ICE NUCLEATION BY SILVER IODIDE-SODIUM IODIDE: A REEVALUATION

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Abstract. New, preliminary, laboratory studies of the 2AgI·NaI ice nucleus are being conducted in the CSU Isothermal Cloud Chamber. Rates and mechanisms of ice nucleation are investigated using chemical kinetic methodology. Interrelationships between ice nuclei effectiveness, rates and mechanisms of nucleation, and chemical composition are studied. The use of chemical kinetics in the study of ice nucleation is described by DeMott, et al. (1983).

The 2AgI·NaI hygroscopic aerosol nucleates the ice phase by a condensation freezing process. This process is sensitive to supersaturation with respect to water. When water supersaturation is increased to a still unknown but critical value, the rate of nucleation increases, the mechanism of nucleation changes, and the effectivity increases significantly. The results have utility in cloud modification.

1. INTRODUCTION

A great many weather modification experiments have made use of silver iodide-sodium iodide (2AgI·NaI) ice nucleus aerosols generated by acetone solution combustion. Research experiments such as the experiments in Israel (Gagin and Neumann, 1974, 1981) and CLIMAX (Grant and Mielke, 1967; Mielke et al., 1981), which utilized these nuclei, have resulted in statistically significant increases in precipitation. Previous laboratory studies of the 2AgI·NaI ice nucleus, for example, Garvey (1975) and Blair et al. (1973), have established the activity spectra (number of ice crystals per gram of AgI as a function of temperature at water saturation). The rates at which nucleation occurs and the nucleation mechanism were not investigated.

This paper decribes preliminary studies of ice nucleus effectivities, rates of ice crystal formation and mechanisms of nucleation of the 2AgI·NaI aerosol. These are correlated with changes in cloud chamber temperature, cloud liquid water contents and transient supersaturations with respect to water. The chemical kinetics methodology used treats nucleation as a function of time and concentrations of nuclei and water vapor. The experimental results were obtained using the CSU Isothermal Cloud Chamber.

2. EXPERIMENTAL

2.1 Approach

Chemical kinetics addresses the rate of a reaction or physical process, or the time required for the process to occur. The rate is a function of the concentration of substances involved in the process. It is based on the Law of Mass Action, first formulated in 1863 by Guldberg and Waage (Moore, 1972). This law states that the rate of a reaction is proportional to the product of the concentrations of reacting substances. At the beginning of the reaction, when the concentrations of reactants are high, the rate is faster than at a later time, when the concentrations have been reduced. The rate is exponential. Phase change and nucleation can be treated by kinetic methodology (Reiss, 1982). Past studies have been concerned with the thermodynamic properties of ice nucleation. The present study addresses the dynamic nature of the process of ice nucleation. The differences in the two disciplines have been summed up by Maron and Prutton (1965) as follows:

> *"In the thermodynamic approach the fundamental laws of thermodynamics are utilized to yield deductions based on the energy relations connecting the initial and final stages of a process. By circumventing the steps intervening between the start and end of a process, thermodynamics enables us to arrive at many valuable deductions without knowing all the intimate details of the intermediate stages. Consequently, although this approach is able to tell us what can happen, and to what extent, it is unable, by its very nature to give us information on how, or how rapidly, a change will actually occur. On the other hand, the kinetic approach requires for its operation an intimate and detailed "picture" of the process. From the mechanism postulated then may be deduced the law for the overall process and its various stages."*

In the CSU Isothermal Cloud Chamber, ice nuclei, gaseous water molecules, and liquid water droplets are present. By varying the concentration of one of the substances and noting the change in rate of production of ice crystals with time, the mechanism of nucleation can be determined. For example, if the droplet concentration is increased and the rate of ice crystal production does not change, then nucleation is not droplet dependent. When the rate increases with increasing droplet concentration the mechanism of ice nucleation is commonly called contact (DeMott et al., 1983). If the concentration of gaseous water molecules (water vapor content) is increased and the rate of nucleation subsequently increases, it is concluded that the mechanism of nucleation is water vapor dependent and thus is condensation freezing or vapor deposition, depending on the physical and chemical properties of the aerosol. Other characteristics of the

mechanism can be determined by the study of rate changes with changes in cloud parameters.

2.2 Procedure

Aerosol Generation and Chamber Operation

The aerosol used in these experiments was generated by combustion of a solution of 2% by weight AgI and 50 mole % (0.6% by weight) NaI in acetone. The generator used was the CSU standard generator.

