

Relationship of Size and Activity for AgI Smoke Particles

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ABSTRACT

The ability of AgI particles to nucleate ice by the freezing mechanism was measured with the Goetz aerosol centrifuge as a function of particle size, temperature and time. When the cooled centrifuge deposit was exposed to a puff of supersaturated nitrogen, each particle was immersed in a supercooled droplet which, if it contained an active AgI particle, froze and formed a visible ice crystal. The fraction of active particles was found by comparing the number of ice crystals with the size distribution of all the particles on the deposit.

The mean nucleation rate per particle depended on particle size for a given temperature, which suggested that the surface of the particles was smooth with respect to the size of the critical ice embryos. The measured rates were about a factor of 10^{4-6} smaller than predicted by Fletcher's theory. Activity spectra, calculated from the measured rates by numerically integrating the activities of all the particles in log-normal size distributions, showed the importance of the nucleation time lag at temperatures warmer than about -12°C or when the AgI generator produces very small particles.

1. Introduction

A complex relationship exists between the sizes of AgI particles and the particles' ability to nucleate ice in a supercooled cloud. Theory suggests that particles lose their activity as ice nuclei if they are too small, and that this effect differs for each of several nucleation mechanisms which may be acting simultaneously in the cloud. Cloud chamber measurements by Vonnegut (1949) showed that a nucleation time lag was a function of particle size as well as temperature, and Young (1974) showed that a diffusion time lag for contact nucleation depended on particle size. The efficiency of the AgI generator depends on the size distribution of the generated particles.

Clearly, a successful model of the influence of AgI in clouds should include all the effects of particle size, which no models yet do. Laboratory experiments designed to establish the relationship of size and activity (e.g., Maruyama, 1956; Sano *et al.*, 1956; Katz, 1962; Edwards *et al.*, 1962; Mossop and Jayaweera, 1969) are difficult to interpret, since none simultaneously relate particle sizes, nucleation mechanisms, and time effects.

For a time it appeared that Fletcher's (1958) extension of Volmer's (1939) theory to a uniform curved substrate successfully predicted the influence of AgI particle size. Fletcher derived an activity spectrum (the maximum number of particles in 1 g of AgI as

a function of temperature) which showed consistent agreement with the spectra determined from ice crystal counts in the cloud chamber. Inherent to the derivation was the assumption that a unique relationship existed between the nucleus size and the nucleation temperature. However, measurements by Katz (1962), Edwards *et al.* (1962) and Mossop and Jayaweera (1969) showed that the activity of the AgI particles was proportional instead to the particles' surface area. That finding led to the concept of nucleation sites on the surface of the particles, which Fletcher (1969) used for new predictions of activity spectra. Questions, however, still remain: How reliable is the concept of nucleation sites when their nature has not been observed directly? If site theory is considered valid, why is there usually good agreement between experimental activity spectra and Fletcher's theoretical spectrum for nucleation by sublimation on particles with a uniform surface? Why is the derivation of activity spectra inconsistent with the nucleation time lag? Do Fletcher's theories require a major revision if the influence of line tension (Evans and Lane, 1973) is included?

An experimental technique proposed by Allee *et al.* (1968) can establish the relationship of size and activity and help clarify the role of nucleation theories. It consists of capturing AgI particles on the collection foil of the Goetz aerosol centrifuge, where their activity is measured as in the Millipore filter technique (Stevenson, 1968). This centrifuge technique has the unique advantage that activity is measured as a function of particle size, since the particles are deposited in a

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pattern which depends on their size. Also, the collection surface is a smooth surface of one's choice, thus avoiding the weakness of the filter method that the number of small nuclei can be underestimated due to losses in filter pores (Wirth and Prodi, 1973). Much of the output of AgI generators can be studied with the centrifuge, since it can efficiently collect particles as small as 100 Å in radius. The centrifuge technique was evaluated at the 2nd International Workshop on Condensation and Ice Nuclei (IWCIN; Grant, 1971), where it was recommended as one of the standard methods for measuring ice nuclei (Bigg, 1971). The ability of the Goetz centrifuge to collect and size aerosol particles was discussed by Goetz *et al.* (1960), Stöber and Zessack (1964), Gerber (1971, 1974) and Stöber and Boose (1973).

This paper describes an application of the centrifuge technique wherein the relationship of size and activity is determined for AgI smoke particles nucleating ice by the freezing mechanism. The results are compared to Fletcher's predictions for AgI particles with a uniform surface and for AgI particles with sites on the surface.

2. Fletcher's nucleation theories

The mean nucleation rate of ice per spherical AgI particle with a uniform surface is given for the freezing

mechanism by the usual expression (Fletcher, 1962)

$$J = 4\pi R^2 K \exp(-\Delta G^*/kT). \quad (1)$$

The rate constant K , determined from the general expression of K for a condensed system (Turnbull and Fischer, 1949), is given for the case of heterogeneous nucleation by the freezing mechanism by

$$K = AS(\sigma T)^{\frac{1}{2}} \exp(-\Delta g/kT), \quad (2)$$

where

$$A = \frac{2p^2 k^{\frac{1}{2}} (3v)^{\frac{1}{2}}}{3h (4\pi)} \approx 2.0 \times 10^{40} \text{ molecules cm}^{-4} (\text{g K})^{-\frac{1}{2}}. \quad (3)$$

McDonald (1953) gave

$$\Delta g = (3.6 + 0.032 T) 10^{-18} [\text{erg}], \quad (4)$$

and according to Wood and Watson (1970)

$$\sigma = (31.4 - 0.187 T) [\text{erg cm}^{-2}]. \quad (5)$$

The value of K given by (2) can differ by several orders of magnitude from Fletcher's (1969) value, which is based on a simplification of the expression given by Turnbull and Fisher; also Eq. (2) includes new dependencies on T , σ and S . Other estimates exist for the values of Δg and σ than are given in (4) and (5).

