Nucleation of water drops by Brownian contact with AgI and other aerosols

By R. I. SAX* and P. GOLDSMITH
Meteorological Office, Bracknell

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SUMMARY

Aitken-sized (0·01μm) particles of AgI, CuI, and 'contaminated' Ag2O were able to nucleate various sized water droplets in free fall (20-80μm in radius) by a direct, diffusive (Brownian) contact mechanism. The AgI aerosol was found to be the most efficient nucleator, showing a probability of 100 per cent at -16°C, 50 per cent at about -14°C, and 1 per cent at -11°C. These nucleation characteristics for AgI can be modelled from heterogeneous nucleation theory if the value of the contact parameter is assumed to be 0·70. Ag2O, passing through carrier tubing previously contaminated with iodine, was found to be only a slightly less efficient nucleating agent than AgI. CuI was found to have a nucleating efficiency corresponding to that which would theoretically be expected from an aerosol with a contact parameter of 0·55. Aerosols of the 'pure' oxides of silver, platinum, and chromium were unable to cause nucleation (to within detectable limits) at temperatures as low as -18°C. Auxiliary experiments indicated that the AgI aerosol had a small, but finite (10^{-3}), nucleating efficiency at -5°C. Aitken-sized particles of AgI did not lose their nucleating ability when captured at temperatures higher than 0°C.

It is postulated that contact nucleation by the Brownian capture of Aitken particles may be an important enough process in the atmosphere to contribute significantly to the large amounts of ice which have been observed at relatively high (-10°C) temperatures in some clouds.

1. INTRODUCTION

During the past decade it has become increasingly evident that, in some instances, a large discrepancy can exist between the observed quantity of ice crystals in clouds and the corresponding detectable concentration of ice-forming nuclei. World-wide surface measurements of ice nuclei generally yield concentrations of the order of one per litre active at -20°C, decreasing by one order of magnitude for every 4°C increase in temperature. However, clouds with summit temperatures no lower than -10°C have often been observed to contain ice crystals in concentrations exceeding 10 l^{-1} (Mossop, Ruskin and Hefferman 1968; Mossop, Ono and Wishart 1970; Koenig 1968; Mee and Takeuchi 1968; Hobbs 1969). Attempts have been made to explain the presence of such large amounts of ice by invoking a multiplication mechanism for secondary crystal production based upon the shattering of freezing drops (Koenig 1966), but the evidence from recent laboratory investigations (Johnson and Hallett 1968; Dye and Hobbs 1968; Hobbs and Alkezweeny 1968; Bovensperge and Thorndike 1968a, b) has indicated that, at least for the case of isolated drops freezing in air at atmospheric pressure, such shattering events are rare. Also Dr. D. A. Johnson (private communication) has found no evidence of significant secondary ice crystal production during the riming process in his laboratory studies.

At this point it seems reasonable to explore an alternative hypothesis that the sometimes severe nuclei-crystal discrepancy is at least partly the result of an efficient nucleating process working in the atmosphere and not being detected by the commonly-used instrumentation presently available. This paper will discuss some laboratory experiments which indicate that the diffusive capture of certain Aitken-sized aerosol particles (\sim 0·01μm radius) is an effective nucleating mechanism for small cloud droplets in thermal and freefall conditions close to those in the atmosphere. A companion paper (Goldsmith, Porter and Sax 1972) deals with the possibility that such sub-micron 'contact nuclei' cannot be readily detected by commonly-used techniques.

* Present Address: Dept. of Air Force, Scott Air Force Base, Illinois.
2. Theory

There are three basic modes of action of ice nuclei—
(a) condensation-freezing, (b) sorption or sublimation and (c) contact nucleation.

The first describes those nuclei which act as, or form part of, the condensation nucleus. They are incorporated into the droplet during the initial condensation process, and may subsequently cause the droplet to freeze when and if it is lowered to the appropriate activation temperature. It can be shown from the basic theory of nucleation thermodynamics that such condensation cannot generally occur on Aitken-sized particulate matter under the just-saturated conditions likely to be encountered in the atmosphere.

