Quantitative Evaluation of Experimental Results an the Heterogeneous Freezing Nucleation of Supercooled Liquids

1 author:

Quantitative Evaluation of Experimental Results on the Heterogeneous Freezing Nucleation of Supercooled Liquids

GABOR VALI

Natural Resources Research Institute, University of Wyoming, Laramie

(Manuscript received 30 October 1970)

ABSTRACT

Freezing experiments using large numbers of small drops are frequently used for the study of both homogeneous and heterogeneous nucleation of water and of other substances. For heterogeneous nucleation, the spread in the observed freezing temperatures of drops has been shown to arise from the presence of nuclei of different activities in the sample. In the past no quantitative assessment of the nucleus content could be given independent of the drop sizes used. It is shown in this paper that from the observed freezing temperatures of the drops one can derive both a differential and a cumulative nucleus spectrum. The differential spectrum represents the concentrations of nuclei which are active at specific temperatures and the cumulative spectrum represents the concentrations of nuclei active at all temperatures warmer than the selected temperature. The accuracies of the derived spectra were examined by Monte Carlo simulation and are shown to be such that the concentrations are reliable to within factors of 2–4. The dependence of the average freezing temperature on drop volume is shown in general to be determined by the shape of the nucleus spectrum but is approximately exponential for many spectra.

1. Introduction and background

The presence of impurity nuclei, or motes, usually limits the amount of supercooling that can be sustained in a liquid. Mendenhall and Ingersoll (1908) were probably the first to recognize that small droplets of a substance can be supercooled to a much greater extent than the bulk material due to sequestering of the impurity nuclei into a few of the droplets and thereby limiting their effect. This approach was later used for the study of nucleation by Vonnegut (1948), Pound (1952), Turnbull (1952), and many others. More recent applications of the droplet technique were reported by Burns and Turnbull (1966), Price and Gornick (1967), and Wood and Walton (1970). The aim in most of these experiments had been to study the kinetics of the nucleation process, primarily for homogeneous nucleation and to some extent for heterogeneous nucleation. In order to arrive at deductions regarding the kinetics of the process, the nature of the heterogeneous nuclei, when present, was for the most part neglected or treated with gross simplifications. Other investigators concentrated on efforts to characterize the activities of the nuclei. Rau (1944) realized that numerous freezing nuclei were present in the water samples he examined and associated a characteristic freezing temperature with each of the nuclei. The distribution of freezing temperatures for a set of drops (in histogram form) was looked upon by Rau as a "spectrum" of the nuclei with peaks in the distributions signifying specific types of nuclei. Dorsey (1948) summarized earlier observations

and presented further evidence to show that special sites on the container walls or on suspended impurities determined the nucleation temperatures. Levine (1950), following the same line of thought as Rau, considered the chance allocation of distinct groups of nuclei of different freezing temperatures into small volumes and found a particular form for the function describing the numbers of nuclei in each of the groups which agreed with the experimental results of Dorsch and Hacker (1950).

Bigg (1953) found that the volume-dependence and the time-dependence of freezing temperatures in his experiments could be explained by the assumption that the probability of freezing per unit volume and per unit time increases exponentially with decreasing temperature. Marshall (1961) suggested that Bigg's formulation is of general validity for heterogeneous nucleation and that the pre-exponential factor in the probability relation characterizes the concentrations of nuclei in the sample. Although not stated explicitly, Bigg's assumption implies that the nucleation process is controlled primarily by molecular kinetics; furthermore, the nucleus content is taken in this theory to be the same for every drop from a sample.

The notion that activation temperatures are specific properties of nucleating particles received strong support from calculations by Fletcher (1962). The results of these computations, which were based on thermodynamic considerations, showed that the nucleation temperatures can be uniquely related to the crystalline characteristics and to the sizes of the particles.

The relative importance of kinetic effects versus the nature of the nucleating particles was investigated by Vali and Stansbury (1966). From experiments on the time-dependence of freezing nucleation they deduced that the probability of freezing for a drop at temperature θ and time t can be written as

$$P(\theta,t) = \int_{-\infty}^{0} P_1(\theta,\theta_c)P_2(\theta_c,t)d\theta_c, \tag{1}$$

where θ_c are the characteristic temperatures of the nuclei. The probability function P_1 characterizes the propensity of nuclei to become active within a unit time interval at temperatures other than their particular characteristic temperatures. The function P_2, a function of θ_c, represents the numbers of those nuclei which at time t have not yet become active. The results of Vali and Stansbury[1] and later results by Vali (1969) indicated that the P_1 function varies so rapidly with temperature that nucleation is almost certain to take place, under conditions usually encountered, within an interval of $\sim\pm0.25C$ about θ_c.

