

A Study of the Mechanism of Contact Ice Nucleation¹

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(Manuscript received 30 January 1975, in revised form 8 April 1975)

ABSTRACT

The nucleation of freezing of supercooled water drops by metaldehyde, phloroglucinol and 1,5-dihydroxynaphthalene was studied. It was found that the threshold temperature for nucleation by contact of the particles with the supercooled drops was 2–3°C warmer than the threshold when the same drops were melted and re-frozen with the nuclei already partly immersed. There was no evidence that the high threshold for contact nucleation was due to active sites that were subsequently destroyed. Rather, it was thought to be associated with the movement of the water front along the surface of the nucleus during the contact process. It is suggested that this process gives rise to a transient high free energy zone which facilitates nucleation. In support of this theory, measurements were made of the contact angles of water on the three compounds.

1. Introduction

The nucleation of ice is important in natural clouds as the first stage in the formation of snow crystals, graupel and hail. There are three known mechanisms of nucleation: by sublimation, by condensation-freezing including immersion freezing, and by contact freezing. The latter is of great interest because there is considerable evidence that it can take place at warmer temperatures than nucleation by the other two mechanisms.

It has long been known that mechanical stimuli can help crystallization of supercooled liquids (Young, 1911; Berkeley, 1912; Young and van Sicklen, 1913). Dorsey (1948) made a careful study of the freezing of supercooled water contained in clean glass bulbs and test tubes by mechanical agitation such as pouring, splashing, impact and rubbing. Of these treatments, only the rubbing of one glass-water interface on another was found to initiate freezing. Rau (1951) reported that a number of materials showed remarkable ability to initiate freezing when sprinkled in dry powder form upon supercooled drops. Pruppacher (1963) found that freezing of supercooled water could be triggered when the boundary line between surfaces of supercooled water, air and solid (plastic) is caused to move along the solid surface by the application of an external electric field.

More recently, Gokhale and Goold (1968), stimulated by previous observations such as those of Blanchard (1957), Medaliev and Sulakvelidze (1965) and Sulakvelidze (1966), showed experimentally that nucleus particles were indeed highly effective when they

collided with supercooled droplets, whereas their activities were relatively poor when they were submerged in water before cooling. Other experimental studies (Gokhale and Lewinter, 1971; Gokhale and Spengler, 1972; Fletcher, 1972; Pitter and Pruppacher, 1973) showed similar results. Isaac and Douglas (1972) discussed the "time lag" for nucleation, taking into account the slowness of the collision process between the nucleus particles and supercooled droplets. The seeding effect of AgI in summertime cumulus clouds was computed by Alkezweeny (1971) on the assumption that contact nucleation was the sole mechanism operating.

In discussing the mechanism of contact nucleation of ice, Fletcher (1970) drew attention to two possible effects: that active nucleating sites on a dry particle colliding with a water drop might subsequently dissolve and be destroyed; and that collision of a supercooled drop with a nucleus might suddenly remove the depression of freezing-point caused by an adsorbed solution layer on the nucleus surface.

In order to decide whether contact nucleation is caused by either of Fletcher's suggested mechanisms, or is due to some other process, carefully designed experiments are necessary. These must take into account that the nucleating ability of seed materials depends strongly upon their method of preparation and subsequent history. The present paper reports an experimental study of contact nucleation using three well-known organic ice nuclei, 1,5-dihydroxynaphthalene (Fukuta, 1966), metaldehyde (Fukuta, 1963) and phloroglucinol (Bashkirova and Krasikov, 1957). To explain these and other results a new mechanism of contact ice nucleation is suggested.

¹Part of this paper was presented at the 8th International Conference on Nucleation, Leningrad, 20–24 September 1973.

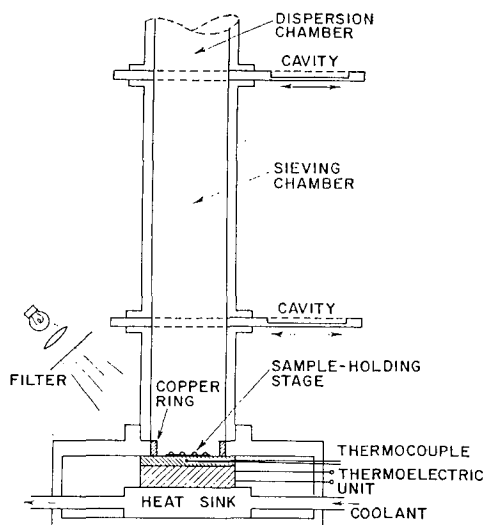


FIG. 1. Schematic representation of experimental apparatus.

