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Freezing-nucleation in aqueous solutions of clathrate forming gases

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ABSTRACT

Experiments were performed to determine the extent to which the nucleating abilities of artificial and natural freezing nuclei are influenced by the presence of clathrate-forming gases dissolved in water. Changes in the supercooling requirement of water saturated with argon, or propane were determined for several nucleant-gas combinations using the drop freezing technique. The nucleants responded differently indicating that the influence of these clathrate-forming gases on heterogeneous freezing nucleation is not due to changes in the bulk water structure, but results from modifications at the nucleant-embryo interface. The measurements revealed an irreversible improvement in nucleating ability for some combinations and demonstrated that these gases can reduce the supercooling requirement of certain nuclei by as much as 3 °C.

1. Introduction

Ice nucleation in the liquid is generally considered to occur by a process of clustering of water molecules to form nuclei or embryos which upon reaching a critical size act as the centres for ice formation. When the embryos form on solid impurities within the water, the nucleation is said to be heterogeneous; otherwise it is called homogeneous.

A number of gases are known to form compounds with water under appropriate conditions. The compounds formed by water and these gases consist of gas molecules surrounded by water molecules in a cage structure. The term "clathrate" was introduced by Powell (1948) to describe such compounds. Davy (1811) reported the first such clathrate or gas hydrate, that of chlorine. It seems reasonable to conjecture that the clathrate-forming gases might affect the clustering behaviour of liquid water at temperatures below 0 °C, and thus have some effect on the process of freezing nucleation. Experiments to test this possibility are described in this paper.

Previous evidence on the influence of dissolved gases on freezing nucleation is sparse and somewhat unclear. Parungo and Lodge (1967) proposed that certain non-polar gases (the rare gases and some hydrocarbons), when dissolved in water, could act as "molecular" freezing nuclei. As a physical basis for this suggestion, they invoked the fact that these gases have negative entropies of solution, and referred to the suggestion by Frank and Evans (1945) that the water molecules surrounding solute gas molecules (or atoms) are in a more crystalline state than elsewhere in the liquid. To test this concept, they conducted comparative drop freezing experiments, using drops saturated with rate gases or hydrocarbons. In all cases they found that the drops containing a dissolved gas froze at a temperature warmer (up to 4.5 °C for argon and 5.0 °C for propane saturated drops) than the control drops which had contacted air only.

Kuhns and Mason (1968) investigated the homogeneous freezing of small (30–40 μ diameter) drops falling through air and other gases with the object of determining the homogeneous freezing temperature of water. From these experiments, Kuhns (1968) determined that with He, H_2, O_2, Ar, CO_2 and air, the nucleation temperature of water varies by at most 1 °C. He and H_2 increased the supercooling very slightly (compared to air), while

Ar decreased the supercooling. In interpreting the results of their experiment, Kuhns and Mason (1968) suggested that the 0.8 °C warmer temperature for the argon tests might be due to the formation of an argon clathrate which assisted in the formation of stable clusters in the supercooled water. Kuhns (1968) also stated that the results of this experiment completely ruled out the possibility that the effect found by Parungo and Lodge was due to "molecular freezing nuclei" and pointed out that heterogeneous rather than homogeneous nucleation temperatures had been altered.

Whether the freezing activity of heteronuclei can be affected by dissolved gases is a question of some importance to our understanding of ice-forming processes in the atmosphere, in part because of the possibility of alterations of nucleation temperatures by anomalous occurrences of high concentrations of certain gases, and in part because of the light such knowledge might shed on the general problem of heterogeneous nucleation processes.

2. Experimental

2.1. *Experimental design*

Three different experimental series were employed to isolate possible influences of dissolved gases on heterogeneous nucleation of liquid water:

(a) tests on effects of the supporting surface of the water drops;
(b) tests with different nucleants and gases;
(c) reversibility experiments.

Experimental procedure for each of these series of tests will be discussed in turn, along with the corresponding results.

2.2. *Materials*

Nucleants selected for the tests were either of natural occurrence or of relevance to cloud seeding. The materials used as nucleants were: kaolin (KLN), leaf-derived nuclei (LDN), artificial zeolites (L-5A & L-3A), mica, silver iodide (AgI), glass, and a number of metallic oxides. The preparation and activities of the KLN, AgI, LDN, and metallic oxides has been described previously (Reischel and Vali, 1975; Reischel, 1978). The remaining nucleants were prepared as hydrosols by adding the dry powder to water at a concentration of 1.0 g nucleant per liter of water just prior to use. The concentrations of the nucleants were:

KLN $2.0\ g\ l^{-1}$
LDN $0.5\ g\ l^{-1}$
AgI $6.2 \times 10^{-3}\ g\ l^{-1}$
others $1.0\ g\ l^{-1}$

The gases used were argon, neon (research grade), propane (fuel grade), and compressed air (breathing grade). All gases were filtered through 0.025 μ pore filters before use.

The water used in the tests had a minimum resistivity of 10 MΩ and was filtered through 0.025 μ pore filters before use. Nucleation temperatures (T_{90}, see following sections) varied between −23 and −26 °C. These nucleation temperatures were typically lower than those of the hydrosols tested.

2.3. *Measurements*

Nucleation temperatures were determined using a thermally controlled cold-plate (Vali and Knowlton, 1970) with appropriate peripheral instrumentation for monitoring and recording the freezing of drops placed on the plate, (detected through the change in transparency of the drops). A matrix of equal-sized drops (0.012 $cm^3 \pm 5\%$) was placed on the cold stage over an aluminum foil coated with dry silicone resin. Cooling rates were held constant at 3.6 °C min^{-1}; lower rates were used for materials that froze at warm temperatures.

