

An Application of Chemical Kinetic Theory and Methodology to Characterize the Ice Nucleating Properties of Aerosols Used for Weather Modification

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ABSTRACT

Chemical kinetic theory and methodology is applied to examine the ice nucleating properties of silver iodide (AgI) and silver iodide-silver chloride (AgI-AgCl) aerosols in a large cloud chamber held at water saturation. This approach uses temporal data on ice crystal formation with changes in key nucleation parameters such as temperature, water vapor concentration and droplet concentrations. The inter-relationships between ice nucleation effectiveness, nucleation mechanisms, nuclei chemical and physical properties, and the rate of appearance of ice crystals can be deduced. The theory and methodology can be applied to atmospheric experimentation.

Ice nucleation effectiveness increases of up to three orders of magnitude over that of AgI aerosols can be achieved with AgI-AgCl solid solution aerosols. Both aerosols are shown to form ice crystals by predominantly contact nucleation at temperatures of -16°C and warmer. Nucleation of the ice phase following collision is identified as a very rapid process, so that the rate of appearance of ice crystals is controlled by the much slower transport rate of nuclei to cloud droplets. The higher efficiency of AgI-AgCl nuclei with respect to the standard AgI nuclei is attributed to an improvement in the relative rates of nucleation versus deactivation or solution following collision of the nuclei with cloud droplets. This increase is most probably due to epitaxy and/or surface "active site" improvements. At a temperature of -20°C , all tested aerosols formed ice crystals by a combination of contact nucleation and deposition nucleation. The percentage of ice crystals formed by deposition correlated well with a minimum particle size of 500 \AA for an appreciable deposition rate.

1. Introduction

Large laboratory cloud chambers have been used for many years to routinely determine the ice nucleation effectiveness of aerosols used in weather modification experimentation. Three facilities in the United States participated in this calibration process: the Naval Weapons Center (Odenkrantz, 1969), the South Dakota School of Mines and Technology (Donnan *et al.*, 1971), and the Colorado State University (CSU) Cloud Simulation and Aerosol Laboratory (Grant and Steele, 1966; Garvey, 1975). Only the CSU facility remains in operation. Properly designed large cloud chambers can be used to study the processes in simulated natural clouds when temperature, supersaturation, and droplet size and concentration are well controlled. Large size minimizes wall effects (vapor and nuclei losses by diffusion). Large samples of nucleating aerosols generated from actual field dispensing systems can be characterized. The CSU chamber also allows for long time constants of nucleation and the resulting slow rates of appearance of ice crystals.

Two parameters of equal importance to the ice nucleation effectiveness, but less understood or considered in the design or conduct of weather modifi-

cation experimentation, are the overall rates of ice crystal formation and the mechanisms of nucleation of field dispensed aerosols. The rate factor was recognized, in a sense, in past nucleation studies (Warner and Newnham, 1958; Warburton and Heffernan, 1964; Isaac and Douglas, 1972) as the "time lag" of ice nucleation. The overall rate processes involved in nucleation and ice crystal formation will influence the subsequent rate of development and fallout of precipitation. Ice crystal formation rates are determined by the mechanisms of nucleation and cloud parameters. An understanding of rates, mechanisms and effectiveness values is necessary for proper application of ice nucleation technology and correct interpretation of weather modification experimentation results. Until the present time, no technique or methodology has been demonstrated to study these inter-relationships in laboratory or natural cloud environments.

In the present study, a chemical kinetics approach is applied to study the nucleating behavior of hydrophobic silver iodide and silver iodide-silver chloride aerosols in the isothermal environment of the CSU cloud chamber. Chemical kinetics is a methodology for the study of the velocities of chemical processes. Phase changes are processes involving the transfor-

mation of matter and are therefore addressable by chemical kinetics. In addition to permitting the better application of laboratory results to the atmosphere, this approach will also find application in the study of nucleation and ice crystal formation in natural and seeded atmospheric clouds.

Four mechanisms or modes of function are presently considered to be important in the formation of ice crystals from ice nucleus aerosols. These are:

- 1) Vapor deposition—direct deposition of vapor to the ice phase on the surface of nuclei.
- 2) Condensation to aqueous embryos followed by freezing—often referred to as sorption nucleation. This mechanism requires the deposition of vapor in the liquid phase, followed by freezing and additional ice growth by deposition.
- 3) Condensation to droplets followed by freezing—nuclei function first as condensation nuclei in this process, forming complete droplets (due to the presence of gross amounts of hygroscopic impurities) which freeze thereafter.
- 4) Contact freezing—requires the collision between ice nuclei and cloud droplets, followed by freezing of the droplets.

Several investigators using cloud chambers, and in a few cases natural clouds, have debated the importance of the various mechanisms given above. Davis and Auer (1972) attempted to separate contact nucleation and vapor deposition nucleation by actual field generator aerosols in an orographic cap cloud. Ice crystal replicas were analyzed for double-structured, frozen-droplet-centered ice crystals which reportedly are associated with contact nucleation events (Auer, 1970). Katz and Pilie (1974), in a cloud chamber experiment, used fluorescent tracer particles within cloud droplets and observations for frozen-droplet-centered ice crystals to determine the percentage of contact nucleation events. This approach has not been employed using an operationally dispensed ice nucleant. Another common method for distinguishing between contact nucleation and a vapor dependent mechanism, is by comparison of ice crystal appearance rates to theoretical collection rates. Blair *et al.* (1973) attempted such a calculation for the AgI aerosols from the $2\text{AgI} \cdot \text{NH}_4\text{I}$ -acetone-water solution combustion system at the South Dakota facility, but concluded only that a simple collision model was inadequate to explain their results. More recently, Federer and Schneider (1981) showed that the total number of ice crystals produced by an AgI aerosol from the Russian Silverspare pyrotechnic, far exceeded the number of possible collisions between nuclei and cloud droplets in a 3 min period. They postulated that this result supports a condensation-freezing mechanism for nucleation by this particular aerosol. Davis (1974), recognizing that contact nucleation is strongly dependent on particle size and

droplet concentration, noted differences in ice crystal formation rates with changes in these parameters for the AgI aerosols from the $2\text{AgI} \cdot \text{NH}_4\text{I}$ -acetone-water system [generated using a field type generator and tested in the CSU isothermal cloud chamber (ICC)]. The changes agreed qualitatively with the concept of contact nucleation. Based on this assumption, very good agreement between experimentally determined and theoretically calculated coagulation rate constants was obtained. This approach is not definitive and is limited to the study of contact nucleation. Employing chemical kinetics principles, the data of Davis (1974) definitively identifies nucleation by contact freezing; the theoretical calculations supply only confirmatory evidence.

Chemical kinetics deals with the rate of chemical processes, with all the factors which relate to the rates of such processes, and with the explanation of the rates in terms of reaction mechanisms. Kinetics thus addresses the continuous temporal nature of processes. Atmospheric ice crystal formation, resulting from ice nucleation, is a continuous temporal process. This is particularly evident in large cloud chamber studies in which the ice crystal formation process can be monitored from start to effective finish. Chemical kinetic theory and methodologies are based on the Law of Mass Action (Guldberg and Waage, 1879). The law states that the rates of such processes are proportional at any instant to the active masses of the reacting substances. Reactant concentrations and temperatures of reaction are varied to determine dependencies, and the results are expressed as rate laws for given or deduced mechanisms. This approach has been successfully applied to such varied processes as photochemical reactions, radioactive decay, crystallizations from solutions, and catalyzed reactions. Silver iodide aerosols, in this study, are treated as catalysts which speed up the rate of the inherent phase change process (homogeneous nucleation) in clouds (Reiss, 1982), rather than as substances which induce the phase change in a quasi-stable system.

The kinetics approach is an experimental methodology which utilizes temporal data on ice crystal formation to give detailed information on the underlying nucleation processes. The methodology can be applied to nucleation studies in natural clouds, as well as in large cloud chambers.

