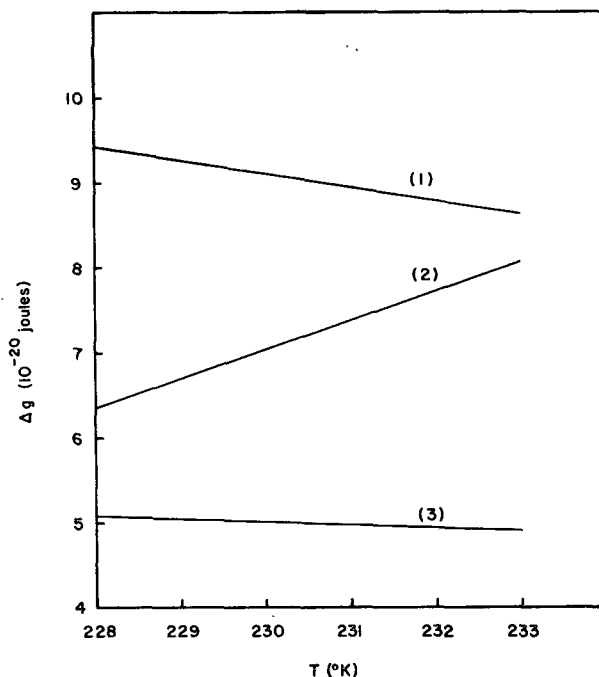


FIG. 6. Experimental determination of Δg . (1) and (3) give the results of a linear extrapolation of the activation energy for the displacement of water molecules in bulk water from Pruppacher and Klett (1978) and McDonald (1953), respectively; (2) is our result for Δg , the activation energy for the transfer of water molecules across the liquid-ice interface.

uncertainty is introduced in assigning the exact time for the initiation of growth. The accumulated uncertainty may easily be an order of magnitude. Such an uncertainty may at first seem large, however, it would require only an error in the droplet radius of about a factor of 2. The effect of an uncertainty of an order of magnitude in the droplet volume is shown by the error bars in Fig. 5. These large error bars are consistent with the scatter between the individual dashed lines.

If we accept the classical expression for ΔG_{LS}^* [Eq. (2)] as correct, then we can combine the data in Fig. 5 with Eq. (2) to extract Δg vs T . This was done, using values for σ_{LS} from Pruppacher and Klett (1978), and the results are shown in Fig. 6. Note that ΔG_{LS}^* is not nearly as sensitive to uncertainties in the classical theory, such as the uncertainty in σ_{LS} , as is J_{LS} (Hobbs, 1974). Δg is the activation energy for the transfer of a water molecule across the ice-water interface. For lack of any other measurement Δg is usually approximated by the energy of activation for the displacement of water molecules in bulk water (Pruppacher and Klett, 1978; McDonald, 1953), which is extracted from experiments that measure the self diffusion coefficient for water (Miles, 1973; Gillen *et al.*, 1972; Pruppacher, 1972) or the viscosity of water (Hallett, 1963; Stokes and Miles, 1965; Kell,

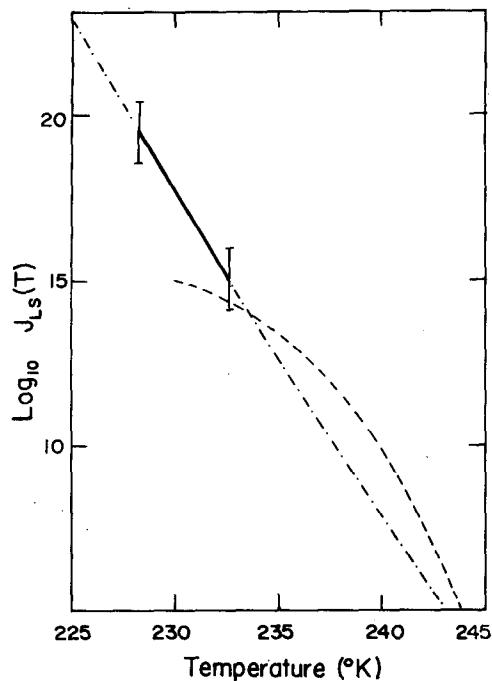


FIG. 7. Spontaneous freezing nucleation rate as a function of temperature. The diagonal line is the resulting rate from measurements over the range given by the solid portion. The dashed line is the rate from McDonald (1953).

