

Freezing Rate Due to Heterogeneous Nucleation

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(Manuscript received 23 March 1993, in final form 18 November 1993)

ABSTRACT

The heterogeneous nucleation of ice from supercooled water is influenced by the nature of the foreign nuclei that serve as the sites for ice embryo formation, and by the stochastic nature of the process of embryo growth to critical size. The relative roles of these two factors have been the subject of some debate, especially as they influence the way nucleation of ice is modeled in clouds. "Freezing rate" is defined as the time-dependent rate at which a population of macroscopically identical samples (e.g., drops in a volume of air) freeze due to the nuclei contained in them. Freezing rate is the combined result of nucleus content and of time dependence. The time-dependent freezing rate model (TDFR) is consistent with available empirical evidence. For droplets cooled at rates of the order of -1°C per min, the nucleus content, or nucleus spectrum, predicts the freezing rate with reasonable accuracy. For samples exposed to a fixed temperature, the time dependence of the freezing rate becomes important, but the probability of freezing is not the same for each individual of the sample population. Stochastic models are not supported by the results. Application of the TDFR model and use of measured freezing nucleus data for precipitation provide a basis for the description of ice formation via immersion-freezing nucleation in cloud models. Limitations to full development of these models arise from inadequate knowledge about the freezing nucleus content of cloud water as a function of cloud evolution.

1. Introduction

The nucleation of ice from supersaturated vapor or from supercooled liquid water is of practical interest in a wide range of contexts—the formation of ice in clouds, artificial cloud seeding, the initiation of frost on plants, the cryobiology of cells, the winter survival of insects, and others. It also poses particularly difficult challenges to both experimental and theoretical examinations of the phenomena. While progress in studies of ice nucleation in clouds has been hardly perceptible over the last 15 years or so, vigorous advances are being made in relation to biological systems.

The lack of reliable theoretical descriptions of heterogeneous nucleation (involving foreign catalysts) leaves such questions as the requirements for effective nuclei, the dependence of nucleation on temperature and on time, the effects of solutes, electric charges, etc., almost completely in the realm of empirical studies. Therefore, the interpretation of experiments in the most general terms possible becomes especially important. This paper addresses such a question of interpretation: the relative importance of time and temperature in the heterogeneous nucleation of ice in liquid water.

The interpretation of heterogeneous ice nucleation experiments proposed by Vali and Stansbury (1966;

VS66 hereafter) is reinforced with additional experimental evidence. Specifically, results are presented from experiments with different temperature versus time profiles. In addition to the earlier constant cooling and constant temperature experiments, intervals of temperature reversal have been included prior to periods at constant temperatures. These experiments provide further support for the VS66 model. The term "freezing rate" is introduced to describe the experimental results. It is defined for a population of identical units drawn from a parent sample, and is described in terms of the nucleation rates of individual nuclei and the numbers of nuclei of different activities. The resulting time-dependent freezing rate (TDFR) model is shown to be consistent with the empirical data here described, and it offers an alternative explanation for the results of Vonnegut and Baldwin (1984).

The TDFR model and previously published data on the nucleus content of precipitation are used to estimate the contribution of immersion-freezing nuclei to ice formation in clouds.

2. Background

The basic theory for heterogeneous nucleation¹ on a uniform and permanent surface is an extension of the

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¹ See, for example, Hobbs (1974), Pruppacher and Klett (1978), and Götz et al. (1991).

description of homogeneous nucleation. The kinetics is fundamentally the same in both cases, being dominated by the attachment and detachment of molecules to the embryo. The resulting fluctuations in embryo size in turn determine the probability per unit time that the critical size for stability is reached, that is, that nucleation occurs. A considerable body of evidence points to the role of surface irregularities as preferred sites of embryo formation, and hence of nucleation, but it proved very difficult to analyze these phenomena either empirically or theoretically. Observations did show that nucleation on surfaces can be influenced by dislocations, grain boundaries, adsorbed molecules, irradiation, and many other factors. However, in most cases, the phenomena could be described only in terms of changes in the "onset" of nucleation (i.e., when the ice formation became appreciable under the particular conditions of the experiment). There is little known about how to model the relevant surface characteristics. One attempt was the modeling of nucleation sites as reentrant cavities (Fletcher 1969), but this formulation could not be related to observations in more than a very general sense. An *a priori* derivation of a temperature-dependent nucleation rate as a function of surface characteristics cannot be attempted on the basis of current knowledge.

Empirical determinations of nucleation probability face the problem that the sample has to be brought to some supercooling or supersaturation from the thermodynamically stable phase, so that the test value of supercooling or supersaturation is, unavoidably, time dependent to some degree. It is therefore necessary to deal with both the time dependence of nucleation probability and its dependence on supercooling or supersaturation. For experiments at constant temperatures, the transient effect of cooling to the test temperature is either neglected or a correction is attempted. In experiments with steady cooling, the separation of time and temperature effects is approached by varying the rate of cooling.

An additional problem for nucleation experiments with materials such as water, whose velocity of crystallization is fast, is that a single nucleation event leads to the solidification of the entire sample before any other events can be observed. The most effective approach to circumventing this problem is to break the sample into many small units. With such an arrangement each nucleation event leads to the solidification of just one unit, and if all the units can be considered representative of the original sample, observations of many events can be combined for the characterization of the sample. Because of this, essentially all studies of the nucleation of ice from supercooled water have been carried out with the samples divided into numerous small units such as drops (suspended in a gas or liquid, or supported on a solid surface), or volumes held in solid containers (test tubes, etc.).

a. Nucleation rate

The measure of nucleation activity is the probability per unit time that a critical size embryo forms (a nucleation event occurs) under given circumstances. Nucleation theory seeks to derive that probability from the energy of the embryo and from the kinetics of molecular attachments. The probability of nucleation per unit volume of sample, or per unit surface of nucleating material, is commonly defined as the rate of nucleation, J . Empirically, for pure water (i.e., homogeneous nucleation) the nucleation rate is given by the fraction of sample units freezing per time interval. For a constant temperature T (in °C), if $N(t)$ is the number of unfrozen sample units, each of volume V , and $\delta N(t)$ is the number observed to freeze between t and $(t + \delta t)$, then $J(T)$ is given by

$$J(T) = - \frac{1}{V} \frac{1}{N(t)} \frac{\delta N(t)}{\delta t} \quad (1)$$

corresponding to first-order kinetics. The negative sign is needed to allow for the fact that δN is negative (a decrease in the number of unfrozen units). According to the definition, $J(T)$ should be independent of time until $N(t)$ approaches zero, but, as mentioned, Eq. (1) can be applied only after transient effects, associated with bringing the sample to T , have decayed.

For steady cooling, the expression is modified to

$$J(T) = - \frac{1}{V} \frac{r(T)}{N(T)} \frac{\delta N(T)}{\delta T}, \quad (2)$$

where the $r(T)$ is the rate of cooling at T (δT and $r(T)$ are negative). Equation (2) is only approximate, as it assumes that cooling is slow in comparison to the rate of increase in magnitude of $J(T)$ with decreasing temperatures, and thereby $J(T - \delta T)$ is negligible compared to $J(T)$. For homogeneous freezing nucleation this assumption is reasonably good, since $J(T)$ increases by an order of magnitude for about each 0.7°C lowering of temperature.

b. Freezing rate

For heterogeneous freezing nucleation (due to particles suspended in the water), Eqs. (1) and (2) cannot be applied, as, in general, the sample units cannot be considered identical even though they originate from the same sample of water. Nuclei of different types (to be defined in more precise manner later) are distributed among the units in a random fashion. Since the relative proportions of nuclei of different types is not known *a priori*, and since the nucleation rate for each type has a different value at every temperature, the meaning of observations of $\delta N/\delta t$ is not immediately obvious. To distinguish this situation from that of identical sample units, for which (1) and (2) apply, we introduce the term "freezing rate," R , in place of the lhs of Eq. (1):

$$R(T, t) = - \frac{1}{N(t)} \frac{\delta N(t)}{\delta t}, \quad (3)$$

where R is explicitly indicated to be a function of time also.

To relate R to a nucleation rate, in the sense of time rate of critical embryo formation, it is necessary to first define that rate for a specific nucleus. Following VS66, let that function be $J_c(T)$, with dimension of inverse time, defined as the probability per unit time that nucleation will take place on the particular nucleus at temperature T . Note that this definition of J_c relates to a specific nucleus, or to be more precise, to a specific nucleating site, of dimensions comparable to the size of the critical embryo. Because of that, a large number of different J_c functions are needed to describe a sample that contains a collection of different nuclei. The nucleation rate J derived from (1) for homogeneous nucleation is a property of water substance.