2. Chemical kinetic theory and experimental methodology

In this approach, a system containing concentrations of nuclei (C_N) which "react" to form ice crystals at a given temperature is considered. Supercooled droplets (C_D) and water vapor (C_V) are also treated as reactants. Ice crystals (C_{IC}) are products. The four overall processes leading to the formation of ice crystals are visualized as follows:

Vapor deposition:	$C_N + C_V \rightarrow C_{IE} + C_V \rightarrow C_{IC}$ (COLLECTED)
Condensation to embryos followed by freezing:	$C_N + C_V \rightarrow C_{AE} \rightarrow C_{IE} + C_V \rightarrow C_{IC}$ (COLLECTED)
Condensation to droplets followed by freezing:	$C_N + C_V \rightarrow C_{DSD} \rightarrow C_{FD} + C_V \rightarrow C_{IC}$ (COLLECTED)
Contact freezing:	$C_N + C_D \rightarrow C_{ND} \rightarrow C_{FD} + C_V \rightarrow C_{IC}$ (COLLECTED).

Here C_{IE} , C_{AE} , C_{DSD} , C_{FD} , and C_{ND} refer to concentrations of ice embryos, aqueous embryos, dilute solution droplets, frozen droplets, and droplets with a nucleus on their surface, respectively. Concentration units are in numbers of particles per cm^3 . For vapor, particles are water molecules. All of the mechanisms can occur in the ICC depending on the cloud conditions and nucleus chemical composition. The ice crystal growth step is not rate determining in any of the four mechanisms. Past observations have demonstrated the rapid initial appearance of ice crystals (always less than 30 s) after the insertion of various nucleants into the ICC. Since the aerosols examined in this study were concluded to be non-hygroscopic, based on results presented in later sections, a discussion of the kinetics of the third mechanism is not included here. The first step is assumed to be rate determining in the other mechanisms.

The kinetic rate law states that the velocity of a reaction, as determined by following the rate of change of concentration of a reactant, can be expressed as the product of the reactant concentrations, each raised to some power, multiplied by a specific rate constant k . Thus, for a vapor deposition or sorption nucleation process,

$$-\frac{dC_N}{dt} = k_V C_N^n C_V^v, \quad (1)$$

where n and v are the orders of reaction with respect to nuclei and vapor respectively. The rate constant is a function of nucleant properties and temperature only. There is no physical reason to believe that n will be any number but 1. Reactions in chemistry that are higher order or non-integer order with respect to a particular reactant generally involve either a decomposition, collision between reactant molecules, or autocatalysis of the reaction by a product to form additional product. These processes are not feasible for ice nuclei. Eq. (1) is then directly compatible with the kinetic expression which forms the basis for classical vapor to condensed phase nucleation theories. In an equilibrium theory, the nucleation rate $J = -dC_N/dt$ in Eq. (1) if k_V is replaced by $k_s K$, where k_s is the specific rate constant of the nucleation step and K is the equilibrium constant for the formation of clusters. In a steady-state theory, a factor Z would precede the equilibrium expression for J (Zettlemoyer, 1969; Hecklen, 1976). The appearance of the equilibrium constant and its subsequent evaluation in terms of standard free energies has disguised the

fact that nucleation is truly a branch of phase change kinetics and not of thermodynamics (Reiss, 1982).

Since C_V is constant (water saturation) at any temperature and liquid water content (LWC) in the ICC, Eq. (1) can be integrated easily for this study. With n equal to 1 and noting that C_N/C_{N0} (the ratio of the nuclei concentration at any time over the total initial nuclei concentration) is equal to $[100 - \text{percent total ice crystal number (IC) formed}]/100$, i.e.,

$$\ln(100 - \%IC) = -k_V C_V^v t + \ln(100), \quad (2)$$

for a deposition or sorption nucleation process.

Similarly, for a contact freezing nucleation process (assuming that the nucleation step is not rate determining) we can write

$$\ln(100 - \%IC) = -k_D C_D t + \ln(100), \quad (3)$$

where k_D is the rate constant. This result follows since C_D is held approximately constant during nucleation at a given temperature by resupplying cloud droplets. The assumption is made that Brownian coagulation and not additional phoretic transport processes, dominates the collision process between nuclei and cloud droplets. Calculations by Davis (1974) show that thermophoresis dominates over diffusiphoresis in the ICC, but for the nucleus and droplet sizes present these capture processes are two orders of magnitude less probable than Brownian diffusion. Inertial impaction and turbulent coagulation are also negligibly important due to the small particle sizes involved (see Fig. 1).

Ice crystal fallout is measured using microscope slides. The slides are periodically removed from the ICC following nuclei aerosol injection. The initial counting period begins with injection and is typically 3 min. Some error is introduced since a finite time will pass before the first ice crystal grows and falls to the slide. In future studies, a continuous sampling detector will help define the exact point at which counting should begin. Simple tests have shown that the neglect of this factor in the present study does not affect the character of the rate data obtained. A rate of ice crystal formation curve is produced by plotting the percentage of the final number of ice crystals formed versus time. Several plots are then averaged for the same set of cloud conditions (temperature and LWC). Plots of $\ln(100 - \%IC)$ versus time are formed from these. They are referred to as kinetic plots. Since at any temperature, C_V is constant, the slope of a

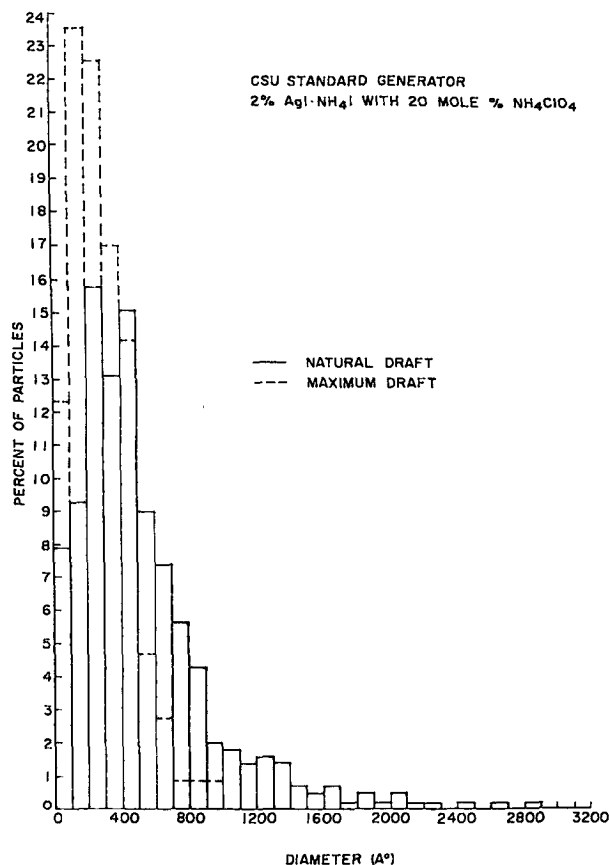


FIG. 1. Aerosol particle size distributions (measured by SEM) produced from the combustion of the 2AgI-NH₄I-acetone-water with 20 mole percent NH₄ClO₄ solution under natural draft (solid lines) and maximum fan (dashed lines) dilution in the vertical wind tunnel.

kinetic plot can only change if C_D changes. Changes in the slope with changes in the supercooled droplet concentration are indicative of a contact nucleation process. The absence of slope changes with changes in droplet concentrations is indicative of nucleation from the vapor. Actual values of rate constants for these processes can also be obtained, demonstrating utility of a kinetic analysis of the experimental data.

As derived, Eq. (2) applies to all deposition or sorption nuclei characterized by a specific rate constant k_V . In reality, there may be, within a nuclei distribution, a distribution of rate constants which may or may not be particle size dependent. There is no current assurance, therefore, that every composite kinetic nucleation plot will be linear. Evidence reported here and elsewhere (Vonnegut, 1949; Warburton and Heffernan, 1963), however, suggests that the rates of nuclei depletion to form ice crystals will always be exponential for processes of nucleation from the vapor onto a distribution of particles at a constant C_V .

In a similar manner, Eq. (3) is valid for a particular

sized contact nucleus and there is no assurance that any particular composite kinetic plot will be linear for a given C_D . However, linearity is a very likely result for nucleus aerosol distributions of the type shown in Fig. 1. For example, a theoretical kinetic plot can be produced if it is assumed that an ice crystal results from every collision between nuclei and droplets. For this purpose, Eq. (3) can be rewritten in the form

$$\ln(100 - \%IC) = \ln\left[\sum_i F_i \sum_j \exp(-k_{Dij} C_{Dj} t)\right] + \ln(100). \quad (4)$$

Here F_i is the fraction of aerosol particles of size i , and j refers to the droplet size. The expression for k_{Dij} (Brownian coagulation coefficient) given by Isaac and Douglas (1972) is used. Using the particle size distributions of Fig. 1 and the ICC droplet size distributions given in the following section, the kinetic plots of Fig. 2a result. The points closely define a straight line. The generality of this conclusion, especially at temperatures where only fractions of the total aerosol distribution function as contact nuclei, will be demonstrated.