The second class of nuclei involves particles which nucleate ice crystals while remaining dry. They may act either by the adsorption of thin films or patches of water on the surface (sorption nuclei) or by condensation on to an ice covered nucleus (sublimation nuclei). Calculations, similar to those performed by Fletcher (1959) indicate that Aitken-sized nuclei have a negligible probability of causing freezing by sorption or sublimation processes, even at temperatures as low as -25°C. Laboratory experiments by Edwards and Evans (1960, 1968) have demonstrated that, within the temperature range -6°C to -18°C, sub-micron sized AgI particles can act at least a hundred times more effectively as freezing nuclei than as sorption nuclei.

In the third mechanism, the freezing nuclei become attached to the water droplets after the initial condensation growth. If such a contact nucleation mechanism is to be important in the atmosphere, then it must involve Aitken-sized particles since the main capture process is a diffusional one which is more efficient for the smaller particles. Capture of particulate matter by kinematic impaction with cloud droplets is not an important atmospheric scavenging process, whilst such impactive capture of particulates by falling raindrops and snowflakes is clearly at the end of the precipitation forming processes and so cannot be an important factor in the initiation of precipitation.

Goldsmith, Delafield and Cox (1963) have shown that diffusiophoresis, the movement of aerosol particles induced by a vapour flux, is not likely to be important as a scavenging mechanism in natural clouds. However, as has been discussed by Greenfield (1957), thermal (Brownian) and/or turbulent (gradient) coagulation can play a significant role in the uptake of Aitken-sized particulate matter by cloud droplets. Standard texts on aerosol physics (e.g. Fuchs 1964) contain the derivation for the general coagulation equation

\[
\frac{-dn_p}{dt} = (K_B + K_T)n_p n_e
\]  
(1)

where \( n_p \) is the concentration of Aitken particles, \( n_e \) the concentration of cloud droplets, and \( K_B \) and \( K_T \) the coagulation constants related to Brownian and turbulent motion respectively. If an atmospheric aerosol can be assumed to consist of Aitken particles, all of radius \( r_p \), and cloud droplets, all of radius \( r_e \), then

\[
K_B = 4\pi(D_p + D_e)(r_p + r_e)
\]  
(2)

where \( D_p \) and \( D_e \) are the diffusion coefficients for the particles and droplets respectively. The corresponding expression for \( K_T \) is

\[
K_T = \frac{4}{3}u(r_p + r_e)^3
\]  
(3)

where \( u \) is the velocity gradient normal to the streamlines. For the case of 0.01μm particles coagulating with cloud droplets of 10μm radius, Greenfield (1957) has shown that \( K_B \) is two orders of magnitude larger than \( K_T \) if reasonable values of \( u \) are assumed. It can be seen from Eq. (3), however, that the \( K_T \) term rapidly gains in relative importance as \( r_e \) increases. If only the effects of Brownian coagulation are considered, then, for \( r_e > r_p \) and \( D_p > D_e \), Eqs. (1) and (2) reduce to

\[
\frac{-dn_p}{n_p} = 4\pi r_e D_p n_e dt.
\]  
(4)
It can be calculated from Eq. (4) that 50μm radius drops falling with a terminal velocity of 25 cm s⁻¹ through a coagulating region 1 cm in vertical extent (dt = 0.04 s) will each collect, on average, one aerosol particle of radius 0.01μm (diffusion coefficient of 10⁻⁴cm² s⁻¹) if the concentration of such aerosol particles is 5 × 10⁶cm⁻³. Small changes in drop size will not significantly affect the above calculation because the drop's terminal velocity (and hence dwell time in the coagulating region) varies inversely with drop radius in the range 40-500μm.

Thus the efficiency of the Brownian contact nucleating mechanism can be measured by experimentally determining the percentage of droplets which freeze after first falling through such a nucleating aerosol.

3. The experimental apparatus and procedure

(a) Aerosol production

An overall understanding of the location and function of the various pieces of apparatus used in the production, counting, and sizing of the aerosol can be gained from the flow diagram shown in Fig. 1. Nitrogen is blown over an electrically heated wire coated with AgI. If the wire is heated to a high enough temperature, an aerosol forms by the vaporization and subsequent condensation of the particulate matter. Such an aerosol can then be sized either by a thermal precipitator (Green and Lane 1964) or by a denuder (Rich 1959), the latter method requiring a weak alpha emitting radioactive source in the line to ensure electrical equilibrium (Pollak and Metnieks 1962). The aerosol concentration was measured by means of a photoelectric condensation nucleus counter of the type originally described by Nolan and Pollak (1946). If the aerosol was found to meet the experimental criteria (i.e. a concentration of 5 × 10⁶ cm⁻³ and a size of the order 0.01μm) for a statistical study of contact nucleating efficiency, it was allowed to by-pass the counting and sizing apparatus and to proceed directly into a nucleation chamber located inside a large cold-room. Because the upper sampling limit of the Nolan-Pollak counter is a concentration of the order 10⁵ cm⁻³, it was necessary to dilute the aerosol with filtered air during the sizing and counting measurements. Filters were placed in the aerosol line for sampling purposes. A means of producing ice crystals was provided to serve as an alternative method of nucleating droplets in order to ensure that the drop-freezing system was functioning properly.
(b) The drop-freezing system