For most purposes the 0.25C uncertainty resulting from the fluctuating nature of the pre-nucleation phenomena is negligible compared to the wide range (10–20C) which is found for the freezing temperatures of drops of the same origin and size. Therefore, as a good first approximation, each nucleus can be taken to be effective at a temperature characteristic of that particular nucleus. Formally, this so-called "singular approximation" is equivalent to replacing $P_1(\theta,\theta_c)$ in (1) by a Dirac δ function at $\theta=\theta_c$. The time-dependence in P_2 can then be omitted so that the probability of freezing, $P(\theta)$, is determined solely by the distribution of characteristic temperatures for the nuclei.

Despite the better understanding of the nucleation phenomenon which arose from the research described above, no immediate improvements were forthcoming in the interpretation of nucleation experiments in terms of quantitative nucleus contents. Experimental results were presented almost universally in the form of histograms. These could be used for qualitative comparisons, but could not provide any absolute bases for evaluation due to the dependence of the results on drop volumes.

It is the purpose of this paper to demonstrate that quantitative evaluations of drop freezing experiments can be made which are true representations of the nucleus contents of the water from which the drops originated. The derived concentration vs temperature functions, or nucleus spectra, have been used successfully to describe the nucleus contents of precipitation samples and the results of those measurements were used to estimate the rate of ice formation in clouds (Vali, 1968, 1971). The technique was also found to be

very useful in unambiguously evaluating the freezing nucleating abilities of artificial sources of nuclei (Vali, 1968; Vali and Finnegan, 1970).

The most convenient experimental method for the determination of the nucleus content is to divide the sample into large numbers of drops of equal volume and to simultaneously cool these drops while observing and recording their freezing temperatures. The analysis given in this paper is formulated primarily for use with experiments of this type, although the results can readily be adapted to other procedures. An extension of the results to the general case of non-uniform drop volumes is presented in the Appendix.

2. Differential nucleus spectra

The starting point for the following derivation is the singular approximation that each particular freezing nucleus becomes active at its characteristic temperature independently of the time rate of change of temperature.

The basic data derived from drop-freezing experiments are the freezing temperatures of the drops. The problem then is to derive from these observations the function $k(\theta)$ describing the concentrations of nuclei active in a unit volume of sample within a unit temperature interval about the temperature θ. This function is similar in form to the usual representation of particle size distributions (dN/dr as a function of radius), or to the presentation of spectral energy as a function of wavelength.

With the foregoing definition of $k(\theta)$, the average number $\bar{n}$ of nuclei which are active within a unit temperature interval θ in a drop of volume V can be written as

$$\bar{n}(\theta) = k(\theta)V. \tag{2}$$

The number of nuclei per drop which are active in the temperature interval θ to $(\theta-d\theta)$ is thus equal to

$$\bar{n}(\theta)d\theta = k(\theta)Vd\theta. \tag{3}$$

For values of $\bar{n}(\theta)d\theta$ smaller than unity, the expression in (3) can be taken to represent the probability that a given drop will contain a nucleus active in the specified temperature interval.

Consider now an experiment in which a total of N_0 drops are observed and let the number of drops still unfrozen at the temperature θ be $N(\theta)$. The number of drops frozen at θ is then given by $N_0-N(\theta)$. Upon further cooling of the temperature to $(\theta-d\theta)$, an additional number dN of the drops may freeze, so that the fraction of unfrozen drops nucleated within this interval is $dN/N(\theta)$. The fraction[2] $dN/N(\theta)$ can be looked upon as the probability of freezing, $Pd\theta$, for one of the unfrozen drops, i.e.,

$$Pd\theta = dN/N(\theta). \tag{4}$$

---

[1] Substantially different results on cooling rate dependence were reported by Gokhale (1965), but these were shown to be the results of temperature lags by Levkov and Genadiev (1966) and Genadiev (1968).

[2] In freezing experiments both $N(\theta)$ and θ decrease with time. In order to avoid the continuous use of minus signs, dN and $d\theta$ have been defined above to be positive quantities, i.e., absolute values are being used for dN, ΔN, $d\theta$ and $\Delta\theta$.

Since the right-hand side of this equation contains quantities which are observable in an experiment, $P d\theta$ can be determined.