Before the experimental methodology can be applied to data from the ICC, aerosol losses due to airflow dilution and diffusion to walls must be considered. A constant airflow into and out of the chamber is necessary to continuously supply supercooled cloud droplets. This airflow evacuates nuclei from the ICC at a rate given by

$$-\frac{dC_N}{dt} = \alpha C_N V^{-1}, \quad (5)$$

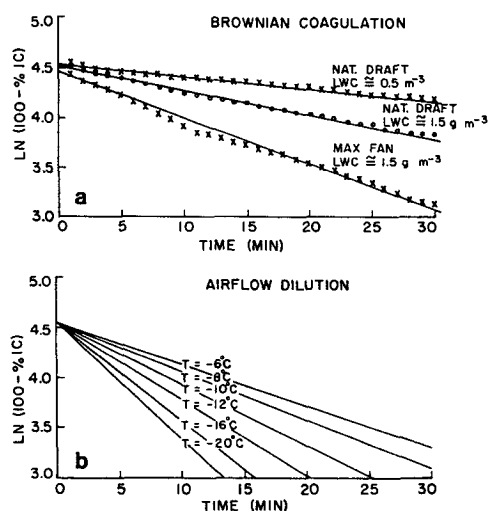


FIG. 2. Kinetics plots which would result from ice crystal formation by Brownian coagulation of the aerosols of Fig. 1 with cloud droplets, followed by 100% efficient freezing at -12°C (a). Also appearing are the kinetics plot corrections for airflow dilution losses of nuclei (b).

where α is the airflow dilution rate ($L s^{-1}$) and V is the chamber volume (L). Alpha varies from $0.50 L s^{-1}$ to $1.93 L s^{-1}$ depending on temperature and LWC, but is known and constant for given conditions. This depletion mechanism can be plotted on a kinetic plot as in Fig. 2b. The slope at any temperature and LWC can be subtracted from the raw experimental kinetic slope to correct for the dilution factor. The quantification of diffusional losses to the walls has not been accomplished satisfactorily. Davis (1974) estimated this depletion mechanism to be of small magnitude, and its effect was neglected in correcting the raw experimental data.

3. Experimental methods

a. Instrumentation and techniques

1) ISOTHERMAL CLOUD CHAMBER

The CSU isothermal cloud chamber has previously been described in detail by Grant and Steele (1966) and Garvey (1975). The chamber volume is 960 L. Chamber temperature is monitored by an array of thermocouples and can be maintained within $\pm 0.2^\circ C$ of that desired over a range from 0 to $-20^\circ C$. Time response is basically controlled by the 35 s period between recording points for each thermocouple. Cloud is continuously produced by the atomization of distilled water with a medical type ultrasonic nebulizer. After mixing with cold filtered air, the droplets equilibrate to the chamber temperature in a central tube and then slowly settle through the chamber. Cloud density is monitored using a Cambridge dewpoint hygrometer. The difference between the saturation mixing ratio corresponding to the dewpoint temperature and that corresponding to the chamber temperature defines the LWC. The LWC can be varied from $0.3 g m^{-3}$ to $3.0 g m^{-3}$ by varying the rate of supply of cloud droplets. The two values and their associated errors used for this research were $0.5 \pm 0.10 g m^{-3}$ and $1.5 \pm 0.15 g m^{-3}$. Fig. 3 displays droplet size distributions at $-12^\circ C$ for the two liquid water contents, determined by a Particle Measuring Systems Forward Scattering Spectrometer Probe (FSSP), modified to sample from the ICC. There was no sampling error detected due to possible evaporative losses in the sampling tube and coincidence errors were effectively eliminated by a restricted sample volume technique (1/25 of atmospheric sample volume). The measurements were used for rough calculations of theoretical coagulation rates of nuclei and droplets. Inferred droplet concentrations were $4300 cm^{-3}$ at a LWC of $1.5 g m^{-3}$ and $2100 cm^{-3}$ at a LWC of $0.5 g m^{-3}$ over a $-6^\circ C$ to $-20^\circ C$ temperature range.

2) AEROSOL DILUTION PROCEDURE

The CSU standard test generator was used to generate the aerosols for this study. This generator is of

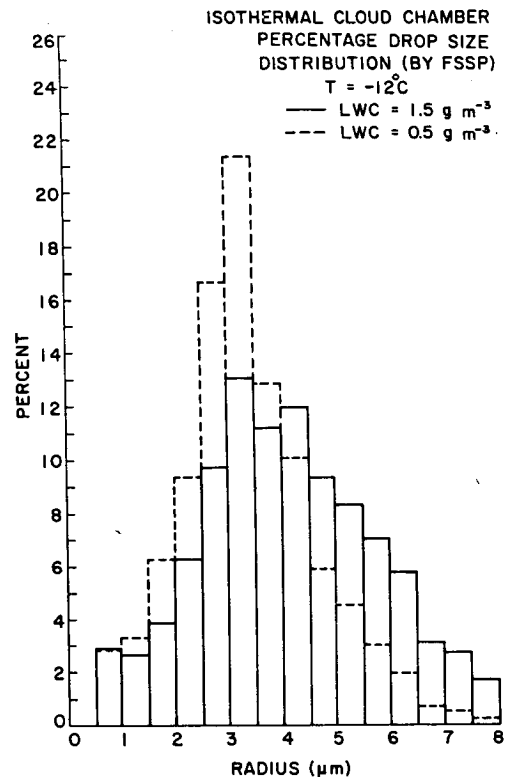


FIG. 3. Cloud droplet size distributions at two liquid water contents at $-12^\circ C$.

the same general design as that for field generators and burns atomized AgI-acetone solutions in an auxiliary propane flame. Initial aerosol dilution is accomplished by allowing the combustion products to rise in a vertical wind tunnel (Garvey, 1975). Updraft velocities were either natural or forced with a high velocity fan. Under the natural draft mode, it was recognized that the updraft can vary due to outside wind and temperature conditions. This method was used, therefore, only under relatively calm conditions. The natural updraft dilution was then taken as $1.0 \times 10^5 L min^{-1}$ at the sampling point. With maximum fan displacement, the updraft dilution was $3.23 \times 10^6 L min^{-1}$. Following sampling with a 4 L syringe, the aerosol was immediately diluted with a known volume of dry ($-40^\circ C$ dewpoint temperature) air. This dilution prevents coagulation of particles within the syringe and the production of transient supersaturations or overseeding after insertion into the ICC.

3) AEROSOL PARTICLE SIZING AND COMPOSITION

Aerosol particles were collected onto a tin substrate using a laboratory designed electrostatic precipitator. These were analyzed using a scanning electron microscope (SEM). Photomicrographs were analyzed manually to size the aerosols. The resolving power

of the microscope is 100 Å and this value was used as a bin size.

The energy dispersive x-ray analysis attachment to the SEM was used to detect the presence of elemental constituents in single particles. For quantitative analysis, neutron activation of aerosol samples (collected on nucleopore filters) was performed at the Rhode Island Nuclear Science Center.