Fig. 2 schematically illustrates the drop-freezing system for the free-fall experiments. Droplets of distilled, de-ionized water were formed on the cold room roof from either a vibrating needle (Mason, Jayaratne and Woods 1963) or an ultrasonic atomiser. The former method was used to produce drops of radius 50-80μm, while the latter method produced drops of either radius 25-50μm (20 KHz source) or 10-25μm (100 KHz source). The number density of the drops was controlled either by the deflection of a selectively charged stream in an electric field (in the case of drops produced from the needle) or by a mechanical shutter (for drops produced from the atomiser). The droplets were allowed to enter the nucleation chamber via a fall-tube which was long enough (≈1m) to ensure that they were in thermal and solution equilibrium prior to intercepting the aerosol. After coagulating with the nucleating aerosol (AgI in this case), the droplets then proceeded to fall into an observation chamber which was illuminated by the beam from a pulsed Hg lamp at 90° to the viewing window. Because water drops scatter least light at right angles to the illuminating beam, while ice particles, on average, do not exhibit preferential light-scattering behaviour, the contrast in brightness between the drops not nucleated and those which are nucleated is easily discernible. It is thus possible to determine from visual observation the percentage of the total number of drops which are nucleated by the aerosol, and a comparison with the calculated value (from Eq. (4)) provides a measure of the aerosol's contact nucleating efficiency. The temperature within both nucleation and observation chambers was dependent only upon that of the large cold room, thus reducing the possibility of thermal gradients along the drop's fall path. The temperature was measured to the nearest ±0.1°C by means of fast response thermocouples.

![Diagram](image)

Figure 2. The drop-freezing apparatus (not to scale).

(c) Operational procedure

The AgI aerosol was produced outside the cold room and was transferred into the nucleating region via some 6m of polythene tubing. Assuming a monodisperse aerosol of 0.01μm spherical particles in an initial concentration of 10^7 cm⁻³ flowing through 5mm i.d. tubing at the rate of 10 cm³ s⁻¹, and considering only the effects of coagulation and diffusion to the walls due to Brownian motion, it can be calculated theoretically that 50 per cent of the particles would be lost by the time the aerosol traversed the distance to the nucleating region. The experimental criterion of an aerosol concentration of 5 × 10^6 cm⁻³ in the nucleating region can therefore be attained with the above experimental conditions. An AgI aerosol of concentration 10^7 cm⁻³ can be produced by heating a short length (10 cm) of AgI-coated resistance wire (e.g. 32 s.w.g. nichrome) to a temperature of up to 700°C in a nitrogen stream.
The operational procedure for the free-fall experiments was to produce a stable stream of droplets of the size of interest and to determine, in the absence of the nucleating aerosol, the natural level of background freezing for a given temperature. The AgI aerosol, having been counted and sized, was then passed into the nucleation chamber, and its nucleating efficiency (relative to the background freezing level) was observed. After about a 10-min experimental run (normally involving a study of some 3,000 drops), the aerosol concentration was once again measured to ensure that the wire's emissive properties had not deteriorated. This procedure was repeated several times for each of a series of temperatures in the range $-8^\circ$C to $-18^\circ$C. Experiments were also carried out at a fixed temperature but with differing concentrations of AgI particles.

4. Characteristics of the AgI Aerosol

It can be seen from Table 1 that the onset of particle emission from an AgI-coated wire is very marked, and the aerosol concentration varies tremendously with small changes in wire current (and hence temperature) in the lower range of values. Fortunately, in the concentration range of interest for the nucleation experiments, the wire's emissivity was considerably more stable. A typical AgI-coated wire was able to emit a particulate concentration of the order $10^7$ cm$^{-3}$ for time periods of as long as 40 min without undergoing any noticeable fluctuations. The experimental lifetime of an AgI-coated wire was normally found to be tens of hours of intermittent usage, at the end of which time it took on a fibrous appearance and its emissive capability very rapidly deteriorated.

