Dependence of Freezing Temperature of Supercooled Water Drops on Rate of Cooling

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ABSTRACT

The dependence of the median freezing temperature of supercooled water drops on rate of cooling is studied over a wide range of cooling rates. A polished metal surface, coated with a water repelling film of liquid paraffin is used to support the water drops being frozen. Deeper supercooling is observed with higher cooling rates in the range 0.3 to 5.0 deg C min⁻¹. However, for cooling rates greater than 5.0 C min⁻¹ a reverse trend is indicated and the drops freeze at warmer temperatures.

The importance of this experimental result is discussed in the case of thunderstorm clouds with strong updrafts. A similar effect for sublimation nuclei tested in cold chambers has been noted by Schults (1947) and by Smith and Heffernan (1950).

1. Introduction

Many researches have been directed toward the study of supercooling and the freezing of water drops, as it is of importance in cloud physics to know the temperatures at which airborne water-drops, varying in diameter from a few microns to about 5 mm, will freeze. The freezing temperatures depend upon the drop volume, the rate of cooling, and the presence of foreign particles.

It is only in recent years that the effect of the volume of the sample on its freezing temperature has been studied systematically. Levine (1950) in discussing the results of Dorsch and Hacker (1950) showed that there was a linear relationship between logarithm of the drop diameter and the mean freezing temperature. Bigg (1953a) confirmed this relationship and interpreting his results in terms of simple probability theory, deduced an equation of the form:

\[ \ln(1-P) = -BV(t^a - 1), \]

where \( P \) is the probability of freezing for a drop of volume \( V \), cm³ maintained at a temperature of \( T(C) \) for \( t \) seconds and \( a \) and \( B \) are constants. \( T = (T_0 - T) \) degrees centigrade, where \( T_0 \) is OC.

However, the effect of rate of cooling has often been ignored or stated to be unimportant; the only exception being the result reported by Bigg (1953a).

Smith-Johannsen (1948) determined the freezing temperatures of small quantities of water in volumes generally less than 1 cc, on a dust free cellulose acetate membrane which was supported on a chilled copper plate. Many freezing runs showed the freezing temperature to be independent of the rate of cooling, over the range employed. Unfortunately the range was not stated in his paper.

Heverly (1949) studied the freezing of drops of water and dilute aqueous solutions. These were supported on a small thermocouple junction or on a waxed paper in a cryostat. The droplets were present either singly or in groups. Spontaneous freezing points were determined for cooling rates, varying from 1 to 20C min⁻¹ and they appeared to be independent of the cooling rate.

A thorough statistical study by Dorsch and Hacker (1950) using large numbers of drops on metal surfaces revealed a much broader distribution of freezing temperatures about the mean. The freezing of 4527 drops with diameters between 8.75 and 1000 µ was studied photomicrographically. The rate of cooling was varied between 6 and 15C min⁻¹. This study did not reveal any effect on freezing temperatures due to changes in rate of cooling. Results obtained with a copper support did not differ essentially from those obtained with a platinum surface.

Bigg (1953a) investigated how the freezing points of water drops were affected by the rate at which they were cooled. The mean freezing point of 164 drops of 1 mm diameter, with a cooling rate of 0.05C min⁻¹, was found to be -21.8C; this was 2.0C above the mean freezing point with a cooling rate of 0.5C min⁻¹, an elevation far too great to be explained by experimental error. Bigg's conclusion was that the cooling rate has a small but real effect on freezing, deeper supercooling being possible with higher cooling rates.

The failure of some of the research workers like Smith-Johannsen (1948), Heverly (1949) and Dorsch and Hacker (1950) to find a dependence of freezing temperature on rate of cooling may be due to one of the following reasons:
i) The variation in the values of cooling rate in some cases may not be sufficient to detect its effect on the freezing temperature. This may be a small effect which was obscured by the scatter in their experimental results.

ii) The freezing process seems to be a random phenomenon and a given sample has only a statistical probability of freezing at a particular temperature. Hence repeated observations on large number of drops are necessary to calculate the median freezing temperature. Insufficient data in some cases did not reveal this effect.

iii) The dependence of freezing temperature on rate of cooling may not be a simple relationship as suggested by Bigg (1953a). On the other hand, it may be more complex in nature.