4) ICE NUCLEUS EFFECTIVENESS DETERMINATION

Ice nucleus effectiveness is defined as the total number of ice crystals produced per gram of nucleating aerosol at a particular temperature. Effectiveness values are calculated from the cumulative number of ice crystals falling onto microscope slides in an experiment as described by Grant and Steele (1966). Effectiveness values must be corrected for nuclei which are lost by chamber airflow before they can initiate ice crystal formation. This correction has not been applied in past studies. The total depletion of effective nuclei in the ICC can be described by an equation combining nucleation and airflow loss processes,

$$C_N = C_{N0} \exp[-(k_1 + k_2)t]. \quad (6)$$

The rate constant k_1 replaces $k_V C_V$ of Eq. (1) or $k_D C_D$ of Eq. (3) and k_2 replaces α/V of Eq. (5) in this equation. Therefore,

$$\frac{dC_{IC}}{dt} = k_1 C_{N0} \exp[-(k_1 + k_2)t]. \quad (7)$$

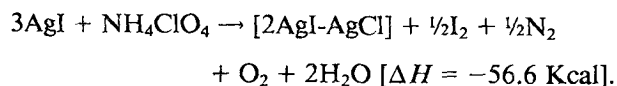
The number terms N_{IC} and N_{N0} can be substituted for the concentration terms C_{IC} and C_{N0} , respectively. Integrating Eq. (7) and taking the limit ($t \rightarrow \infty$) gives

$$N_{N0} = \left(\frac{k_1 + k_2}{k_1} \right) N_{IC(\text{total})}. \quad (8)$$

The actual effectiveness ($N_{N0} g^{-1} AgI$) is thus calculated from the measured effectiveness [$N_{IC(\text{total})} g^{-1} AgI$] weighted by the ratio of the experimentally measured kinetics slope ($k_1 + k_2$) over the dilution corrected slope (k_1).

b. Materials

The kinetics methodology has been applied to the characterization of a new ice nucleant (AgI–AgCl) for weather modification use. The production of AgI–AgCl aerosols is thermodynamically and experimentally possible by the addition of ammonium perchlorate (NH_4ClO_4) to the $2AgI \cdot NH_4I$ –acetone–water solution combustion system for aerosol generation. For example,



Upon condensation of the generator flame products, the AgI and AgCl combine to form solid solution aerosols with Cl atoms replacing I atoms in the AgI lattice. Similar ion substitution products showing improved nucleating abilities have been discussed by Vonnegut and Chessin (1971). These mixed AgI–AgCl nucleants might be expected to have a lattice constant closer to ice than silver iodide. Based on the nucleation catalysis theory of Turnbull and Vonnegut (1952), the AgI–AgCl nuclei would then have an improved ability to nucleate ice. Sax *et al.* (1979) postulated that intimate mixtures of AgI and AgCl might be responsible for the high efficiency of the aerosol from the Nuclei Engineering, Incorporated TB-1 (with C_6Cl_6) pyrotechnic. Effectiveness, however, was not correlated with a measured chlorine content of that aerosol. That was done in this study.

Ammonium perchlorate was added to the standard solution in 10 mole percent (with respect to the AgI) increments, in order to optimize ice nuclei effectiveness of the combination aerosols. The aerosol produced from the solution with 20 mole percent NH_4ClO_4 added was chosen for complete kinetic analysis. Energy dispersive x-ray analysis using the SEM detected Ag, I and Cl in single particles large enough to be analyzed. Neutron activation analysis was performed on single samples of the aerosols generated from the solutions with 20, 30 and 40 mole percent NH_4ClO_4 . Samples were collected on nucleopore filters of 0.4 μm pore size over several minute periods. This technique insured the collection of all particle sizes without significant bias in collection efficiency toward any particular size. After subtracting background filter concentrations, mass ratios of chlorine to iodine were converted to molar ratios. The mole percentage of chlorine in the aerosol is then

$$\text{mole percent Cl} = \left(\frac{\text{molar ratio}}{1 + \text{molar ratio}} \right) \times 100. \quad (9)$$

Table 1 summarizes these values.

It can be seen that the conversion is about 75% efficient. The chlorine unaccounted for may appear as gaseous HCl.

From Fig. 1 it is seen that generator operation under maximum fan conditions results in a marked reduction of the mean particle size (289.6 Å vs 521.8 Å diameter under natural draft dilution of the aerosols). In general, particles >1000 Å diameter are aggregates of smaller particles. Assuming spherical particles, 1.07×10^{15} and 7.30×10^{15} particles g^{-1} are

TABLE 1. Neutron activation analysis results for aerosol composition. Values in mole percentage.

Chlorine in solution	Chlorine in aerosol
20	15.6
30	21.9
40	30.0

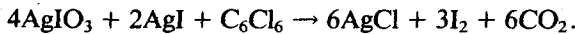
calculated to be produced under natural draft dilution and maximum fan dilution respectively. Size distributions for other aerosols were measured for natural draft dilution. These were very similar to Fig. 1a, with a slight trend toward a broader peaked distribution and loss of smaller particles as the mole percentage of NH_4ClO_4 in solution is increased.

4. Results and discussion

a. Ice nuclei effectiveness

The aerosols from combustion of all solution variations were tested repeatedly at any given temperature in the ICC to determine their effectiveness in forming ice crystals. The test temperatures normally used were -5 , -6 , -8 , -10 , -12 , -16 and -20°C . Fig. 4a is an example of the unaveraged results and the correction which accounts for the airflow dilution factor. Average effectiveness results for five of the aerosols tested are shown in Fig. 4b.

The superiority in effectiveness of the AgI-AgCl nucleus aerosols, over the AgI aerosol at warmer temperatures, is immediately evident. The effect is maximized with the addition of 30 mole percent NH_4ClO (22 mole percent Cl^- replacing I^- in the aerosol particles) to the standard solution. The threshold temperature for detectable ice crystal formation is 1°C warmer (-5°C) than for the standard AgI aerosols (-6°C). Increases in ice nuclei effectiveness (g^{-1}AgI) over that of the standard aerosols range from one order of magnitude at -12°C to three orders of magnitude at -6°C . It should be noted that the use of the $\text{AgI-I}_x\text{-Cl}_y$ ($x = 0.78$, $y = 0.22$ in this case) nucleant mass rather than the mass of AgI define effectiveness would actually raise these values by about 9%. This factor is well within the error margins of values and since the actual nucleant structure is unknown, this slight correction has been ignored. It is interesting to note that should the chlorine in the NEI TB-1 pyrotechnic (with the 3% C_6Cl_6 found to maximize effectiveness) be efficiently converted to form $\text{Ag-I}_x\text{-Cl}_y$ aerosols, 22.8 mole percent of the iodine atoms would be replaced by chlorine in the resulting aerosol. This result follows since silver chloride can be produced from silver iodate and hexachlorobenzene as follows:



With the addition of 40 mole percent NH_4ClO_4 to the standard solution, the resultant aerosol effectiveness values are seen to drop substantially. Particle sizes, though, are very similar to the aerosols from the 30 mole percent solution. This lowered activity when elemental substitution exceeds a critical value is consistent with an epitaxial argument for changes in ice nuclei effectiveness. The epitaxy of the new nucleant would be expected to improve to a certain point, but when too much chlorine is present the

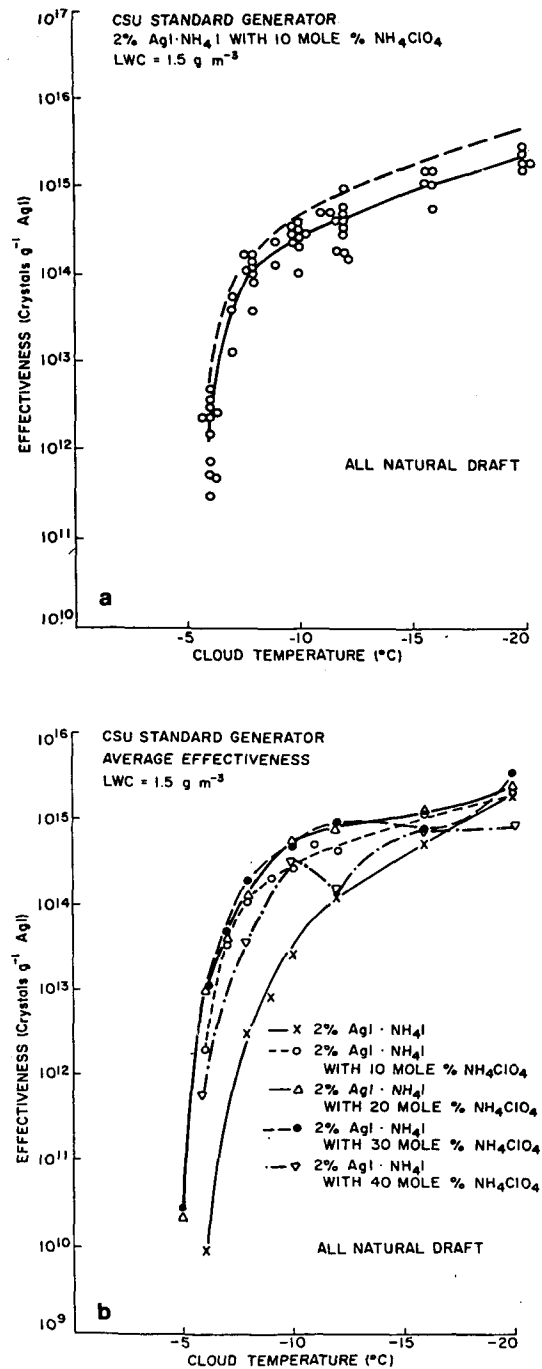


FIG. 4. Effectiveness values versus temperature for a particular aerosol with the chamber airflow dilution correction applied (dashed line) to the average (a), and average effectiveness curves for five aerosols generated with natural draft dilution (b).