<table>
<thead>
<tr>
<th>TABLE 1. Variation of AgI Emission with Wire Current</th>
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<tr>
<td>Current (amps)</td>
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<td>Concentration (cm$^{-3}$)</td>
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A detailed size distribution of the AgI aerosol was obtained from an analysis of electron microscope photographs of thermal precipitator specimens. Four such photographs are shown in Fig. 3. Samples (a) and (b) were taken from an 'aged' wire, while samples (c) and (d) were taken from a wire never before used. The AgI aerosol pictured in (a) and (c) was sampled at the source, while that shown in (b) and (d) was sampled after it had traversed the six meters of carrier tubing to the nucleation chamber. The corresponding histograms of particulate size distribution are shown in Fig. 4. The smooth curves represent an attempt to fit a theoretical distribution of the type described by Khrgian and Mazin (1956)* to the experimental histograms. It is readily apparent from Figs. 3 and 4 that the AgI aerosol is not monodisperse. In all cases, however, the mean particle radius is between 0.01 $\mu$m and 0.02 $\mu$m. As could be expected from a coagulating aerosol, at the nucleation chamber the size spectrum is shifted towards slightly larger radii relative to that at the aerosol source. Although the actual AgI aerosol proved to have a polydisperse size distribution, the experimentally-determined decrease in particle concentration due to losses by coagulation and diffusion within the carrier tubing was found to agree closely with the theoretically-calculated 50 per cent loss which would be experienced by a monodisperse aerosol of 0.01 $\mu$m particles with a similar initial concentration.

Newly-coated AgI wires consistently produced a wider spectrum of particle sizes than did the wires which had previously been used. Fig. 4(d) represents the widest AgI size

* The Khrgian-Mazin distribution: $n(r) = \pi a^2 e^{-br}$ where $a = n_0b^{1/2}$ with $n_0$ the total concentration, $r$ the particle radius, and $b = 3/\bar{r}$, $\bar{r}$ the mean particle radius.
Figure 3. Electron microscope photographs of some AgI aerosol samples.
Figure 4. Some AgI aerosol size spectra analysed from electron microscope photographs.

spectrum observed from any of the thermal precipitator specimens, while the most mono-
 dispersed spectrum (not shown) resulted from an aged wire and indicated a mean particle
radius as small as 0.007µm. The composite average of all of the thermal precipitator sam-
pling showed a mean particle radius of 0.012µm at the source and 0.016µm at the nucleation
chamber. It should be mentioned that newly-coated AgI wires were not utilized in the drop
freezing experiments without first allowing for some burn-off of the coating, so the aerosol
size distributions shown in Fig. 4(a) and (b) were the most typical.

The operational sizing analysis carried out with the denuder, though limited by the
relatively low resolution of the Pollak counter near its upper sampling limit, confirmed that
the AgI aerosol's 'equivalent monodisperse radius' at no time exceeded 0.03µm. An inde-
dependent check on particle size was also made with a 17-channel diffusion battery, and it
was found that the diffusion coefficient of the AgI particles corresponded to an aerosol
possessing a mean radius of about 0.01µm.

5. The Experimental Results

A graphical summary of the contact nucleating efficiency of the AgI aerosol (from aged
wires only) as a function of temperature is presented in Fig. 5. The natural background

Figure 5. Experimentally observed contact nucleating efficiency, as a function of temperature, of the AgI
and CuI aerosols.
freezing percentage in all cases was found to be less than the detectable visual threshold which, for an experiment of this type, is probably not better than about 1 per cent (i.e. less than one droplet freezing per hundred drops cannot be readily detected). Each data point in Fig. 5 represents an integrated average of the freezing behaviour of several thousand drops of sizes ranging from 20µm to 80µm in radius. To within any reasonable error caused by the subjectivity of the visual analysis, the contact nucleating efficiency of the AgI aerosol appeared to be independent of drop size within that range. The zero freezing percentage indicated in Fig. 5 should be regarded as implying only that the aerosol's nucleating efficiency is below the visual threshold, and not necessarily that no nucleation can occur. An experimentally-determined curve of nucleation probability for a CuI aerosol is also presented in Fig. 5, and this will be discussed in the next Section.