It can be shown that the probability $P d\theta$ also represents the probability of finding a nucleus active between θ and $(\theta - d\theta)$ in any one of the original number of drops (N_0). The basis for this assertion is that the chance allocations of the various nuclei of different activities into the drops are independent of one another. Thus, the drops that were observed to freeze at temperatures warmer than θ had the same chance for containing nuclei active between θ and $(\theta - d\theta)$ as the other drops which did not contain nuclei active above θ and which therefore remained unfrozen up to that point. Hence, the empirical probability of freezing from (4), although derived from observations on the N unfrozen drops, can be equated to the expected value for the probability of containing a nucleus in any one of the N_0 drops as given by (3), so that

$$dN/N(\theta) = k(\theta)Vd\theta, \qquad (5)$$

from which the final expression for the concentration can be written as

$$k(\theta) = \frac{1}{VN(\theta)} \frac{dN}{d\theta} \quad [\mathrm{cm}^{-3}(^\circ\mathrm{C})^{-1}]. \qquad (6)$$

The concentration function $k(\theta)$ is termed the "differential nucleus concentration" and its graphical representation is described as a "differential nucleus spectrum."[3]

The use of infinitesimal temperature decrements $d\theta$ in the foregoing derivation ensured that no more than one nucleus could have been responsible for the observed freezing of a drop in that interval. With the probability for an active nucleus to be found in a drop over the interval $d\theta$ being very small, the probability of two or more nuclei of the same activity occurring in the same drop becomes negligible. This can be readily seen by an application of Poisson's law (Hoel, 1962) from which the probability $p(x)$ for finding x nuclei of the same activity in the same drop can be obtained as

$$p(x) = e^{-\mu}\mu^x/x!, \qquad (7)$$

where $\mu = \bar{n}(\theta)d\theta$, i.e., the average number of nuclei per drop. The probabilities of one, two, three, etc., nuclei of the same activity occurring in a drop are thus proportional to

$$\mu, \ \mu^2/2, \ \mu^3/6, \ \ldots, \qquad (8)$$

respectively. For an infinitesimal temperature change $d\theta$ the average number μ is also infinitesimal so that terms with higher powers of μ are negligible.

For practical application (6) has to be modified somewhat due to the fact that in an experiment with finite

---

[3] Roulleau (1957) presented her experimental results by plotting dN/N as a function of temperature in a way which is very similar to the differential spectra defined in this paper; however, no physical interpretation was attached to the quantity dN/N.

numbers of drops one has to use temperature intervals $\Delta\theta$ which are sufficiently large to yield appreciable numbers of freezing events, ΔN, in each interval. Since the value of μ is then not infinitesimal, all the terms in (8) have to be considered. In other words, the only statement that can be made in this case is that observation of the freezing of a drop in a particular temperature interval is an indication for the presence in that drop of one or more nuclei all having characteristic temperatures in that interval. The probability that at least one nucleus of the same "kind" (in the sense of having characteristic temperatures within the same interval) will occur in a drop is given by Poisson's law as

$$p(1,2,\ldots) = 1 - p(0) = 1 - e^{-\mu}, \qquad (9)$$

where μ is now equal to $\bar{n}(\theta)\Delta\theta$. Equating this probability to $P\Delta\theta$ from (4) and using (3), it follows that

$$\Delta N/N(\theta) = 1 - \exp[-k(\theta)V\Delta\theta], \qquad (10)$$

from which

$$k(\theta) = -(1/V\Delta\theta)\ln[1 - \Delta N/N(\theta)]. \qquad (11)$$

Eq. (11) is the formula used to calculate $k(\theta)$ from the observed values of ΔN. The term $N(\theta)$ is readily obtained as

$$N(\theta) = N_0 - \Sigma\Delta N. \qquad (12)$$

The volume V is fixed for any given experiment, and equal temperature decrements are usually used throughout (this is not a requirement, however).

3. Cumulative nucleus spectra

The differential nucleus concentration $k(\theta)$ is the most useful representation of the nucleus content of a sample, since it describes the variation of activity with temperature in a direct fashion. It may be of interest, however, especially in considering the freezing of a population of drops upon cooling from 0C, to form a cumulative nucleus concentration $K(\theta)$, which is an indication of the numbers of nuclei which are active at all temperatures warmer than θ in a unit volume of water.

The cumulative concentration $K(\theta)$ can readily be derived by integrating (6) over the temperature range θ to 0C; it thus takes the form

$$K(\theta) = [\ln N_0 - \ln N(\theta)]/V \quad [\mathrm{cm}^{-3}]. \qquad (13)$$

This equation is also consistent with the finite-difference form of (11) as can be seen by writing

$$k(\theta) = [K(\theta - \Delta\theta) - K(\theta)]/\Delta\theta, \qquad (14)$$

which, upon substitution for $K(\theta)$ from (13) and by putting $N(\theta - \Delta\theta) = N(\theta) - \Delta N$, reduces to (11). The cumulative spectrum may thus be obtained either directly from (13) or by summation of the $k(\theta)\Delta\theta$ terms.