2. Experimental

a. Sample preparation for ice nucleation studies

Samples for the nucleation studies were prepared in the following manner:

METALDEHYDE (MA)

Sublimed metaldehyde was washed with clean hexane several times, followed by several washes with distilled water. Drying was carried out in a silica gel desiccator.

Smoke: About 1 mg of MA was blown by pumping action of a syringe through a copper pipe of 3 mm i.d., wound around a hot temperature-controlled soldering iron. MA sublimed while moving along the pipe and deposited when quenched with cold outside air. Smoke was injected into the sedimentation setup shown in Fig. 1.

Ground: The cleaned MA was ground, using agate mortar and pestle, and sieved in the sedimentation setup.

Washed: The ground MA was washed with distilled water, using a suction filter, dried, and then used in the same manner as mentioned above.

PHLOROGLUCINOL (PG)

Commercially available PG was purified by dissolving in hot water and cooling it slowly to room temperature. The deposit was filtered, washed, dried, and used in the same manner as MA.

1,5-DIHYDROXYNAPHTHALENE (DN)

The DN sample was prepared by washing a commercial variety with clean hexane several times, followed by several washes with distilled water. Drying

was carried out in the silica gel desiccator. Again it was used in the same manner as MA.

b. Sample preparation for contact angle measurements

Samples for contact angle measurements were prepared in the following manner:

METALDEHYDE

The cleaned MA was made into small pellets using a compressing type pellet-making machine.

PHLOROGLUCINOL AND 1,5-DIHYDROXYNAPHTHALENE

Cover glasses were cleaned using a chromic acid mixture, followed by several washes with distilled water. The cleaned chemical was placed between two cover glasses, melted, and cooled. One cover glass was removed and measurements were carried out using material deposited on the other.

The prepared samples were used in the following three surface conditions: as prepared, cleaned with a razor blade, and cleaned by wiping with a filter paper.

c. Contact angle measurements

A water droplet about 1 mm in diameter was placed by a clean glass capillary on a horizontally placed sample surface and was viewed in a microscope of long working distance. For the advancing contact angle measurements, the slight advancement of the droplet rim was confirmed just before each run by carefully adding a very small amount of water. Similarly, for the retreating contact angle measurements, the retreating rim was created by removing a small amount of water using the capillary action of a filter paper.

Photomicrographs of droplets were taken and from the droplet heights and widths, the contact angles were estimated (Adamson, 1967). For each angle measurement, at least five runs were made.

d. Contact ice nucleation study

A clean circular cover glass, 0.15 mm thick and 22 mm in diameter, was coated with ethylene dichloride solution of Plexiglas and dried. The cover glass was placed on a mineral oil-coated surface of a thermoelectric unit whose temperature was measured by an attached thermocouple. Twenty droplets of a 4% aqueous solution of high molecular weight polyvinyl alcohol were placed on the coated glass. The droplets were about 1 mm in diameter. Then they were cooled to the temperature of the study. The solute, as a soluble high polymer, does not affect the nucleation behavior of water (Fukuta, 1966).

When the droplets were cooled to the temperature of the measurements, sample particles were introduced from the top of the sieving chamber located above the droplet holding glass (see Fig. 1). By opening the upper

TABLE 1. Contact angle (deg) of water on organic crystals.

Ice nuclei crystal	Preparation	Contact angle	
		Ad- vanc- ing	Re- treat- ing
Metaldehyde	(i) pellet	99	59
	(ii) cleaned with razor blade	76	71
	(iii) cleaned with filter paper	84	47
1,5-Dihydroxy-naphthalene	(i) melted	71	39
	(ii) cleaned with filter paper	59	41
Phloroglucinol	(i) melted	28	17
	(ii) cleaned with filter paper	43	9

sliding window, the particles entered the chamber. While the particles descended through the chamber, they were sieved and a desired fraction was led into the lower compartment by opening the second window. Particles of uniform size fell onto the droplets, making contact. The condition was adjusted so that at least two particles hit each droplet on the average.