The most significant feature of Fig. 5 is the marked increase in AgI nucleating ability at temperatures lower than −12°C. Although the subjective visual method of analysis makes it impossible to guarantee the absolute accuracy of the freezing percentage to within about ±15 per cent in the middle of the range, it can be concluded from the experiments with some certainty that the AgI aerosol changes from a relatively poor contact nucleator to a very good contact nucleator at a temperature of about −13°C. Detectable nucleation was not observed to occur at temperatures higher than about −10°C, while 100 per cent of the drops were always found to nucleate at temperatures lower than about −16°C. A limited number of experiments using the new-wire aerosol with a size distribution as shown in Fig. 4(d) gave 75 per cent nucleation at −17°C, compared with 100 per cent for the aerosol shown in Fig. 4(b) at the same temperature. Such a decrease in freezing percentage with increasing particle size lends support to the assumption that the capture process was diffusive and not kinematic.

It is desirable to relate the experimental results shown in Fig. 5 to theoretical freezing probabilities derived from the basic thermodynamics of heterogeneous nucleation. The concepts involved in the interpretation of the theoretical thermodynamical treatment have been discussed in considerable detail by Fletcher (1962). Fletcher (1969) also has recently modified the theory to account for the possibility of 'active sites' upon the surface of the nucleating substrate and to explain experimental results indicating that particles of a given size are able to cause nucleation (with a varying degree of probability) at a variety of temperatures under a given set of conditions. The probability that a particle will cause nucleation becomes, in the final analysis, a function of \( R \), the particle radius, \( T \), the environmental temperature, \( m \), the cosine of the contact angle between the particulate substrate and ice, \( \sigma \), the free energy per unit area at the ice-water interface, and \( \alpha \), a parameter indicating how much of the particulate surface contains active nucleation sites.

For any given \( m \), \( T \), and \( \sigma \), the mean nucleating probability for a population of aerosol particles can be expressed by

\[
P_R = \int_{R=0}^{\infty} \frac{P(\alpha, R)N(R)}{N_T} dR
\]

where \( P(\alpha, R) \) is the nucleating probability for a particle of radius \( R \) (Fletcher 1969), \( N(R) \) is the concentration of particles of radius \( R \), and \( N_T \) is the total concentration of aerosol particles. Eq. (5) is too cumbersome to solve analytically, thus making it necessary to resort to numerical procedures. Fig. 6 shows the results of such a computation of mean nucleating probability, \( P_R \), as a function of temperature for a polydisperse, Khrgian-Mazin distributed, aerosol of mean radius 0.015µm and various values of contact parameter ranging from \( m = 0.50 \) to \( m = 0.75 \). The experimentally-determined nucleation curves for AgI and CuI shown in Fig. 5 are also included in Fig. 6 for comparison with the theoretical curves.

It can be seen that the experimental nucleating probabilities agree well with the theoretical curves if the values of the contact parameter \( m \) is assumed to be about 0.70 for the case of the AgI aerosol and 0.55 for the CuI aerosol. The divergence between the theoretical and experimental curves at high nucleating probabilities can be attributed, at least in part,
to the departure of the actual aerosol size spectrum from the idealized Khrgian-Mazin distribution at small values of particle radius. In view of the many assumptions and uncertainties inherent in any theoretical treatment of heterogeneous nucleation (Fletcher 1962, 1969), it would be unwise to draw too many quantitative conclusions from Fig. 6. It is apparent, however, that the general shape of the curve of nucleating behaviour displayed by the experimental AgI and CuI aerosols can be quite successfully modelled by incorporating an appropriate value of $m$ into the theory of nucleation thermodynamics.

It should be mentioned that the $m$ value of 0.70 needed to reconcile reasonably thermodynamic theory with the results from the contact nucleation experiments is higher than that ($m = 0.50$) deduced by Fletcher (1969) as being necessary to explain the results from the more conventional type of nucleation experiments (Mossop and Jayaweera 1969). This could possibly indicate that direct contact between a dry particle and a water drop is a more efficient nucleating mechanism than either condensational or sublimational freezing, and there is some experimental evidence (Sulakvelidze 1969) as well as intuitive reasoning (Fletcher 1970) to support this idea.