1972). Pruppacher and Klett (1978) give an empirical expression for this energy of activation in bulk water, good down to -30°C . This data was linearly extrapolated from -30°C down to -45°C and is shown in Fig. 6. McDonald (1953) also exhibits data for the bulk water activation energy which he extrapolated much farther, from -10°C to -60°C ; this also is included in Fig. 6. As McDonald points out this data was extrapolated far beyond measurement, and he expects it to underestimate the true energy barrier.

At $T = -40^{\circ}\text{C}$, just above the spontaneous freezing temperature, our Δg is quite close to that from the linearized Pruppacher and Klett extrapolation, however they diverge as the temperature is lowered. The bulk water activation energy exhibits a negative slope, which is reasonable. As the temperature is lowered the local water structure becomes more organized and hence a higher energy barrier must be surmounted before a molecule can be temporarily broken loose in the process of diffusion. Our Δg , on the other hand, has a positive slope; it decreases as the temperature is lowered. However, it reflects a different physical process, the transfer of water molecules across the liquid-ice interface, or perhaps better said as the passage of the interface across the water molecules' positions. This is another indication that the local water structure is becoming more icelike as the temperature is lowered (Pruppacher and Klett, 1978). Perhaps as the temperature is low-

ered the freezing process becomes more of a cooperative phenomenon, that is, groups of molecules transfer across the liquid-ice interface without breaking their internal hydrogen bonds except at the ends of the group, and hence a plausibility argument may be offered for why Δg , the energy barrier per molecule, goes down.

This is a good example of using data from homogeneous nucleation experiments to extract microscopic information which also play a role in heterogeneous nucleation. The Δg calculated here can be applied to the heterogeneous problem, since there water molecules also must transfer across the liquid-ice interface. ΔG_{LS}^* will be different for heterogeneous nucleation but the same Δg will appear in the kinetics.

An empirical freezing rate may be obtained by inserting Eq. (9) into Eq. (1). The resulting temperature dependent freezing rate (number of ice embryos $\text{cm}^{-3} \text{s}^{-1}$) represented by the solid line in Fig. 7 is valid from about 228 to 233 K. The dashed-dotted line is the extrapolation of the freezing rate to temperatures outside this range. The error bars again indicate the uncertainty that would result from the determined droplet volumes being in error by an order of magnitude. The theoretical freezing rate of McDonald (1953) (dashed-curve) is also exhibited in Fig. 7 where local agreement with experiment is obviously fortuitous.

4. Conclusions

The expansion cloud chamber has proven itself to be a tool that is able to generate quantitative information about homogeneous freezing nucleation in water. Quantitative measurements are made possible, despite high nucleation rates on the order of $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$, by the use of small water droplets on the order of 10^{-5} cm radius and by keeping short the time during which nucleation can occur. The short pulse technique limits this time to $\sim 0.01 \text{ s}$. The resulting freezing nucleation rate is shown in Fig. 7. When our results are put into the classical nucleation rate Eq. (1) we find $J_{LS} = 5.92 \times 10^{22} T \times \exp(1.260 \times 10^5/T - 588.1)$, where J_{LS} is the freezing nucleation rate (number $\text{cm}^{-3} \text{ s}^{-1}$) and T the temperature (K). The nucleation rate results can be combined with the classical expression for the free energy of formation of a critical size ice embryo to get a result for the activation energy for the transfer of a water molecule across the ice-water interface. This is shown in Fig. 6, and is well fit by the linear expression $\Delta g = -71.18 \times 10^{-20} + 0.3400 \times 10^{-20} T$, where Δg is in joules and T kelvins.

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