It seems reasonable to assume that the nucleation probability for a given nucleus is a monotonic function of decreasing temperature, so that a temperature T_c can be defined for every nucleus such that $J_c(T_c) = C$, where C is a constant. Since T_c at least partially specifies the nucleating ability of the particular nucleus, it is termed the "characteristic temperature" of that nucleus, or nucleating site. This definition does not necessitate that J_c have the same form (same dependence on temperature) for different values of T_c .

Given the J_c functions for the different nuclei, the additional quantity needed for defining the overall nucleation probability is the number concentration of nuclei of different characteristic temperatures. Let this function be $k(T_c, t)$, with dimensions of $[L^{-3}\theta^{-1}]$. Its meaning can be made clear by noting that $\{k(T_c)\delta V\delta T_c\}$ represents the probability that a volume δV will contain a nucleus whose characteristic temperature is between T_c and $(T_c + \delta T_c)$ and has not yet initiated a nucleation event at time t .

The observed freezing rate, $R(T, t)$, in general is a function of both temperature and time. For $N(T, t)$ still unfrozen sample units at temperature T and time t , the freezing rate can be expressed in terms of $k(T_c, t)$ and the corresponding $J_c(T)$ as

$$\begin{aligned} R(T, t) &\equiv - \frac{1}{N(T, t)} \frac{\delta N(T, t)}{\delta t} \\ &= V \int_{T_h}^0 J_c(T) k(T_c, t) dT_c, \end{aligned} \quad (4)$$

where V is the volume² of each sample unit, and the

integration limits are the melting point (0°C) and the temperature of homogeneous nucleation (T_h). The time-dependent concentration function, $k(T_c, t)$, is given by

$$k(T_c, t) = k(T_c, 0) - \int_0^t J_c(T) k(T_c, t) dt \quad (5)$$

with the integration started at $t = 0$, $T = 0^\circ\text{C}$.

To facilitate the forthcoming discussions, the freezing rate defined in (4) and (5) will be termed the time-dependent freezing rate (TDFR). It is important to maintain the distinction between freezing rate and nucleation rate. The former refers to the observable rate of freezing events in individual volumes that can be considered units of the same sample but differ from one another due to the random allocation of different nuclei among them, while the latter describes the probability per unit time that nucleation will occur on a particular nucleus.

The rhs of (4) expresses the fact that the freezing rate is determined by the prevailing nucleation rate on each nucleus summed over all nuclei in the sample. Furthermore, for evaluating the number of nuclei of type T_c (i.e., with characteristic temperature equal to T_c) only that fraction of the original number, $k(T_c, 0)$, of that type should be counted that has not yet caused nucleation at time t . This gives rise to the time dependence expressed in (5). The solution of (5) depends on the time-temperature history of the sample.

c. Approximations

The two functions $J_c(T)$ and $k(T_c, 0)$ are not known from a priori considerations. Thus, Eqs. (4) and (5) can be related to previously proposed models for the analysis of nucleation experiments only after some simplifying assumptions.

1) STOCHASTIC HYPOTHESIS

If the rhs of (4) is a function of temperature only, and is equally applicable to all sample units, then (4) reduces to the "stochastic hypothesis" formulated by Bigg (1953). The distinction between freezing rate R and nucleation rate J then becomes nearly unimportant, since the probability of freezing of a sample unit is simply the nucleation rate times the volume of the unit.

2 It could be argued that such a uniform probability of freezing should apply if there are so many particles in each sample unit that variations among them become insignificant. However, this would have to hold for nuclei active at any temperature, even close to 0°C , where in practice active nuclei are rare. The assumption is inconsistent with the interpretation that the probability of nucleation increases monotonically with decreasing temperature; Bigg (1953) and others have found exponentially increasing probabilities with decreasing temperature.

² For volumes of finite size, allowance has to be made for the probability that more than one of a given type of nucleus might be found in the sample unit. The treatment for this would be similar to that given by Vali (1971a).

Vonnegut and Baldwin (1984) and Wang and Vonnegut (1984) interpreted their experimental results as support for the stochastic hypothesis. In their experiment, a sample contained in a U-tube was repeatedly brought to the same supercooling, held there until freezing occurred, and then melted (above 0°C). They observed that nucleation took place in times that ranged from a few seconds to many hours. The frequency distribution of delays until nucleation was found to decrease exponentially. The observed variation in the time delay until freezing was equated by Vonnegut and Baldwin with the variation that could be expected for many "nearly identical"³ samples in a single test. Hence, they deduced that the "rate of nucleation," that is, the probability of nucleation per unit time, increased relatively slowly with decreasing temperature (approximately 4 to 10-fold increase for each degree lowering of the test temperature).

Observations with cells in emulsified water droplets led Franks et al. (1983) to conclude that heterogeneous nucleation was taking place and interpreted their results, as did Vonnegut et al., in terms of a nucleation rate that applied uniformly to all droplets.

2) SINGULAR HYPOTHESIS

An alternative simplification of Eqs. (4) and (5) can be reached by assuming that nucleation on a given nucleus takes place at a clearly defined temperature. This assumption was made by Langham and Mason (1958) and by many other investigators; it was termed the "singular hypothesis" in VS66. The assumption can be stated as $J_c = 0$ for $T > T_c$ and $J_c = \infty$ for $T \leq T_c$. Time dependence is then removed from $k(T_c, t)$ because the integrand in (5) is zero for any time t prior to reaching the $T = T_c$. Equation (4) then has meaning only if a rate of change of temperature with time is specified.

Independence of freezing temperatures from the duration of supercooling was concluded by Kornfeld (1916), Tamman and Büchner (1935), and by Dorsey (1948, p. 308). Other studies in which freezing temperatures were noted to be determined by nucleus content, and to be almost independent of the time-temperature history of the sample, were those of Dorsey (1938), Brewer and Palmer (1951), Hosler and Hosler (1955), Carte (1956), Levkov and Genadiev (1966), and Salt (1966).

Specific evidence in favor of the singular hypothesis derives from experiments in which the rate of cooling is varied. It was shown by Carte (1956), Levkov and Genadiev (1966), and VS66 for water droplets, and by Salt (1966) for insect larvae, that the number of freezing events per temperature interval is almost indepen-

dent of the time taken to reach that temperature and of the time taken to traverse it, while the freezing rate R (per unit time interval) varies almost in direct proportion to the rate of cooling. A factor 10 change in rate of cooling corresponds to a shift of approximately 1°C in average freezing temperatures. The singular hypothesis is also supported by experiments at constant temperatures: it is observed that the freezing rate R decays rapidly to near zero, even with large fractions of the sample units still unfrozen. Results of this type were given by VS66 for supercooled water, and by Okamoto and Yamada (1970) for supercooled indium.

With the limitation described above, the time-independent concentration function, or differential nucleus spectrum, $k(T)$, was defined by Vali (1971a) as

$$k(T) = \frac{1}{V} \frac{1}{N(T)} \frac{\delta N}{\delta T}, \quad (6)$$

where the subscript c in $k(T)$ and the indication of time dependence in $N(T)$ have been dropped. As before, the quantity $k(T)$ gives the number of nuclei per unit volume with activity within unit interval of the observation temperature T , but with the singular approximation this means freezing initiated at T , not just having the abstract definition of T_c apply there. If the rate of cooling at T is $r(T)$, the rhs of (6) is equal to $R(T)/[-V \cdot r(T)]$. Equation (6) and its integral form, called the cumulative spectrum, have found application in the characterization of immersion-freezing nuclei in precipitation samples (Vali 1971b, 1978), and in studies of biological ice nuclei (e.g., Schnell and Vali 1972, 1976; Lindow 1982; Rogers et al. 1987; Kieft 1988).

3. Experiments on time dependence

The experiments to be described were designed to shed further light on the temperature and time dependence of freezing nucleation. They extend the experiments described in VS66 by including more complex time variations of temperature. The experiments were carried out in 1964; they are being reported now because they are particularly helpful for evaluating the stochastic and singular hypotheses, and for comparison with the results of Vonnegut and Baldwin (1984).

a. Experimental procedure

Arrays of 36 drops of 0.01 cm³ were placed on a cold plate whose temperature could be controlled according to predetermined time-temperature patterns. The drops were dispensed from a syringe containing 10 cm³ of the water sample; the syringe in turn was filled from a container that held enough water for all experiments of a series. When distilled water from a glass still was used in these experiments, drops of this water froze generally in the temperature range -14° to -22°C. Drops were placed on an oil-coated aluminum foil on the cold stage. Freezing of the drops was re-

³ The quotation marks indicate phrases that in the cited papers have different definitions from those used in this one.