Fig. 1 shows nucleation rates which were calculated

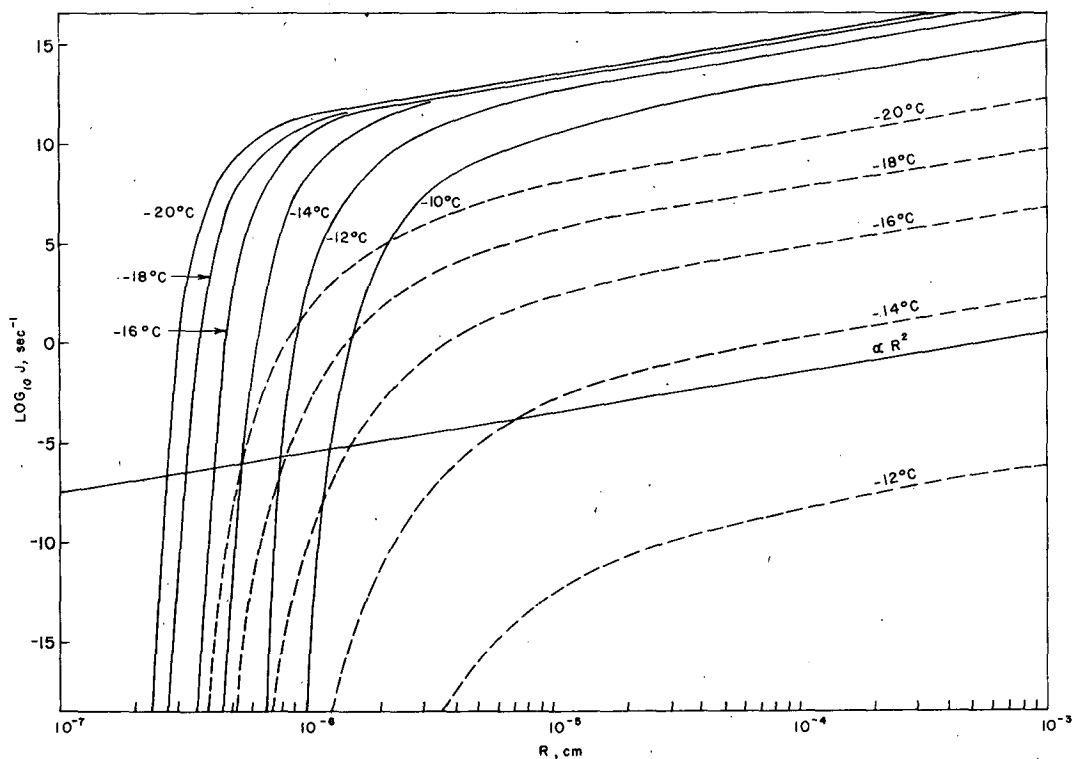


FIG. 1. Theoretical nucleation rate J of ice in water for a spherical AgI particle with radius R and a uniform surface characterized by $m=0.9$ (solid lines) and $m=0.7$ (dashed lines).

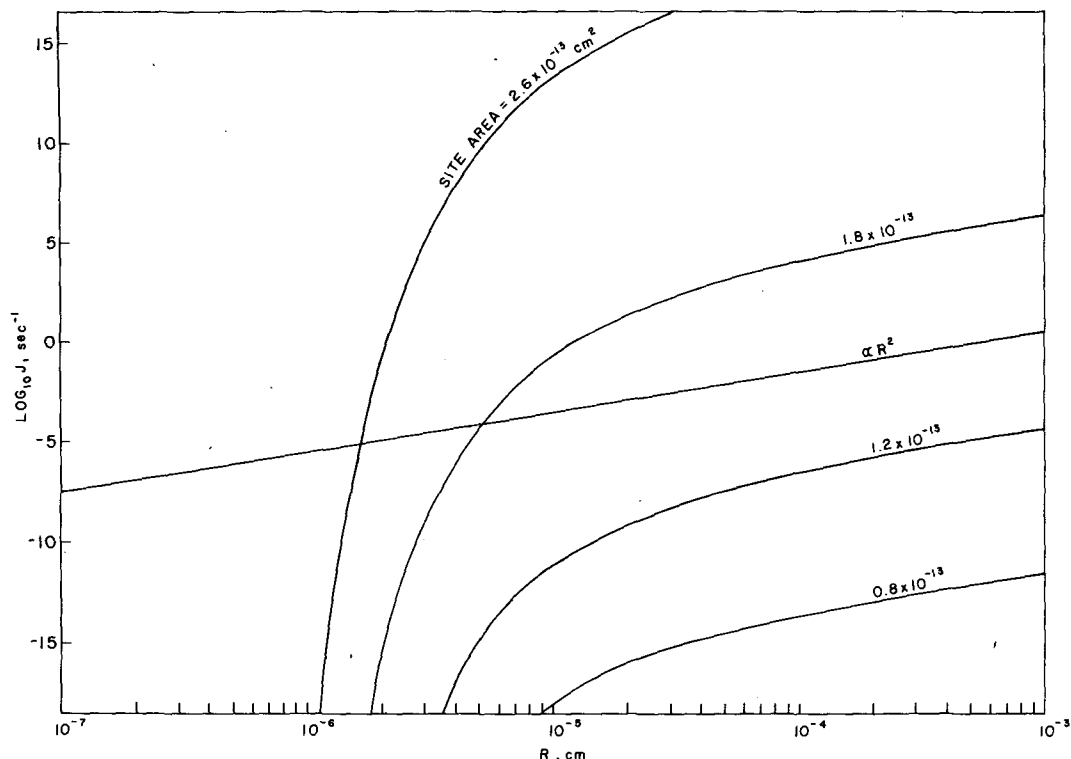


FIG. 2. J for a spherical AgI particle with an active site on its surface as a function of site area; $T = -14^\circ\text{C}$, and $m = 0.5$ for the surface adjacent to the site.

from the preceding equations as a function of R , T and m . For large particles Fig. 1 shows that the separation of the curves for different values of T is a strong function of m . Later on use will be made of that behavior to compare theory with experimental results.