The CSU Isothermal Cloud Chamber design and mode of operation is described in detail by DeMott (1982). Correction factors such as chamber air dilution and wall losses, aerosol generation and delivery are also discussed. The 1000ℓ chamber can be maintained at any constant temperature between 0°C and -20°C. Liquid cloud is produced and maintained by continuous atomization of distilled water by an ultrasonic nebulizer. Mixing cloud droplets with cold air before they enter the chamber allows the droplets to equilibrate thermally to the chamber temperature. Cloud density can be controlled so that liquid water content can be varied from 0.3 to 3.0 g/m^3. For liquid water contents of 0.5 and 1.5 g/m^3, droplet concentrations in these experiments were about 2000 and 4250/cm^3, respectively.

Aerosol samples are collected in a vertical wind tunnel under natural draft dilution conditions and further diluted as necessary using a 4.25ℓ syringe. The sample is then injected into the chamber. Stacked microscope slides at the bottom of the chamber collect the ice crystals that are produced. The slides are taken from the chamber at regular time intervals and the ice crystals are counted using a cold stage microscope. The cumulative number of ice crystals produced in the chamber, is then used in effectivity calculations. The percent of total crystals counted at any time is used in determining the rate of nucleation.

Test Conditions

Table 1 is a summary of the preliminary experiments conducted to date. The column labeled test conditions refers to the method of aerosol delivery to the chamber. 'Dry' denotes experiments when the sample was delivered to the cloud chamber after dilution with -30°C dew point, filtered air. The 'wet' experiments differ in that the last syringe dilution was made with ambient outside air. Shortly before sampling, air temperature and dew point temperature were measured. From the dew point temperature, the amount of water vapor, in grams, in the syringe was calculated. This figure is presented in the column 'H_2O_v excess' in Table 1.

Water saturation is maintained under normal operating conditions because of a constantly replenishing droplet supply. By introducing additional water vapor with the aerosol sample, water saturation is temporarily perturbed and the chamber becomes supersaturated with respect to water for a short time and perhaps in a localized area near the syringe. Steady-state saturation is quickly reestablished, as evidenced by dew point temperature measurements made in the chamber, but not before affecting the ice nucleus population.

The degree of the local supersaturation in the chamber cannot readily be measured or calculated. Classical droplet growth equations and droplet nucleation theory are based on equilibrium and steady-state non-equilibrium thermodynamic theories (Pruppacher and Klett, 1980). Transitory processes occuring in the chamber cannot be adequately addressed by such theories. Microphysical determinations of droplet growth and droplet nucleation may be possible in the cloud chamber. The response time of currently available instruments is probably longer than the time scale of the processes involved. Efforts will be made in the future to study the extent of such supersaturations. Presently, 'H_2O_v excess', in grams, denotes the relative water vapor excess and thus supersaturations encountered in the chamber.

Kinetics

Following DeMott et al. (1983), the process of ice nucleation by condensation freezing and its rate can be expressed kinetically as:

$$N + V \rightarrow IE \quad \text{or} \quad N + V \rightarrow [O]$$

$$\frac{dC_N}{dt} = -KC_V^y C_N = -K'C_N$$

where N is nuclei, V is water vapor, IE is ice embryos, and [O] is frozen droplets. C is used to denote concentration and its subscipts

TABLE 1 - TEST CONDITIONS

# of runs	temp(°C)	liquid water content (g/m^3)	# syringe dilutions	test conditions	H_2O_v excess(g)
3	-16	1.5	2	dry	--
3	-16	0.5	2	dry	--
3	-16	1.5	2	wet	0.03
1	-16	1.5	2	wet	0.038
2	-16	1.5	2	wet	0.045
3	-16	1.5	3	wet	0.06
1	-10	1.5	1	dry	--
3	-8	1.5	0	dry	--
2	-8	0.5	0	dry	--

represent the species, nuclei or vapor, t is time, K is a rate constant ($K'=KC_v^y$), and y is an exponent which determines the order of reaction. Integrating this expression and considering that the number of ice nuclei depleted is inversely related to the number of ice crystals formed,

$$\ln (100-X\%) = -K't$$

where X is number percent of ice crystals formed at any time t. This expression can be plotted on a graph of ordinate ln (100-X%) versus time. The slope of a straight line on such a graph is -K', the rate constant of nucleation.

3. RESULTS

3.1 Ice Crystal Production Rates and Kinetics

Figure 1 shows changes in the rate of ice crystal production for 2AgI·NaI ice nuclei at -16°C. It can be seen from this figure that whereas complete nucleation in the cloud chamber requires about 50 minutes during water saturated conditions, less than 10 minutes are required for complete nucleation when supersaturated conditions exist.

