

## Conditions Governing Drop Freezing at Warm Temperatures

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### ABSTRACT

In an attempt to investigate conditions under which ice crystals can form at comparatively warm temperatures in supercooled regions of a cloud, the scope of experiments on drop freezing, previously undertaken by the authors, has been enlarged. The results of the present extensive series of experiments have confirmed that supercooling drops, when subjected to evaporation, freeze more readily due to what has been called the "dynamic effect" of evaporation. When sodium sulphate was added to the drops in arbitrary concentration, their freezing probability also showed a significant increase. These findings indicate that, in supercooled regions of a cloud where prevailing conditions are similar to those of the reported experiments, the ice crystal concentration should be two to three orders of magnitude higher than the existing ice nucleus concentration.

### 1. Introduction

Measurements in cumulus clouds (Murgatroyd and Garrod, 1960; Koenig, 1963; Braham, 1964; Mossop *et al.*, 1970) have indicated unusually large concentrations of ice crystals over a temperature range extending even close to 0°C. On occasions, the reported concentrations have been as much as three to four orders of magnitude more than the estimated ice nucleus concentration. Although many mechanisms for explaining this anomaly have been suggested, *viz.*, shedding of whiskers from evaporating surfaces (Ruskin, 1969), electro-freezing of water drops (Abbas and Latham, 1969), contact nucleation by dry particles (Gokhale and Gould, 1968), shattering of crystals due to thermal shock on the nucleating supercooled drops (Hobbs, 1969), and production of secondary ice particles by the process of riming in supercooled cloud (Mossop, 1970), laboratory confirmation of these mechanisms, capable of operating on a scale large enough to be of importance in natural clouds, has not as yet been found. A new approach to the problem is, therefore, warranted.

The authors have been carrying out experiments on ice nucleation in supercooled drops under conditions similar to those in nature: drops have been used which contain natural aerosols, and processes have been simulated which are known to control the formation and development of a cloud. One effect considered has been that of the influence of evaporation on freezing probability. Droplets in different supercooled regions of a cloud experience evaporation due to various causes, *viz.*, differences in equilibrium vapor pressure over drops of different sizes, co-existence of solid and liquid phases, entrainment from cloud boundaries, and initia-

tion of downdrafts. The evaporative cooling of cloud droplets at cloud boundaries could be as much as 6°C below the ambient temperature (Koenig, 1965), suggesting an increase of drop freezing events by one order of magnitude. The question being considered by the authors, however, is whether, apart from the evaporative cooling which may help increase drop freezing events, other effects accompanying the process of evaporation could further influence nucleation.

It is known from the theory of heterogeneous nucleation (Fletcher, 1962; Mason, 1971) that the important factors which control drop freezing, apart from the nature of the function  $f(m, x)$  of the nucleating particle present within the drop and the temperature  $T$  of the drop, are 1) the activation energy per molecule for self-diffusion in water and, particularly, 2) the surface free-energy  $\sigma_{SL}$  of the ice-water interface. The expression for the nucleation rate of freezing per particle is given by

$$I \approx \frac{n_c k T}{h} 4\pi r^2 \exp\left[-\frac{(U + \Delta G^*)}{k T}\right],$$

where

$$\Delta G^* = \frac{16\pi M^2 \sigma_{SL}^3 f(m, x)}{3[\rho_S R T \ln(p_{\alpha, w}/p_{\alpha, i})]^2}.$$

Here,  $n_c$  is the number of liquid molecules in contact with unit area of the nucleating particle,  $r$  the radius of the nucleating particle considered as a sphere,  $M$  and  $\rho_S$  the molecular weight and density, respectively, of the solid phase,  $p_{\alpha, w}$  and  $p_{\alpha, i}$  the equilibrium vapor pressures over plain surfaces of liquid water and ice,