nucleant would resemble AgCl. Silver chloride is less effective as an ice nucleus. A change in the nature of surface "active sites" may be important in determining the nucleation ability as well, since organized water clusters on surface sites are precursors to epi-

taxial effects (Zettlemoyer *et al.*, 1961). Substitution of some Cl^- for I^- may have a synergistic effect on ice nucleation. However, too much Cl^- could create surface patches and reduce the ice nucleating activity by surface charge effects (Edwards and Evans, 1961). It is not within the scope of this paper, however, to discuss the relative importance of epitaxial versus surface "active site" improvements in explaining differences in ice nuclei effectiveness.

b. Rates and mechanisms for ice crystal formation

The following analysis is primarily based on the data obtained on the combustion aerosol from the solution with 20 mole percent NH_4ClO_4 added. Fig. 5 displays the rate of ice crystal formation curves for these aerosols under both conditions of wind tunnel dilution. Data are averaged at each temperature for several tests. All curves demonstrate the temporal nature of the ice crystal production process and its exponential nature. Rate curves for the standard AgI solution resemble closely those in Fig. 5a. Strong differences are noted between the rate curves for the natural draft dilution and maximum fan dilution aerosols. Differences occur with temperature as well. These differences are all meaningful in terms of mechanisms for ice crystal formation.

Kinetic plots of the raw data at -12 and -20°C , and two liquid water contents, are presented in Figs. 6a and 6b, respectively. These plots are corrected for chamber airflow dilution in Fig. 6c. Nucleus behavior at -12°C was found to be characteristic of all temperatures -16°C and warmer for both AgI-AgCl and AgI aerosols. The entire data set displayed strong linear correlations at -16°C and warmer. The mechanism at these temperatures is singular as noted by the singular slope of Fig. 6a. The apparent rate constants increase with increases in droplet concentration (droplet concentration is directly related to LWC in the ICC as stated earlier). The relative increase is not changed when corrections for airflow dilution are applied in Fig. 6c. It is concluded that the singular mechanism is contact nucleation, following the discussion of Section 2. This conclusion is substantiated quantitatively by dividing the slopes at the two water contents by the respective droplet concentrations to obtain the composite rate constant k_D . At a LWC of 1.5 g m^{-3} , this value is 1.49×10^{-5} ; at a LWC of 0.5 g m^{-3} , it is 1.70×10^{-5} . The values are essentially equivalent within experimental error, as expected. Effectiveness values do not change with a change in LWC. This is also expected in a contact nucleation process.

The high cloud droplet concentrations present in the ICC might mask other mechanisms for ice crystal formation at temperatures -16°C and warmer. If, however, any other mechanism is functioning, it would necessarily have a characteristic rate of ice crys-

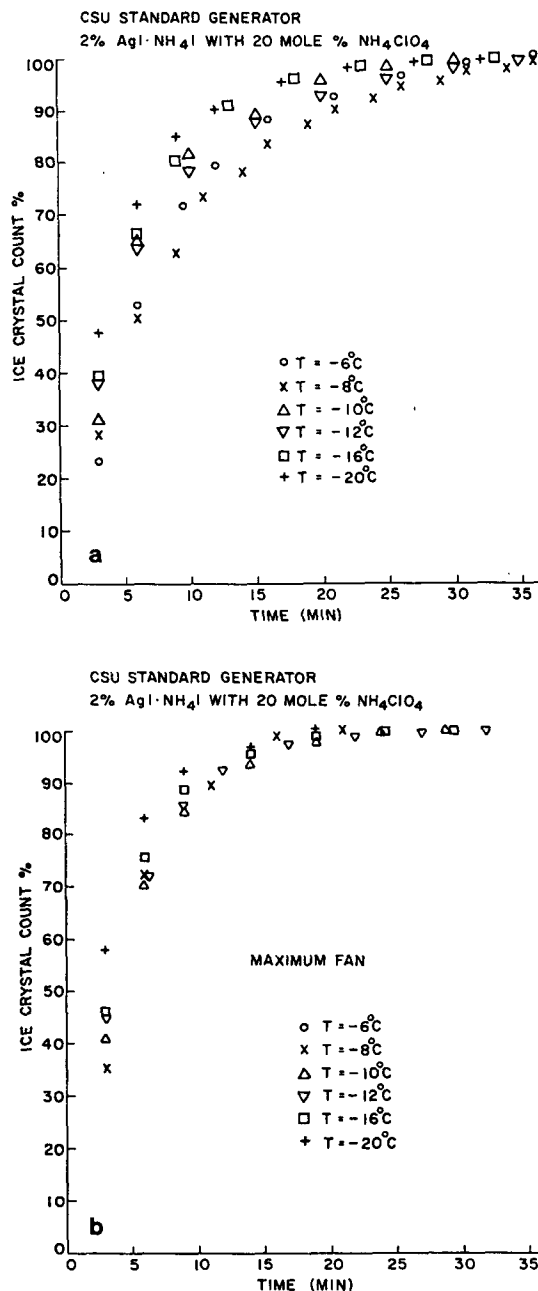


FIG. 5. Rate of ice crystal formation plots by the nuclei produced from the combustion of the $2\text{AgI}\cdot\text{NH}_4\text{I}$ -acetone-water with 20 mole percent NH_4ClO_4 solution generated under natural draft (a) and maximum fan (b) dilution.

tal formation very much slower than the already slow contact rate at either LWC. Otherwise, contact nucleation would not dominate.

In the two-stage collision and freezing process (a series first order reaction), the rate which governs the formation of ice crystals will be the slowest process or a combination of the two rates which is not pseudo-first order (see, for example, Frost and Pearson, 1953,