By applying the kinetic rate equation for a condensation freezing process, ln (100-X%) = -K't, to data in Fig. 1, a kinetic rate plot, Fig. 2, is produced with a slope equal to the kinetic rate constant, K'.

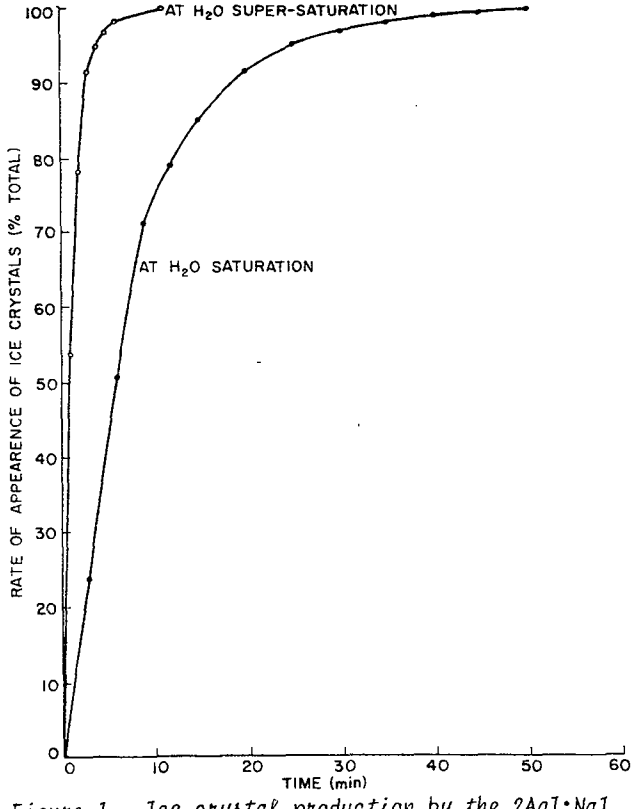

Figure 1. Ice crystal production by the 2AgI·NaI ice nucleus at -16°C. 'At water saturation' refers to 'dry' experiments as explained in the text, at 0.5 and 1.5 g/m^3 liquid water content. 'At water supersaturation' refers to 'wet' experiments with 1.5 g/m^3 liquid water content and water vapor excess of 0.045 g. Production rates for experiments with water vapor excess less than 0.045 g were similar to the dry results.

Fig. 2 demonstrates that the process of ice nucleation is condensation freezing as opposed to contact nucleation since the kinetic plot for experiments conducted for both 1.5 and 0.5 g/m^3 liquid water contents are represented by the same line. The change of droplet concentration did not alter the rate of ice crystal production. The slope of kinetic plots for the condensation freezing mechanism is $-K' = -KC_v^y$. Concentration of droplets, C_D, does not appear as it would for a contact nucleation mechanism (DeMott et al., 1983). The absence of a rate change when cloud droplet concentration changes eliminates contact nucleation as the mechanism.

Figure 3 shows the kinetic rates for experiments conducted at -16°C and -10°C, both at 1.5 g/m^3 liquid water content. As the temperature in the chamber is increased, water vapor content is increased from 1.4 g/m^3 to 2.1 g/m^3. The increase in water vapor concentration results in an increased rate of ice crystal production since $-K'=-KC_v^y$. Experiments conducted at -8°C, though not plotted on Fig. 3 because of limited ice crystal detectability when activity decreases, support the

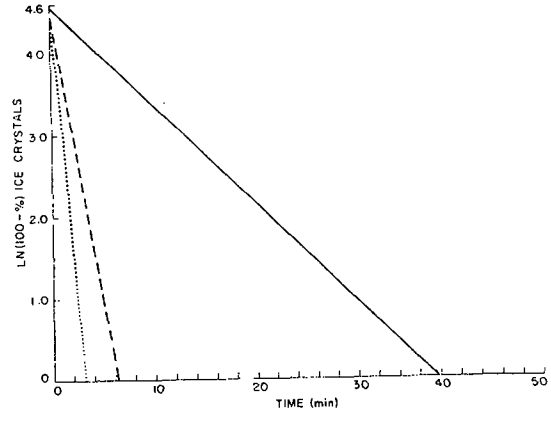

Figure 2. Kinetic rate plots for experiments conducted at -16°C. The solid line denotes the plot for averaged 'dry' experiments with 0.5 and 1.5 g/m^3 liquid water content and 'wet' experiments with water vapor excess less than 0.045 g. Dashed and dotted lines denote averaged 'wet' experiments with water vapor excess of 0.045 and 0.06 g respectively and 1.5 g/m^3 liquid water content.