The frozen droplets were easily distinguished because of their white color. The percentage of frozen droplets was recorded at this temperature of first droplet freezing, T_0 . Then the stage was warmed up to 10°C , and cooled again at the rate of 2°C min^{-1} . The percentage of droplets frozen was recorded with respect to this slowly decreasing temperature, T_1 . There was no appreciable delay in temperature between the stage and the thermoelectric unit during the cooling or warming process. This was confirmed by the fact that the melting point of ice formed on the stage and the temperature reading in the unit coincided. The same procedure was repeated and the spectra with respect to T_2 , T_3 , ..., were similarly recorded. At least five runs were made using fresh samples each time to determine the nucleation behavior of the selected kind of sample.

3. Result and discussion

The observed contact angles are given in Table 1. The melted sample surfaces apparently are enriched with impurities and the results are not consistent. Surfaces cleaned either by razor blade or filter paper give

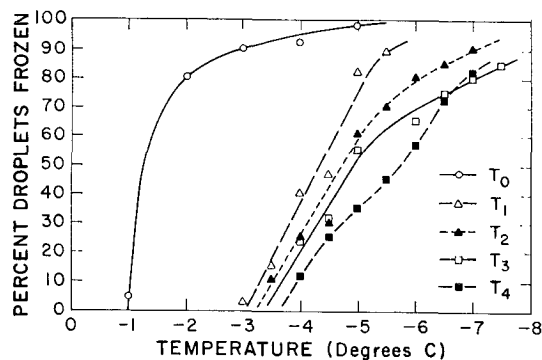


FIG. 2. Freezing of supercooled water droplets by metaldehyde smoke particles (Fukuta, 1972).

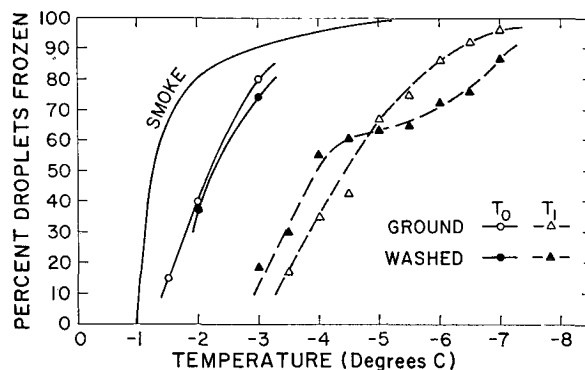


FIG. 3. Freezing of supercooled water droplets by ground or washed metaldehyde crystals (Fukuta, 1972).

more consistent values though they still show some scatter. As anticipated, MA gives the highest advancing as well as retreating contact angles. PG has the lowest values. This is one of the reasons why the percentage of active MA nuclei is small in normal tests despite the fact that the nucleation threshold is very high; under the supersaturation in the laboratory and nature, it is difficult for water condensation to take place on MA nuclei. This is in accordance with what appears to be the prerequisite for ice nucleation under slight supercooling, i.e., the existence of liquid phase on the surface. This also explains why MA nuclei show a strong vapor activation effect (Fukuta, 1968).

The result of the contact ice nucleation study for MA smoke is shown in Fig. 2. It is immediately apparent that there is a large gap between T_0 and subsequent freezing temperatures. As the repeated freezing studies are continued, the activity spectra shift to the right suggesting an additional deactivation of the nuclei. Fig. 3 illustrates the result for MA powders. Both ground and washed samples show a similar behavior and there is a 1.5°C gap between the contact and the repeated freezing nucleation. During the repeated freezing tests, sample particles were seen sitting on the surface of droplets.

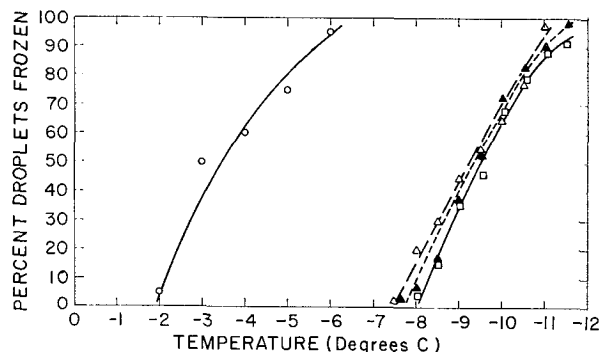


FIG. 4. Freezing of supercooled water droplets by phloroglucinol smoke particles (Fukuta, 1972).