respectively,  $k$  Boltzmann's constant,  $h$  Planck's constant, and  $R$  the universal gas constant. The function  $f(m, x)$  is always less than unity and is a function of the geometry of the nucleating particle and the habit of the embryo. Since factors 1) and 2) are susceptible to the surface molecular disturbances caused by evaporation, these same factors may well change during the evaporation of supercooled drops. The extent of those changes in the characteristics of the water substance would depend upon the rate of evaporation, and a feedback would be established affecting the drop freezing probability. Should the values of 1) and 2) decrease, then the nucleation rate  $I$  would increase. The problem, in the manner posed, can be investigated by studying drop freezing not only as a function of the supercooling but also under the simultaneous superposition of supercooling and evaporation, at least to the point where the cooling effect due to evaporation does not become the over-riding factor in freezing. The results of preliminary experiments with large drops containing natural aerosols have been reported (Ramachandra Murty and Ramana Murty, 1972a). These results indicated that drops froze more readily under conditions of simultaneous supercooling and evaporation than with supercooling alone, despite the fact that there was no noticeable difference in the drop temperatures. This new effect of evaporation on drop freezing has been called the "dynamic effect" of evaporation. This effect has now been confirmed by further experiments under a wider variety of physical conditions.

Another feature which we now consider is the effect of certain soluble components on the freezing behavior of droplets containing natural aerosols (Hosler and Hosler, 1955; Hoffer, 1961; DePena *et al.*, 1962; Pruppacher, 1963, 1965; Evans, 1967). It is known that sulphate is present nearly everywhere in the atmosphere and its concentration in rainwater and sea water insures its presence in cloud droplets. Therefore, experiments have been carried out with large drops which indicated that sodium sulphate enhances freezing.

We present and discuss here the results of the investigation of the two features, evaporation and solubility, as they help to explain at least partly, the discrepancy between the observed and anticipated ice crystal concentrations in cumulus clouds. It has been assumed in this context that the results for large size drops are equally applicable to droplets of micron size range (cloud droplets), because experiments with smaller but non-uniform size drops produced by a home-spray atomizer have indicated similar results (Ramachandra Murty and Ramana Murty, 1972b). Moreover, investigations with large drops are relevant because observations made by The University of Chicago Clouds Physics Laboratory, showing unduly large concentrations of ice crystals, emphasized the frequent presence of large drops (about 1 mm in diameter) in cumulus clouds before ice crystals were detected (Braham, 1964).

## 2. Water samples used and the size of water drops investigated

As rainwater contains natural aerosols and chemically resembles cloud water, samples of rainwater were collected on the third floor terrace of the Institute at Poona (18°32'N, 73°51'E, 559 m MSL). Because uniform large size drops can be easily produced with hypodermic needles, all drops studied had diameters of 2.2 mm.

## 3. Experimental set-up

The details of the equipment and the observation method adopted for the study of freezing drops under simultaneous supercooling and evaporation have been described earlier (Ramachandra Murty and Ramana Murty, 1972a). A brief outline of the essential features is given below.

Drops (diameter 2.2 mm) are placed in equal numbers onto two identical metal dishes of large thermal capacity (mass 590 gm), each of which has a special groove all around the region where the drops are placed. Before placing the drops the dishes are coated with a water repellent Dow Corning silicone lubricant. Two milliliters of water from the sample under investigation are then placed in the groove of one of the dishes, leaving the groove of the other dish empty. Both dishes are sealed with glass covers and subjected immediately to identical rates of cooling by transferring them simultaneously to the cold stage of a very large thermal capacity metal block (mass 100 kg), kept precooled to the desired temperature with a Freon 22 system. The drops which are placed on the dish containing water in the groove, while undergoing supercooling, are also subjected to the process of evaporation because the water in the groove freezes earlier than do any of the drops on the dish, giving rise to a solid-liquid vapor pressure difference in the dish. The numbers of drops freezing in each dish at successive time intervals are observed with the naked eye until all 30 drops in each dish are frozen. The temperature of the dishes as well as that of the drops in the dishes are measured with thermocouples and recorded with a Hewlett-Packard recording microvoltmeter.

For studying the effect of sodium sulphate on the freezing behavior of the drops, the same experimental set-up as above is used, but with the grooves of both the dishes left empty. One of the dishes contained drops with sodium sulphate and the other drops without it.