It has not been emphasized sufficiently that the usual derivation of activity spectra depends strongly on the value of m . The curves in Fig. 1 for $m = 0.9$ show that for small particles the nucleation rates are steep and are nearly independent of the particle sizes. Fletcher solved (1) for those sizes by assuming that it was not important to specify the exact nucleation rates but only an appreciable rate, which was chosen as 1 s^{-1} . Those sizes are the threshold sizes from which the familiar activity spectrum is calculated. On the other hand, the curves for $m = 0.7$, especially those for the warmer temperatures, correspond to much smaller nucleation rates, so that they no longer have rates independent of particle sizes in the vicinity of an appreciable rate. Thus for that value of m it is not possible to compute the activity spectrum in the usual manner. Fletcher (1959) gave $m \approx 0.95$ for freezing by AgI particles with a uniform surface. When the concept of nucleation sites appeared to provide an explanation of the experimental activities, Fletcher (1969) suggested a value of $m = 0.5$ for the AgI surface between the sites. Sax and Goldsmith (1972) found the best fit with their experiment for

$m = 0.7$. Thus there has to be a lack of confidence in the activity spectrum reflecting the uncertainty in the value of m .

Fig. 1 shows further that the nucleation time lag is inconsistent with activity spectra which depend on the concept of an appreciable nucleation rate. If, for example, $m = 0.9$ and a typically polydisperse smoke is considered, then those particles with sizes below the threshold size have essentially a theoretical $J = 0$. Above the threshold the nucleation rate is large, so that those particles will nucleate ice in a fraction of a second. The time effect predicted theoretically by Fletcher (1959) for AgI particles with a uniform surface is thus impossible for nucleation by the freezing mechanism. Experimental observation of the nucleation time lag requires that $-10 \text{ s}^{-1} \lesssim \log J \lesssim 0 \text{ s}^{-1}$ for a substantial fraction of the particles in a polydisperse smoke.

The only change in (1) for Fletcher's (1969) site theory is in ΔG^* , which is now also a function of the fraction of the particle's surface covered by nucleation sites. Fig. 2 gives nucleation rates for AgI particles with site sizes permitted by the log-normal site-size distribution which was thought to give good approximation with experiment. The accuracy of activity spectra which depend on the curves in Fig. 2 is questionable, since there are rate curves for which the assumption of an appreciable rate has no meaning.

Later it will be shown that the observed propor-

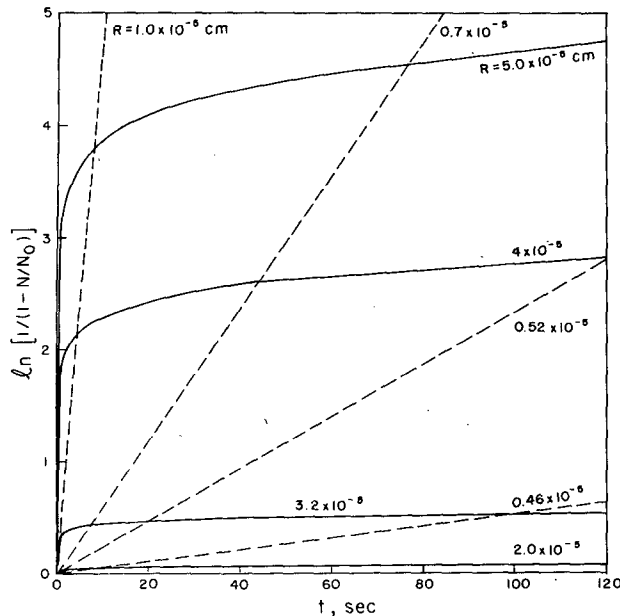


FIG. 3. Theoretical fractional activity N/N_0 of monodisperse AgI particles with uniform surfaces (dashed lines) and surfaces with sites (solid lines) as a function of R and activation time t at -14°C .

tionality of activity to particle area does not lead invariably to the concept of nucleation sites. Another way exists, however, to determine whether the particle surface behaves as if it were uniform or covered with sites. Making the reasonable assumption that nucleation is a stochastic process, Fletcher (1959) gave the fractional activity of monodisperse nuclei as

$$N/N_0 = 1 - \exp(-Jt), \quad (6)$$

where J is given by (1).

The fractional activity was calculated for particles with both types of surfaces by using nucleation rates given in Figs. 1 and 2. The results, given in Fig. 3, show a marked difference in the behavior of (6) for the two types of surfaces. Particles with a uniform surface give a straight line whose slope is their nucleation rate. On the other hand the fractional activity for particles with sites shows a rapid increase initially and a slow rise thereafter, since particles with the most active sites cause an initially large effective nucleation rate. Although the curves in Fig. 3 were calculated for specific numerical values of the nucleation parameters, the two distinct types of curves will persist as long as particles from one population all have the same mean nucleation rate while the others have a large spread in their rates. Thus, in principle, it is possible to determine whether the particles have a uniform surface or a site surface by measuring the fractional activity of monodisperse AgI particles as a function of time.

3. Experiment

The AgI particles were generated by heating a known amount of reagent-grade AgI in a ceramic boat placed in a stream of nitrogen. Since a separate AgI generator run was used for each test of the particles' activity, it was necessary to assume that each run produced particles with the same size distribution. The required consistent operation of the generator was suggested by a constant duration of AgI smoke leaving the generator for each run.

In a calibration experiment the generator output was passed directly into the Goetz centrifuge, where the particles were deposited on electron-microscope grids attached to the collection foil. Evaluation of the grids gave a calibration curve relating foil coordinates to Stokes' diameters of the particles; good agreement was found with a calibration curve given earlier (Gerber *et al.*, 1970). The relative size distribution of the particles was log-normal with $R_0 = 67 \text{ \AA}$ and $\sigma_0 = 2.21$. The particles were predominantly bullet-shaped, with pyramids at one or both ends of hexagonal prisms; they all showed the hexagonal geometry of β -AgI, and their crystalline planes had sharp intersections. Since the particles were all nearly isometric and more than 90% uncoagulated, it was possible to equate without much error their Stokes' diameters and shadow widths on the grids.

For the activity measurements the centrifuge sample was obtained inside an aluminized Mylar bag in which the output of one generator run had been mixed with room air. After sampling, the foil was removed from the centrifuge and placed in a cold box, where it was cooled to the desired temperature. A freeze trap inside the box kept the water vapor pressure at less than ice saturation. At the desired temperature a 2 s puff of nitrogen saturated with water vapor at room temperature was blown over the foil. It was assumed that each particle was enclosed in a water droplet, which froze if it contained an active nucleus. The appearance of ice crystals was recorded as a function of time with dark-field photography.