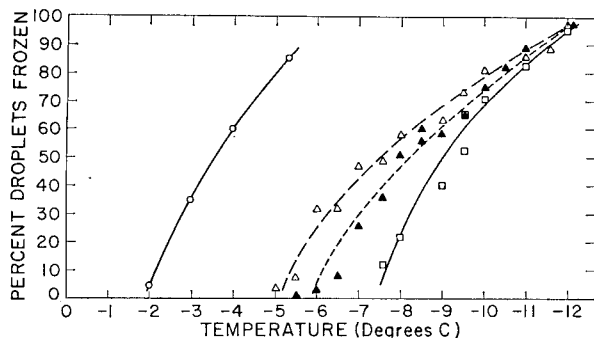


FIG. 5. Freezing of supercooled water droplets by ground phloroglucinol crystals.

The higher threshold for contact nucleation on smoke particles gives the impression that highly active sites exist on these particles but are absent on powder particles. However, considering the lack of difference in observed nucleabilities between the washed and the ground powders, and remembering that MA tends to decompose slowly and the decomposition products make the stored sample less active compared with the freshly prepared material (Fukuta, 1972), the higher activity of the smoke is likely due to the cleaner surface condition.

An even larger gap may be seen between T_0 and repeated freezing temperatures for PG smoke (see Fig. 4). This may be attributed to some extent to the solubility of PG in water, although small. In comparison with the result with ground powders shown in Fig. 5, it seems that the spectra given by repeated freezings of the smoke are similar, indicating that decay of activity is complete. As can be interpreted from the shift of T_2 , T_3 and T_4 lines at low percentiles toward lower temperatures, the decaying tendency is stronger for the particles of higher activation temperatures.

The results for the smoke and the washed as well as the ground powder of DN are shown in Figs. 6, 7 and 8, respectively. Although this compound gives the lowest threshold temperature among the three, the repeated freezing does not significantly deactivate the smoke

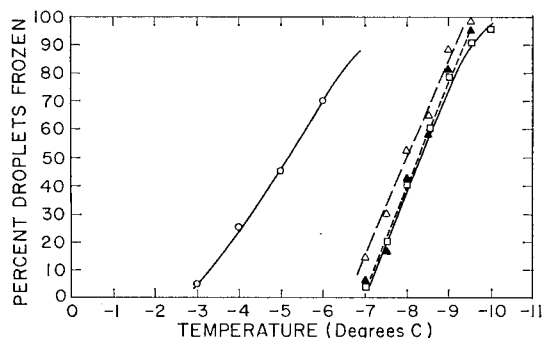


FIG. 6. Freezing of supercooled water droplets by 1,5-dihydroxynaphthalene smoke particles (Fukuta, 1972)

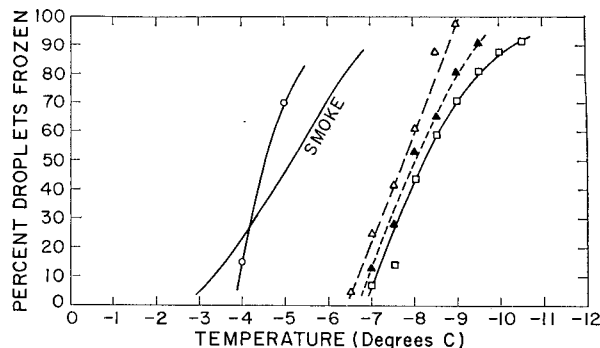


FIG. 7. Freezing of supercooled water droplets by washed 1,5-dihydroxynaphthalene crystals.

particles. The washed as well as ground powders again demonstrate almost identical behavior.

The 50 percentiles of the T_0 spectra of all the smokes coincide with the previously reported thresholds of ice nucleation (Fukuta, 1966). The large gap between T_0 and temperatures for subsequent repeated freezing, particularly in PG smoke, is partly due to nuclei dissolving in water. Medaliev and Sulakvelidze (1965) reported rather low freezing temperatures for AgI particles which were precaptured on a drop at a warm temperature. Their result also appears to be caused by this particle dissolution effect. The rate of dissolution of a particle in a water droplet is controlled by the solubility which is a function of solute and solvent masses as well as the temperature. Small particles are thus more likely to be subjected to dissolving deactivation. For these reasons, a hasty extrapolation of laboratory results to the real atmosphere without proper consideration of this nuclei dissolution effect should be avoided.