## 4. Results of experiments under simultaneous supercooling and evaporation as compared to supercooling alone

Placing and enclosing batches of 30 drops in each of the two dishes and adding a small quantity of water in the groove of one, the freezing events were counted in each dish in successive intervals of 1 min, starting

after transfer of the dishes onto the cold stage. The experiments were conducted using drops from a number of rainwater samples and also with the cold stage initially brought to various predetermined temperatures, namely,  $-20$ ,  $-15$ ,  $-10$  and  $-5$ C. With these initial temperatures, the dishes attained, under quasi-equilibrium conditions, temperatures of  $-19.7$ ,  $-14.7$ ,  $-9.8$  and  $-4.7$ C, respectively. The fraction of drops frozen at successive intervals for various cold stage temperatures is given for a typical sample of rainwater, collected on 17 July 1969, in Figs. 1-4. The following observations are of interest.

1) Cold stage at  $-20$ C: Drops under simultaneous supercooling and evaporation started freezing at a temperature of  $-12.9$ C, i.e., 4 min earlier than the drops under supercooling alone ( $-16.8$ C). The first set of drops froze within 19 min, the second within 30 min.

2) Cold stage at  $-15$ C: Drops under simultaneous supercooling and evaporation started freezing 6 min earlier ( $-7.5$ C) than the drops under supercooling alone ( $-12.7$ C). The first set of drops froze within 21 min, the second within 70 min.

3) Cold stage at  $-10$ C: Drops under simultaneous supercooling and evaporation started freezing from the 9th minute ( $-4.2$ C) and all froze within 41 min. The drops which were subjected to supercooling alone never showed signs of freezing, even after 100 min.

4) Cold stage at  $-5$ C: Drops under simultaneous supercooling and evaporation started freezing from the 46th minute ( $-4.7$ C); all 30 drops froze within 125 min.

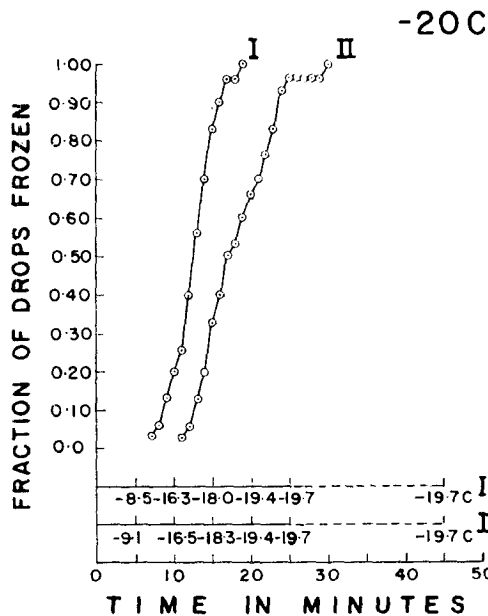


FIG. 1. Fraction of rainwater drops frozen with the cold stage initially at  $-20$ C. Curve I is for the dish containing a small quantity of rainwater in the groove, curve II for the empty-groove dish. Temperatures are given at 5-min intervals.

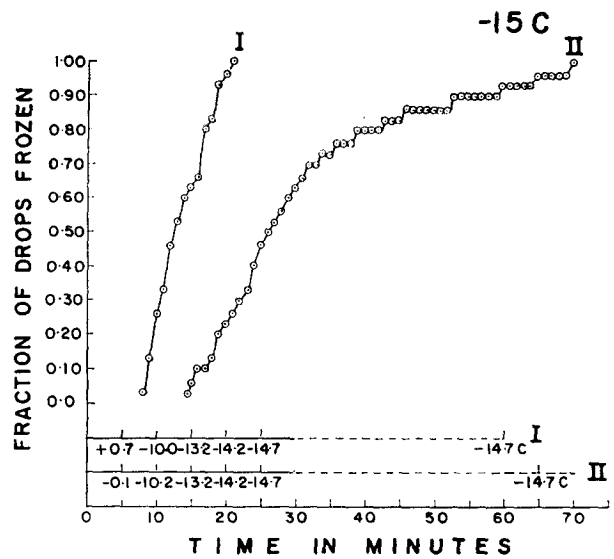


FIG. 2. As in Fig. 1 except for cold stage initially at  $-15$ C.