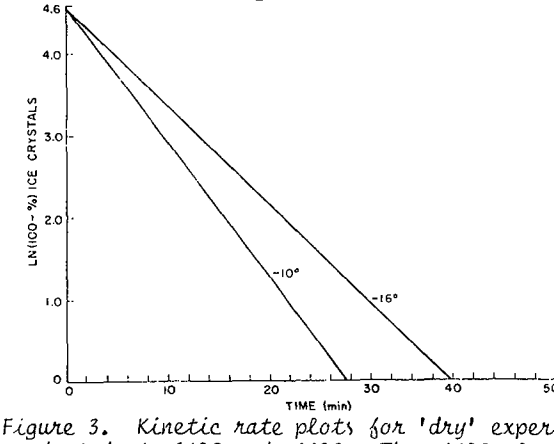

Figure 3. Kinetic rate plots for 'dry' experiments conducted at -16°C and -10°C. The -16°C plot is representative of experiments conducted with 0.5 and 1.5 g/m^3 liquid water content. The -10°C plot is only for experiments conducted with 1.5 g/m^3 liquid water content.

condensation freezing mechanism. 100% ice crystal production was completed in about 15 to 20 minutes at -8°C with no difference when cloud droplet concentration was changed.

Additionally, saturation ratio with respect to ice, at water saturated conditions, increases with decreasing temperature (Pruppacher and Klett, 1980). Ice crystal formation rates would be expected to increase with decreasing temperature for vapor deposition ice nucleation. Figure 3 shows this not to be the case, where rates increased with increasing temperature, further supporting the conclusion that AgI-NaI is a condensation freezing ice nucleus.

The Condensation Freezing Mechanism

The experiments conducted at -16°C where supersaturations were induced provide more detail about the ice nucleation mechanism. At a critical level of water supersaturation of at least 0.045 g water vapor excess introduced into the chamber, the mechanism of ice nucleation apparently changes. The noticeably increased rate of nucleation in Fig. 2 leads to this hypothesis. Further increased water excess promotes even faster rates of nucleation.

There are two possible forms of condensation freezing ice nucleation: 1) condensation freezing to embroyos which grow to produce ice crystals, and 2) condensation to droplets which freeze and grow to produce ice crystals. The rate constant, K', increases from 0.025/min to 0.714/min (a factor of nearly 30) at a critical level of supersaturation, suggesting that a change from one of these mechanisms to the other is occuring. At water saturation and small transient supersaturations, ice nucleation is slow. A mechanism involving complete droplet formation prior to freezing may be predominant in this case. At some critical supersaturation and higher, only limited condensation of water prior to ice formation may be required. This process is intrinsically faster than the process whereby a complete droplet is formed.

The physical environment may force the aerosol into different chemical phases as St. Amand et al. (1971) have outlined, and thus different modes of nucleation. Future research will attempt to define the two mechanisms.

Kinetic Plot Corrections

Because of chamber operational requirements, the loss of aerosol sample in the chamber is unavoidable, due to chamber air dilution. Corrections can be made to kinetic plots to take these losses into account, as outlined by DeMott (1982). Such corrections were made to Figs. 2 and 3 and shown in Figs. 4 and 5. These rates are more representative of how the nuclei may behave in the atmosphere. At moderately low temperatures, considering a cloud with little or no significant water supersaturation, 2AgI·NaI ice nuclei may be dispersed over large cloud areas before nucleation of all dispensed aerosols occurs. It is not easily seen in Fig. 4, but at -16°C, 100% nucleation requires approximately 2 1/2 hours and 27 minutes for 50% nucleation. In contrast, above some critical transitory supersaturation at -16°C, complete nucleation occurs within 10 minutes, with 50% nucleation in less than a minute.

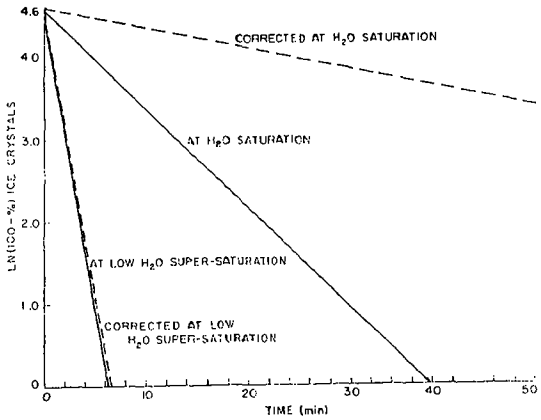

Figure 4. Same as Fig. 2, except corrected for chamber air dilution. 'At water saturation' line is the same as the solid line in Fig. 2. 'At low supersaturation' line is the same as the dashed line of Fig. 2. Dashed lines above are kinetic rates after chamber air dilution correction has been made.