A remarkable fact detected in the present study is that the extrapolation of T_1 , T_2 , T_3 , ..., for all the compounds tested under the different preparations, does not lead one to T_0 . The difference between T_0 and the extrapolated temperature at low percentiles of drop freezing is about 2–3°C for powders. Powders are less affected by dissolution loss of particles due to their larger masses. The contact nucleation thresholds, T_0 ,

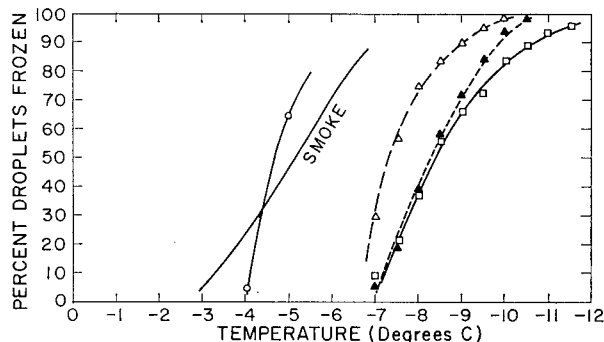


FIG. 8. Freezing of supercooled water droplets by ground 1,5-dihydroxynaphthalene crystals.

do not depend appreciably on the method of sample preparation, except for MA which may be contaminated by its own decomposition products, as discussed above. This implies that the duration of the condition suitable for the nucleation is short so that even small particles can act as contact nuclei without dissolution deactivation.

These analyses clearly suggest that there exists at least a mechanism by which freezing nucleation takes place at warm temperatures during the process of *mechanical contact*. This is in agreement with the observation made by Pruppacher (1963); freezing took place at warm temperatures when the liquid-gas interface moved along the solid surface, although the movement was created by the applied electric field. In the following section, we shall discuss possible factors that may affect the mechanism.

4. A possible mechanism of contact ice nucleation

In order to discuss possible mechanisms for contact ice nucleation, let us summarize the general conditions experimentally detected. First of all, the nucleus surface, which apparently provides the place for ice germ formation, must not carry bulk or visible liquid water on its surface, so that it appears dry although the surrounding air environment is virtually saturated with respect to water due to coexisting droplets. Second, the mechanism requires a relative movement of the supercooled water surface along the air-nucleus boundary due to the contacting motion (see Fig. 9).

On such a nucleus surface, although it appears dry, one can expect a population of ice clusters forming and disintegrating in the adsorbed water layer at the temperature where contact nucleation is about to take place. The clusters are all below the critical size for ice nucleation. Under such a condition, the thermodynamic approach (Fletcher, 1962) has had considerable success in describing the macroscopic behavior of heterogeneous ice nucleation, and it is mainly attributed to the large critical embryo size which permits application of such a treatment. A claim has been made with respect to the contact ice nucleation mechanism that some of the clusters in the adsorbed layer on a dry-looking particle can serve as critical embryos when the nucleus surface is placed in the supercooled water by contact action (Cooper, 1974). The argument was based on this thermodynamic treatment of heterogeneous ice nucleation. Clusters of this category can, of course, serve as embryos for sublimation nucleation at lower temperatures. Since the clusters at a given size in the adsorbed layer are less numerous than those on the nucleus immersed in the water under the same temperature and even the more numerous of the latter cannot produce any critical embryos, it is not possible for the former to nucleate ice when immersed in the supercooled water (Fukuta, to be published). For this reason, the idea that the immersed deposition clusters in the adsorbed layer

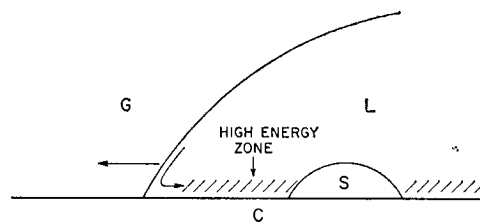


FIG. 9. The system of contact ice nucleation. Letters G, L, S and C stand for gas, liquid, solid, and nucleus crystal.

serve as critical embryos of freezing upon contact with supercooled water cannot be accepted.