The drops which were subjected to supercooling alone never showed signs of freezing.

### 5. Results of experiments showing effects of sodium sulphate on drop freezing

Fresh solutions of sodium sulphate of ANALAR grade (analytical reagent) were prepared with rainwater as a solvent at an arbitrary concentration of  $20 \text{ gm liter}^{-1}$ ; these were compared with corresponding unaltered rain samples serving as reference. The experiment was conducted with the cold stage initially brought to  $-10$ C, a temperature at which drops subjected to supercooling alone never showed freezing.

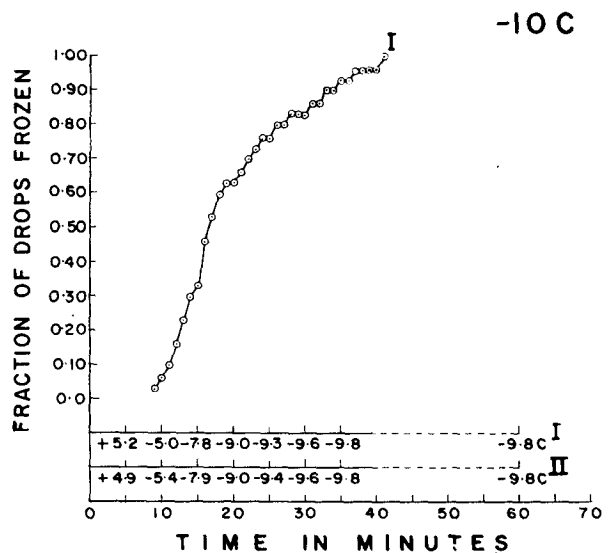


FIG. 3. As in Fig. 1 except for cold stage initially at  $-10$ C. No freezing event was observed even after the 100th minute in the empty-groove dish.

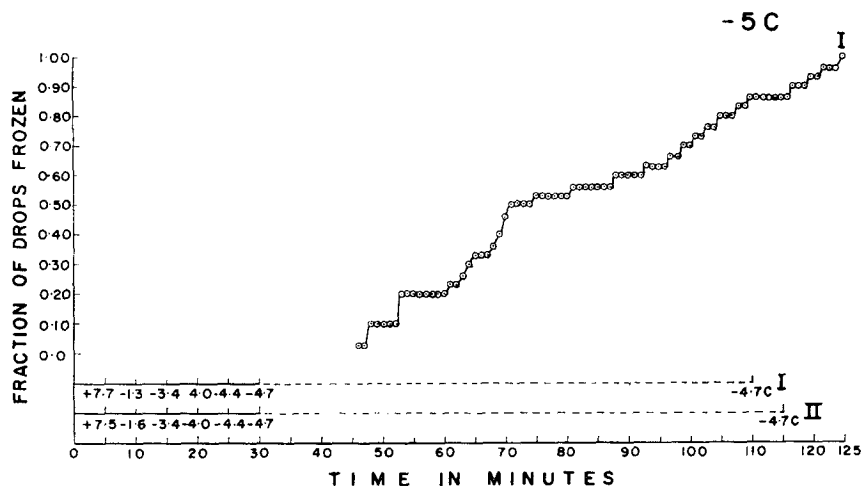


FIG. 4. As in Fig. 1 except for cold state initially at  $-5^{\circ}\text{C}$ . No freezing event was observed up to the end of the experiment in the empty-groove dish.

Typical fractions of the drops frozen at successive intervals of time are given in Fig. 5.

Freezing of drops began at the 12th minute ( $-6.5^{\circ}\text{C}$ ). All 30 drops froze within 39 min whereas none of the reference rainwater drops showed signs of freezing, even after 100 min.