Measurements of individual freezing temperatures were accurate to within ±0.05 °C. Mean and T_{90} temperatures for a given run were reliable to about ±0.2 °C because of statistical sampling errors. When the results of several runs are combined, the accuracies are dominated primarily by run-to-run sample variabilities; sedimentation losses and aging introduce an average uncertainty of about ±0.5 °C in the nucleation temperatures.

2.4. *Derived quantities*

Concentration versus temperature functions, or nucleus spectra, have been derived by Vali (1971). The differential spectra, $k(T)$, describe the concentration of nuclei active in a unit volume of sample within a unit temperature interval about the supercooling T:

$$k(T) = \frac{1}{VN(T)} \frac{dN}{dT}\ [cm^{-3}\ °C^{-1}], \qquad (1)$$

where V is the drop volume; $N(T)$ is the number of drops still unfrozen at the supercooling, T; dN is the number of drops frozen during the temperature interval dT. By integrating eq. (1) from 0 °C to T, cumulative spectra which give the concentration of nuclei active at all temperatures warmer than T can be obtained:

$$K(T) = \frac{1}{V} \ln \frac{N_0}{N(T)} \text{ [cm}^{-3}\text{]} \quad (2)$$

where $N(T)$ and V are the same as in eq. (1) and N_0 is the total number of drops in the experiment.

As seen from eq. (2), the fraction of drops frozen at T:

$$F(T) = 1 - (N(T)/N_0) \quad (3)$$

is directly related to $K(T)$.

In comparing the nucleating ability of different samples, it is often convenient to use a single quantity rather than the entire spectrum. Any fraction of drops frozen, $F(T)$, provides one such measure. Thus, each $F(T)$ corresponds to a fixed value of $K(T)$ and can be readily determined even during the course of an experiment from eqs. (2) and (3) above. $F(T)$ corresponds to a temperature above which there are $K(T)$ nuclei active per unit volume of sample. Values of $F(T)$ and $K(T)$ used in these experiments are shown in Table A1 and Fig. A1.

3. Results

3.1. *Effects of the support surface*

Comparative drop freezing experiments were conducted using sets of control drops (free of test gas) and sets of drops saturated with the test gas. Similar to Parungo and Lodge (P & L), microscope cover glass slips were used to support the drop sets while the temperature was lowered at a rate of 1.5 °C min^{-1}. The saturated water was obtained by precooling to 0 °C a portion of the sample water and then bubbling the test gas through it for 5 min. The freezing experiments were conducted in clean air (the drops being covered by a plastic box) with no attempt made to control the partial pressure of the test gas over the surface of the drops. The possibility thus existed for desorption of the gases from the drops during cooling.

The results of these experiments are shown in Fig. 1 as cumulative number of freezing nuclei per cm^3 versus temperature; the range of temperatures in different tests for given $K(T)$ is shown by the horizontal bars on the spectra. For comparison purposes, the P & L results are also shown. The distilled water froze at relatively warm temperatures on the glass substrate and the variabilities for any $K(T)$ were large, similar to the report of P & L. Considering the scatter in the data,

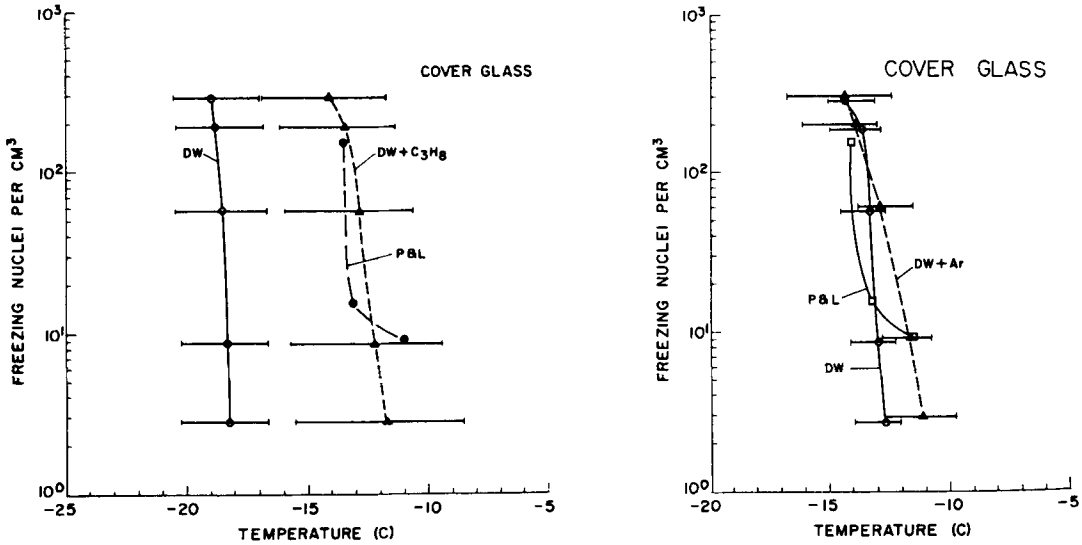

Fig. 1. Nucleus spectra for distilled water saturated with C_3H_8 (left) or Ar (right) and supported by glass surface.

agreement with P & L is fair, and it is clear that, at least for C_3H_8, the presence of the gas does affect the freezing behavior of the samples. The fact that the spectra for distilled water shows considerable variability on the cover glass slips suggests that the sites provided by these glass surfaces were due to contaminants; moreover this variation shows that a substrate can provide nuclei in sufficient number to overwhelm the nuclei of interest. A number of substrates were tested to find a surface that repeatably provided few background nuclei (see Appendix). The final choice of a silicone resin (DF-88) was based on its ease of application as well as its cleanliness with regard to spurious nuclei.