As can be seen from (13), $K(\theta)$ is dependent only on $N(\theta)$, so that it may be expected that this quantity

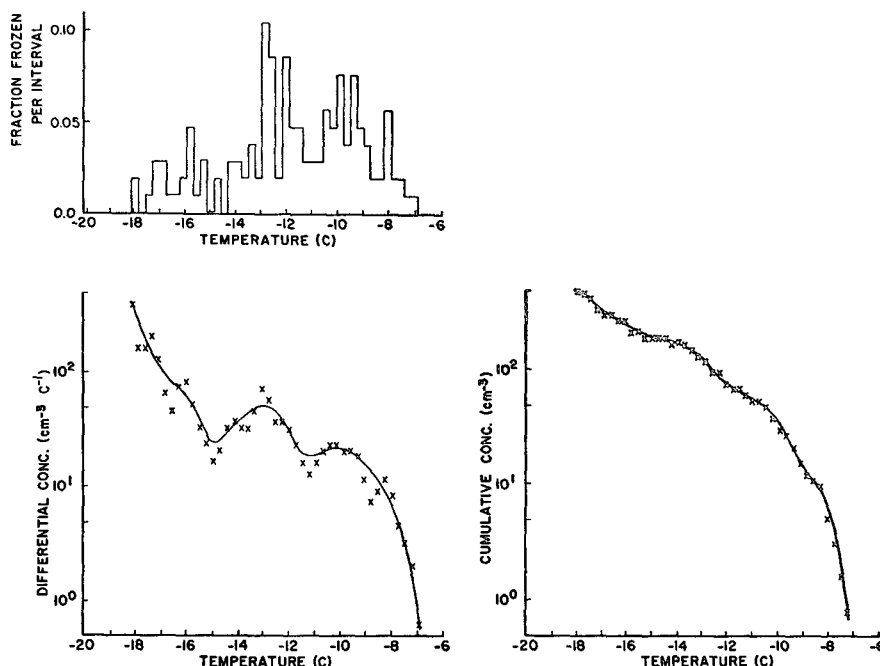FIG. 1. Different representations of the experimental results for 144 drops of 0.01 cm³ volume from a sample of rain. Part (a), upper left, is a histogram, part (b), lower left the differential spectrum obtained from (11), and part (c), lower right, the cumulative spectrum calculated from (13).

alone could be used to derive $K(\theta)$. This can be done, in fact, by considering $N(\theta)/N_0$ (the fraction of drops unfrozen at θ) as representing the probability that a drop contains no nuclei active above θ. Expressing this relation, with reference to (7), we obtain

$$N(\theta)/N_0 = \exp[-K(\theta)V],\qquad(15)$$

which is equivalent to (13).

4. Application

As mentioned in the introduction, the most convenient experimental procedure for the determination of the nucleus spectra is the steady cooling of a set of drops until all the drops freeze. The details of the experimental procedure have been presented by Vali and Stansbury (1966). In Fig. 1 the results of a typical experiment are shown for a sample of rain. Part (a) of the figure is a histogram representation of the numbers of drops frozen in each 0.27C interval expressed as percentages of the 144 drops tested. Parts (b) and (c) show the corresponding differential and cumulative spectra. The concentrations were calculated at each 0.27C interval and a three-interval weighted smoothing $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$ was applied. The curves were then fitted to the points subjectively. Frequently there are peaks, more or less pronounced, in the differential nucleus spectra; these indicate the presence of specific groups of nuclei in the samples. The general tendency, however, is toward an exponential increase in concentration with decreasing

temperature. In this respect, these results for freezing nucleus concentrations in water samples are very similar to those deduced from cloud-chamber measurements. The deviations from the simple exponential form are in general greater for samples which contain nuclei active at temperatures $\gtrsim -15$C. On the other hand, singly-distilled water, which has relatively low concentrations of nuclei, has a very nearly exponential spectrum with an exponent typical of cloud-chamber measurements for atmospheric nuclei (a factor of 10 increase in concentration for a 4C decrease in temperature).