Hence, a more careful investigation of this relationship is suggested, with observations on a large number of drops and the varying rates of cooling over a much wider range.

2. Theory

The freezing equation (1) may be written in the form

\[ \Delta N/N = BV(e^{\alpha T_s} - 1)\Delta t, \]

(2)

where \( N \) is the number of drops unfrozen at time \( t \) and \( B, V \) and \( \alpha \) have the meanings already stated, and \( T_s = (T_0 - T) \) where \( T_0 = OC \).

When \( e^{\alpha T_s} \gg 1 \), this equation reduces to

\[ \Delta N/N = BV e^{\alpha T_s} \Delta t. \]

(3)

The fractional rate at which drops will freeze at a given supercooling is assumed to be the same whether they have formerly been held there at a constant temperature or have been cooled steadily down to that temperature.

Let the temperature of water drops be reduced at a constant rate, given by

\[ T_s = \alpha t. \]

(4)

Then from Eq. (3), for the condition \( e^{\alpha T_s} \gg 1 \), one may by substituting \( T_s = \alpha t \) and solving, derive

\[ \ln(-\ln N/N_0) = \ln(BV/\alpha) + aT_s. \]

(5)

or

\[ \ln a = Z + aT_m, \]

(6)

where \( Z \) is a constant and is equal to \( \ln(BV/\alpha) - \ln(\ln(N_0/N)) \) and \( T_m \) is the median freezing temperature when \( N/N_0 = \frac{1}{2} \).

Thus, if \( \ln a \) is plotted against \( T_m \), the median freezing temperature, one should expect a linear relationship from Eq. (6). The slope of this line is the value of \( \alpha^2 \), one of the constants in Eq. (1).

3. Experimental technique

A polished brass plate which is three inches in diameter and 0.37 inch thick, is cooled from a much larger copper reservoir, surrounded by dry ice in a Dewar flask as shown in Fig. 1. The thermal conduction is through a copper stem and a copper plate, firmly attached to it. The temperature of the top surface of the brass plate was uniform. The rate of cooling can be adjusted by inserting suitable thermal resistors such as a piece of thin cardboard or plastic material between the two plates. The cooling rate is fairly constant over the temperature range necessary to freeze twenty drops placed on the brass plate.

The use of a polished metal surface, coated by a water repellent film of liquid paraffin, to support the water drops being frozen, is similar to the procedure described by Brewer and Palmer (1951). These authors established that the freezing temperatures of drops under these conditions were not dependent on the supporting surface.

The method of suspending the drops between two immiscible liquids is not suitable for this study, especially for observations with high cooling rates.

Twenty water drops from a sample of laboratory distilled water were arranged on the water repellent surface of the brass plate. Each drop had a volume 0.01 cm\(^3\) and so was equivalent to a sphere of diameter 0.27 cm. Adequate precaution was taken to minimize convection currents around the plate by the use of a glass cover over the drops and the plate. Nucleation of a water drop from its neighbours was avoided by placing them far apart from each other. No dependence of freezing temperature on drop position could be detected.

The instantaneous temperature of the top surface of the brass plate was recorded as a function of time.
by a thermocouple. It was firmly attached to the surface by a small screw, and thus was making a good contact, approximately a quarter of an inch from the edge of the plate, as shown in Fig. 1. The thermocouple was made out of AWG 28 size copper-constantan wires. An automatic null-balance indicator in which balance is accomplished through the use of an electronic amplifier was used to read the temperature and the accuracy of this indicator was 0.5°C. Thus, the temperatures, at which the first, tenth and twentieth drop froze, were noted. The investigation reported herein includes data on the freezing temperatures of 2560 water drops. The cooling rate was calculated for each set of observations and it was ascertained to be constant over the temperature range in question.