To clarify whether the result with C_3H_8 was due to a gas-heteronuclei effect or a gas-substrate effect, tests were conducted in duplicate fashion with the exception that a silicone resin film was used to support the drops.

The results of these experiments are shown in Fig. 2, where it is seen that the freezing temperatures (T_F's) are considerably colder using the resin substrate than when using a glass substrate; a difference of nearly 10 °C was observed in T_{90} for C_3H_8 saturated drops, and for Ar saturated drops this difference was nearly 8 °C. Comparison of these two experiment sets suggests that the results obtained with the glass substrates were in fact influenced by that substrate, i.e. the glass substrate was providing nucleation sites that were affected by the presence of the gases in the water. Whether the nucleation sites were due to contaminants on the glass surface or due to the glass surface itself was not revealed by these tests.

3.2. *Tests with different nucleants*

Since the resin film seemed to have provided few nuclei interactive with the gases, the other nucleants were tested using this substrate. The nucleants and gas combinations tested are given in Table 1 with the results of the repeated tests reported as the difference between the supercoolings of the saturated and non-saturated drops containing the same nucleant:

$$\alpha = T_F \text{ (gas-saturated)} - T_F \text{ (control)}. \quad (4)$$

A value of <0 implies that the gas reduced the amount of supercooling necessary to initiate nucleation, since supercooling is taken as a positive quantity (Reischel and Vali, 1975).

The results of these tests were subjected to a statistical analysis using a t-test (Dixon and Massey, 1969). A null hypothesis of equality of the means was applied to the T_1, T_{10}, T_{50}, T_{90} and T_{99}'s of these experiments. Before using the t-test, and F-test (Dixon and Massey, 1969) for equality of the variances was applied. In cases where the F-test resulted in rejection at the 0.01 level of significance, a modified form of the t-test was used (Dixon and Massey, 1969). In Table 1, the differences in supercoolings are reported along with the number of tests (N) and the number of drops frozen for each test (N_0). Differences which caused rejection of the null hypothesis at the 5% level of significance appear in italics. Few of the differences appear

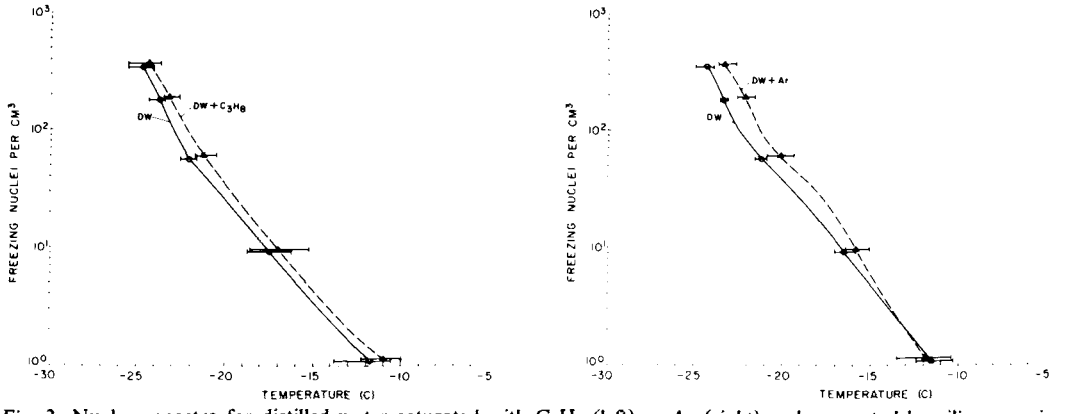

Fig. 2. Nucleus spectra for distilled water saturated with C_3H_8 (left) or Ar (right) and supported by silicone resin surface.

significant and even then not for all T_F values, so that the physical significance is probably little.

3.3. *Reversibility experiments*

The above tests indicated that the effect of the test gases on the activity of the nucleants was slight. The possibility was present that this effect was lessened by the desorption of the test gases from the hydrosols during their cooling even though solubility increases with decreasing temperature for these gases (Linke, 1965). A test was devised to explore some of these factors and to detect residual effects after gas desorption.

The procedure is described in Fig. 3. A sample of drops was first deposited on the resin surface (point A) and frozen (point B). After freezing, the drops were warmed to +15 °C and the test gas admitted to an airtight chamber (point C) which covered the drops. After 5 min at +15 °C (point D), the drops were cooled to 0 °C, held at this temperature for 10 min, and cooled again. After freezing (point E), the drops were warmed to +15 °C (point F) at which point the chamber was removed, flushed with filtered air and replaced. The drops were then frozen again (point G) to test for possible residual effects. Fig. 3 has been idealized to represent a case in which a reversible lowering of the supercooling might be observed. An estimate of the time required for saturation of water drops with a gas that does not react with water (Postma, 1970) shows that about 5 min would be required for a stagnant spherical drop of equivalent surface area. It cannot be said with certainty that all of the gas had desorbed from the drops after the 15 min period allowed. However, the driving force for absorption in this case is primarily the equilibrium partition coefficient (i.e., Henry constant: concentration of solute in liquid/concentration of solute in gas) and since these gases do not react with the water, it seems reasonable to assume that the desorption time is close to that required for absorption. Transfer processes occurring when gases are desorbed from solution are poorly understood, and for gases which do react with water, absorption and desorption may be quite different in nature (Thomas and Ray, 1975).