This effect of  $\text{Na}_2\text{SO}_4$  was confirmed by other experiments at warmer temperatures where finely powdered silver iodide, of L-R grade (laboratory reagent), was dispersed in an (arbitrary) concentration of  $2 \text{ gm liter}^{-1}$  into the samples of rainwater. Sodium sulphate was added to a part of the mixture as before, in concentration of  $20 \text{ gm liter}^{-1}$ . The freezing of drops produced from rainwater samples containing both AgI and  $\text{Na}_2\text{SO}_4$  was then compared with the freezing of rainwater drops containing only silver iodide. The initial cold stage temperatures were  $-5$  and  $-3^{\circ}\text{C}$ . The fraction of drops frozen at successive intervals of time in a typical run is given in Figs. 6 and 7. The results were as follows:

1) Cold stage at  $-5^{\circ}\text{C}$ : The drops containing both AgI and  $\text{Na}_2\text{SO}_4$  started freezing 16 min earlier ( $-2.9^{\circ}\text{C}$ ) than the drops containing silver iodide alone ( $-4.7^{\circ}\text{C}$ ). The first set of drops froze within 42 min whereas it took 122 min for the others.

2) Cold stage at  $-3^{\circ}\text{C}$ : The drops containing both AgI and  $\text{Na}_2\text{SO}_4$  started freezing from the 32nd minute ( $-2.2^{\circ}\text{C}$ ). All 30 drops froze within 102 min. However, none of the 30 drops which contained only silver iodide showed signs of freezing within this period.

## 6. Discussions and conclusions

The cold stages used at different initial temperatures enabled the drops to attain different temperatures at different rates of cooling. The present study again revealed that 2.2-mm drops freeze more readily under conditions of simultaneous supercooling and evapora-

tion than under conditions of supercooling alone. It is, therefore, concluded that this behavior is not dependent on such other features in the experiment as the degree and rate of the supercooling. The new findings, therefore, confirm that the process of evaporation is always accompanied by the dynamic effect, favoring increases in temperatures of ice nucleation by  $4$ – $5^{\circ}\text{C}$ . For more rapid evaporation the rise in temperature could even be higher; this may not be uncommon at cloud peripheries.

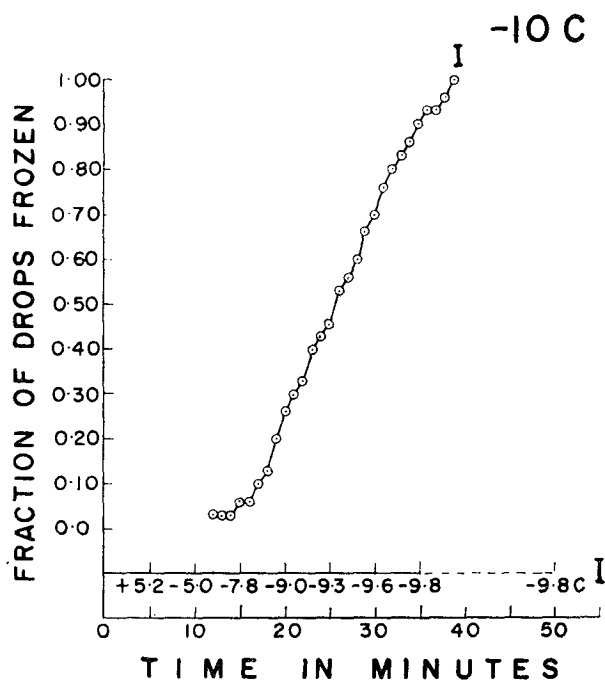


FIG. 5. Fraction of rainwater drops containing sodium sulphate frozen when the cold stage was initially at  $-10^{\circ}\text{C}$ . No freezing event was observed in the case of rainwater drops not containing sodium sulphate. Temperatures are given at 5-min intervals.