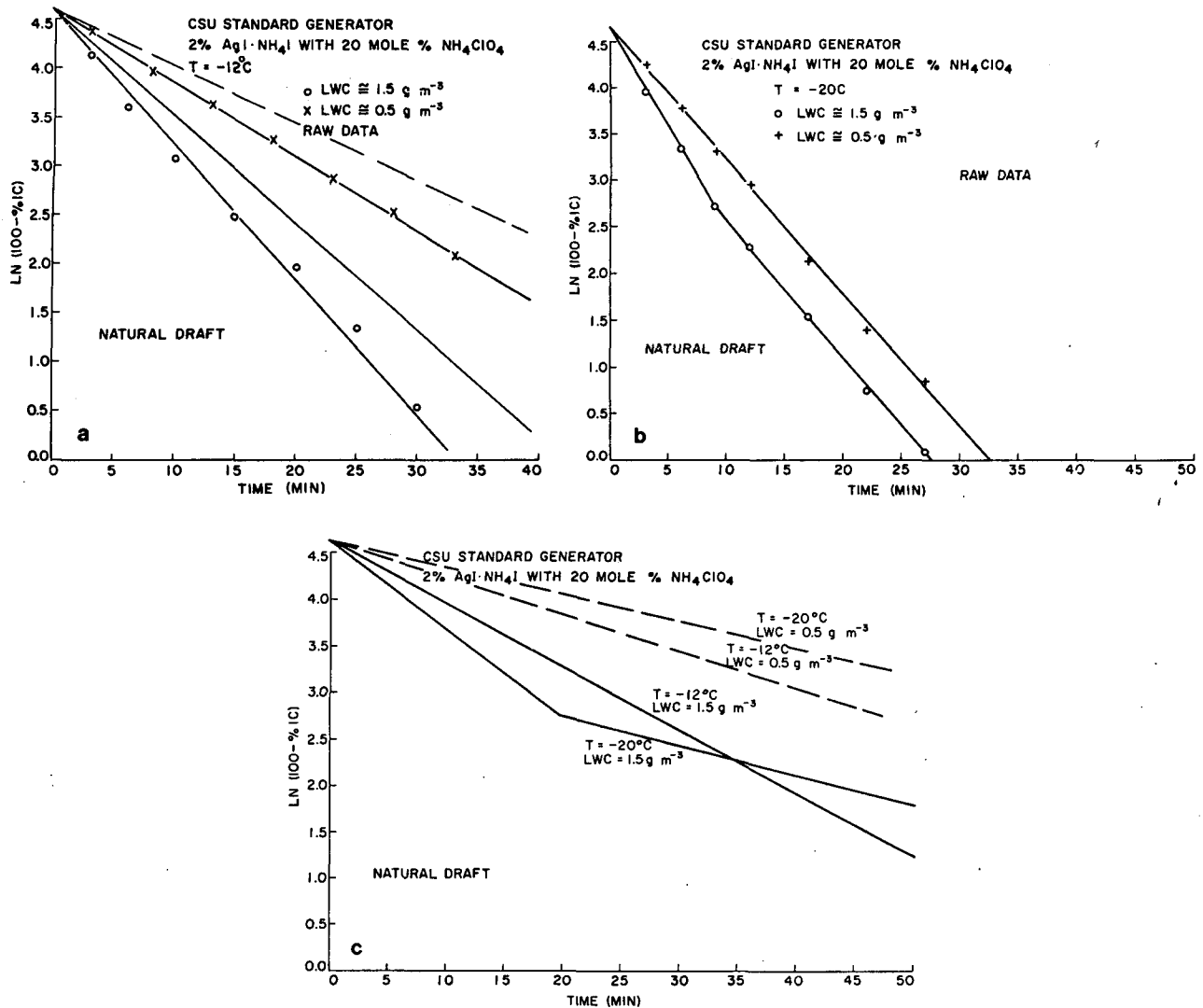


FIG. 6. Raw kinetics plots of ice crystal formation by AgI-AgCl nuclei at -12°C (a) and -20°C (b), and the plots corrected for airflow dilution (c). Also appearing in (a) are the theoretical plots which would result if every nuclei-droplet collision (based on Brownian diffusion) produced an ice crystal at LWC's of 1.5 g m^{-3} (single solid line) and 0.5 g m^{-3} (dashed line).

p. 153). The results presented then substantiate that the rate of nucleation following collision (at $T \geq -16^{\circ}\text{C}$) is necessarily very much faster than the rate of transport of effective nucleating aerosols to droplets. Nucleation or the destruction of the ice nucleating ability of the particle is nearly instantaneous following collision.

The addition of chlorine to AgI aerosols does not change the basic nucleation mechanism. The change in effectiveness must result because the apparent improvements in epitaxy and/or surface active sites introduced, have enhanced the rate of nucleation following contact compared to the rate of deactivation or solution. Competitive deactivation processes, such

as "etching" of active sites or nuclei dissolution (Matthews *et al.*, 1972) are apparently unchanged in rate or possibly decreased.

For contact nucleation by AgI-AgCl aerosols, changes in rates of ice crystal formation with temperature should be inversely related to changes in the mean effective particle size catalyzing the formation of ice crystals. The temperature coefficient of the kinetic rates then gives information on the particle size dependency of contact nucleation for AgI-AgCl aerosols. For all the data considered, temperature and kinetic rate appear to relate inversely as one might expect. This is displayed in Fig. 7 with some exceptions. These exceptions likely result from the variable

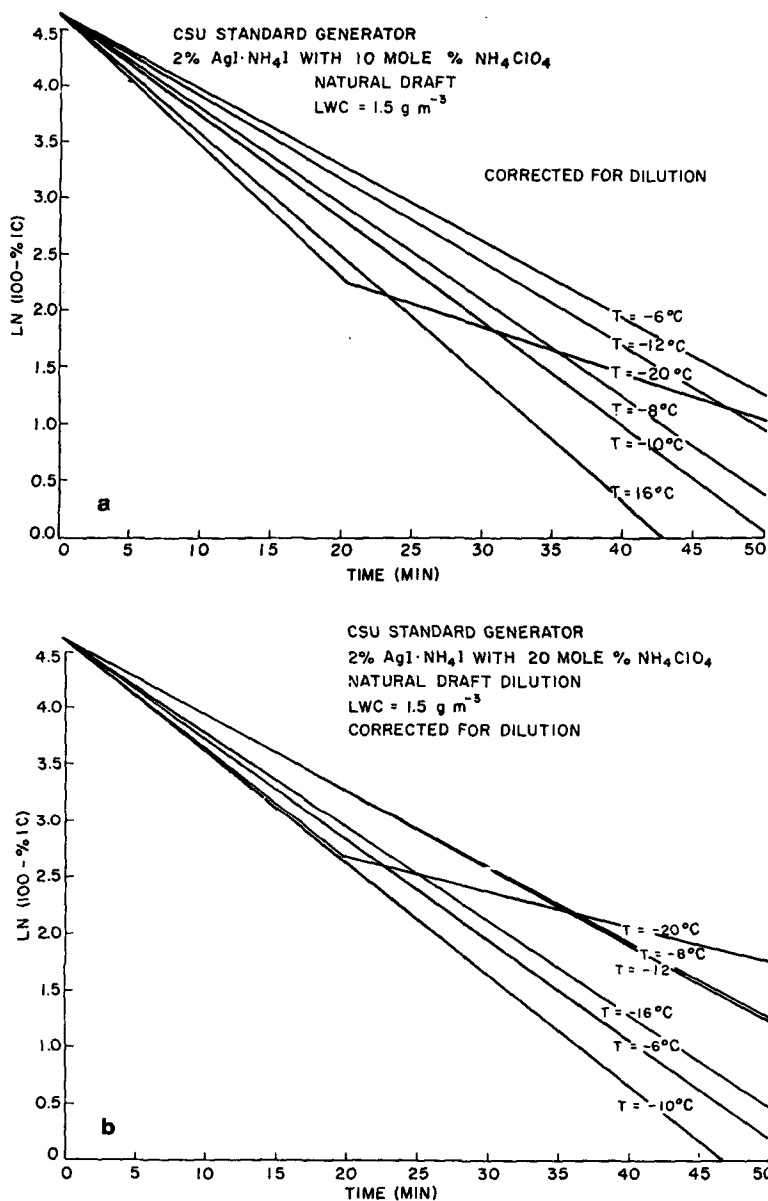


FIG. 7. Corrected kinetics plots of the aerosols from the 2AgI·NH₄I-acetone-water solution with 10 (a) and 20 (b) mole percent NH₄ClO₄ added.

wind tunnel updraft under natural draft conditions, which may have drastically changed the particle size distribution of the combustion products on certain days. [Generator operation with maximum fan updraft produced a more consistent and nearly monodisperse aerosol. In this case, only the direct relationship between kinetic rate and temperature that is inherent in Brownian coagulation, is apparent at temperatures -16°C and warmer (see Fig. 8).]

The inverse relationship between temperature and kinetic rate substantiates the conclusion that smaller sized AgI and AgI-AgCl aerosols are less efficient nucleants for freezing cloud droplets than larger aero-

sols at any temperature. This is confirmed by Fig. 9, which displays the composite nucleation efficiency (based on 100% efficiency at -20°C) of three particle size distributions as a function of mean particle size. As plotted, the lowest curve is the most efficient. However, since such a larger magnitude change in effectiveness is necessary to effect only a small change in the rate constant (Fig. 7 vs Fig. 4), probably all particle sizes are involved to some degree in ice crystal formation at a given temperature.

Comparison between Figs. 7 and 8 demonstrates the large increase in the rates of formation of ice crystals which occurs on the smaller sized aerosols (with

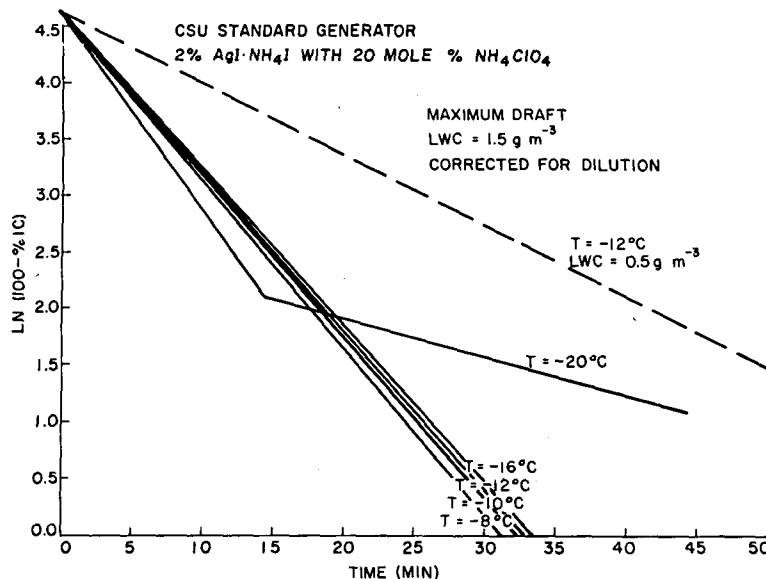


FIG. 8. Corrected kinetics plot of ice crystal formation produced by the nuclei from the $2\text{AgI} \cdot \text{NH}_4\text{I}$ -acetone-water solution with 20 mole percent NH_4ClO_4 added and generated with maximum fan dilution.

larger diffusion coefficients). This is further proof that the mechanism producing ice crystals at -16°C and warmer is contact nucleation and controlled by the rate of aerosol transport to droplets. A comparison can also be made between theoretical kinetic plots at -12°C (produced by adding the Brownian coagulation and airflow dilution slopes of Fig. 2) and the experimental plots in Fig. 6a. The theoretical plots assume 100% utilization of particles to form ice crystals. These should not have smaller slopes than the respective experimental plots. That they do suggests that a dilution mechanism, perhaps the yet-to-be-quantified wall effects, still needs to be accounted for. The change in slope experimentally with LWC is more consistent with what is predicted theoretically.