The question of statistical validity arises with respect to the calculated concentrations, especially with respect to the scatter which makes the resolution of the peaks in the differential spectra uncertain. Due to the fact that each point along the curve is based on the observed freezing of a different number of drops, the statistical significance of each point is different. This rules out the application of standard methods. The problem was therefore approached by Monte Carlo simulation of the experiments on a computer. Consecutive sets of numbers were assigned to each successive temperature interval in proportion to the assumed concentrations for the intervals. Random numbers generated in the computer were then compared to the assigned numbers and the temperatures to which those numbers belonged were taken as the freezing temperatures of drops. The spectra were calculated from (11) and (13) and compared to the input concentrations. Fig. 2 shows the results of such a simulation. The numbers of drops per sample,
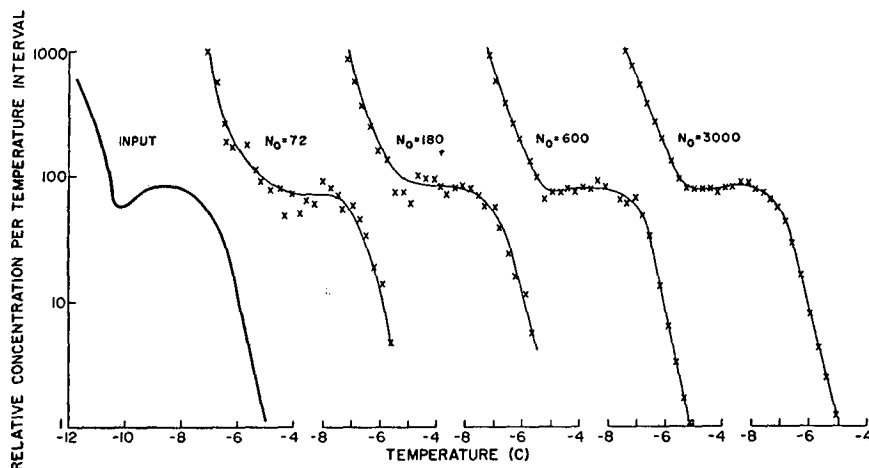
FIG. 2. Differential nucleus spectra for computer-simulated experiments. The "input" curve represents the assumed concentration in a sample from which N_0 drops were taken for the simulated experiment.

N_0, were varied for an input spectrum having relatively fine detail. As can be seen from the figure, the main features are already reproduced for N_0 as small as 72, but even at $N_0 = 3000$ there is some uncertainty in the definition of the small dip in concentration at $-10C$. It may also be noted that the scatter of points is greater over portions of the spectrum which have smaller negative slopes and that the definition is best over the steep portions of the spectrum.

The probable errors associated with a spectrum for an experiment with $N_0 = 150$ can be estimated from Fig. 3 which shows the envelopes drawn to ten spectra obtained from ten independent simulations for the same experiment. The maximum discrepancies in concentrations appear at the warm temperature end of the spectrum, whereas the maximum range in temperatures for a given concentration is in the middle part of the spectrum. The error band associated with a nucleus spectrum is thus seen to be dependent on the shape of the spectrum. In general, differential spectra are accurate to within approximately a factor of 2 over most of the range covered, with uncertainties of perhaps factors of 4 toward the ends of the spectra. The cumulative spectra tend to show somewhat less scatter. The figures quoted above are for spectra derived from experiments with $N_0 \approx 200$; accuracies can be improved by increasing the numbers of drops tested per sample.

Although the simulated experiments can serve to provide a rough indication of the degree of confidence that can be placed in the calculated concentrations, a more thorough and rigorous treatment of the statistical reliability of the spectra remains to be developed.

5. Volume dependence

Many previous experiments on the freezing of water drops have yielded logarithmic relations between the mean freezing temperatures and the volumes of the drops [see summary by Fletcher (1962)]. It is therefore worthwhile to examine the volume dependence that follows from the theory outlined in this paper.

It can be readily seen from applications of (5) to some simple forms of $k(\theta)$ that the mean freezing temperatures of N_0 drops of volume V depend on V in different ways for the different forms of $k(\theta)$. A general volume-temperature relation therefore cannot be given.

The special case, when $k(\theta)$ is of the form

$$k(\theta) = A \exp(-B\theta), \tag{16}$$

where A and B are constants, deserves consideration. For the distribution that follows from (16), Stansbury (1961) has shown the mean freezing temperature $\bar{\theta}$ to be given by

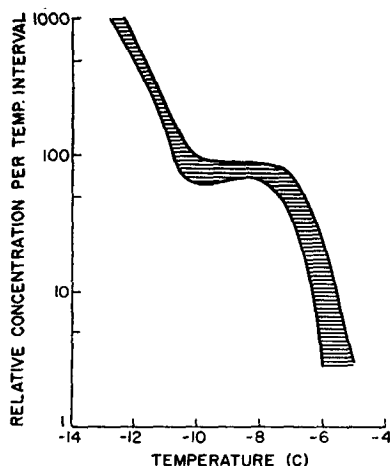$$\bar{\theta} = \ln(AV/B^2) + \Gamma'(1)/B, \tag{17}$$