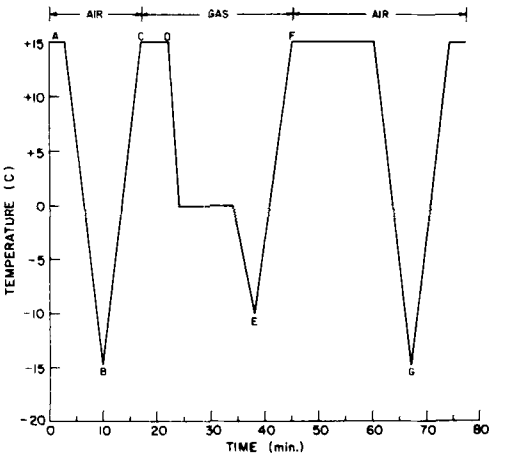

Fig. 3. Cooling and gas exposure sequence used for reversibility experiments.

Table 1. *Changes in supercoolings* (α's) *for the nucleant salt combinations tested in these experiments*

		$F(T)$						
Gas	Nucleant	1	10	50	90	99	N_0	N
C_3H_8	None	−0.8	−0.5	*−0.8*	*−0.5*	−0.3	150	6
C_3H_8	None	*+0.1*	−0.9	*−0.7*	*−0.5*	−0.2	150	6
C_3H_8	None*	−0.3	−1.2	−1.2	−1.0	−0.8	150	6
C_3H_8	LDN	*+0.7*	+0.5	+0.1	+0.1	−0.4	150	6
C_3H_8	AgI	+0.1	*+0.7*	*+1.3*	+0.7	*+1.0*	150	6
C_3H_8	L-3A	−1.7	*−1.4*	+0.6	*+2.6*	*+3.6*	150	5
C_3H_8	L-5A	+0.1	+0.9	*+1.8*	*+2.0*	*+1.1*	150	3
Ar	None	+0.3	*−0.7*	*−1.1*	*−1.2*	−1.0	150	6
Ar	LDN	−0.5	−0.8	*−0.5*	*−0.5*	*−0.7*	150	6
Ne	None	−1.0	−0.1	−0.5	*−0.9*	*−1.3*	200	5

* Singly distilled water.

N_0 is the number of drops per test; N is the number of tests.

For each gas-nucleant combination, 3 replicate experiments were conducted. The data points represent the averages of these 3 runs; the bars on the spectra labelled 1, represent the ranges of T_{10} and T_{90} for the initial cooling cycle (point B) without gas. The 3 spectra labelled 1, 2, and 3 correspond, respectively, to the points B, E, and G in Fig. 3.

Since the previous test series had shown a small effect of C_3H_8 on the background particles present in the water, an experiment using C_2H_8 as the test gas was performed with this water (no nucleant intentionally added). The results show (Fig. 4) that the activity of the particles has increased slightly.

The results of the tests using mica are shown in Figs. 5 and 6. Fig. 5 shows the results of a "blank" run (performed for each nucleant) in which compressed air was used as the test gas; the spectra for the 3 consecutive freezings agree well and are within experimental errors. The tests using air as the test gas were conducted to ensure that the repeated freeze-melt cycles did not influence the activity of the nucleant. The tests with mica indicate that a change in freezing temperature is caused by C_3H_8.

For the tests with KLN (Figs. 7 and 8), similar effects were noted, but in this case the effects are not as clear, both decreases and increases in freezing temperatures being observed. However, if just the results at T_{90} are considered (which are best suited to characterize a nucleant, see Appendix), it appears that both of these gases do increase the activity of KLN by a small amount.

Using LDN as a nucleant in experiments with C_3H_8 and Ar, no effects larger than $\pm 0.3\,^{\circ}C$ in T_{90} were found. Additionally, tests using C_3H_8 with a rain sample collected at Laramie, Wyoming, showed no effect larger than $\pm 0.6\,^{\circ}C$ in T_{90}.

The final nucleant to be used for these tests was ground glass obtained by pulverizing some microscope cover slips used in the earlier experiments (see Section 3.1) with a Diamonite mortar and pestle. Figs. 9 and 10 show results of similar tests using the pulverized glass with the gases. No effect due to these gases was present when glass was used as the nucleant. These reversibility tests gave results quite different from when the glass was used as a solid substrate upon which the drops rested (Sections 3.1 and 3.2): (a) drops on the glass substrate exhibit warmer freezing temperatures than when the glass is suspended in the drops; (b) the scatter (i.e., range of T_F's) is larger on the glass substrate. It thus seems reasonable to conclude that the effects of the test gas (in previous tests using glass supporting surfaces) were not of the nature of a heteronuclei-water interaction. The explanation was found when it was observed that frost formed

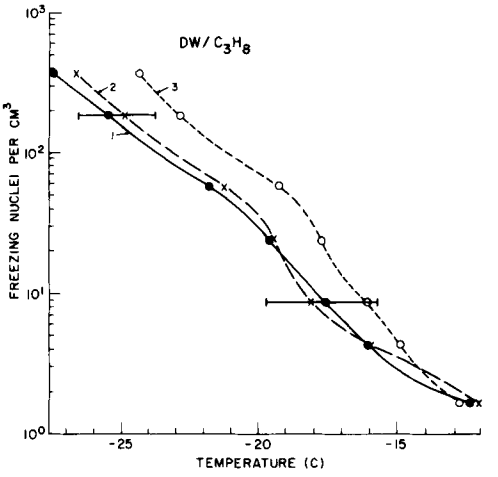

Fig. 4. Successive nucleus spectra for distilled water saturated with C_3H_8. Numbers refer to successive freezings of the sample.