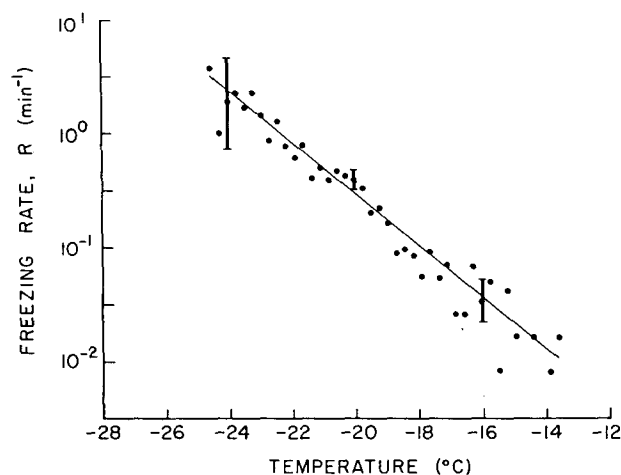


FIG. 1. Freezing rate, R , for a sample of distilled water cooled at $1^{\circ}\text{C min}^{-1}$. The overall sample size was 468 drops. Error bars indicate the calculated statistical uncertainty in selected data points. The line was fitted to the data by weighted least squares.

corded photographically together with a temperature display; for the temperatures of these tests, nucleation in a drop is associated with an abrupt change in opacity, so that nucleation points were quite unambiguous. Further details of the experimental arrangement are given in VS66.

Results will be presented for three different cooling patterns: continuous cooling (at $-1^{\circ}\text{C min}^{-1}$), constant temperature, and overshoot experiments. The constant temperature intervals were of 15-min duration; they were preceded and followed by cooling at the standard rate. The overshoot experiments involved a reversal of cooling at the desired temperature, warming by 0.5° to 1.3°C , maintaining a constant temperature for 10 min, and then resuming cooling. The lowest temperature in all tests was the temperature at which the last drop froze.

Repeatability of the tests was within the errors expected from statistical fluctuations, so the results of 4 to 13 experiments of a given type are combined for analysis. Temperatures were determined with approximately 0.1°C accuracy. Freezing of drops was resolved to 0.125°C .

b. Constant cooling

The results of 13 experiments (468 drops) are combined in Fig. 1 to show the freezing rate R (min^{-1}) as a function of temperature. The freezing rate is seen to be increasing exponentially with decreasing temperature. To quantify this trend, a weighted least-square regression line was calculated for $\log R$ versus T . The weighting factors were inversely proportional to the variances of the data points. The variances were estimated from the standard deviations, $s_{\log R}$, expected on

the basis of Poisson distributions for the observed values of dN and N : $s_{\log R} = 0.434(1/dN + 1/N)^{0.5}$. Since fewer drops contribute to the points at the ends of the temperature range than at its middle, the errors are larger there. This is shown by the error bars in Fig. 1. The correlation coefficient for the exponential trend is 0.97.

The freezing rate was also calculated for the cooling portions of the constant temperature and overshoot experiments. Data from the first minute after resumption of cooling were omitted; justification of this will be given with the results of the constant temperature and overshoot experiments. Regression lines were calculated in the manner described above for each experiment and for each group of experiments. These results are listed in Table 1 in terms of the constants a and b of corresponding exponential functions $R = a \exp(bT)$.

Regression lines for the different groups match fairly closely; the maximum discrepancy is a factor of 1.4 in R at the cold end of the temperature range, typical variation is a factor 1.2. Averages for the groups were obtained after weighting according to the number of drops used in each experiment. It may be noted that the spread in values for the constant a is much larger than the differences in R within the actual temperature range of the experiments.

c. Constant temperature intervals

Four sets of such experiments were carried out: one set at $T = -16^{\circ}\text{C}$ with 144 drops, two sets at different times at $T = -18.7^{\circ}\text{C}$ each with 144 drops, and one set at $T = -21.3^{\circ}\text{C}$ with 288 drops. The results for one of the -18.7°C sets is shown in Fig. 2. The upper panel shows temperature as a function of time, the middle panel the fraction of drops frozen, and the bottom panel the freezing rate. As soon as cooling was stopped the freezing rate

TABLE 1. Freezing rates observed in the experiments.

Experiment	Type*	N_0 **	a	b
1	CC	468	7.6×10^{-6}	-0.52
2	CT— 16°C	144	8.9×10^{-7}	-0.64
3	CT— 18.7°C	288	8.1×10^{-6}	-0.55
4	CT— 21.3°C	288	3.2×10^{-5}	-0.46
	avg. CT	720	6.5×10^{-6}	-0.56
5	OS— $18.7/0.5^{\circ}\text{C}$	288	1.7×10^{-6}	-0.60
6	OS— $18.7/1.3^{\circ}\text{C}$	360	1.9×10^{-5}	-0.48
7	OS— $20/0.5^{\circ}\text{C}$	144	2.0×10^{-5}	-0.49
8	OS— $20/1.3^{\circ}\text{C}$	180	4.2×10^{-7}	-0.67
	avg. OS	972	5.1×10^{-6}	-0.55
Overall average		2160	4.4×10^{-6}	-0.56

* CC: continuous cooling; CT: constant temperature at indicated T ; OS: $T/\Delta T$: overshoot of temperature T by ΔT .

** N_0 : number of drops.

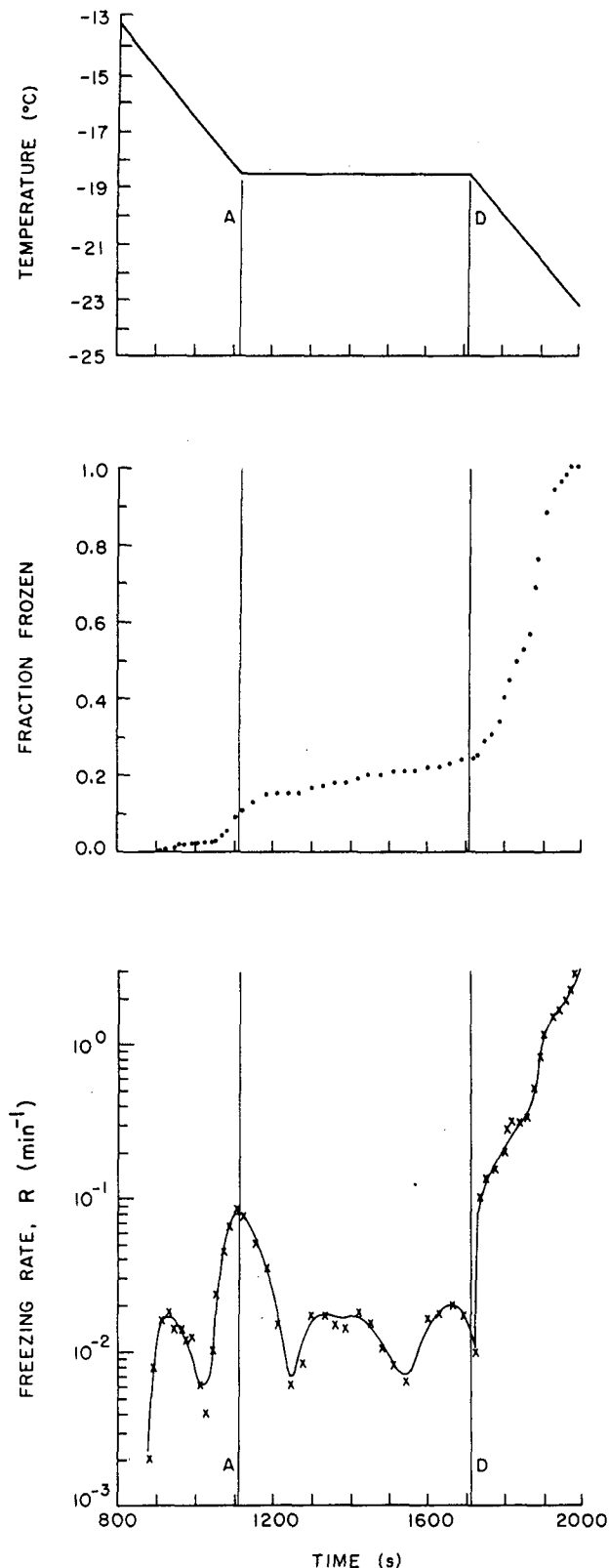


FIG. 2. Freezing rate (lower panel) and the fraction of drops frozen (middle panel) for an experiment with a constant temperature period A–D at $T = -18.7^\circ\text{C}$ (upper panel). Sample size $N = 144$.

started to diminish, and very soon after cooling was resumed it rose sharply. This pattern agrees with that reported in VS66 for a different set of experiments.