The results of a series of experiments testing drop-freezing probability, $P_r$, as a function of aerosol concentration are presented in Fig. 7. Fig. 7 also serves to illustrate some of the major considerations which must be taken into account when interpreting the experimental results on aerosol nucleating effectiveness. The theoretical curve A represents the nucleating efficiency of a Khrgian-Mazin distributed polydisperse aerosol of mean radius 0.015$\mu$m, assuming a contact parameter ($m$) value of 0.70. Curve B represents the nucleating efficiency of a monodisperse aerosol of mean radius 0.015$\mu$m and $m$ value of 0.70. The slightly higher drop-freezing probability for the polydisperse case results because the number of drops frozen is a function of the product of the particle’s diffusion coefficient and the particle’s nucleating probability, and, for the case of a water drop collecting a Khrgian-Mazin distributed aerosol, the increase in capture rate (relative to a monodisperse aerosol of the same mean radius) outweighs the corresponding effect of a lower mean nucleating probability.

It is apparent from Fig. 7 that the experimentally-determined curve of nucleating efficiency for AgI is not well represented by the theoretical curves A and B. There is, however, experimental evidence (Nolan and Kennan 1949) to suggest that particulate size, as well as concentration, is a strong function of wire temperature for aerosols produced by the heated wire technique. They found that the particulate size increased very nearly
linearly with wire temperature over their experimental range of values. Such a dependency of particle size on wire temperature was confirmed in the present experiments by 'dynamically' measuring the diffusive characteristics of the AgI aerosol with a 17-channel diffusion battery. The geometric mean particle radius for initial aerosol concentrations (a function of wire temperature) of $1 \times 10^7$, $5 \times 10^6$, and $1 \times 10^6$ cm$^{-3}$ was found to be 0.015, 0.010 and 0.007µm respectively. A general theoretical curve reflecting a variable mean particle radius which decreases linearly with decreasing aerosol concentration takes the form

$$
\tau = \tau_L + \frac{(\tau_U - \tau_L)}{(n_U - n_L)} (N - n_L)
$$

where $\tau_L$, $\tau_U$, $n_L$, $n_U$ are the lower and upper limits of the particle radii and particle concentration considered, and $N$ is the particle concentration at the aerosol source. Specifically, for the case of Curve 'C' in Fig. 7, $\tau_L = 0.5 \times 10^{-6}$ cm, $\tau_U = 1.5 \times 10^{-6}$ cm, $n_L = 1 \times 10^6$ cm$^{-3}$, and $n_U = 8 \times 10^6$ cm$^{-3}$. Curve 'C' also takes into account the effects of the aerosol's diffusive loss to the carrier tubing (a function of particle size), so the abscissa of Fig. 7 represents the aerosol concentration at the nucleation chamber, not at the source.

It can be seen that, in a general manner, the experimental results shown in Fig. 7 can be explained by a combination of the theories of diffusive capture and heterogeneous nucleation, but not without first introducing an aerosol size dependency on output concentration. The divergence between theory and experiment can again be taken to represent the departure of the actual aerosol size spectrum from the assumed idealistic Khrgian-Mazin distribution.

6. RELATED EXPERIMENTS ON BROWNIAN CONTACT NUCLEATION

(a) Nucleation of freely-falling drops by aerosols other than AgI

During the course of the experimentation with freely-falling droplets, attempts were made to induce nucleation by the capture of aerosol particles other than AgI. The various types of particles were produced by the heated wire technique in the same manner as the AgI, except that air was substituted for nitrogen as the carrier gas when oxide aerosols were desired.

From a nucleating point of view, the most consistently successful aerosol (other than AgI) was cuprous iodide (CuI), and the experimentally-determined nucleation probability curves for this aerosol have already been produced in Figs. 5 and 6. From Fig. 6 it can be
seen that the value of the contact parameter, \( m \), which gives the best agreement between theory and experiment for CuI is 0.55. It should be pointed out here that because of refrigeration problems it was not possible to perform experiments at temperatures lower than about \(-18^\circ\text{C}\), thus making it necessary to terminate the CuI experimental curve at a nucleation probability of about 25 per cent.