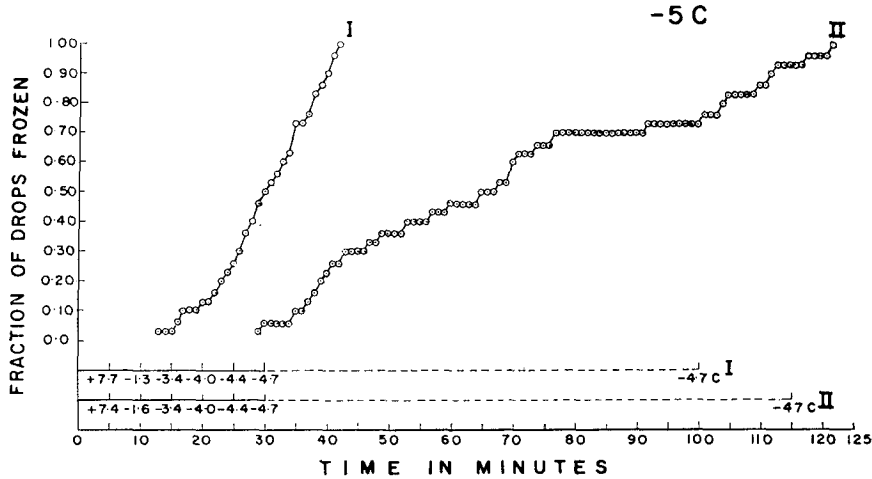


FIG. 6. Fraction of drops frozen when the cold stage was initially at  $-5^{\circ}\text{C}$ . Curve I is for dish with rainwater drops containing silver iodide and sodium sulphate, curve II for rainwater drops containing only silver iodide. Temperatures are given at 5-min intervals.

The presence of the soluble salt  $\text{Na}_2\text{SO}_4$  in the super-cooling drops produced remarkable increases in their freezing probability. Repeated observations, made with the cold stage temperature initially at  $-10^{\circ}\text{C}$ , have shown that the first freezing takes place as soon as the drops attain a temperature of about  $-6^{\circ}\text{C}$ . This means that the presence of  $\text{Na}_2\text{SO}_4$  in the drops has raised the temperature at which the first freezing takes place by more than  $6^{\circ}\text{C}$  because the reference rainwater drops froze only at temperatures below  $-12^{\circ}\text{C}$  (see Section 4). The conditions in the dish containing solution drops may not be exactly identical to those in the other dish containing the reference rainwater drops, for there will be a difference in the evaporation rate due to the sodium sulphate. Since the presence of  $\text{Na}_2\text{SO}_4$  lowers the vapor pressure of the solution, it is

likely that the evaporation rates are smaller, at all stages, for solution drops than they are for the reference rainwater drops. Consideration of this feature suggests that the rise noticed in the freezing temperatures of the solution drops could not be ascribed to the difference in evaporation rate due to sodium sulphate.

As already stated, there are indications that the effect of evaporative cooling alone at cloud peripheries could occasionally be as high as  $6^{\circ}\text{C}$ . Also, it has been noticed that the combined influence, on drop freezing, of the dynamic effect of evaporation and of the solution effect, is more than that of either of these effects separately (Ramachandra Murty and Ramana Murty, 1971). If the droplets containing soluble salts such as sodium sulphate [ammonium and magnesium sulphates have also been found to behave like sodium sulphate

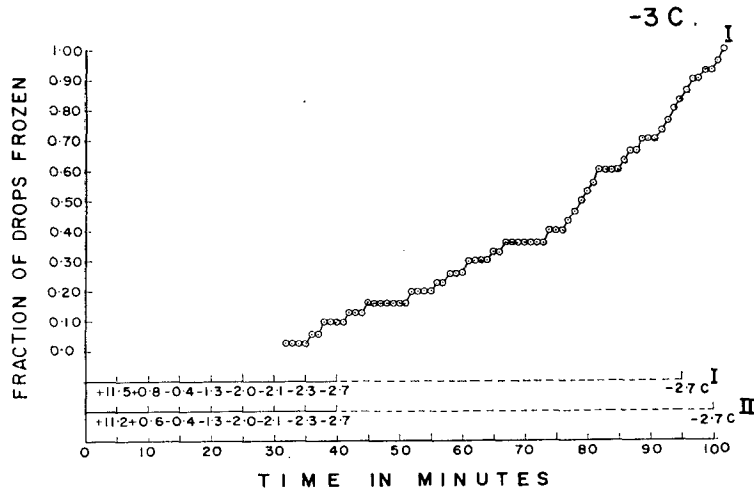


FIG. 7. As in Fig. 6 except for cold stage initially at  $-3^{\circ}\text{C}$ . No freezing event was observed for rainwater drops containing silver iodide only until the end of the experiment.