The kinetic behavior of the ice crystal formation processes at -20°C differs from that observed at warmer temperatures. At this temperature, the kinetic plots for all aerosols tested were curves, concave downward (see Fig. 6b). Such kinetic behavior is characteristic of two first-order processes (mechanisms) producing the same product (see, for example, Frost and Pearson, 1953, p. 149). The curves can be analytically separated into two lines: the first (initial slope) representing ice crystal formation by a combination of two mechanisms and the latter (persistent slope) representing ice crystals continually formed by the slower of the two mechanisms. After airflow dilution corrections are made, as in Fig. 6c, the kinetic slopes for the separate mechanisms can be determined.

When droplet concentrations were nearly halved (by reduction of the LWC to 0.5 g m^{-3}), the composite

slope became very nearly parallel to, but slightly faster than, the slower mechanism (at an LWC of 1.5 g m^{-3}) as shown in Fig. 6c. It is concluded that the fast mechanism with a 1.5 g m^{-3} LWC was contact nucleation, being strongly dependent on droplet concentration.

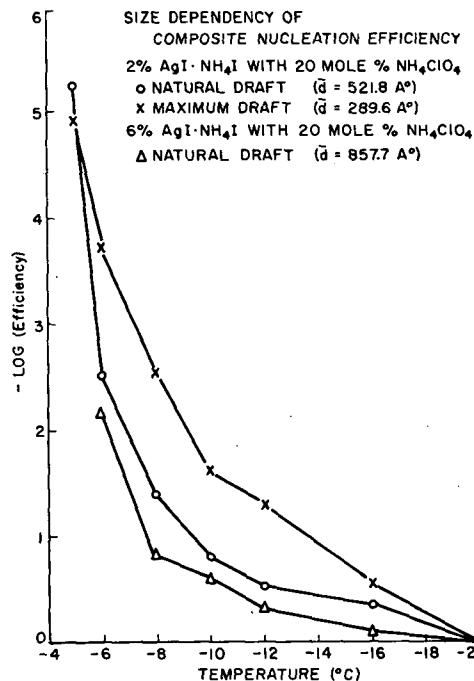


FIG. 9. Nucleation efficiency of the AgI-AgCl particle size distribution as a function of mean particle size. Efficiency is based on 100% at -20°C .

The second mechanism is insensitive to droplet concentration and has a rate of ice crystal formation comparable to the contact rate when the LWC is 0.5 g m^{-3} . This second mechanism must be either vapor deposition or sorption nucleation. Due to the hydrophobic nature of the aerosols, the deposition nucleation mechanism is more probable.

In order for two mechanisms to appear in the kinetic plots at -20°C , it is necessary that each mechanism predominantly utilizes a different segment of the total nuclei population. Past experimental studies (Gerber, 1976) and theoretical studies (Sax, 1970; Young, 1974) have demonstrated that there is generally a critical sized nucleus for which the instantaneous vapor deposition or sorption nucleation rate becomes appreciable. Gerber (1972), for example, gives size cutoffs for appreciable vapor deposition nucleation as 500 \AA radius at -20°C and 1500 \AA radius at -16°C . It is therefore likely that the hypothesized deposition nucleation mechanism is functioning on the larger aerosols. The deposition nucleation rate on these larger aerosols is much faster than the collision rate (contact nucleation rate) of the same aerosols with cloud droplets at -20°C . This is not so at much warmer temperatures.

It is interesting to compare the percentage of ice crystals produced by the apparent deposition mechanism to a minimum particle size which might be utilized. For this purpose, the 500 \AA value given by Gerber (1972) was chosen. It can be shown that the equation of the deposition kinetic plot is

$$\ln[100 - \%IC_t] = \ln[\%IC(\text{deposition})] - K_2 t, \quad (10)$$

where K_2 is negative the slope. Thus, the percentage of the total number of ice crystals formed by the deposition mechanism is obtained from the exponent of the y -intercept. These values are correlated in Fig. 10 with the percent of aerosol particles greater than 500 \AA diameter (determined by SEM), for six aerosols tested. The line in Fig. 10 represents a one-to-one relationship. Four of the six points are observed to lie very close to this line. Although it must be assumed that all aerosols greater than 500 \AA diameter can and do nucleate ice by vapor deposition, this figure does suggest that a size cutoff for measurable deposition nucleation on non-hygroscopic nuclei at near 500 \AA (at -20°C) is validated for freely suspended nuclei.

Although there appears to be a minimum size dependency to the hypothesized deposition nucleation, the rate of ice crystal formation by this mechanism is very nearly independent of the mean size of the aerosols $\geq 500 \text{ \AA}$ diameter. This is particularly noticeable in comparing the kinetic slopes (for deposition) by the natural draft (Fig. 7) and maximum draft (Fig. 8) AgI-AgCl nuclei. Apparently, all nuclei $\geq 500 \text{ \AA}$ diameter contain similar "active sites."

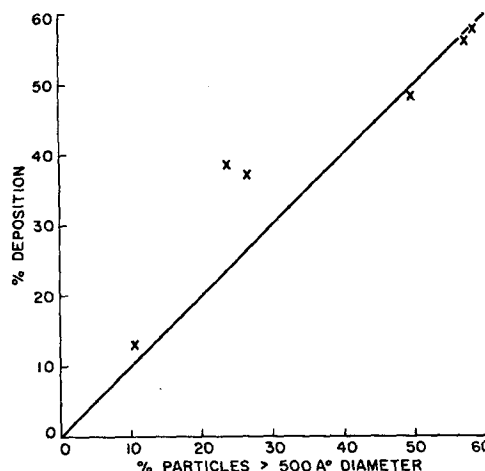


FIG. 10. Relationship between the percentage of ice crystals formed by deposition and the percentage of particles $> 500 \text{ \AA}$ for six aerosols tested. Line gives 1:1 relation.

5. Summary and implications

In this paper, physical chemistry methodology has been applied to the study of the rates of ice crystal formation in order to delineate ice nucleation mechanisms and to gain information into the nucleation characteristics of mixed AgI-AgCl nuclei at water saturation. Mixed AgI-AgCl nuclei were generated using a laboratory acetone burner similar in design to many used for operational weather modification. These aerosols were tested in a large cloud chamber for comparison with standard AgI aerosols generated from the $2\text{AgI} \cdot \text{NH}_4\text{I}$ -acetone-water solution combustion system. The major results and conclusions may be summarized as follows:

- 1) The chemical kinetics methodology has proved useful and valid to study single and simultaneously occurring nucleation processes.
- 2) Ice nucleation effectiveness increases have been directly associated with the introduction of chlorine to a standard AgI aerosol. By the addition of 30 mole percent NH_4ClO_4 (with respect to the AgI) to the standard solution, AgI- NH_4I aerosol ice nucleation, effectiveness increases of approximately one order of magnitude at -12°C to three orders of magnitude at -6°C can be achieved ($\text{LWC} = 1.5 \text{ g m}^{-3}$ in these tests). This new aerosol contained 21.9 mole percent chlorine.
- 3) For conditions simulated in the ICC, the kinetics analysis showed that contact nucleation dominates ice crystal formation on both AgI-AgCl nuclei, and AgI nuclei aerosols at temperatures -16°C and warmer.
- 4) The measured overall rates of ice crystal formation by contact freezing nucleation of the aerosols tested were determined by the transport rate to drop-

lets of the nuclei effective in forming ice crystals at a given temperature. The relative rates of nucleation following collision compared to the rates of deactivation or solution, determined primarily the ice nucleation effectiveness at any temperature. The mixed AgI–AgCl nuclei are more efficient than the standard AgI nuclei at relatively warm temperatures below 0°C because epitaxy and/or surface “active site” improvements increase the rate of nucleation following collision compared to the rates of deactivation or solution. The relative rates of nucleation indirectly influenced the rate of ice crystal formation because larger nuclei (with slower transport rates) are more efficient compared to smaller particles in forming ice crystals. However, all particle sizes participate in contact nucleation at any temperature indicating that nucleation probably occurs at “active sites.”