To examine the pattern of decrease in freezing rate during the periods of constant temperature, data from all four sets of experiments were combined. While the actual rates differed, depending on temperature, the time trends were found similar, as were the ratios of the observed freezing rates to the freezing rate with constant cooling at the same temperature. This ratio of freezing rates is shown in Fig. 3, demonstrating a reduction in freezing rate to 46% during the first 30 s, to about 10% of initial values by 300 s, and an average of about 3% for the period beyond that. As can be seen from the data in the middle panel of Fig. 2, these reductions in freezing rates are observed in spite of having large fractions of the drops still unfrozen (about 80% for the example in Fig. 2, 30% for the experiments with $T = -21.3^\circ\text{C}$, and 97% for $T = -16^\circ\text{C}$).

When cooling is resumed, the freezing rate quickly recovers. This is clearly seen in the example of Fig. 2, and is further illustrated with data from all constant temperature experiments combined. The freezing rate is shown in Fig. 4 for the first 3°C cooling following the constant temperature period, as a ratio to the freezing rate observed with continuous cooling at the same temperature. The freezing rate is seen to recover to values near those expected within about 1°C of cooling.

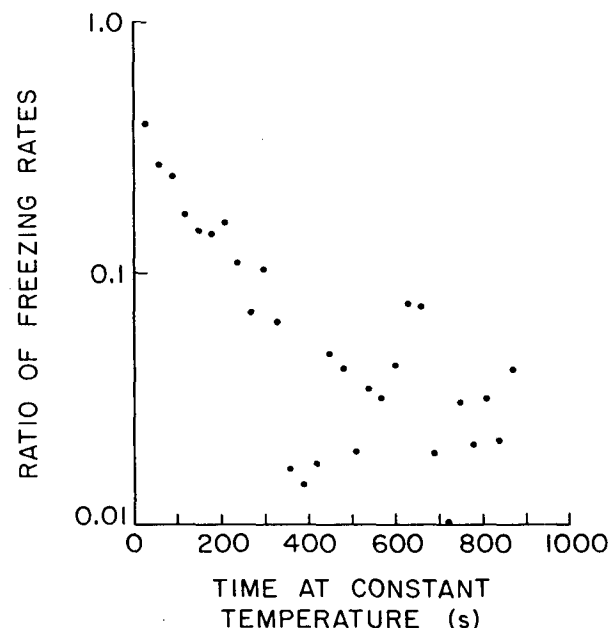


FIG. 3. Combined result from several groups of experiments with periods of constant temperature. The observed freezing rate is given as a ratio to the freezing rate observed during cooling at the same temperature. The time $t = 0$ is the beginning of the constant temperature period.

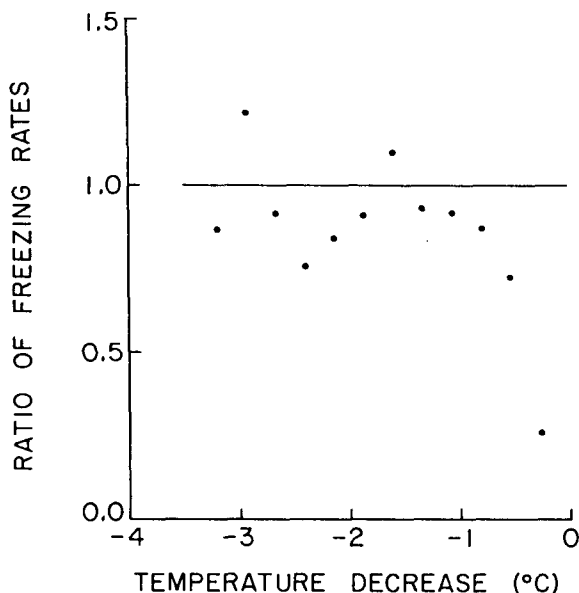


FIG. 4. Similar to Fig. 3 except for the period immediately after resumption of cooling. Temperature decrease is from the right to left, beyond the temperature that was held constant. The ratio of freezing rates is to the rate observed at the same temperatures during cooling.

d. Temperature overshoots

Four sets of experiments of this kind were performed, with two different steady temperatures (-18.7° and -20°C), preceded by two different degrees of temperature overshoots (0.5° and 1.3°C). Results are shown in Figs. 5 to 8.

Similarly to the constant temperature experiments, as soon as cooling is replaced by warming the freezing rate diminishes. The decrease is even more abrupt than when the cooling is simply stopped. The average value of the freezing rate over the first 30 s is 3% of the rate observed with continuous cooling at the same temperature. Over the remaining period, with the temperature held constant, the freezing rate changed little, as shown in Fig. 9. No systematic differences could be detected between runs with smaller or larger degrees of temperature overshoot, mostly because of small sample sizes.

The large decreases in freezing rates occurred in spite of having large fractions of the drops still unfrozen, as shown by the middle panels in Figs. 5 to 8. Thus, the decreases in rates must be accounted for on the basis that previous nucleation events, during cooling, depleted the numbers of nuclei active near the temperature held constant. In terms of the TDFR model this depletion is expressed by the negative term in the rhs of Eq. (5). As these experiments show, the time available during cooling at 1°C per minute is sufficient to produce a reduction of $k(T_c, t)$ to near zero.

When cooling was resumed, the freezing rates increased rapidly. Past point D (see Figs. 5 to 8), that is,

the lowest temperature reached before warming, the rate of freezing was comparable to that observed in experiments without interruption of the cooling. This fact is demonstrated in Fig. 10, where observed values of R are plotted for the various experiments, with the segments A–D removed. Vertical lines indicate where those segments were. Curve a in Fig. 10 is for the experiments with constant cooling and the broken lines are repetitions of the regression line to those data. Data for the -18.7°C constant temperature experiment (from Fig. 2) are shown in panel b, and data for the overshoot experiments are shown as c, d, e, and f. It is seen that freezing rates subsequent to the periods of constant temperature were altered little by the introduction of those periods.

4. Summary of experimental results

The experiments clearly demonstrate that the rate of freezing of units (drops) drawn from a sample is both temperature dependent and time dependent. Specifically:

(i) The rate of nucleation increases steadily if the sample is cooled at a constant rate (cf. Fig. 1). For a cooling rate of $-1^{\circ}\text{C min}^{-1}$, the rate R (min^{-1}) can be described as

$$R(T) = \bar{a} \exp[-\bar{b}T], \quad (7)$$

where $\bar{a} = 4.37 \times 10^{-6} \text{ min}^{-1}$ and $\bar{b} = 0.564$, the average values for the eight sets of experiments listed in Table 1. It should be emphasized that (7) is valid only for the particular sample used and for the specified cooling rate; wide variations from the exponential temperature dependence are found for precipitation samples (cf. section 6) and for samples with artificial nuclei.

(ii) In terms of the singular approximation, using (6), the freezing rate given in (7) can be stated as the result of cooling at the rate $r = -1^{\circ}\text{C min}^{-1}$ sample units of volume V and with nucleus content given by

$$k(T) = -\frac{\bar{a}}{rV} \exp(-\bar{b}T). \quad (8)$$

In (8), the units of $k(T)$ are $[\text{cm}^{-3} \text{ } ^{\circ}\text{C}^{-1}]$. The expression represents the differential spectrum (cf. Vali 1971a), that is, the concentration of nuclei per unit volume with characteristic temperatures within a degree of T .