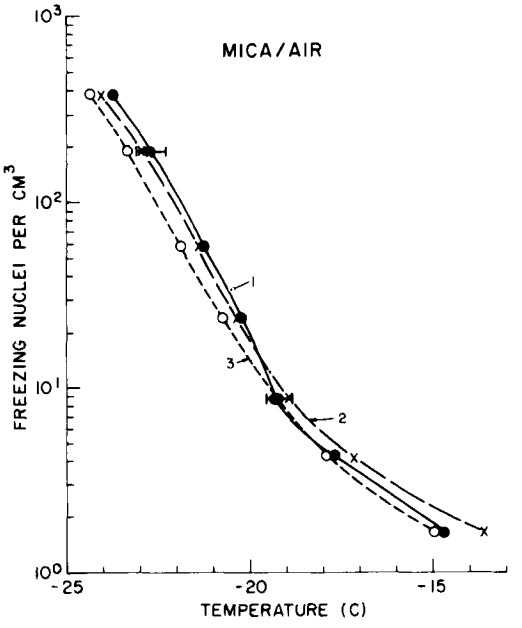

Fig. 5. Successive nucleus spectra for mica–air combination. Numbers refer to successive freezings of the sample.

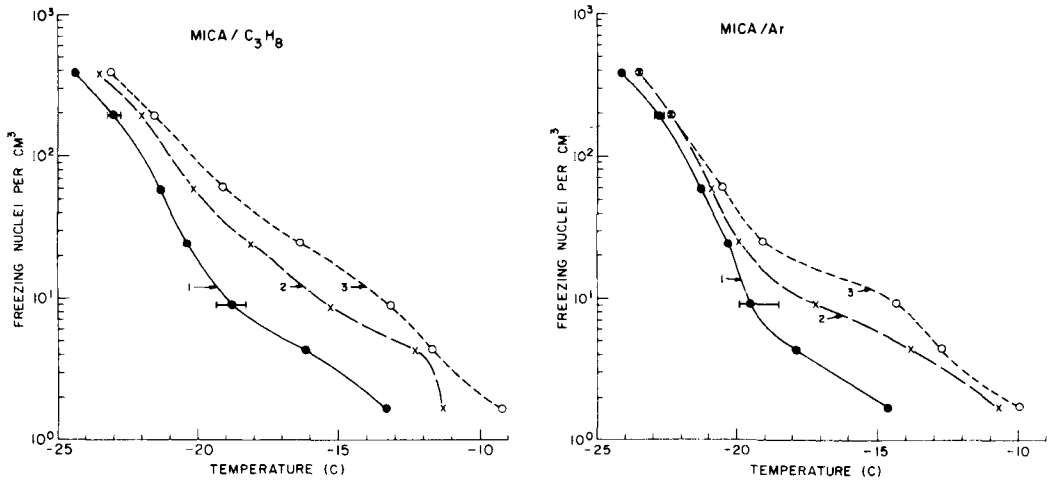

Fig. 6. Successive nucleus spectra for mica–C_3H_8 (left) or Ar (right) combinations. Numbers refer to successive freezings of the sample.

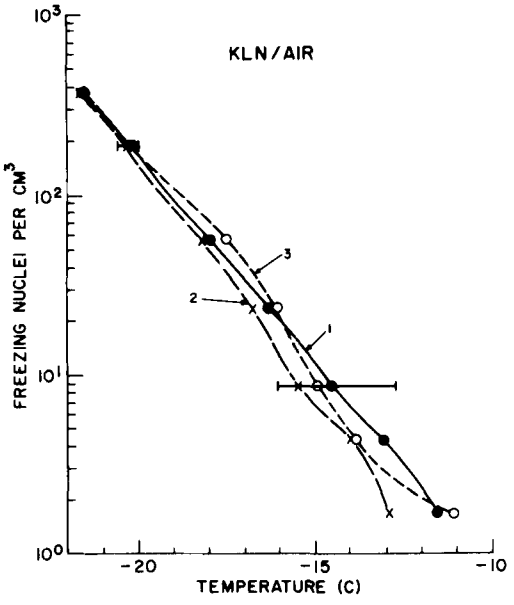

Fig. 7. Successive nucleus spectra for KLN—air combinations. Numbers refer to successive freezings of the sample.

on the glass cover slips at unpredictable temperatures and spread rapidly to nucleate the drops. Such problems were not encountered with the resin surface. From the above discussion and the results obtained on differing surfaces (see Section 3.2), it can be seen that the selection of a suitable surface on which to conduct drop freezing experiments is a matter of central importance and can lead to erroneous results (see Appendix, below).

That the effects observed in these experiments were not simply due to a gas–water interaction is supported by the fact that there were differences in freezing temperatures between the tests using different nucleants, indicating a dependency on the nature of the nucleant. That the effects are not due to interactions between the gases and the silicone resin is supported by the lack of any effect with the pulverized glass, as well as by the differing behaviours of the nucleants.

4. Discussion

While the magnitudes of the observed changes were not large, the tendency for certain nucleants of natural occurrence (mica and kaolin) to become more active after exposure to C_3H_8 or Ar is of interest regarding our fundamental concepts about the nature of immersion nucleation sites. The observations reported here suggest that an irreversible improvement of the active sites (or the creation of totally new sites) occurred due to the influence of the dissolved gases. Studies of the effects of dissolved amines (also clathrate formers, Jeffrey and McMullan, 1967) on heterogeneous freezing nucleation have shown that the activities of hetero-nuclei can be decreased or improved (Reischel et al., 1974). That pre-activation of