(Ramachandra Murty and Ramana Murty, 1972b)] are subjected to the effect of evaporative cooling, then the cumulative effect at cloud peripheries due to evaporative cooling, the dynamic effect of evaporation, and the solution effect could be a raise of the drop freezing temperature by at least 10C. Such rises in the nucleating temperature would correspond to an increase in ice crystal concentration by two to three orders of magnitude. It is pertinent to note in this regard that some of the observations reported (Moore *et al.*, 1958) had shown ice crystals only at the edges of cumulus clouds, not in their interior.

The dynamic effect of evaporation also exerts a control on the total time required for freezing of all the drops. At  $-20^{\circ}\text{C}$ , it took 19 and 30 min, respectively, for all the drops to freeze with and without the effect; at  $-15^{\circ}\text{C}$ , 21 and 70 min. At  $-10^{\circ}\text{C}$ , it took 41 min with the effect while none of the drops had frozen without the effect after 100 min. Therefore, the dynamic effect of evaporation speeded up the freezing of all the drops by 11 and 49 min at  $-20$  and  $-15^{\circ}\text{C}$ , respectively. At  $-10^{\circ}\text{C}$ , the time difference exceeded 59 min. At  $-5^{\circ}\text{C}$  no comparison can be drawn because the drops never froze without the aid of the dynamic effect. The observed features suggest that, as warmer temperatures are approached, the dynamic effect plays a more significant role in the initiation of the ice phase. Applied to actual clouds where the dynamic effect of evaporation prevails, the discrepancy between the observed and anticipated ice crystal concentrations becomes larger at warmer temperatures. Observations confirm this conclusion.

It will be noted in the above connection that the rates of cooling experienced by the drops in the experiments are smaller the warmer the initial temperatures of the cold stage. However, for any given initial temperature of the cold stage, both the reference and the test drops experience identical rates of cooling. The marked increase of the dynamic effect of evaporation suggested at warmer temperatures should not, therefore, be due to the cooling rate. In any case, it is known that the cooling rate does not markedly affect the freezing temperature (Gokhale, 1965; Vali and Stansbury, 1966).

Other discrepancies between the observed and anticipated ice crystal concentrations should arise in a cloud as a result of the solute effect. But it is not as yet clear just how this would vary with height inside a cloud. Only a conditional guess is possible. The finding that the addition of an arbitrary amount of sodium sulphate to rainwater drops has remarkably increased their freezing probability shows that drops containing soluble salts such as sodium sulphate freeze more readily before they become unduly diluted. The concentration used in the present study would correspond to salt nucleus masses of about  $10^{-11}$  gm in cloud droplets  $10\ \mu$  in diameter. The possibility of approaching such

conditions in actual clouds cannot be ruled out in view of recent measurements of hygroscopic nuclei in cloud droplets (Naruse and Maruyama, 1971). Cloud droplets, in the form of concentrated solution droplets, may freeze more readily in early stages of growth if they contained the right type of salt or salts in solution. In case the supercooled droplets present in a cloud at warmer temperatures (lower levels) are smaller in size, and the aerosol concentration in the cloud air decreases with height (such features help make the droplets more concentrated at warmer temperatures), the discrepancy between the observed and the anticipated ice crystal concentrations in a cloud becomes even larger in warmer regions due to the solute effect. However, available data on drop size distributions in supercooled clouds are too scanty to throw more light on this aspect. Also, mixing is generally considered excellent in cumulus clouds.

The study revealed that solution drops containing sodium sulphate show a remarkable increase in their freezing probability. Although it is known that solutes alter the surface free energy of the solvent, the observed increase in freezing probability may not be due exclusively to this effect, since experiments with all similar solutes do not yield similar results. It should be mentioned in this regard that the present finding with  $\text{Na}_2\text{SO}_4$  is not in agreement with that by Hoffer (1961), whose experiments with saturated solution drops  $\sim 100\ \mu$  in diameter, using pure water as solvent, showed a depression of the freezing temperature. To further our understanding of these effects, the present experiments should be extended to smaller drop sizes, using uniform rates of cooling. With the presently available equipment only non-uniform rates of cooling are possible.