A separate experiment was performed to obtain the time-lag constant of the thermocouple. The method used was similar to the one described by Middleton and Spilhaus (1953). The thermocouple was detached from the brass plate and was held at a constant temperature. It was then inserted in a bath when the difference in temperature between them was about 4°C and the time behavior of the reading of the thermocouple was observed. The time-lag constant thus determined was 0.9

### Table 1. Rate of cooling and the correction for $T_m$.

<table>
<thead>
<tr>
<th>Rate of cooling (deg C/min)</th>
<th>Correction (to be added) deg C for $T_m$</th>
<th>Mean deviation in $T_m$ deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>+0.01</td>
<td>0.5</td>
</tr>
<tr>
<td>5.0</td>
<td>+0.07</td>
<td>0.5</td>
</tr>
<tr>
<td>20.0</td>
<td>+0.30</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**DISTILLED WATER**

*Drop Diameter = 2.7mm*

![Sample 1](image1)

![Sample 2](image2)

**Fig. 2.** Plots of freezing temperatures of supercooled water drops of distilled water versus rate of cooling for the first, tenth and twentieth drop. Each point plotted is the mean value of eight similar observations. Fig. 2a (left) is for sample 1 and Fig. 1b (right) is for sample 2 of distilled water.
second. The corrections necessary for the observed values of $T_m$ on this account are presented in Table 1.

Thus the correction due to the lag of thermocouple, even at very high cooling rate is small as compared to the mean deviation in $T_m$. However, the values of $T_m$ reported in this paper are corrected for this small time-lag of the thermocouple.

The median freezing temperature ($T_m$) is the temperature at which the tenth drop freezes, the total number being twenty. The procedure was repeated to get eight such observations for the same cooling rate, and the mean value of freezing temperature was calculated from these observations. This was accepted as the value of $T_m$ for that particular cooling rate. Thus each value of $T_m$ is obtained from the freezing of 160 water drops. With this procedure it was possible to reproduce the results.

Cooling rate was varied between 0.3°C min$^{-1}$ and 22.0°C min$^{-1}$ and corresponding values of $T_m$, determined. The observed mean deviation in $T_m$, is 0.5°C for low cooling rates. For cooling rate 20.0°C min$^{-1}$, it was 1.3°C. This may perhaps be due to observational error because of very high cooling rate.

4. Experimental results

Fig. 2a includes three curves showing variation of freezing temperature with cooling rate. Curves 1, 2 and 3 are for the freezing temperatures of the first, tenth and twentieth drop, respectively. Each point plotted in this figure represents the mean value of temperature from eight similar observations. All curves indicate that the freezing temperature decreases as the cooling rate increases up to a certain value. However, for cooling rates higher than 6°C min$^{-1}$, the freezing temperature increases, indicating a reverse trend. Similar observations were taken on a different sample of distilled water referred to as sample 2. The results are plotted in Fig. 2b, which confirm the trend in earlier observations.

From Eq. (6), one expects a linear relationship, if $\ln \alpha$ is plotted against $T_m$, the median freezing temperature. Such plots are shown in Fig. 3, for sample 1 and sample 2. A linear relationship is obtained in both cases for the cooling rates varying from 0.3 to 5.0°C min$^{-1}$, indicating that deeper supercooling is possible for higher cooling rates. An increase in the rate of cooling by a factor of 10, increases $T_m$ by 1.9°C, in one case and 2.4°C in the other. The slopes of these lines give the values of $\alpha'$ as 1.2 deg$^{-1}$ and 0.9 deg$^{-1}$.

Dorsch and Hacker (1950) and Bigg (1953a) studied the freezing of supercooled water drops of widely different volumes and established the freezing temperature dependence upon volume. The values of $\alpha'$ calculated from their results are 1.25 deg$^{-1}$ and 1.0 deg$^{-1}$, respectively. These values compare very well with those obtained in the present study.