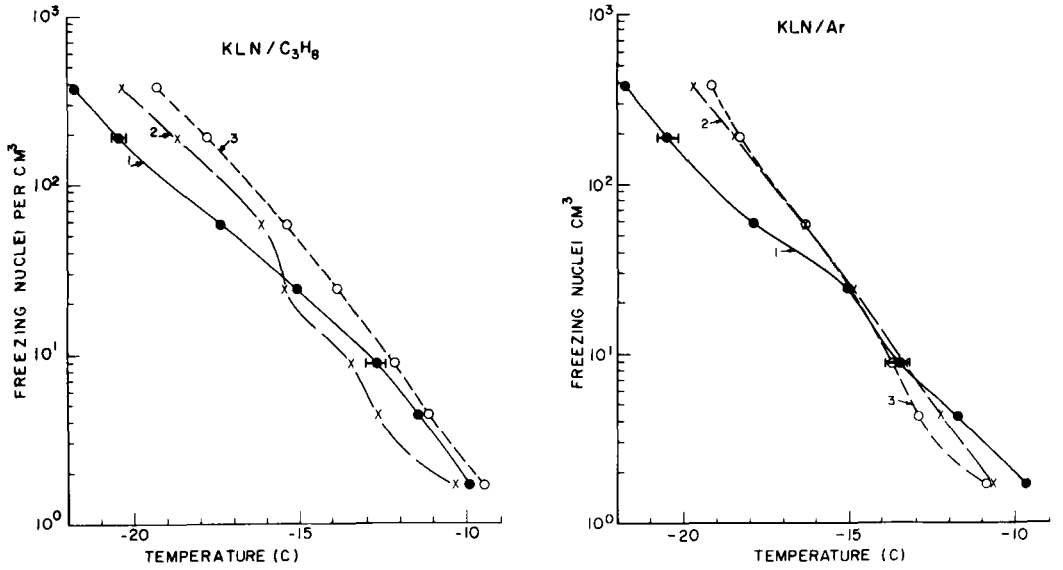

Fig. 8. Successive nucleus spectra for KLN–C_3H_8 (left) or Ar (right) combinations. Numbers refer to successive freezings of the sample.

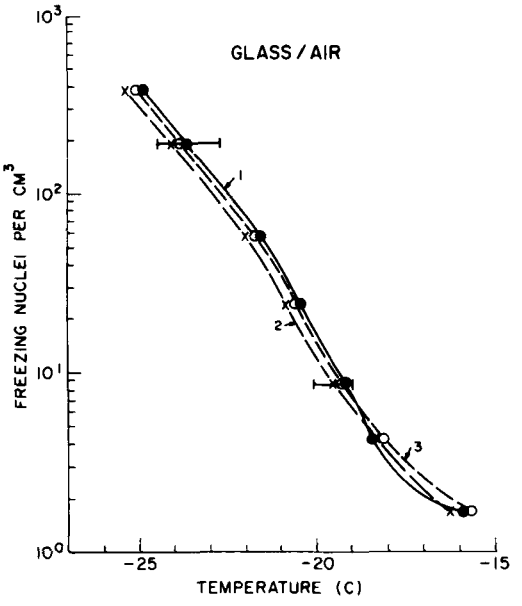

Fig. 9. Successive nucleus spectra for glass—air combination. Numbers refer to successive freezings of the sample.

freezing nuclei can occur has been shown by Edwards et al. (1970), but the explanation of the effect relies on the formation of a monolayer of ice (under high pressure) at the surface of the nucleant or the formation of ice in capillaries. These types of surface ice (and pre-activation) cannot survive temperatures above about +5 °C and so are quite different from the pre-activation which occurred in these experiments (samples were heated to +15 °C).

Another interesting aspect of this pre-activation is the possibility that C_3H_8 dissolved in a droplet could alter the nucleation behavior of natural nuclei upon refreezing of the droplet downwind of a propane-seeding site. These experiments have shown, however, that the effect is dependent on nucleant type and thus any such effect would depend on the type of natural nuclei present, as well as the presence of C_3H_8.

The experiments have shown that the clathrate-forming gases can affect heterogeneous freezing nucleation processes and that these effects are not due to changes in the bulk water structure but to modifications occurring at the nucleant–embryo interface.

5. Acknowledgements

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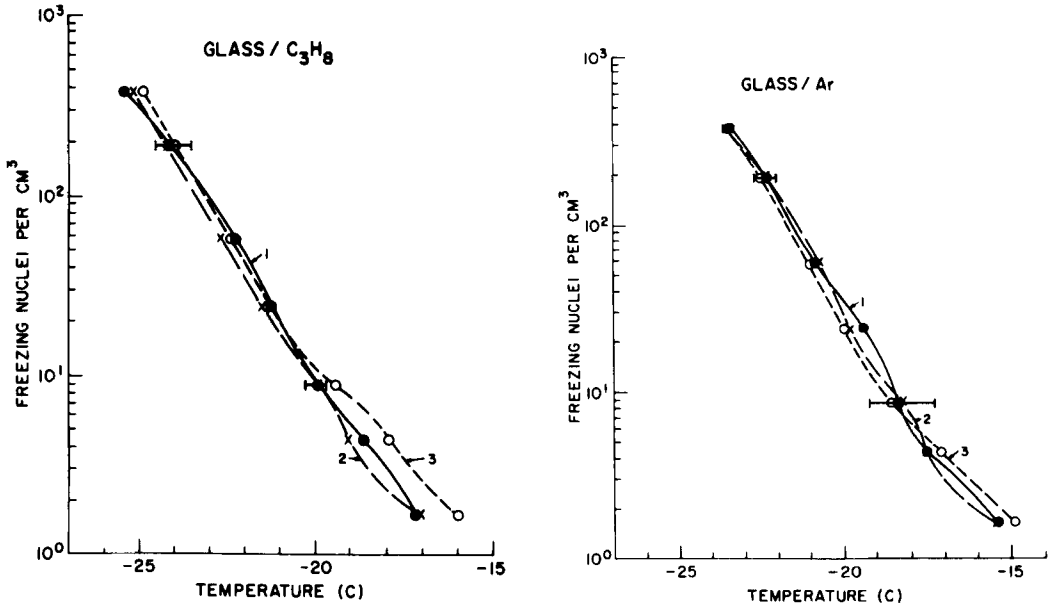

Fig. 10. Successive nucleus spectra for glass–C_3H_8 (left) or Ar (right) combination. Numbers refer to successive freezings of the sample.

ments for the Ph.D. degree at the University of Wyoming. This research was partially supported by the Universities Space Research Association under Contract NAS8-33882 sponsored by the NASA Materials Processing Office directed by Richard Halpern. I am also grateful to Karen Emmitt who typed the manuscript.