Let us therefore carefully examine what can be expected to change in relation to ice nucleation during the contact process. As we have discussed above, there exists an adsorbed layer of water on the nucleus surface which is in or near equilibrium with the supercooled water. This implies that there is no free energy difference between the adsorbed layer and the supercooled water. As the nucleus particle makes contact with a supercooled droplet, the air-liquid-nucleus boundary line moves along the nucleus surface. If the movement is slab-like, the surface free energy change is $\gamma_{CG} - \gamma_{CL}$, where subscripts C, G and L stand for nucleus crystal, gas and liquid, respectively. During the movement, however, the liquid surface is likely to be pulled onto the nucleus surface. In this case, the surface free energy change becomes $\gamma_{CG} + \gamma_{LG} - \gamma_{CL}$. The nucleus surface is thus forced to get wet with bulk water (cf. Fig. 9).

When a solid surface is immersed in a liquid, it is known that heat of immersion or of wetting is evolved. This heat can be described by the difference of specific total surface energies between the gas-nucleus and the gas-liquid interfaces (Bikerman, 1970). However, the heat generation is merely the result of a thermodynamic change, and what permits such a change to occur is the free energy difference between the initial and final states. The free energy also controls the nucleation process. Therefore, we now look into the free energy behavior during the contact process.

Concerning the adsorbed molecules existing on the nucleus surface, if the layer is infinitely thick, the surface is wettable, but if the layer is finite, further addition of molecules to it increases the free energy of the system. Depending upon how the free energy increases by adding molecules, hydrophobic surfaces of different degrees can be defined, and according to the hydrophobic nature of the surface, liquid water on it shows the contact angle phenomenon. Adamson and Ling (1964) convincingly treated the contact angle phenomenon using an interfacial potential and a decay function of the interfacial effect. According to them, the Gibbs' free energy difference between the adsorbed water and the bulk can be given as

$$kT \ln \frac{P}{P_0} = \Delta e^{-ax} - \frac{E_{CL} d_{CL}^3}{x^3}, \quad (1)$$

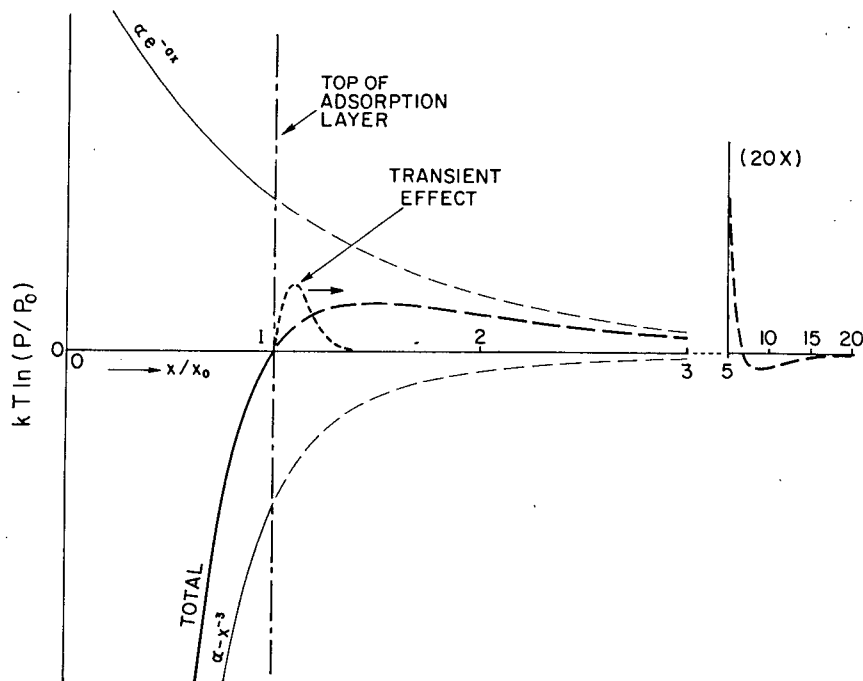


FIG. 10. The Gibb's free energy variation with distance from the nucleus crystal surface. The subscript (0) stands for the bulk liquid.

where k is Boltzmann's constant, T the absolute temperature, P and P_0 are the vapor pressures of adsorbed molecules and of bulk liquid, respectively, Δ the deviation in the free energy from the normal liquid at the nucleus-liquid boundary, a the decay constant, x the distance from the boundary, E_{CL} the free energy per nearest neighbor interaction between the adsorbed molecule and the molecule in the nucleus surface, and d_{CL} is the distance (see Fig. 10). The x^{-3} term is due to the choice of dispersion potential and it can be changed depending on the kind of potential one selects for the interaction. The situation at the top adsorption layer is such that the two terms on the right-hand side of (1) match to make the free energy exactly at the bulk liquid level. Nevertheless, the derivatives of the two terms with respect to the distance remain uncanceled there.