#### REFERENCES

- Abbas, M. A., and J. Latham 1969: The electrofreezing of supercooled water. *J. Meteor. Soc. Japan*, **47**, 65-74.
- Braham, R. R., Jr., 1964: What is the role of ice in summer rain-showers? *J. Atmos. Sci.*, **21**, 640-645.
- DePena, R. G., J. V. Irebarne and E. M. Detchavel, 1962: The freezing of supercooled droplets of electrolytic solutions. *J. Atmos. Sci.*, **19**, 302-308.
- Evans, L. F., 1967: Ice nucleation under pressure and in salt solution. *Trans. Faraday Soc.*, **63**, 3060-3071.
- Fletcher, N. H., 1962: *The Physics of Rain Clouds*. Cambridge University Press, p. 214.
- Gokhale, N. R., 1965: Dependence of freezing temperatures of supercooled water drops on rate of cooling. *J. Atmos. Sci.*, **22**, 212-216.
- , and J. Gould, 1968: Droplet freezing by surface nucleation. *J. Appl. Meteor.*, **7**, 870-874.
- Hobbs, P. V., 1969: Ice multiplication in clouds. *J. Atmos. Sci.*, **26**, 315-318.
- Hoffer, T. E., 1961: A laboratory investigation of droplet freezing. *J. Meteor.*, **18**, 766-778.
- Hosler, C. L., and C. R. Hosler, 1955: An investigation of the freezing of water in capillaries. *Trans. Amer. Geophys. Union*, **36**, 126-132.
- Koenig, L. R., 1963: The glaciating behaviour of small cumulonimbus clouds. *J. Atmos. Sci.*, **20**, 29-47.

- , 1965: Ice-forming processes in relatively warm clouds. *Proc. Intern. Conf. Cloud Physics*, Tokyo, Japan, 242-246.
- Mason, B. J., 1971: *The Physics of Clouds*, 2nd ed. Oxford, Clarendon Press, p. 219.
- Moore, C. B., B. Vonnegut and A. T. Botke, 1958: Results of an experiment to determine initial precedence of organized electrification and precipitation in thunderstorms. *Recent Advances in Atmospheric Electricity*, New York, Pergamon Press, 333-360.
- Mossop, S. C., 1970: Concentrations of ice crystals in clouds. *Bull. Amer. Meteor. Soc.*, **51**, 474-479.
- , A. Ono and E. R. Wishart, 1970: Ice particles in maritime clouds near Tasmania. *Quart. J. Roy. Meteor. Soc.*, **96**, 487-508.
- Murgatroyd, R. J., and M. P. Garrod, 1960: Observations of precipitation elements in cumulus clouds. *Quart. J. Roy. Meteor. Soc.*, **86**, 167-175.
- Naruse, H., and H. Maruyama, 1971: On the hygroscopic nuclei in the cloud droplets. *Papers Meteor. Geophys. Japan*, **22**, No. 1, 1-21.
- Pruppacher, H. R., 1963: Some relations between the supercooling and the structure of aqueous solutions. *J. Chem. Phys.*, **39**, 1586-1594.
- , 1965: The crystallization velocity of ice in pure water and aqueous solutions. *Proc. Intern. Conf. Cloud Physics*, Tokyo, Japan 192-195.
- Ramachandra Murty, A. S., and Bh. V. Ramana Murty, 1971: Freezing of rain water drops at warmer temperatures. *Preprints Intern. Weather Modification Conf.*, Canberra, 6-11 September, Amer. Meteor. Soc., 72-76.
- , and —, 1972a: A new effect of evaporation accelerating ice phase in super-cooled water. *J. Atmos. Sci.*, **29**, 781-784.
- , and —, 1972b: Freezing characteristics of rain water drops with different solutes and their implication on anomalous ice crystal concentrations in clouds. *Tellus*, **24**, 150-160.
- Ruskin, R. E., 1969: Multiplication of ice embryos by ice-whisker shedding. *Science*, **166**, 906.
- Vali, G., and E. J. Stansbury, 1966: Time-dependent characteristics of the heterogeneous nucleation of ice. *Can. J. Phys.*, **44**, 477-502.