6. Appendix
Reliability of the nucleation temperatures

Vali (1971) has shown from Monte Carlo simulation of drop freezing experiments that for N_0 = 150, maximum discrepancies in concentrations appear at the warm temperature ends of nucleus spectra. Vali has also shown that a nucleus spectrum can be determined with fair reliability using only 72 drops and that improvement in resolution is slow with increasing numbers of drops. In general, the error band associated with a nucleus spectrum is dependent on the shape of the spectrum. Uncertainties of a factor of 2 over most of the spectra with perhaps factors of 4 towards the ends were suggested as reasonable error bands for $k(T)$, while $K(T)$ showed somewhat less scatter. A rigorous treatment of the statistical reliability of the spectra has not been developed.

It was thus of some interest to determine empirically the repeatability of the supercoolings measured for a given concentration ($K(T)$). A number of different nucleants were tested repeatedly and the standard deviations, S, of T (for $K(T)$ as shown in Table A1) were determined for the N tests of each nucleant. The value of N was 7 for TiO_2, PbO(1) and PbO(2), while for Sb_2O_3, AgI (precipitated from $(NH_4)_2AgI_3$) and mica, N was 12, 13, and 14, respectively. The results of these experiments are shown in Fig. A1, where the standard error, S/N, is plotted as a function of $K(T)$. The results show that the standard error of the measurement decreases for greater $F(T)$ values in agreement with the Monte Carlo simulation analysis.

The two nucleant samples, PbO(1) and PbO(2), were both of analytic reagent grade but of different origin. The widely differing results for these two samples show the inherent variability in materials used as nucleants (i.e., even though the two materials are chemically similar, they exhibit quite different nucleation behavior).

Drop freezing tests invariably require a support-

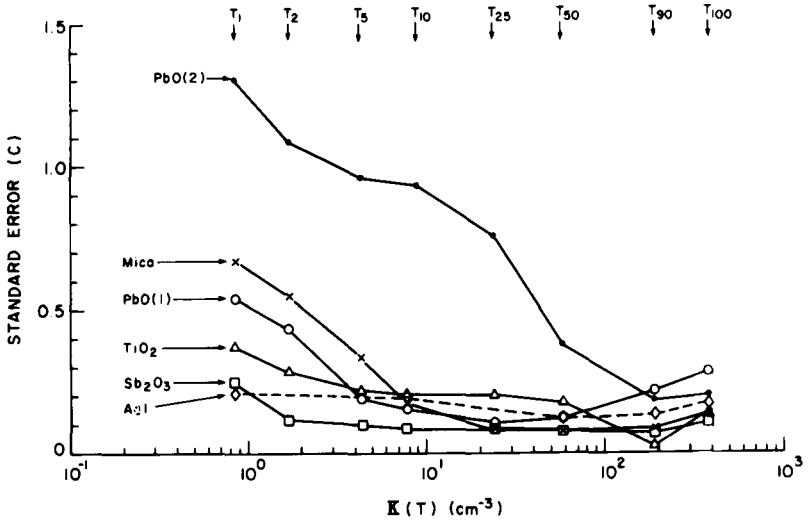

Fig. A1. Standard error in the measurement of T as a function of $K(T)$ for 6 nucleants.

Table A1. *Values of $F(T)$ and associated $K(T)$'s for the drop volume used in these experiments*

$F(T)$	0.01	0.02	0.05	0.10	0.25	0.50	0.90	0.99
$K(T)$	0.84	1.68	4.27	8.78	24.0	57.8	192	383

ing surface. To inspire confidence that the supporting surface used in these tests was inert, experiments were conducted using 8 different hydrophobic surfaces. All of the surfaces were commercial products used without further treatment. The surfaces used were: petrolatum (VSLN), a silicone base resin (DF-88), Mylar plastic film (MYL), plastic food wrap (SW), wax paper (WP), a motor oil additive (STP), and two samples of a silicone base grease (DC-7). All surfaces were taken from previously unopened containers except for DC-7(2) which was taken from a tube which had been deliberately left open for several weeks prior to the tests. This was done to check for possible effects of moisture uptake by DC-7 since it contains silica particles suspended in a grease and also because silicone grease has been reported to be a good nucleator of both ice and AgI (Knight, 1969). The distilled water used was filtered through a 0.22 μ pore filter, a single sample being used throughout the tests. The tests were conducted in random sequence (with regard to surface) so that sampling bias would not occur. Four separate tests of 100 drops each were run and values of $K(T)$, as shown in Table A1, were determined. The results of the tests are shown in Fig. A2.

The following points are suggested from these results.

(1) A larger spread in T is apparent for low $K(T)$ compared to high $K(T)$.
(2) Some surfaces give quite high $K(T)$ (for a given T) compared to others; WP, MYL and DC-7(2) give the warmest spectra.
(3) VSLN appears to give the "cleanest" spectra (i.e., coldest freezing temperatures) followed by DF-88 and DC-7(1).