FIG. 3. Envelopes of the spectra from ten simulated experiments with $N_0 = 150$. This represents a rough estimate of the error-band associated with such a spectrum (due to the small number of experiments no precise confidence values were attached to these limits).

with Γ' denoting the first derivative of the gamma function [numerically, $\Gamma'(1) = 0.5772$]. In this case, then, there is a logarithmic dependence of $\bar{\theta}$ on V. Since many spectra tend toward an exponential form such as (16), the measured dependence of $\bar{\theta}$ on V can be expected to be nearly logarithmic for most cases (in accordance with earlier results); a strict logarithmic relation holds, however, only in the special case given by (16).

The nucleus spectra given by (6) and (13) represent the nucleus content per unit volume and they should therefore be independent of the drop size used in the experiment from which the spectra were derived. Verification of this statement, by experiments using drops of different sizes, is, in fact, a good check on the reasoning that led to (6) and (13), as well as on the acceptability of the experimental procedures. Effects proportional to the area of contact between drops and the supporting surface, for example, would negate the independence of derived concentrations from drop volume. Fig. 4 shows an example of differential concentrations derived from experiments with different sizes of drops; the consistency among these three curves appears quite satisfactory.[4] It is also evident from Fig. 4 that the calculated concentrations cover different ranges for the three sets of experiments, with the overlap existing over portions of the spectra only. This is a general consequence of (6) and of (13) according to which V and N_0 determine what range of values will be covered by $k(\theta)$ and $K(\theta)$. With larger drops, fewer nuclei per cubic centimeter of water will suffice to freeze all the drops in the sample; thus, information is obtained from the experiment for relatively low concentrations. Conversely, with drops of smaller volume nuclei of greater concentrations are examined. The influence of N_0 is similar in that the larger the number of drops tested, the greater the chance that a rare (low concentration) nucleus of high activity will be detected. For example, differential concentrations of 10^{-1}–10^3 cm^{-3} ($^\circ$C)$^{-1}$ can be measured by using 100–300 drops of 10^{-2} cm^3 volume. As an alternative to changing V or N_0 for increasing the ranges of the spectra, the sample can be diluted with water of much lower nucleus content (Vali, 1968); this is a very convenient method but its application is limited to measurements at temperatures $\gtrsim -20$C due to the unavailability of nucleus-free water.

---

[4] The same analysis technique has been applied to the measurements of Rau (1953) which extended to a much larger range of drop volumes. The histograms for ten sets of drops (Fig. 1 in Rau's paper) indicated gradual shifting of peaks from warm temperatures toward colder temperatures as the sizes of the drops were decreased. Qualitatively, this behavior is expected from the further partitioning of nuclei into smaller and smaller drops. However, the calculated concentrations of nuclei, using (11), were found not to be constant for the different experiments but to increase for decreasing drop sizes, contrary to the arguments of this paper. Thus, the qualitative reasonableness of Rau's results cannot be carried over into a quantitative statement, indicating perhaps that the same sample of water was not used in all of the experiments or that some factor other than nucleation by suspended impurities entered the experiments.

6. Summary

A method has been presented for the quantitative evaluation of drop freezing experiments. It was shown that the specific nucleus contents of samples can be determined and be described by the differential nucleus spectra (6). The freezing behavior of a population of drops can be predicted by simple calculations (Vali, 1968) based on the use of the cumulative spectrum (13). These spectra are independent of the particular drop sizes used in the experiments and are therefore con-
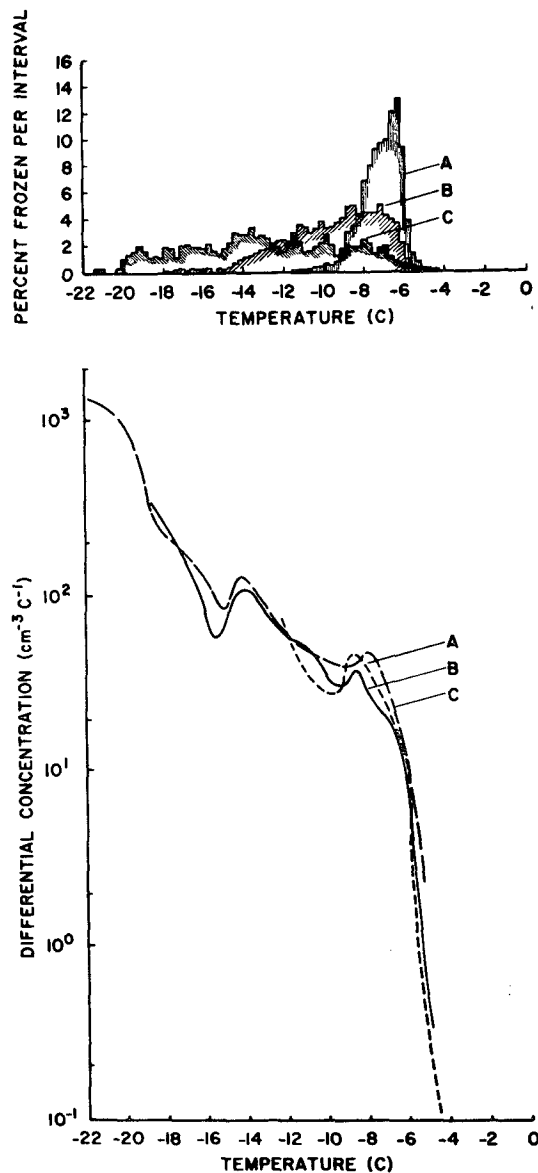