Attempts to cause nucleation with an aerosol composed of silver oxide (Ag$_2$O) particles met with very inconsistent results. The nucleating probability of the Ag$_2$O aerosol generally was improved as the time delay between the Ag$_2$O experiments and previous AgI and CuI experiments became shorter. This suggests that the carrier tubing may have contained residual amounts of free iodine at the conclusion of the AgI and CuI experiments, thus making possible some contamination of the Ag$_2$O aerosol. A reaction of the type

\[
2 \text{Ag}_2\text{O} + 2 \text{I}_2 \rightarrow 4 \text{AgI} + \text{O}_2 \quad \Delta G_{298} = -58.2 \text{ Kcal mole}^{-1}
\]

is strongly favoured thermodynamically, so it is not implausible that some AgI may have been present on the particle surface, during the Ag$_2$O experiments. With fresh, uncontaminated carrier tubing, no nucleation was observed to occur with an Ag$_2$O aerosol, even at temperatures as cold as \(-18^\circ\text{C}\). One group of experiments was performed by switching the Ag$_2$O aerosol alternately back and forth between new carrier tubing and contaminated tubing when a difference in drop freezing percentage of approximately 50 per cent was observed.

Attempts to cause nucleation with oxide aerosols of both chromium and platinum did not, to within the visual limit of detection, meet with any success at temperatures higher than \(-18^\circ\text{C}\). An aerosol composed of particles of PbI$_2$, produced by the heated wire technique, was also unsuccessful in causing nucleation, but when the exhaust from a small internal combustion engine (fuelled by leaded gasoline) was passed through an iodine-saturated environment, the resulting compound of lead and iodine (plus probably other contaminants) was found, at a temperature of \(-18^\circ\text{C}\), to be nearly as efficient a nucleating agent as CuI. The engine exhaust without the iodine vapour, however, did not cause noticeable nucleation, nor did just the iodine vapour alone.

An electron microscope analysis of the PbI$_2$ aerosol produced by the heated wire technique revealed that its particulate size spectrum was considerably different from that of the AgI and metallic oxide aerosols produced in a similar manner. The PbI$_2$ size spectrum was strongly bi-modal, with a mixture of very small particles of radius 0.01\(\mu\text{m}\) and large particles (possibly spallation products) of radius 0.1\(\mu\text{m}\). Also, the maximum output concentration of PbI$_2$ particles was found to be consistently a factor of two or three lower than the maximum output concentration of AgI particles. This serves to point out that comparisons between the nucleating capabilities of various aerosols should be regarded with some caution unless it can be ascertained that the manner of aerosol production does not itself lead to differences in the microphysical and chemical properties of the substances under investigation.

(b) Nucleation of suspended drops

It is desirable to provide a method of determining an aerosol's contact nucleating efficiency at temperatures for which drop freezing is too rare (less than one event per hundred) to detect visually from observations of the behaviour of freely falling drops. It can be calculated from Eq. (4) that one drop of radius 500\(\mu\text{m}\), exposed to a monodisperse nucleating aerosol of concentration \(5 \times 10^6 \text{ cm}^{-3}\) and radius 0.01\(\mu\text{m}\), would have particles diffusing on to its surface at the approximate rate of \(2.5 \times 10^2 \text{ s}^{-1}\) if effects of turbulence and diffusiophoresis can be neglected. From this type of argument, the time interval between a suspended water drop's first exposure to the aerosol and the instant of nucleation can be utilized to provide a quantitative measure of the aerosol's contact nucleating efficiency.

For the experiments on the freezing of drops held in suspension, the nucleation chamber shown in Fig. 2 was sealed from both the fall tube and the observation chamber. A mm-sized diameter drop was formed on the shellac-coated tip of a thin strand of terylene
fibre and was inserted into the coagulating region. After the drop had remained suspended for a period of time long enough to ensure that it did not freeze naturally, it was exposed to the nucleating aerosol and the time until nucleation was measured. A stereo microscope was used to aid the visual observations of the drop's freezing behaviour. Temperature was measured with a thermocouple in close proximity to the drop.

The results from a series of experiments indicated that the order of $10^3$ AgI particles were required to nucleate a drop at $-5^\circ C$, with about half that amount required at $-8^\circ C$. The drops nucleated 'instantly' (i.e. after exposure to about 250 particles or less) at temperatures of $-10^\circ C$ or colder for the case of AgI and 'contaminated' Ag2O. 'Pure' oxides of silver, platinum, and chromium failed to cause nucleation at $-10^\circ C$ even when the drop had been exposed to $10^3$ particles. The most significant result from these experiments was to show that Aitken-sized AgI particles possess a small but finite nucleating efficiency at temperatures warmer than $-10^\circ C$.