(iii) When temperature is held constant, ending cooling to that temperature, the rate of nucleation decreases abruptly (Fig. 3). For the distilled water sample, freezing rate in the first 30 s was 46% of the rate during cooling at the same temperature, and after 2 min the rate was less than 20%. The decrease in freezing rate was roughly exponential, with a time constant of 4.3 min. From the limited data available, the time con-

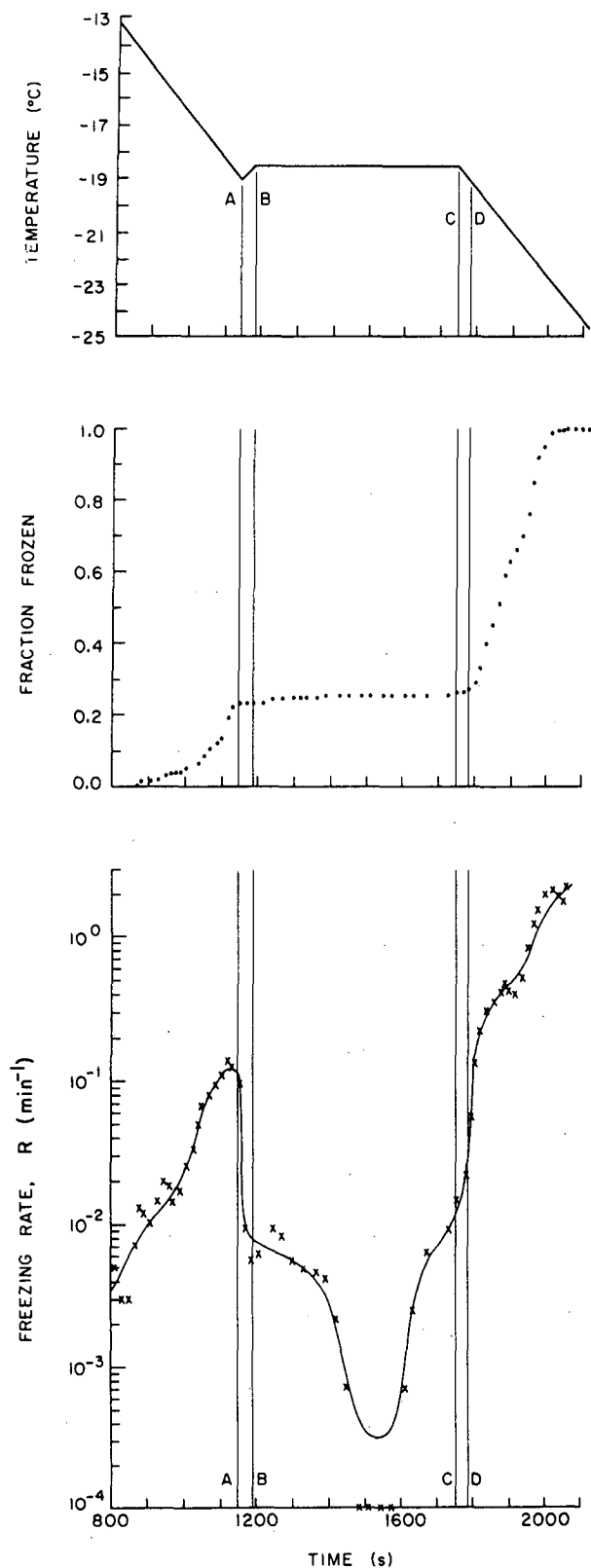


FIG. 5. Similar to Fig. 2 but with a 0.5°C overshoot (A-B) preceding the constant temperature period (B-C) at $T = -18.7^\circ\text{C}$. Cooling at the standard rate is resumed at C. Sample size $N = 288$.

stant of this relationship does not appear to be dependent on temperature.

(iv) If cooling is reversed, and the sample is warmed at 1°C min^{-1} , the nucleation rate drops immediately (first 30 s) to about 3% of the value it had before the cooling was reversed (Fig. 9).

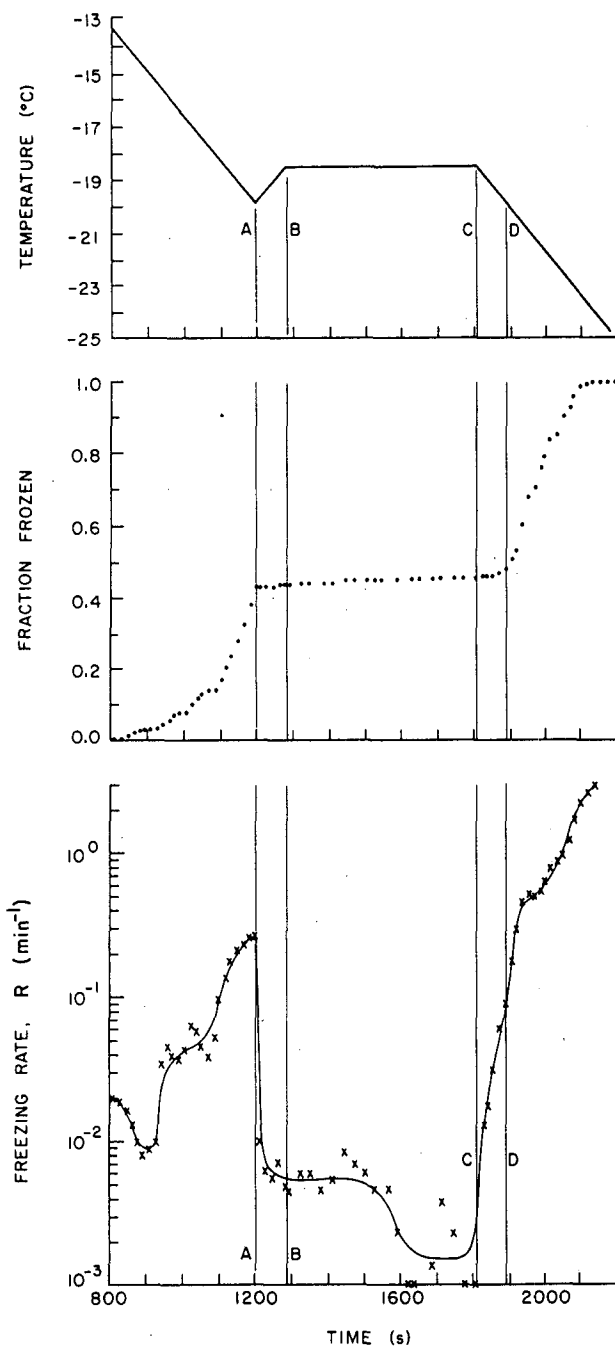


FIG. 6. Same as Fig. 5 but with an overshoot (A-B) of 1.3°C prior to the constant temperature interval (B-C) at $T = -18.7^\circ\text{C}$. Sample size $N = 360$.

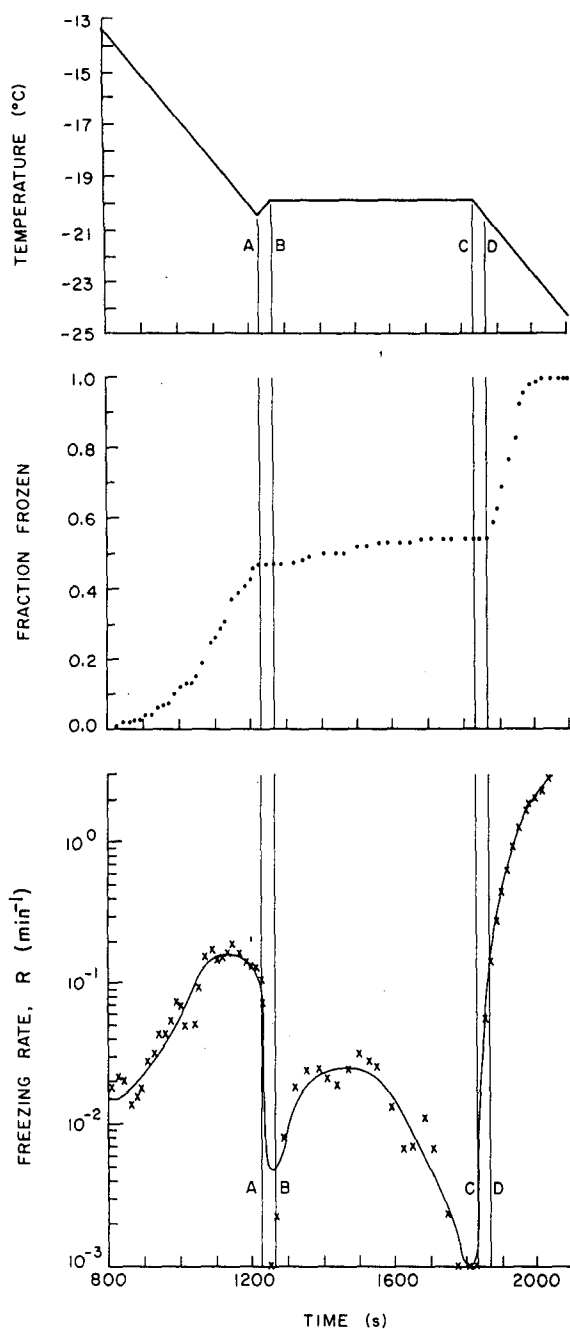


FIG. 7. Results for experiments with a 0.5°C overshoot (A–B) preceding the constant temperature period (B–C) at $T = -20^\circ\text{C}$. Sample size $N = 144$.