Only VSLN and DF-88 gave a low value of all T's (<−20 °C), compared to other surfaces (T_1 = −9.5 to −12.8) and thus seem preferable to WP, MYL, STP, or SW. These observations suggest that only a few surfaces can be used to determine T reliably for low values of F. The results also point out a problem in determining the nucleus spectra for a very inactive material, i.e., if the material is only active at temperatures below about −20 °C, background activity from the water or support surface could become significant and invalidate the

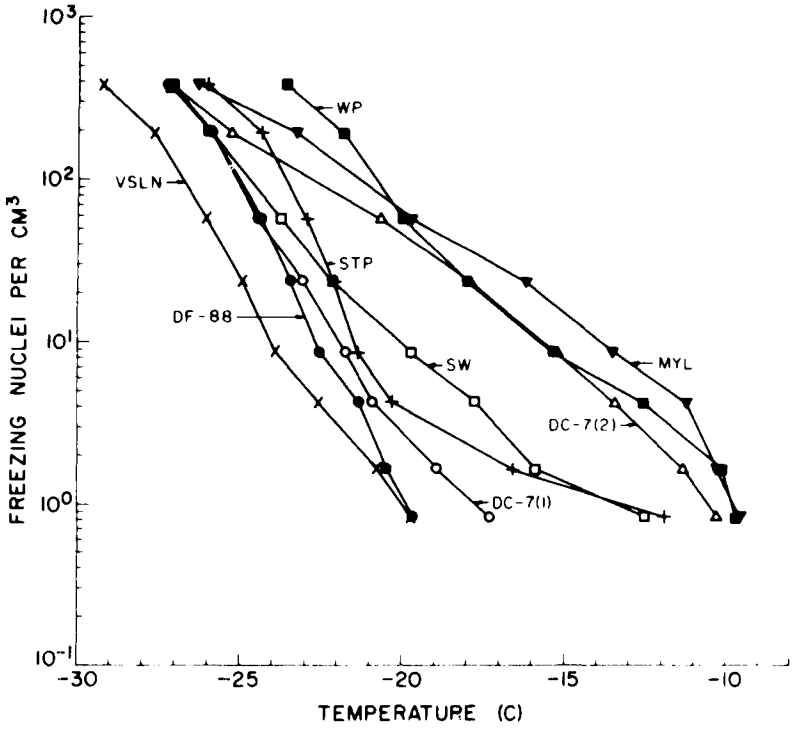

Fig. A2. Nucleus spectra for the distilled water using 8 different support surfaces.

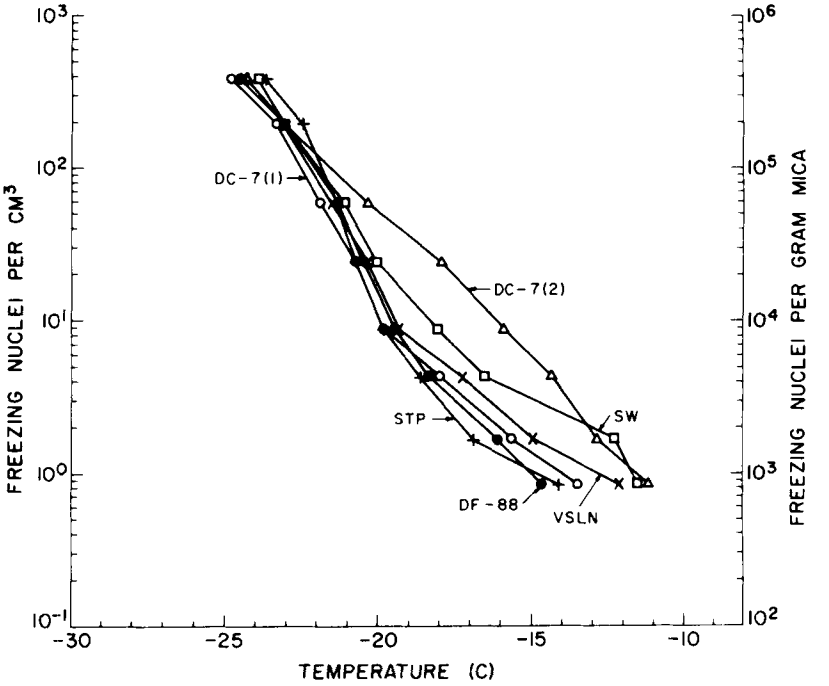

Fig. A3. Nucleus spectra for mica using 6 different support surfaces.

spectrum unless special precautions are taken (such as filtering the water and using a surface—water combination of known nucleation activity).

In the above tests, some surfaces appeared to exhibit lower nucleation activity than others. However, since the actual nucleus content of the water was unknown, it was possible that some substances from these colder surfaces dissolved in the drops and "poisoned" the freezing nuclei. To test this possibility, 6 of the surfaces were tested with drops containing mica as a nucleant (10^{-3} g ml^{-1}). The results of these tests are shown in Fig. A3 and represent the average of 3 runs for each surface. For higher $K(T)$ values, agreement was quite good; at lower $K(T)$ values there was still considerable scatter. There was good agreement in T at all values of $K(T)$ for DF-88 and DC-7(1). The DC-7(2) results were still very close to those obtained with this surface and DW when no intentionally-added nucleant was present in the water, showing how the surface may act to obscure the activity of a nucleant.

The above tests do not prove that the surface used in these studies (DF-88) was inert to all possible combinations of nuclei and dissolved material; they do, however, suggest that this surface has no innate tendency to affect nucleation temperatures.

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