The assumption of a one-to-one relationship between particles and droplets on the foil is supported by the following observations: Microscopic examination of the foil following humidification at -10°C showed about one 5–10 μm diameter droplet per $10^3 \mu\text{m}^2$ of deposit area. That concentration was close to the concentration of AgI particles which was expected on the deposit considering the relative size distribution of the particles, the mass of the AgI vaporized, and the volume of the dilution bag and of the aerosol sampled by the centrifuge. The concentration of the droplets was about the same at both ends of the deposit, as should have been the case for the measured size distribution. The background concentration of droplets on control areas on the foil to either side of the particle deposit suggested that the clean surface

of the foil, made hydrophobic with a silicone film, required a high supersaturation for droplet formation. Droplets on the control areas were about one order of magnitude fewer than the droplets on the deposit area, were much larger, and were about equidistant from each other. On the other hand, the droplets on the deposit area were randomly distributed, suggesting that the humidification caused sufficient supersaturation to condense water even on particles close to each other on the deposit. Although no measurements were made of the supersaturation achieved over the foil, it must have far exceeded the 5% found by Justo and Kocmond (1968) to be necessary for AgI smoke particles 200 Å in diameter to form condensation droplets. The interaction between the droplets on the foil was minimal, since the condensate did not change its appearance when left long times at a constant temperature.

Condensation during humidification could possibly be less rapid than the rate of ice nucleation, but that appears unlikely, since the vapor-liquid-solid transition is preferred over the vapor-solid transition; also,

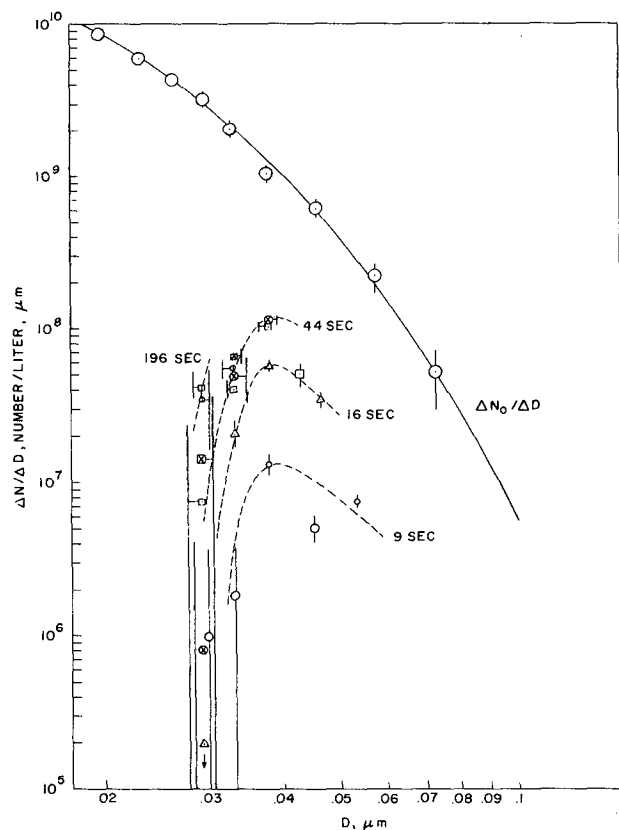


FIG. 4. Size distributions $\Delta N_0/\Delta D$ of all AgI smoke particles and the size distribution $\Delta N/\Delta D$ of those particles that activate ice by the freezing mechanism at -14°C for $t=9$ (\odot), 16 (Δ), 34 (\square), 44 (\otimes), 63 (\oplus), 96 (\boxtimes) and 196 seconds. The vertical line on each data point is twice the sample standard deviation. (Values at 196 s are shown by a square with a vertical line.)

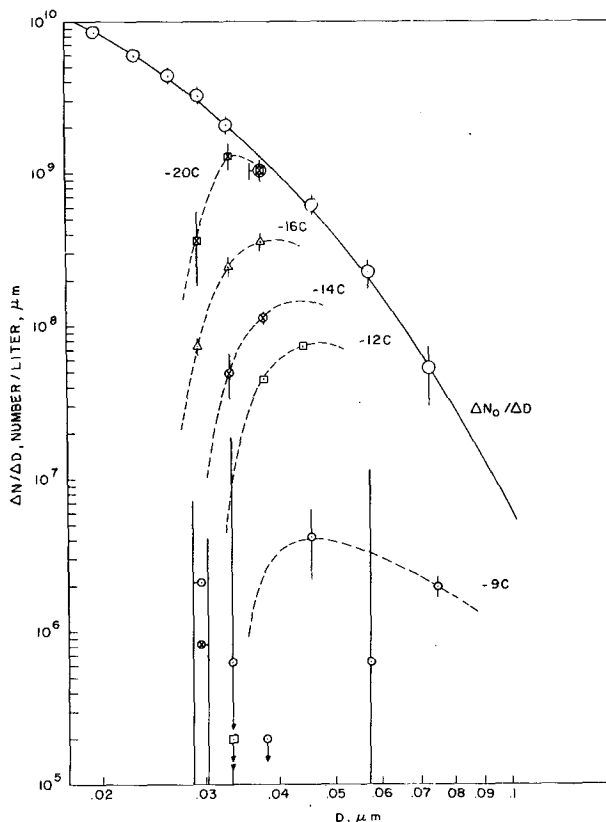


FIG. 5. $\Delta N_0/\Delta D$ and $\Delta N/\Delta D$ at various temperatures for $t=118$ (\odot), 86 (\square), 44 (\otimes), 45 (Δ) and 50 (\boxtimes) seconds.

a time lag was seen between the formation of the droplets and the appearance of ice crystals.

It was necessary to assume that the surface of the foil did not interfere with the nucleation of ice; that assumption appears reasonable, because Edwards and Evans (1968) studied ice nucleation on various hydrophobic substrates and found no difference in nucleation behavior as a function of substrate.

The volume of each condensation droplet on the foil was less than about $250 \mu\text{m}^3$; hence 200 Å particles, which were the smallest particles tested, should not have dissolved.

The problem of different particles interacting when nucleating ice was minimized by limiting the count of ice crystals to those areas of the foil where at least 75% of the area still consisted of supercooled water droplets.