(v) After about 5 min at a constant temperature, or after warming by 0.5° to 1°C , and extending to about 15 min, the freezing rate is 2%–4% of the rate with steady cooling at the corresponding temperature (Figs. 3 and 9). No observations are available for times in excess of 15 min.

(vi) Following periods at constant temperatures (with or without overshoots), when cooling is resumed, the nucleation rate assumes the same values as those observed with continuous cooling for the same temperatures, except over the first 1°C interval (Fig. 4).

(vii) The results here stated were obtained with distilled water containing freezing nuclei of unknown

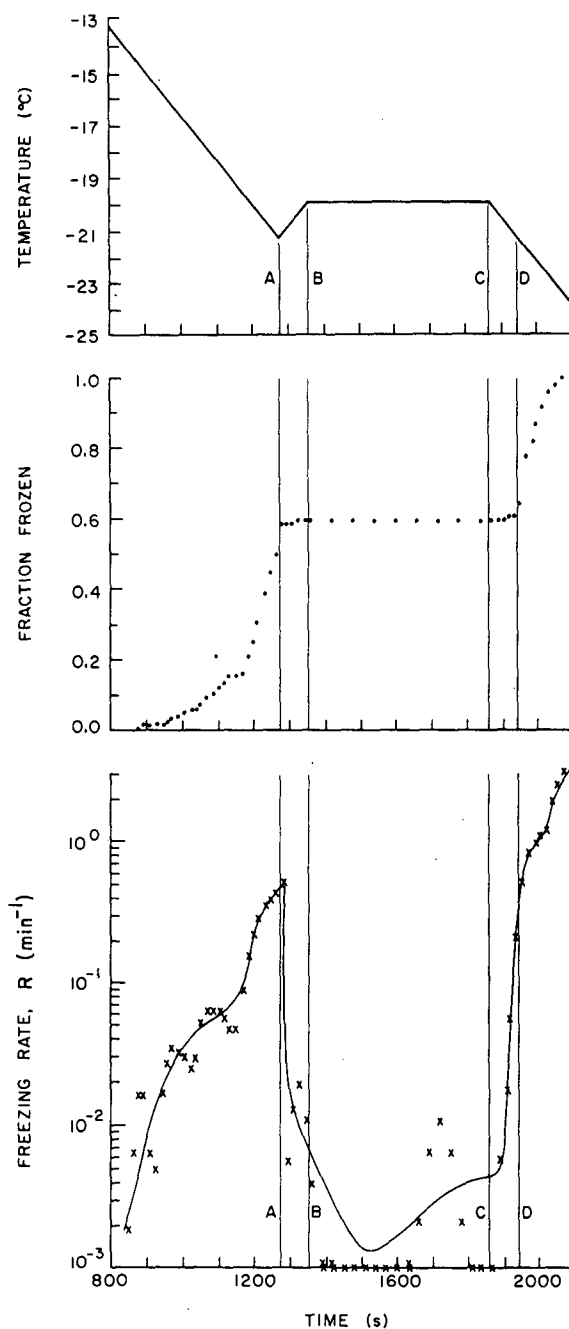


FIG. 8. Results for an overshoot (A–B) of 1.3°C preceding the constant temperature period (B–C) at $T = -20^\circ\text{C}$. Sample size $N = 180$.

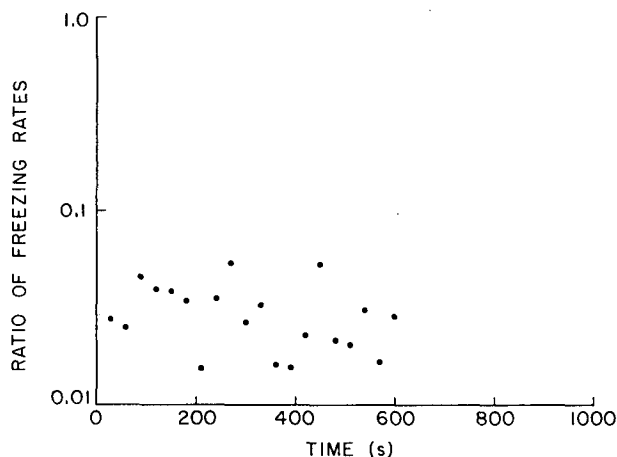


FIG. 9. The observed freezing rate over the periods A–C in Figs. 5 to 8, as a ratio of the freezing rate observed during cooling.

composition, and for the temperature range -16° to -21°C . While the results are not expected to be very sensitive to the type of nuclei involved, or to be significantly different at warmer temperatures, further work will be needed to extend the results to those conditions.

5. Discussion

The results presented here support the TDFR model. Perhaps the key observation related to the balance of time dependence and temperature specificity is the

large reduction in freezing rate when cooling is stopped at some temperature, or when the sample is brought there from a slightly lower temperature (points iii, iv, and v above). To take one example, at -18.7°C the 10-min averages of R were found, in two experiments, to be 8% and 10% of the rate observed at the same temperature while cooling. After reaching -18.7°C from 0.5° and 1.3°C lower temperatures, the rate of freezing reduced to 2.9% and 2.6%, respectively, in the two experiments. The point can be also demonstrated by noting that, for the case considered, just 0.1°C of further cooling (over 6 s) would have produced the same number of nucleation events as 3 min of exposure at the constant temperature. In contrast with these findings, according to the stochastic hypothesis the probability of nucleation, and hence the freezing rate, would remain constant at a given temperature.

While these results do not allow the explicit form of J_c to be determined, the results indicate, most clearly perhaps from the experiments with temperature overshoots, that the function J_c rises sharply with decreasing temperatures—one or more orders of magnitude within 1°C . Thus, neglecting time dependence in obtaining $k(T)$ from an experiment with steady cooling, using Eq. (6), is equivalent to about a 1°C uncertainty in temperature. If cooling of a sample is stopped, then the rate of freezing will drop and decrease with time. The total number of nucleation events expected over some time period can be calculated on the basis of the exponential decrease noted in (iii). The expected number of events over a 10-min period is 1.56 times the

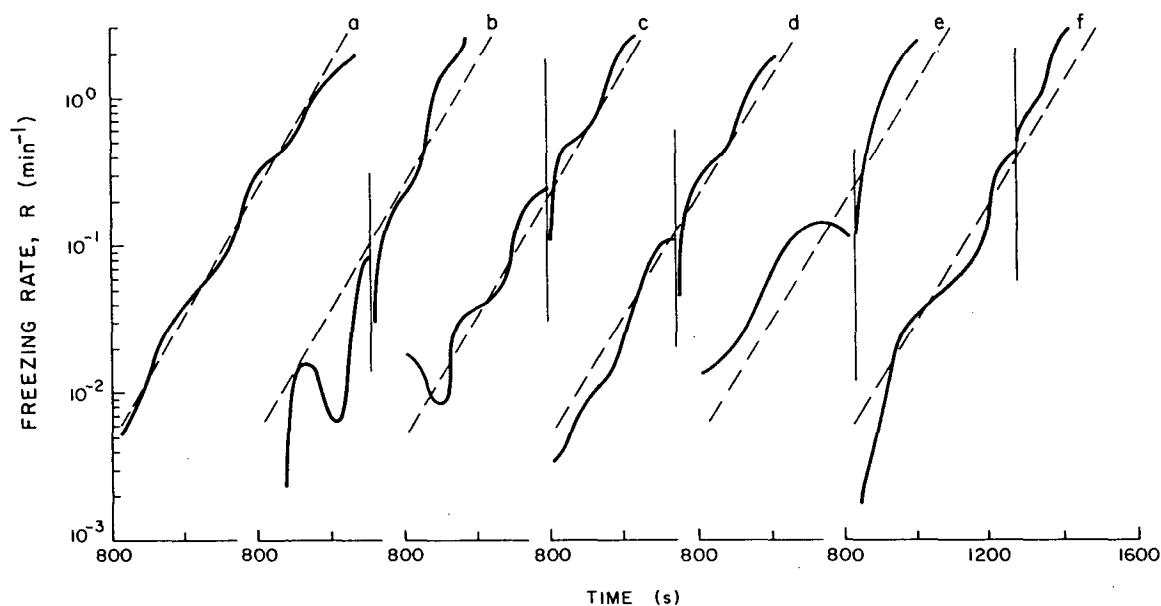


FIG. 10. Comparison of the observed freezing rates for periods of cooling. Data are for experiments with continuous cooling (a), with a constant temperature interval (b), and with temperature overshoot plus constant temperature period (c to f). Vertical lines indicate where the cooling was interrupted; the total duration of the interruptions varied from 12 to 15 min. The sloping dashed line is fitted to the data in (a) and repeated over the other curves for comparison.