FIG. 4. Experimental results for three sets of runs with different sizes of drops, all from the same sample of a melted hailstone: A, 725 drops of 0.04 cm^3 each; B, 720 drops of 0.01 cm^3 each; and C, 704 drops of 0.0025 cm^3 each. The upper diagram is a histogram representation of the numbers of drops frozen per 0.27C interval, the lower diagram the corresponding spectra derived from (11).

sidered to be better representations of experimental re-
sults than the frequency distributions of freezing events
which are in common use at present.

From the point of view of physical significance, drop
freezing experiments of the kind analyzed in this paper
are the most convenient and at the same time the most
rewarding ways to determine the "freezability" of
water or of any other substance, and to quantify many
of the characteristics of heterogeneous freezing nuclei.
For atmospheric research, this technique offers a way to
unambiguously identify both natural and artificial
freezing nuclei, with the attendent advantage of equal
sensitivity of detection at all temperatures below the
melting point. Since freezing induced by particulates
within a water drop is not the only mode of ice forma-
tion in the atmosphere, it appears that other types of
measurements, used in conjunction with these freezing
nucleus measurements, will be necessary to obtain a
complete measure for ice-forming potential in the
atmosphere.

APPENDIX

Calculation of Spectra for Polydisperse Population of Drops

If a drop freezing experiment is performed in which
drops of various sizes are being used, it is expected, on
the average, that the larger drops will freeze at warmer
temperatures than the smaller drops. With this addi-
tional complication there appear to be two possible
approaches for the derivation of nucleus spectra from
experimental data.

Provided that the dispersion in drop sizes is relatively
small and that all the drops are small compared to the
total volume tested, the only modification necessary in
(6) is to replace $VN(\theta)$ by $V(\theta)$, the volume of water
which is unfrozen at θ. In this case drops are considered
equal, irrespective of their sizes, in determining dN;
the greater chance of freezing for larger drops is not
neglected, however, as $V(\theta)$ is diminished by a larger
amount due to the freezing of a large drop than it would
be for a smaller drop.

An adaptation of (11) can be made by considering
the following expression as the best estimate for the

probability of freezing in place of (4):

$$P\Delta\theta = \frac{\Delta N}{N(\theta)} \frac{V(\theta)/N(\theta)}{\Delta V/\Delta N}, \qquad (18a)$$

or

$$P\Delta\theta = [\Delta N/N(\theta)]^2[V(\theta)/\Delta V], \qquad (18b)$$

where the second factor in (18a) is a correction for the
volume effect in the form of the ratio of average un-
frozen drop size to the average size of the drops freezing
in $\Delta\theta$. The average number of nuclei per drop can be
written for the unfrozen drops, whose average volume
is $V(\theta)/N(\theta)$, as

$$\bar{n}(\theta)\Delta\theta = k(\theta)\Delta\theta V(\theta)/N(\theta). \qquad (19)$$

Hence, by analogy with (10), we have

$$\left[\frac{\Delta N}{N(\theta)}\right]^2\left[\frac{V(\theta)}{\Delta V}\right] = 1 - \exp\left[\frac{-k(\theta)\Delta\theta V(\theta)}{N(\theta)}\right], \qquad (20)$$

from which $k(\theta)$ can be obtained.

An alternate approach which may be used is to
classify the drops of different radii r_i into groups with
nominal volumes $V(r_1)$, $V(r_2)$, etc., and to treat each
group separately, finding a $k(\theta)$-value from each group
and applying a volume-weighted averaging.