4. Results

a. Fractional activity

A time-dependent phenomenon was observed after humidification of the foil on which a sample of AgI particles had been collected from the dilution bag. Ice nucleated first on portions of the deposit corresponding to large particles. As time progressed, the

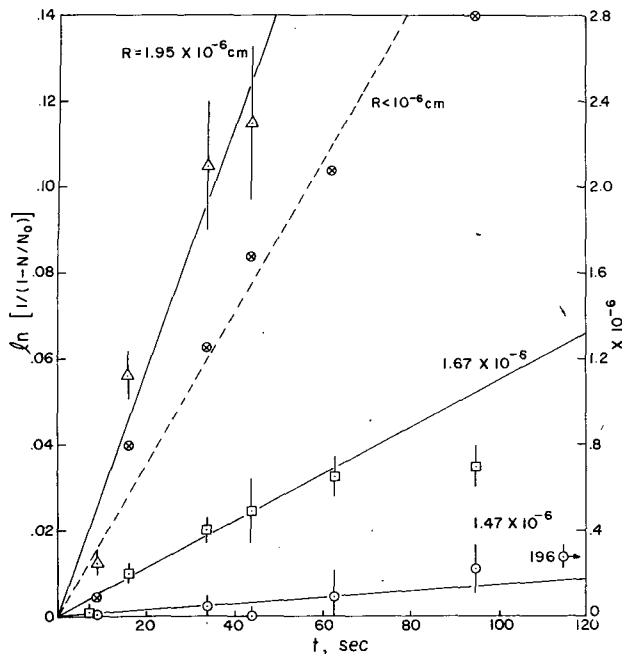


FIG. 6. Fractional activity N/N_0 of the AgI smoke particles as a function of R and t at -14°C . The right-hand ordinate corresponds to $R < 10^{-6}$ cm.

formation of ice crystals advanced along the deposit toward areas occupied by increasingly smaller particles. At -20°C that advance was rapid, but at -9°C it was slow. Those observations showed that the AgI particles nucleated ice at a rate which depended on particle size as well as on temperature. Those trends are identical to those found much earlier by Vonnegut (1949) in the cloud chamber.

In Fig. 4 the number of particles which nucleated ice at -14°C is compared to the total number of the particles on the foil as a function of time and particle size. Fig. 5 gives the fractional activity of the particles at -20 , -16 , -14 , -12 and -9°C for one value of time. A new deposit of AgI particles was used for measurement at each temperature, with the exception that for -9°C the crystals grown on the -12°C deposit were sublimed before the foil was again humidified. At temperatures warmer than -8°C no activity was found.

The size distribution $\Delta N_0/\Delta D$ of all the particles, shown in Figs. 4 and 5, has the shape of the relative size distribution determined from the calibration grids, and the position of $\Delta N_0/\Delta D$ along the vertical axis was fixed by assuming that 100% of the particles $>400 \text{ \AA}$ in diameter nucleated ice at -20°C . That 100% activity size limit was reported at the 2nd IWCIN for similar work with AgI smoke particles (Gerber and Allee, 1972).

The curves in Figs. 4 and 5 show that the effectiveness of the AgI particles drops off more rapidly with particle size than predicted by theory; that effect had

been seen previously by Mossop and Jayaweera (1969) and Gerber (1972).

b. Nature of the AgI particle surface

The -14°C data were used to determine the behavior of the AgI particle surface as was described in the theory section. The results, given in Fig. 6, should be compared with the theoretical predictions in Fig. 3. The data in Fig. 6 follow a linear pattern, which infers that for nucleation by freezing the AgI particle surface behaves as if it were homogeneous. The data do not show the rapid increase of fractional activity for small values of t which would have indicated a behavior consistent with sites on the surface of the particles.

Although the surface behaves as if it were homogeneous, the presence of certain sites is still physically possible. Similar curves to those in Fig. 6 would have been found for sites of nearly uniform activity or for sites with small sizes compared to the size of the critical ice embryo. The latter is a reasonable possibility.

c. Experimental and theoretical nucleation rates

Experimental nucleation rates can be calculated by using (6) with the fractional activity data given in Figs. 4 and 5, since particles of the same size have the same mean nucleation rate. Those rates, given in Fig. 7 as a function of particle size and temperature, can be compared directly with the theoretical rates for AgI particles with uniform surfaces.

Since the value of m is unknown and, as shown in the theory section, has a strong influence on the nucleation rates, the comparison was made by evaluating (1) with many different values of m in an attempt to match the separation of the theoretical and the experimental rates for different temperatures. A match was found for $m = 0.88 \pm 0.02$, as shown in Fig. 7. However that value of m gave theoretical rates which overestimated the experimental rates by a factor of 10^{14} . When a smaller value of m was used with (1), the theoretical rates decreased, as would be expected from Fig. 1; however, their separation for different temperatures increased rapidly, so that a match with the experimental rates was impossible. Also the decrease in the experimental rates for particles of $R \approx 10^{-6}$ was for significantly larger particles than predicted by theory.

The 10^{14} difference between the theoretical and experimental rates for the larger AgI particles must be considered approximate due to the many uncertainties in the theory. Assumptions in the theory which may bear on that discrepancy include the use of thermodynamic properties in the description of the ice embryos, the steady-state assumption and the particular model of embryo growth used in the development of the rate constant, and the description of the AgI