However, as the cooling rate is increased and is greater than 5°C min$^{-1}$, a reverse trend is noted. The median freezing temperature ($T_m$) now decreases, a result one would not expect from Eq. (6) or from Eq. (1). This trend is further confirmed by observations on sample 2 of distilled water. This curve is displaced towards colder temperatures, indicating purer sample.

The present investigation is concerned with heterogeneous nucleation as the water samples used, certainly contained foreign particles. It is interesting to compare these results on freezing nuclei imbedded in drops of laboratory distilled water with the experimental results of Schulz (1947) and Smith and Heffernan (1954) on the behavior of sublimation nuclei, in cold chambers.

5. The behavior of sublimation nuclei

a. Natural sublimation nuclei. Schulz (1947) expanded air initially at 10 atmospheres to one atmosphere and thereby obtained equivalent vertical speeds of 5 to 100 m sec$^{-1}$. The volume of the chamber was 0.65 m$^3$. With different rates of cooling, he determined the highest temperature at which 'type 1' nuclei became
active. The vertical speeds can be changed to the appropriate cooling rates, assuming the wet adiabatic lapse rate as 6.5C km\(^{-1}\).

At lower speeds of 5 to 30 m sec\(^{-1}\), the temperature at which 'type 1' nuclei became active decreased with increasing cooling rates. But at higher speeds, a reverse trend was shown; the threshold temperature now became higher during more rapid expansions.

Thus, the effect of changing the rate of cooling is similar in two cases. Further, in Schulz's experiment, both mechanisms, sublimation and freezing, may have been responsible for the formation of ice-crystals. It is possible that a very thin film of water condensed on a nucleating particle which may be sufficient for this purpose, so that no macroscopic droplet was formed.

b. Artificial sublimation nuclei. Smith and Heffernan (1954) in a controlled-cooling chamber, carried out tests to determine the effect of rate of cooling on the estimated crystal concentration at various temperatures. A smoke sample of AgI was introduced into the observation chamber as artificial nuclei and cooled at steady rates of 5C min\(^{-1}\) and 1.25C min\(^{-1}\). The observations were repeated several times to plot the mean values. The concentration of ice crystals at a particular temperature was always higher for cooling rate 5C min\(^{-1}\) than for 1.25C min\(^{-1}\).

6. Summary and conclusions

The present study shows that the freezing temperatures of water drops are affected by the rate at which they are cooled. Further, one very interesting and significant observation is, that deeper supercooling with the increase in cooling rate as expected from Eq. (1) is indicated only up to a rate of about 5C min\(^{-1}\). A reverse trend is shown for the cooling rates higher than this value. Thus the Eq. (1) for freezing of water drops derived from statistical considerations seems to be true only for cooling rates less than 5C min\(^{-1}\), indicating the need for further investigations.

Because there is a maximum for \(T_m\) indicated by the curve of \(\ln \alpha\) against \(T_m\), two different values of cooling rate indicate the same value for \(T_m\); e.g., from Fig. 3 (sample 1) both the rates, 2C min\(^{-1}\) and 12C min\(^{-1}\) give one value of \(T_m\), namely 14.6C. This may be one explanation why some of the earlier workers could not detect the dependence of freezing temperature on rate of cooling.

Vertical velocities of about 20 m sec\(^{-1}\) have been measured in cumulonimbus clouds. Extreme updraft speeds in thunderstorms with large hailstones, may be of the order of 30 m sec\(^{-1}\). Moreover, radar observations show that updraft speeds in the upper levels of such extreme thunderstorms could be as high as 50 m sec\(^{-1}\). On the basis of saturated adiabatic cooling, this updraft would correspond to a cooling rate of about 19.5C min\(^{-1}\). Thus the cooling rates employed in this study bracket those to which a cloud droplet may be subjected in nature.

From this study, it appears, that in a cumulonimbus cloud, updrafts resulting in vertical velocities greater than 13 m sec\(^{-1}\), equivalent to a cooling rate of about 5C min\(^{-1}\), help the ice-crystal process by freezing the drops at warmer temperatures. Thus these results point to a new effect of the variations in the speed of strong updrafts in a thundercloud.

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REFERENCES