freezing rate for continuous cooling at that temperature. By comparing this with (7), it is found that the same number of events would result from cooling from T to $(T - 1.1)^\circ\text{C}$.

a. Comparisons with Vonnegut's results

Vonnegut (1948) presented results on the number of drops freezing as a function of time, and Vonnegut and Baldwin (1984) and Wang and Vonnegut (1984) reported on the variation in time intervals until freezing at constant temperatures. The basic observation of Vonnegut et al. is that a sample might freeze very soon, or only after a considerable interval of time, when repeatedly brought to the same temperature. From this observation the conclusion was drawn that nucleation is a "largely stochastic" process; the results were interpreted in terms of a rate equation analogous to the decay of radioactive nuclei.

The question arises: Can the experiments of Vonnegut et al. be reconciled with the TDFR model? In terms of the description given in section 2b, the observed variations in time intervals until freezing can be viewed as a result of bringing a sample to a temperature slightly warmer than the characteristic temperature of the most effective nucleus contained in the sample. At such a temperature, J_c has a small but non-negligible value, leading to an average time to nucleation of $1/J_c$, or more correctly to a nucleation probability per unit time equal to J_c . A spread in time intervals to nucleation would be expected due to the nature of the nucleation phenomenon, that is, the stochastic character of embryo growth on a particular nucleus, or nucleating site. The expected frequency distribution of times, for repeated trials, would be

$$P(t)\Delta t = (1 - J_c\tau)^m J_c\Delta t, \quad (9)$$

where $t = m\tau$, with τ denoting unit time. This equation expresses the fact that the probability of nucleation in the interval t to $(t + \Delta t)$ is equal to the probability that no nucleation took place in the preceding time interval t , times the probability of nucleation in Δt . Equation (9) leads to an exponentially decreasing likelihood of the sample remaining unfrozen after time t , since

$$e^{-x} = \lim_{n \rightarrow \infty} \left(1 - \frac{x}{n}\right)^n.$$

This is also what Vonnegut and Baldwin (1984) concluded, but for a different reason. They considered the repeated tests with a single sample as equivalent to a single test with a large number of sample units, and argued that the probability of a nucleation event decreased with time due to the reduced number of sample units remaining available, each unit retaining the same likelihood of nucleation. Indeed, the probability of nucleation is constant, but in the situation envisaged here, namely, with a single nucleus being subjected to re-

peated tests, it is the probability of survival that decreases with time, not the number of possible nuclei that might cause a nucleation event.

The experiments of Vonnegut et al. and those described here agree in showing exponentially decreasing frequencies of freezing events with longer times at a constant temperature. For a single sample, that result is explained as above. However, in the experiments described in this paper, large numbers of sample units are observed simultaneously and the sample units are not assumed to be identical. They differ in the chance allocation of nuclei with different sets of T_c values. Therefore, the approximate exponential decrease in freezing rate is less readily explained; it is likely to be a result of a combination of the decreasing probability of survival for any nucleus with appreciable magnitudes of J_c at the test temperature, and the roughly exponential increase in likelihood with ΔT that any particular sample unit contains a nucleus with T_c in the interval T to $T - \Delta T$. It is possible that other than exponential patterns would be found with samples of differing nucleus contents, although the results of Vonnegut et al. were quite similar for distilled water and for a silver iodide suspension.

The two analyses lead to differing predictions regarding the total number of nucleation events expected after long times. The stochastic model of Vonnegut would lead to the freezing of all sample units after sufficiently long times, whereas our model would predict that sample units lacking nuclei with T_c close to the test temperature would have negligible probabilities to freeze. The constant temperature periods in our tests were not sufficiently long to evaluate this, but with further experiments this point can be checked.

The Vonnegut experiments yielded information on the increase in nucleation probability with decreasing temperature. That temperature dependence in fact specifies the J_c function for the particular nucleus of the sample. The rapid rise of nucleation probability with decreasing temperature is in accord with the assumptions described in section 2b about J_c . However, this interpretation critically depends on the assumption of one nucleus only per sample, and the validity of that assumption is in question for the colder test temperatures. The probability of more than one nucleating site with similar characteristic temperatures increases rapidly with decreasing temperatures (roughly factors of 2–10 per $^\circ\text{C}$). A further limitation arises for very short nucleation times (few seconds), since for these cases it is probably incorrect to assume that freezing took place at the test temperature rather than while cooling the sample to that temperature. Baldwin and Vonnegut (1982) give the time to reach the test temperature within the tube as 8 s, yet some of the reported average times to freezing were even shorter.

Because of the abrupt cooling, Vonnegut's experiments cannot show the decrease in nucleation rate when cooling is replaced by a constant temperature.

In summary, the observations of Vonnegut et al. are qualitatively consistent with the prediction of the TDFR model for a sample brought to a temperature close to the critical temperature of the most active nucleus in the sample. Vonnegut's interpretation of the results as deriving from a stochastic phenomenon is also part of the TDFR model, but the TDFR model restricts that description to nucleation on a particular nucleus, and not to a population of identical appearing units drawn from a parent sample. The distinction is important for the modeling of freezing nucleation; application of the stochastic model would lead to significant overprediction of the number of nucleation events for constant or slowly changing temperatures, or where the temperature is raised from a lower to a higher value.

b. The experiments of Ashworth et al. (1985)

Experiments aimed at studying the freezing of plant samples were reported by Ashworth et al. (1985). One of the characteristics examined was the fraction of identical samples or sample units of suspensions frozen as a function of time, at constant temperatures. For a variety of plants, and for a kaolin suspension, they found similar patterns: portions of the samples freezing within a very short time, and much slower increases over the remainder of the 24-h periods of the tests. Lower temperatures for the sample resulted in a higher initial fraction frozen. The rate of freezing beyond the initial rapid freezing appeared to vary little with temperature. These results are similar to those reported in this paper, and appear consistent with the TDFR model.

6. Ice formation in clouds

The results and analyses given here refer to the nucleation of ice on immersion-freezing nuclei (as defined in the article "Nucleation Terminology" 1985), that is, foreign nuclei suspended in water. This nucleation mode is only one of the pathways in which ice is formed in the atmosphere; the relative role of this mode is not well known, and is likely to be variable from situation to situation.

Even though the general problem of determining how many and what kinds of ice nuclei exist in the atmosphere is much more complex, it might be helpful to examine how the immersion-freezing mode might be modeled with some simplifying approximations. Let us assume that the spectrum of immersion freezing nuclei, $k(T)$, is predicted from a detailed model of cloud evolution or is determined empirically from a sample of the cloud water. For full generality, the nucleus content would have to be known as a function of four dimensions, taking into account the transport of the nuclei into the cloud, their sizes, and the likelihood that either condensation or collection transfers the nuclei into cloud droplets. If nucleus content is obtained from an analysis of a cloud water sample, the original dis-

tribution of the nuclei among droplets of different sizes need not be considered for the prediction of the numbers of ice particles, since the number of freezing nuclei is always much smaller than the number of cloud droplets, but it may have some impact on the subsequent evolution of the ice particles.