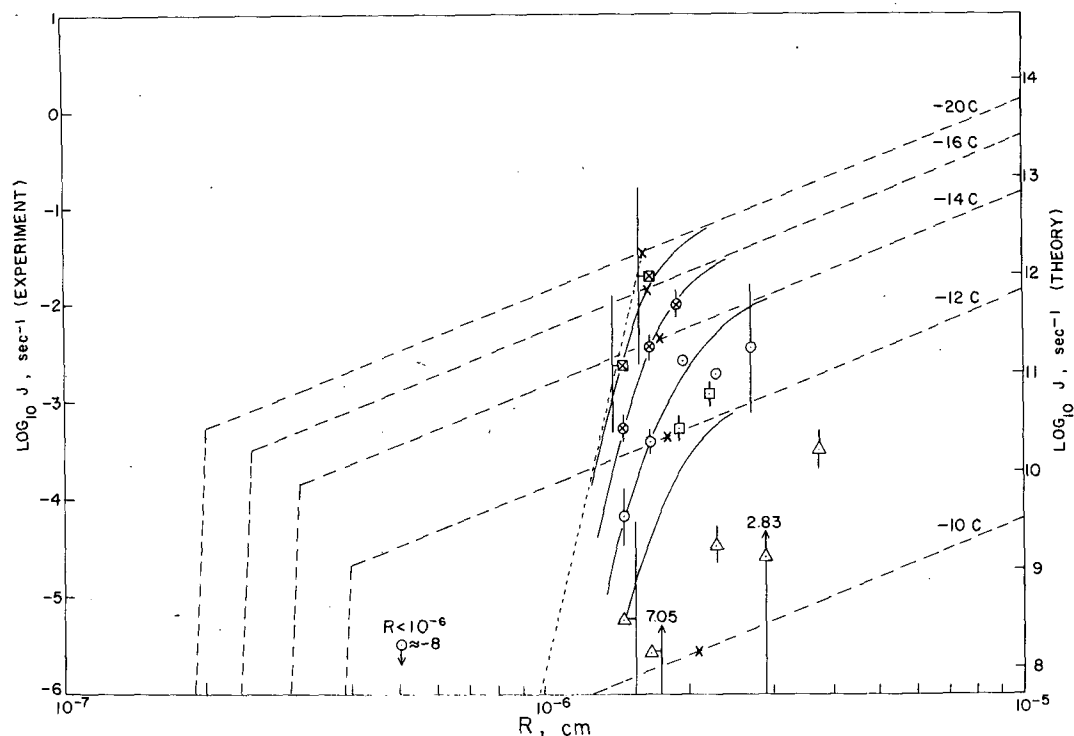


Fig. 7. Experimental nucleation rate of ice by freezing per AgI smoke particle for -9°C (Δ), -12°C (\square), -14°C (\circ), -16°C (\otimes) and -20°C (\boxtimes). The theoretical rate is from Fletcher's theory for nucleation on the uniform prism faces of a AgI particle with $m=0.88$. The significance of the dotted line and the points marked (\times) are explained in the text.

particle surface by only a single parameter. In addition, there are large uncertainties in the numerical values of σ and Δg and in their temperature dependencies. The value of σ in (5) can be in error by about $\pm 10 \text{ erg cm}^{-2}$ according to recent estimates of that parameter (Jones, 1974); the temperature dependence of σ can differ by $\pm 0.15 \text{ erg cm}^{-2} \text{ K}^{-1}$ (Jacobi, 1955; Carte, 1956; Dufour and Defay, 1963). Those uncertainties in σ translate to a $10^{14\pm 3}$ difference between the rates. A value of 60 erg cm^{-2} for σ would eliminate the difference. The use of another estimate for Δg (Dufour and Defay, 1963) increases theoretical J by more than 10^2 , and the inclusion of line tension decreases J by about 10^3 .

The shape of the AgI smoke particles has only a small influence on the 10^{14} difference; hence the theoretical curves in Fig. 7 for nucleation on the prism faces of the particles could, with minor differences, represent spherical particles. Nor does the shape of the critical ice embryo affect the mismatch, since when the comparison was made between the rates for hexagonal ice embryos, the factor of 10^{14} was found again, but this time reflecting particles with $m=0.96 \pm 0.02$. That value of m corresponds to ice embryos with an unrealistically small size.

The preceding considerations show that at best about a 10^8 difference remains between experimental and theoretical rates. It is unknown whether that difference

must be attributed to inaccuracies in the basic assumptions of the theory or to additional uncertainties found in the numerical values of the nucleation parameters.

The much-lower-than-expected experimental rates suggest an explanation for the observed proportionality of activity to particle area which does not depend on the concept of nucleation sites. Since experimentally $0 \text{ s}^{-1} < J \lesssim 1 \text{ s}^{-1}$, Eq. (6) reduces to $N/N_0 \approx Jt$ for values of t often used in laboratory experiments. Furthermore it is reasonable to assume that $J \propto R^2$ for particles large enough that the surface curvature no longer strongly influences the interface areas of the ice embryos. Thus for N_0 and t constant, for large AgI particles, and especially for warmer nucleation temperatures, $N/N_0 \propto R^2$, even though those particles have a uniform surface.

d. Activity spectra

Although a value of $m=0.9$ was shown in Fig. 1 to be consistent with the usual technique of calculating the theoretical activity spectrum, the nearly identical value of m found in the preceding comparison between theory and experiment does not permit a similar technique for the experimental rates. The experimental rates all have $J < 1 \text{ s}^{-1}$; thus particle sizes do not exist which show the required independence of the rates in the vicinity of $J=1 \text{ s}^{-1}$. Activity spectra

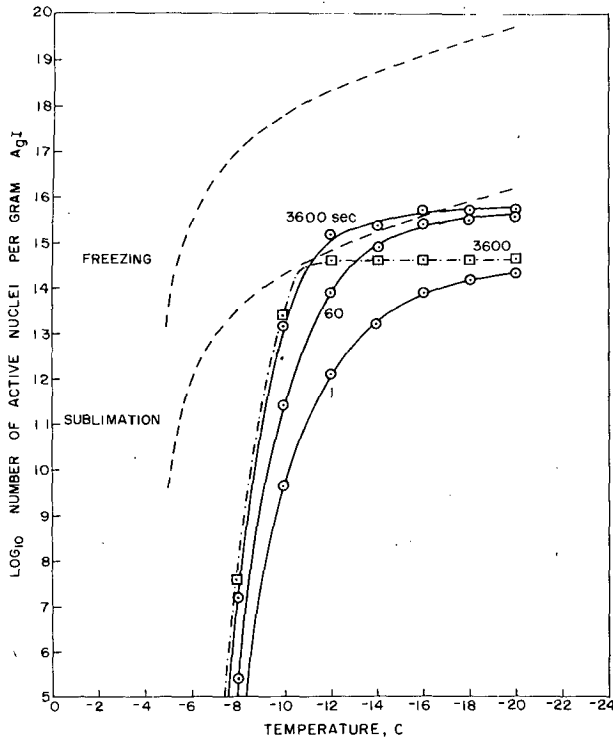


FIG. 8. Freezing activity spectra for the AgI smoke particles calculated from the experimental nucleation rates for a log-normal particle size distribution with $\sigma_g = 1.8$ and $R_g = 4 \times 10^{-7}$ cm (\odot) and $R_g = 4 \times 10^{-6}$ cm (\square); values of t are given with each curve. The dashed curves are Fletcher's predictions of activity spectra for nucleation by the freezing and sublimation mechanisms.