(c) Capture of AgI at temperatures warmer than 0°C

In order to determine if the Brownian capture of AgI aerosol particles at temperatures warmer than 0°C could influence subsequent freezing behaviour when the drop moved into a colder environment, a short series of free-fall contact nucleation experiments were carried out with the nucleation chamber on the cold-room roof. Drops produced from the vibrating needle were thus allowed to capture the aerosol prior to entering the cold-room. Any subsequent freezing behaviour was then viewed in the observation chamber in a similar manner to the previous experiments. It was found that no nucleation occurred without the presence of the AgI aerosol at temperatures as low as $-18^\circ C$. With the AgI aerosol, no nucleation was found to occur at a cold-room temperature of $-10^\circ C$ or higher, but 50 per cent of the drops appeared to nucleate at a temperature of $-17^\circ C$. Such behaviour is similar to that which was found for drops nucleated by contact at sub-zero temperatures.

Knowing that the solubility of AgI is of the order $10^{-7}$ gm in 100 ml of water, one can calculate that up to 10 AgI particles of radius 0-015μm should be capable of completely dissolving in one 50μm radius water drop. From the above experimental results, however, it is apparent that, for AgI, the rate of dissolution is not fast enough to impair significantly the captured particle's nucleating efficiency during a time interval of at least a few seconds (with the chamber on the cold-room roof, a 50μm radius drop takes approximately four seconds to fall from the capture area into the observation area). Further experiments will be necessary to determine the length of time needed for various types of particles to lose their nucleating capabilities following capture.

7. Relevance of the Experiments to the Atmosphere

If changes in the aerosol concentration are small compared to the initial aerosol concentration, then, for a cloud of water droplets with a Khrgian-Mazin distribution, the Brownian capture Eq. (4) can be re-expressed as:

$$\frac{dn_p}{n_p} = \frac{1.35 w D_{pd} dt}{\gamma^2} \ldots \ldots \ldots\ldots (7)$$

where $w$ is the cloud's liquid water content and $\gamma$ is the mean radius of the cloud drops. Table 2 gives the percentage ($100 \frac{dn_p}{n_p}$) of 0-01μm aerosol particles scavenged from a cloud during a 10-min time interval. It can be seen, for example, that a cloud of water content 1.5g m$^{-3}$ and a mean drop radius of 15μm will remove, during a 10-min interval, about 5 per cent of the aerosol particles initially available. The ramifications which such scavenging can have on a cloud's ice budget can be readily appreciated when it is realized that Aitken-sized particles exist in average concentrations exceeding 200 cm$^{-3}$ in clear air throughout the troposphere, with considerably higher concentrations (in excess of $10^3$ cm$^{-3}$) measured at many ground locations (Junge 1963). A cloud with reasonable microphysical properties could thus be expected to collect, in 10 minutes, Aitken particles in concentra-
Table 2. The percentage of 0.01μm aerosol particles removed after 10 min as a function of cloud liquid water content and mean drop radius

<table>
<thead>
<tr>
<th>Mean drop Radius (μm)</th>
<th>Liquid water content (g m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>8.1</td>
</tr>
<tr>
<td>1.5</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The problem of directly relating the experimental results to the atmosphere is further compounded because the dynamical processes occurring on the scale of individual cloud elements, at least in cumuli, are not understood well enough to lend themselves to confident numerical modelling. Since time is a critical factor in any diffusion process, it is possible that large concentrations of ice crystals could be produced in the dormant regions of supercooled cumuli by a Brownian contact mechanism, while practically no ice occurs in the neighbouring, actively rising towers. The observations of large amounts of ice at 'high' (-10°C) temperatures in cumuli have thus far not discriminated between the stagnant and the updraught regions.

In conclusion, it can be stated that Aitken-sized particles of some types of aerosols (AgI, CuI, and 'contaminated' Ag₂O) are effective contact nucleators under realistic conditions, while those of other types of aerosols ('pure' oxides of silver, platinum, and chromium) are not. In the atmosphere, the concentration and composition of the Aitken aerosol may, at some time and in some locations, be such as to produce, by a diffusive (Brownian plus, perhaps, turbulent) contact nucleating mechanism, significant quantities of ice. Because of the very important role which the ice phase plays, both in the production of middle-latitude precipitation and in the possible dynamic modification of convective clouds (see Simpson and Wiggert 1969), the efficiency of the atmospheric Aitken aerosol as a diffusive contact nucleator warrants further study.

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