5) At a temperature of –20°C, all aerosols tested formed ice crystals by both contact nucleation and a mechanism independent of cloud droplet concentrations, which is hypothesized to be deposition nucleation.

6) The overall rate of formation of ice crystals by the deposition mechanism at –20°C is independent of mean particle size. However, the percentage of particles formed by deposition correlated well with a minimum particle size of 500 Å diameter for an appreciable deposition rate.

The kinetics methodology presented should allow better understanding of the nucleating characteristics of actual field generator nuclei by providing a relatively simple method for determining the nucleation mechanisms and their sensitivity to environmental parameters. Care must be taken, however, in applying the quantitative rate results presented in this first study. The ice crystal formation rates measured apply only at water saturation and for the droplet concentrations present in the ICC. Composite rate constants (k_D) obtained by dividing the corrected kinetic slopes by the average droplet concentrations are functions of temperature only. These are useful values, but could change slightly when wall effects in the chamber are quantified. Useful extensions to this study would examine kinetically the ice nucleation behavior of artificial nucleants under varied conditions of supersaturation, as well as varied temperature and cloud droplet concentrations and sizes. Such quantitative data could be reduced to a single rate constant for ice crystal formation (under a given set of conditions and by a given mechanism) on an entire particle size distribution of nuclei. Simple empirical relations for the ice nucleation behavior of aerosols would result that would be of utility in proper seeding effect models. The ultimate quantitative test of the chemical kinetic methodology would be provided by tests with discrete size cuts of nucleating aerosols. This was not allowed

in this study. Such tests would better define size effects in nucleation and provide understanding of the first-order linearity of the composite nucleation kinetics of the dispersive aerosols in this study.

The fact that the interpretation of the macro-kinetics was not complicated by an aerosol distribution, suggests the possibility of using this approach to study natural and artificially induced ice evolution in atmospheric clouds. This would be facilitated by the use of cloud physics aircraft which can characterize the spatial and temporal changes in ice crystal concentrations and environmental parameters.

Although the use of mixed AgI–AgCl nuclei in cold clouds can result in the formation of 10–1000 times the number of ice crystals formed by the standard AgI aerosol over some time period, the consideration of ice crystal formation rates is vital to their use. It is apparent that ice crystal formation within a cold, stable cloud at water saturation (with a typical LWC of 0.2 g m⁻³ and a typical droplet concentration of 200 cm⁻³), would be a prolonged process which might not produce the desired ice crystal concentrations over the allowed time and space frame unless seeding rates were adjusted upward. In such a case, Brownian coagulation of the entire aerosol distribution with droplets would represent the upper limit to the ice crystal formation rate and the actual rate would be much lower at warmer temperatures below 0°C. For many applications, a nucleant population which forms ice crystals rapidly and independently of cloud droplet concentrations might be desirable.

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REFERENCES

- Auer, A. H., 1970: Observations of ice crystal nucleation by droplet freezing in natural clouds, *J. Rech. Atmos.*, **4**, 145–160.
- Blair, D. N., B. L. Davis and A. S. Dennis, 1973: Cloud-chamber tests of generators using acetone solutions of AgI–NaI, AgI–KI and AgI–NH₄I. *J. Appl. Meteor.*, **12**, 1012–1017.
- Davis, C. I., 1974: The ice nucleating characteristics of various AgI aerosols. PhD. dissertation, University of Wyoming, 267 pp.
- , and A. H. Auer, 1972: The possibility of collision nucleation by an AgI aerosol in natural orographic cap cloud. *J. Rech. Atmos.*, **6**, 107–115.
- Donnan, J., D. N. Blair and D. A. Wright, 1971: A wind tunnel/cloud chamber facility for cloud modification research. *J. Wea. Mod.*, **3**, 123–133.
- Edwards, G. R., and L. F. Evans, 1961: The effect of surface charge on ice nucleation by silver iodide. *Trans. Faraday Soc.*, **58**, 1649–1655.
- Federer, B., and A. Schneider, 1981: Properties of pyrotechnic nucleants used in Grossversuch IV. *J. Appl. Meteor.*, **20**, 997–1005.
- Frost, A. A., and R. G. Pearson, 1953: *Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions*. Wiley, 147–151.
- Garvey, D. M., 1975: Testing of cloud seeding materials at the

- cloud simulation and aerosol laboratory, 1971-1973. *J. Appl. Meteor.*, **14**, 883-890.
- Gerber, H., 1972: Size and nucleating ability of AgI particles. *J. Atmos. Sci.*, **29**, 391-392.
- , 1976: Relationship of size and activity for AgI smoke particles. *J. Atmos. Sci.*, **33**, 667-677.
- Grant, L. O., and R. Steele, 1966: The calibration of silver iodide generators. *Bull. Amer. Meteor. Soc.*, **47**, 713-717.
- Guldberg, C. M., and P. Waage, 1879: Ueber die chemische Affinität. *J. Prakt. Chem.*, **19**, 69-114.
- Heicklen, J., 1976: *Colloid Formation and Growth—A Chemical Kinetics Approach*. Academic Press, 87-96.
- Isaac, G. A., and R. H. Douglas, 1972: Another "time lag" in the activation of atmospheric ice nuclei. *J. Appl. Meteor.*, **11**, 490-493.
- Katz, U., and R. J. Pilie, 1974: An investigation of the relative importance of vapor deposition and contact nucleation in cloud seeding with AgI. *J. Appl. Meteor.*, **13**, 658-665.
- Matthews, L. A., D. W. Reed, P. St.-Amand and R. J. Stirton, 1972: Rate of solution of ice nuclei in water drops and its effect on nucleation. *J. Appl. Meteor.*, **11**, 813-817.
- Odenrantz, F., 1969: Freezing of water droplets: Nucleation efficiency at temperatures above -5°C . *J. Appl. Meteor.*, **8**, 322-325.
- Reiss, H., 1982: Common problems in nucleation and growth, chemical kinetics, and catalysis. *Heterogeneous Atmospheric Chemistry, Geophys. Monogr. Ser.*, No. 26, Amer. Geophys. Union, 1-5.
- Sax, R. I., 1970: Drop freezing by Brownian contact nucleation. PhD thesis, Imperial college of Science and Technology, University of London, 257 pp.
- , D. M. Garvey and F. P. Parungo, 1979: Characteristics of AgI polytechnic nucleant used in NOAA's Florida Area Cumulus Experiment. *J. Appl. Meteor.*, **18**, 195-202.
- Turnbull, D., and B. Vonnegut, 1952: Nucleation catalysis. *Ind. Eng. Chem.*, **44**, 1292-1298.
- Vonnegut, B., 1949: Nucleation of supercooled water by silver iodide smokes. *Chem. Rev.*, **44**, 277-289.
- , and H. Chessin, 1971: Ice nucleation by coprecipitated silver iodide and silver bromide. *Science*, **174**, 945-946.
- Warburton, J. A., and K. J. Heffernan, 1964: Time lag in ice crystal nucleation by silver iodide. *J. Appl. Meteor.*, **3**, 788-791.
- Warner, J., and T. D. Newnham, 1958: Time lag in ice crystal nucleation in the atmosphere: Part I: Experimental. *Bull. Obs. Puy de Dome*, **1**, 1-10.
- Young, K. C., 1974: A numerical simulation of orographic precipitation, Part I: Description of the model microphysics and numerical techniques. *J. Atmos. Sci.*, **31**, 1735-1748.
- Zettlemoyer, A. C., N. Tcheurekdjian and J. J. Chessick, 1961: Surface properties of silver iodide. *Nature*, **192**, 653.
- , 1969: *Nucleation*. Marcel Dekker Inc., 606 pp.