for AgI particles which do not qualify for the assumption of an appreciable rate and whose sizes show dependence on nucleation rates in the interval $-10 \text{ s}^{-1} \lesssim \log J \lesssim 0 \text{ s}^{-1}$ must be calculated by numerically integrating (6) for particles of all sizes found in the particular AgI aerosol under consideration. If n different particle sizes with J_n different rates are given, the fraction of active particles is

$$\frac{M}{M_0} = 1 - \frac{1}{M_0} \sum_{i=1}^n N_{0i} \exp(-J_i t) \quad (8)$$

A choice must be made of the form of the size distribution for the AgI particles in order to specify values of N_{0i} in (8). The log-normal size distribution was the logical choice, since particle sizes in AgI aerosol often closely follow that distribution (e.g., Mossop and Tuck-Lee, 1968). It follows that

$$N_{0i} = M_0 f(R) dR, \quad (9)$$

where the fraction $f(R)dR$ of the particles of size R is given by Fuchs (1964) as

$$f(R)dR = \frac{0.434}{(2\pi)^{1/2} R \log \sigma_g} \exp \left[-\frac{(\log R - \log R_g)^2}{2(\log \sigma_g)^2} \right] dR. \quad (10)$$

Since the activity spectra are usually computed for 1 g of AgI, M_0 was normalized to that value as a function of the parameters of the log-normal size distribution:

$$M_0 = 1 \text{ g} \left\{ \frac{2\pi\rho R_g^3 \exp(3.45\delta^2)}{3} \left[\text{erf} \left(\frac{\log R_b/R_g - 3.45\delta^2}{\delta} \right) - \text{erf} \left(\frac{\log R_a/R_g - 3.45\delta^2}{\delta} \right) \right] \right\}^{-1}, \quad (11)$$

where $\delta = (2)^{1/2} \log \sigma_g$ and $R_a \ll R_g \ll R_b$.

Eqs. (8)–(11) were combined to calculate activity spectra using the measured values of J in Fig. 7. Due to the scatter and limited range of the experimental rates, values of J were extrapolated by following the dashed lines for particle sizes above the points marked by crosses and by reading values of J from the experimental scale. Below the crosses the dotted lines were extended downward from each cross in the direction parallel to the dotted line for -20°C . For values of $\log J \leq -8$ it was assumed that $J = 0$. That procedure was not expected to provide exact activity spectra; however, it was expected to resolve the trends in the spectra as a function of particle size, temperature and time.

Spectrum calculations made for some typical values of R_g and σ_g were compared (Fig. 8) to Fletcher's predictions for the freezing and sublimation mechanisms. The large difference between Fletcher's freezing spectrum and the calculated freezing spectra reflects the decrease in the theoretical rates for AgI particles with sizes that are much smaller than those shown by the present experiment. On the other hand, the good agreement of Fletcher's sublimation spectrum

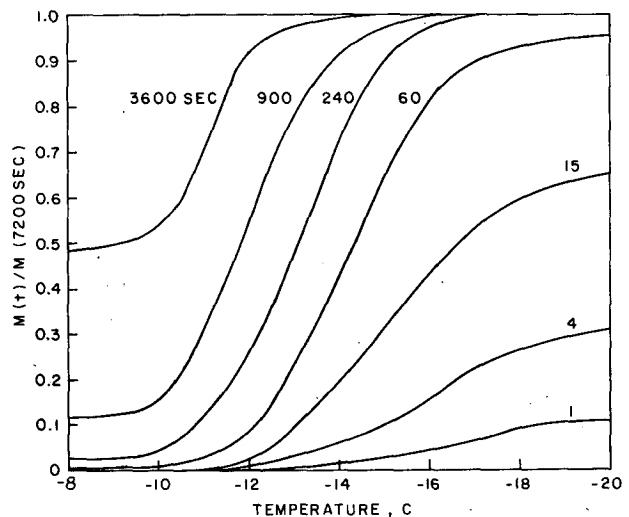


FIG. 9. Fraction of active AgI smoke particles, $M(t)/M(7200 \text{ s})$, as a function of temperature and t for $\sigma_g = 2.0$ and $R_g = 1.25 \times 10^{-6}$ cm.

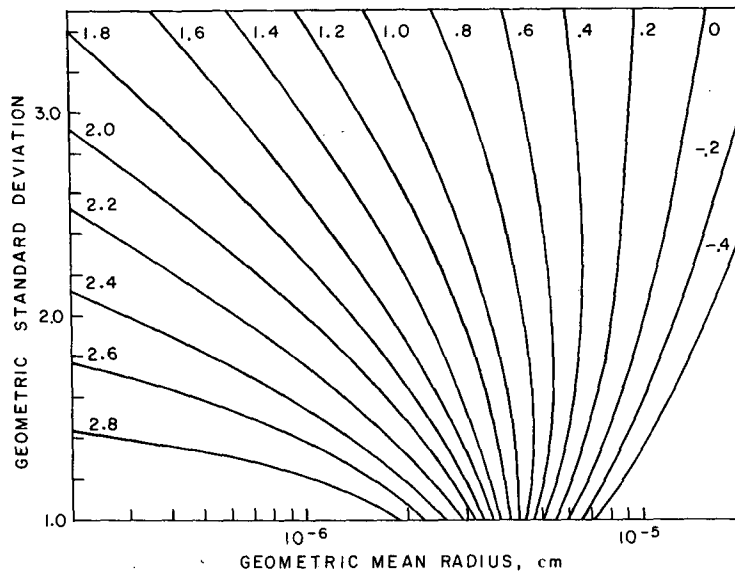


FIG. 10. Values of K_2 used with Eq. (12).

with the calculated spectra occurs because the nucleation rates corresponding to both spectra decrease sharply for about the same particle sizes. That finding suggests that the good agreement usually found between Fletcher's sublimation spectrum and spectra measured in cloud chambers seeded with AgI is fortuitous. Those cloud chamber spectra may have instead reflected nucleation by a freezing mechanism.