The best way to derive $K(\theta)$ from an experiment with
polydisperse drops appears to be by summation of the
$k(\theta)\Delta\theta$-values.

REFERENCES

Bigg, E. K., 1953: The supercooling of water. *Proc. Phys. Soc.,*
    B66, 688–694.
Burns, R., and D. Turnbull, 1966: Kinetics of crystal nucleation
    in molten isotactic polypropylene. *J. Appl. Phys.,* **37,**
    4021–4026.
Dorsch, R. G., and P. T. Hacker, 1950: Photomicrographic
    investigation of spontaneous freezing temperatures of super-
    cooled water droplets. Natl. Adv. Comm. Aeronautics, Tech.
    Note 2142, 57 pp.
Dorsey, N. E., 1948: The freezing of supercooled water. *Trans.
    Amer. Phil. Soc.,* **38,** 247–328.
Fletcher, N. H., 1962: *The Physics of Rainclouds.* Cambridge
    University Press, 386 pp.
Genadiev, N., 1968: De la corrélation entre la vitesse de refroid-
    issement et la température de congélation de gouttes d'eau
    refroidies sur plaque métallique. *J. Rech. Atmos.,* **3,** 125–132.
Gokhale, N. R., 1965: Dependence of freezing temperatures of
    supercooled water drops on rate of cooling. *J. Atmos. Sci.,*
    22, 212–216.
Hoel, P. G., 1962: *Introduction to Mathematical Statistics,* 3rd ed.
    New York, Wiley, 427 pp.
Levine, J., 1950: Statistical explanation of spontaneous freezing
    of water droplets. Natl. Adv. Comm. Aeronautics, Tech.
    Note 2234, 27 pp.
Levkov, L., and N. Genadiev, 1966: Relation between freezing
    temperature of supercooled waterdrops and cooling rate.
    Compt. Rend. Akad. Bulgare. Sci., **19,** 1139–1142.
Marshall, J. S., 1961: Heterogeneous nucleation is a stochastic
    process. *Nubila,* **4,** 39–42.
Mendenhall C. E., and L. R. Ingersoll, 1908: On certain phenom-

ena exhibited by small particles on a Nerst glower. *Phil. Mag.*, **14**, 205–214.

Pound, G. M., 1952: Liquid and crystal nucleation. *Ind. Eng. Chem.*, **44**, 1278–1283.

Price, P., and F. Gornick, 1967: Estimation of nucleation parameters from continuous cooling droplet experiments. *J. Appl. Phys.*, **38**, 4182–4186.

Rau, W., 1944: Gefriervorgange des Wassers bei tiefen Temperaturen. *Schr. Deut. Akad. Luftfahrtforschg.*, **8**, 65–84.

——, 1953: Uber den Einfluss des Tropfenvolumens aut die Unterkuhlbarkeit von Wassertropten und die Bedeutung des Gefrierkernspektrum. *Z. Naturforsch.*, **8a**, 197–204.

Roulleau, M., 1957: Mechanisms de la congélation de l'eau. *J. Sci. Meteor.*, **9**, 127–147.

Stansbury, E. J., 1961: Stochastic freezing. McGill Univ., Stormy Weather Group, Sci. Rept. MW-35, 43–52.

Turnbull, D., 1952: Kinetics of solidification of supercooled liquid mercury droplets. *J. Chem. Phys.*, **20**, 411–424.

Vali, G., 1968: Ice nucleation relevant to hail formation. McGill Univ., Stormy Weather Group, Sci. Rept. MW-58, 51 pp.

——, 1969: The characteristics of freezing nuclei. *Proc. 7th Intern. Conf. Condensation and Ice Nuclei*, Prague and Vienna, 387–393.

——, 1971: Freezing nucleus content of hail and rain in Alberta. *J. Appl. Meteor.*, **10**, 73–78.

——, and W. G. Finnegan, 1970: Freezing nucleation by silver iodide complexes. *Preprints of Papers, Conf. Cloud Physics*, Fort Collins, Colo., Amer. Meteor. Soc., 29–30.

——, and E. J. Stansbury, 1966: Time-dependent characteristics of the heterogeneous nucleation of ice. *Can. J. Phys.*, **44**, 477–502.

Vonnegut, B., 1948: Variation with temperature of the nucleation rate of supercooled liquid tin and water drops. *J. Colloid Sci.*, **3**, 563–569.

Wood, G. R., and A. G. Walton, 1970: Homogeneous nucleation kinetics of ice from water. *J. Appl. Phys.*, **41**, 3027–3036.