If bulk water makes a sudden contact with this adsorbed layer during the process of contact nucleation, these two terms controlling the layers of adsorbed water molecules immediately start affecting the water. As soon as fields begin propagating, one can reasonably assume that the two terms behave differently by extending the corresponding two lines originating from the adsorbed layers. A transient high free energy zone will thus form in the water just like the supersaturation wave in a warm, moist and nuclei-free slab of air suddenly making contact with a cold wall (Fukuta and Saxena, 1973). This trend can also be judged by extending the total free energy line in the adsorbed layer on the

hydrophobic substrate, although the line falls below the bulk water level once before converging to it (see Fig. 10). The transient free energy line will move toward the broken line of the total free energy which represents the equilibrium condition. If the liquid water surface is pulled to the surface of the nucleus during the contact as mentioned before, the additional γ_{LG} must also dissipate at the C-L boundary. This further increases the free energy at least temporarily.

For heterogeneous ice nucleation, it is the free energy of critical embryo formation, ΔG^* , that sharply controls the nucleation rate (Fletcher, 1962). Under the transient condition on the nucleus shortly after making contact with supercooled water,

$$\Delta G^* = \Delta\mu V + A_{CS}(\gamma_{CS} - \gamma_{CL}^\dagger) + A_{SL} \gamma_{SL}, \quad (2)$$

where $\Delta\mu$ is the free energy difference between ice and water per unit volume of ice, V the volume of the ice germ, and A the area. Since the surface-free energy at water-nucleus interface (indicated by the \dagger) is thus raised as discussed above, ΔG^* is reduced, making the ice nucleation easier. The nucleation rate equation is

$$J = K \exp(-\Delta G^*/kT), \quad (3)$$

where K is the kinetic constant. The situation can also be interpreted in terms of decreased $\Delta\mu$ due to the increase in free energy of water, rather than increased γ_{CL} , leading to the same final effect. The duration of the effect may be short but considering the depth of the

adsorbed layer and time involved in the ice germ formation which are comparable to those of this transient effect, and further remembering the strong ΔG^* dependency in heterogeneous ice nucleation, it appears possible that this effect is responsible for the observed enhancement of ice nucleation during the contact process. Contact nucleation, if the proposed mechanism were correct, must be specific to hydrophobic nuclei. The three organics studied here are, as the measurements showed, indeed hydrophobic.

From this viewpoint, it is quite obvious why Dorsey (1948) failed to detect contact nucleation; he used extremely clean glass surfaces which were wettable and therefore could not induce this transient high free energy zone upon contact. The requirement Rau (1951) found for freezing ability of a particle, i.e., dried condition, can be interpreted as a means of exposing the hydrophobic surface. Most materials are more or less hydrophobic, although the hydrophobic surface is only a necessary condition for contact nucleation and it alone is not sufficient to let the nucleation take place at warm temperatures.

5. Summary and conclusion

From the analyses and discussions we had above, the following conclusions may be drawn:

- 1) Small particles tend to dissolve and create a larger gap between T_0 and T_1
- 2) The threshold temperature of contact freezing is not a function of the solubility and size of nucleus particles. This suggests that the time suitable for contact nucleation is short.
- 3) Dissolution of high activity sites on the nucleus surface during the contact nucleation cannot account for the mechanism.
- 4) There exists a gap of about 2–3°C between T_0 and that extrapolated from T_1 , T_2 , etc., to the time of contact nucleation.
- 5) Contact nucleation is associated with the liquid-air interface movement along the nucleus surface during the mechanical contact process of the nucleus particle with the supercooled water.
- 6) Clusters existing in the adsorbed layer at the air-nucleus interface cannot become critical embryos for freezing nucleation when they are brought in the water-nucleus interface due to contact with supercooled water.
- 7) The transient high free energy condition, which is considered to appear on the nucleus surface when the air-nucleus surface is brought inside of the supercooled water as the result of the contact process, can explain the effect of contact ice nucleation.

Acknowledgments. The author thanks Mr. V. Shridhar for his help in experiments, and Dr. S. C. Mossop of CSIRO, Australia, for his discussion on the results. This study was supported by the Atmospheric Sciences

Section, National Science Foundation, under Grant GA-12569.

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