The influence of the nucleation time lag is demonstrated in Fig. 9, where the fraction of active particles is calculated as a function of t and T for one value of σ_g and R_g . The importance of the time lag is seen

to increase rapidly for temperatures warmer than about -12°C ; it also increases for smaller values of R_g and decreases for larger values.

An empirical expression was developed from Eqs. (8)–(11) to simplify the calculation of activity spectra for all reasonable combinations of σ_g , R_g , t and T . Spectra calculations for those combinations showed that

$$\frac{M}{M_0(T)} = 1 - \exp \left\{ -t \exp \left[- \left(\frac{K_1}{T^4} + K_2 \right) \right] \right\}, \quad (12)$$

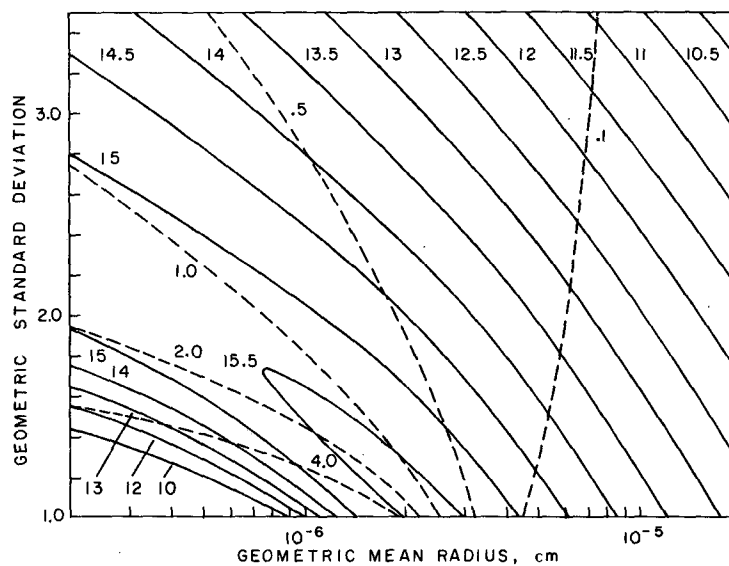


FIG. 11. \log_{10} of the number M_0 (-20°C) of active AgI smoke particles per gram of AgI for $t \gg 0$ (solid lines). Values of K_3 used with (13) are shown as dashed lines.

where $K_1=8.9 \times 10^4$, K_2 is a function of σ_0 and R_0 as shown in Fig. 10, and

$$M_0(T) = \exp[\ln M_0(-20^\circ\text{C}) + K_3(|T|^{1/2} - 4.77)] \quad (13)$$

gives the number of active AgI particles as a function of T for t in the order of hours. Eq. (13) takes into account the values of R and T for which $\log J = -8$. Values of $M_0(-20^\circ\text{C})$ and K_3 are given in Fig. 11 as a function of σ_0 and R_0 .

The application of (12) requires only a knowledge of σ_0 and R_0 , with the necessary constants being found in Figs. 10 and 11. The values of M given by (12) are within plus or minus one order of magnitude of the more accurate values determined from (8)–(11).

5. Concluding remarks

A unique relationship between AgI particle size and nucleation threshold temperature was not found in this experiment. Instead only a fraction of the particles, depending in a complicated way on particle size, temperature and time, nucleated ice. By applying the assumption that nucleation is a stochastic process following the Poisson distribution, matters were simplified, since now the particles had in common a mean nucleation rate which depended only on particle size and temperature. That behavior permitted the derivation of a simple empirical expression for the particles' activity spectra which included particle size, temperature and time effects. That expression showed that the nucleation time lag became important at temperatures warmer than about -12°C and that the number of active particles had a pronounced maximum for certain values of the parameters of the log-normal particle-size distribution.

Care must be taken in applying that expression to other nucleation experiments, since it may reflect the unique intrinsic activity and the specific shape of the particles used in this experiment. Also, it applies only to a freezing mechanism in which the particles are immersed in supercooled droplets at $t=0$ and in which the droplets are not large enough to dissolve the particles. To judge the reliability of the predicted spectra, comparisons should be made with other measured spectra. However, proper comparisons are difficult at present, since the measured spectra are usually determined only from ice crystal counts, whereas the comparison should include the nucleation mechanisms involved, the particle size distribution, and time effects.

The unique relationship between particle size and nucleation rate for a given temperature suggested that the results of this experiment should be compared with Fletcher's theory for nucleation on particles with a uniform surface instead of a surface with nucleation sites. That comparison showed that the activity of small particles dropped off more rapidly than pre-

dicted by theory and that the experimental nucleation rates of large particles were many orders of magnitude less than given by theory. Those differences make the theoretical technique of calculating activity spectra invalid for AgI particles with similar behavior, since the concept of threshold temperature and an appreciable nucleation rate no longer hold.

This study has demonstrated a new technique for determining the activity of AgI particles. It should be applied to AgI particles generated by other means and nucleating ice by other mechanisms. It is necessary to rely at this time on experiments of this type, since the theory of heterogeneous ice nucleation does not appear to be sufficiently sophisticated to provide practical results.

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APPENDIX

List of Symbols

D	Stokes' diameter
h	Planck's constant
J	mean nucleation rate of ice per particle in water
k	Boltzmann's constant
K	nucleation rate constant
m	particle surface parameter (cosine of the angle between the ice embryo and the particle surface in water)
M	number of active particles out of M_0
$M(t)$	M for a given t
M_0	number of particles with a total mass of 1 g in a log-normal size distribution of particles
$M_0(T)$	those particles out of M_0 which nucleate ice at T and $t \gg 0$
p	number of water molecules in contact with a unit area of particle surface
N	active number of monodisperse particles
N_0	total number of monodisperse particles
R	Stokes' radius
R_0	geometric mean particle radius for a log-normal size distribution of particles
S	ice-water interface area of the critical ice embryo
t	time elapsed after AgI particles are enclosed in supercooled water droplets
T	temperature ($^\circ\text{C}$), except K in (1) and (2)
v	ice molecule volume
Δg	activation energy for viscous flow of water

- ΔG^* free-energy change in the formation of the critical ice embryo
 σ free energy of the interface between the critical ice embryo and water
 σ_p geometric standard deviation of the radii of particles with a log-normal size distribution

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