For cloud volumes undergoing steady cooling, in the range of few tenths to few degrees per minute (from <1 to 10 m s^{-1} updrafts), the experimental results obtained from drop-freezing experiments are directly applicable. The first approximation is to neglect the effect of the cooling rate and predict the number of ice particles as a function of temperature alone. The differential and cumulative nucleus spectra [cf. Eq. (6)], when converted from concentration per cubic centimeter of water to concentration per unit volume of air (via the liquid water content, LWC), provide a direct answer:

$$N_{\text{ice}}(T) = \int_0^T \frac{k(T)}{\rho_w} \text{LWC} dT = \frac{K(T)}{\rho_w} \text{LWC} \quad (11)$$

where $\rho_w = 1 \text{ g cm}^{-3}$ (the density of water), $K(T)$ is the cumulative nucleus spectrum (cf. Vali 1971a), LWC is expressed in $[\text{g m}^{-3}]$; and N_{ice} is in units of $[\text{m}^{-3}]$. Estimation of N_{ice} can be improved by taking into account the rate of cooling. In VS66 a 0.2°C change in mean freezing temperature is reported for each doubling of the cooling rate, while there were no detectable changes in the shapes of the spectra. Using that result, (11) can be modified to

$$N_{\text{ice}}(T) = \int_0^{T-\alpha} \frac{k(T)}{\rho_w} \text{LWC} dT = \frac{K(T-\alpha)}{\rho_w} \text{LWC}, \quad (12)$$

where $\alpha = 0.66 \log_{10}|r|$, $|r|$ is the absolute value of the rate of cooling in $[\text{°C min}^{-1}]$. The cooling rate is readily obtained, in a simple situation, from the updraft velocity and the in-cloud lapse rate. In effect, with Eq. (12) the actual cloud temperature is replaced by one shifted to a somewhat higher value for fast rates of cooling (lower N_{ice}), and toward a lower value (higher N_{ice}) for slow rates of cooling. The adjustment reflects the fact that more time available leads to more nucleation events. The magnitude of the adjustment in Eq. (12) is modest; compared to other uncertainties, specifically in $k(T)$, it is minor, but it is physically sound, and is supported by empirical evidence for the range of cooling rates stated above. Outside that range no data are available, so (12) should be applied with caution, though the trend expressed in (12) is likely to hold. Based on limited data, Levkov and Genadiev (1966) reported even weaker dependence of freezing temperatures on cooling rate than Vali and Stansbury (1966).

In clouds remaining at a constant supercooled temperature over periods of a few minutes to tens of minutes, the number of ice particles due to immersion freezing can be obtained, based on the results stated in point (iii) of section 4, as

$$N_{ice}(t) = N_{ice}(T) \int_0^t 0.46 e^{-0.23t} dt$$

$$= 2N_{ice}(T)(1 - e^{-0.23t}), \quad (13)$$

where $t = 0$ is the beginning of the constant temperature period. This number is to be added to that which formed during cooling:

$$N_{ice}^{total} = N_{ice}(T) + N_{ice}(t). \quad (14)$$

Formula (13) is less reliable than (11) or (12) as the rate of decrease of nucleation events might in fact be a function of the slope of the nucleus spectrum, while the constants used in (13) are derived from experiments with only one sample and for temperatures -16° to -20°C . At warmer temperatures, the slopes of the $k(T)$ spectra are usually quite steep, so application of (13) will probably lead to an underestimate in the number of nucleation events. It may also be noted that the number of additional ice particles that forms while the cloud is at a constant temperature approaches [as $t \rightarrow \infty$ in (13)] about the same magnitude as the number that has formed [according to (11)] while cooling the cloud. The precise proportion that this additional number represents is determined by the slope of the nucleus spectrum.

If the temperature of a cloud is increased, the number of additional freezing nucleation events will drop to near zero, so that the total number of ice particles will remain almost unchanged from what it was before the temperature increase started.

Analyses of the concentrations of immersion freezing nuclei in precipitation samples provide some estimates of $k(T)$ and of $K(T)$, although there are some possible complicating factors due to changes particles might undergo in the water during the evolution from cloud droplets to precipitation on the ground. An adequate description of freezing nucleus concentrations in precipitation is given by the expression

$$K(T) = A \left(\frac{T}{T_0} \right)^B, \quad (15)$$

where T_0 is a suitable reference temperature. The power-law function is used here in order to represent the vanishing of $K(T)$ at $T = 0^\circ\text{C}$ (and to keep the dimension of A independent of the numerical value of B). For summertime rain in Colorado and Alberta, Canada, the data given by Vali (1971b, 1978) can be fit with $T_0 = -10^\circ\text{C}$, $A = (0.5 \text{ to } 50) \text{ m}^{-3}$, and $B = (3.5 \text{ to } 6.5)$. Schnell and Vali (1976) presented evidence that there is a systematic variation of nuclei content in precipitation with climate type; for example, samples from Florida thunderstorms showed much lower nucleus content, better fit with $T_0 = -16^\circ\text{C}$, $A = 0.05$, and $B = 10$.

As can be seen from the values quoted above, the concentrations of immersion-freezing nuclei are low relative to typical values of observed ice particle con-

centrations. For example, with 1 g m^{-3} LWC, and using the integral of (11), N_{ice} for High Plains clouds is 1.1 to 67 m^{-3} at -10°C . It is noteworthy that the immersion-nucleus content of precipitation is far more variable, on local and global scales, than other modes of nucleation, and that nuclei are found on occasion in precipitation even at temperatures as warm as -5°C . The apparent systematic variation of immersion-freezing nucleus concentrations with climatic zone is also of potential significance. It is important to remember that the precipitation data provide only a first estimate for the nucleus content of cloud water.

The potential importance of immersion-freezing nuclei for precipitation initiation was argued by Braham (1986), drawing parallels between the observations in Project Whitetop (Braham 1964), in Florida (Sax et al. 1979), and in Australia (Mossop 1985), recognizing the role played by the freezing of large drops formed by coalescence. Also, secondary ice generation by the Hallett-Mossop process relies on the early development of a few large ice particles, which may be frozen raindrops or graupel.

7. Conclusions

Experimental evidence so far available on the time dependence of heterogeneous freezing nucleation can be given adequate qualitative interpretation in terms of the TDFR model described in section 2b. The model emphasizes the dominant role of foreign particles in immersion-freezing nucleation, but also takes into account the time dependence introduced by the stochastic nature of embryo growth. The major unknown, restricting application of the model at present, is the quantitative description of J_c as a function of temperature for nuclei of different composition and of a wide range of characteristic temperatures. It is clear that the assumption that nucleation on a given site takes place at a well-defined temperature is untenable, but evidence points to a rapid increase in J_c over temperature intervals of about 1°C . Practical manifestations of this finite rate of rise in nucleation rate with decreasing temperature appear in processes where the temperature is changing slowly with time, or is held constant.

The equations described in section 6 provide a first approximation for the prediction of ice formation in clouds by immersion-freezing nuclei. For situations where steady cooling is occurring, the nucleation spectra provide an adequate prediction, and the rate of cooling can be taken into account. For clouds at constant temperatures the number of nucleation events is predicted to diminish rapidly with time and to reach a value approximately double the number that formed during cooling to that temperature. Application of the proposed formulas presupposes knowledge of the freezing-nucleus content of the cloud droplets, yet there are considerable obstacles to obtaining that information from either theory or from direct sampling. Best esti-

mates now available are from determinations of the nucleus content of precipitation samples and of a limited number of cloud water samples.

The formation of ice in clouds being one of the foremost questions of concern in meteorological research, the nucleation processes involved need to be addressed with vigor. The development of instruments for field use, as well as laboratory experiments, could make significant contributions. This paper, dealing with immersion freezing only, is a partial response to that need. While questions remain regarding this process, and those questions are of fundamental importance, further elaboration of those questions is not expected to make a large difference in the precision of predictions for ice formation in clouds.

Acknowledgments. The experiments described in this paper were carried out by John Stevenson. The impulse for this study came from the late Dr. J. S. Marshall and from Dr. E. J. Stansbury. Discussions and correspondence with Dr. B. Vonnegut led to the clarifications of several ideas. Dr. C. A. Knight and three anonymous reviewers are thanked for their suggestions for improvements of the paper.

APPENDIX

$J(T) \text{ s}^{-1} \text{ cm}^{-3}$	nucleation rate per unit volume
$J_c(T) \text{ s}^{-1}$	nucleation rate per particle
$k(T_c, t) \text{ cm}^{-3} \text{ }^{\circ}\text{C}^{-1}$	time-dependent concentration of nuclei with characteristic temperatures within 1°C of T_c
$k(T) \text{ cm}^{-3} \text{ }^{\circ}\text{C}^{-1}$	nucleus concentration; differential spectrum
$K(T) \text{ cm}^{-3}$	cumulative nucleus spectrum
$N_{ice} \text{ m}^{-3}$	ice particle concentration in cloud
$r(T) \text{ }^{\circ}\text{C min}^{-1}$	cooling rate
$R(T, t) \text{ min}^{-1}$	freezing rate
$T^{\circ}\text{C}$	temperature
$T_c^{\circ}\text{C}$	characteristic temperature of nucleus (site).

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