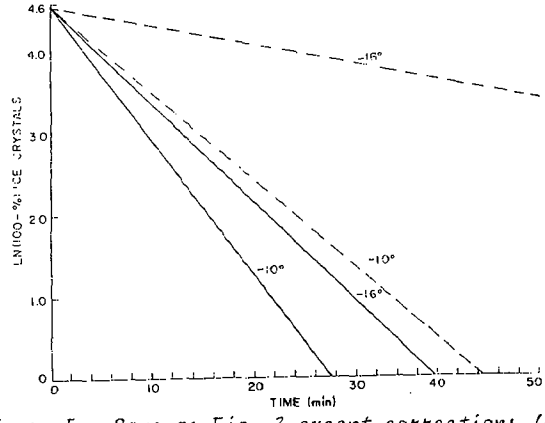

Figure 5. Same as Fig. 3 except corrections for chamber air dilution are added. Dashed lines are the corrected kinetic rates.

3.2 Ice Nuclei Effectivities

Ice nuclei effectivities is defined as the number of ice crystals produced per gram of AgI at varying cloud temperatures. Figure 6 shows the effectivity spectra of 2 AgI·NaI ice nuclei. The data points were obtained from the present study, while the curve shows the average effectivity of the nucleant, established during previous tests at water saturation in the cloud chamber. From data obtained at -16°C, it is evident that as the transient concentration of water vapor increases (i.e., transient supersaturation), at a constant temperature, the effectiveness increased by a factor of 8.

There is reason to believe that since the effect of supersaturations is to raise the effectivity of AgI-Nai nuclei at -16°C, this same effect should occur at warmer temperatures. Therefore, the threshold of activity, commonly taken to be -8°C for AgI-NaI, may actually be higher in supersaturated conditions. Activity may possibly be raised to as much as -6°C. Further tests will be conducted to determine the threshold of activity in supersaturated condition.

4. SUMMARY AND CONCLUSIONS

In this preliminary investigation of the ice nucleating characteristics of silver iodide-sodium

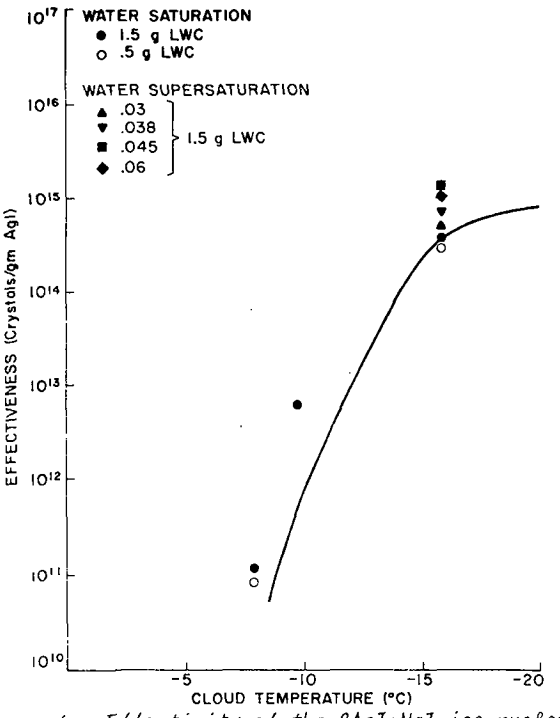

Figure 6. Effectivity of the 2AgI·NaI ice nucleus aerosol. The data points were obtained from this study using the CSU standard aerosol generator. The curve is from previous test using the North American ground generator.

iodine ice nucleus aerosols, it has been shown that the mechanisms of nucleation is dependent on water vapor concentration only. Thus it has been determined that 2AgI·NaI is a condensation freezing ice nucleus. Additionally, at -16°C, when conditions are such that only water saturation is maintained, the condensation freezing process is a slow one, requiring approximately 50 minutes in the chamber (2 1/2 hours, corrected) for complete nucleation. If a transient supersaturation is induced, the entire population of ice nuclei is affected and complete nucleation at -16°C then occurs in less than 10 minutes. This shows that the nucleation rate is dependent on the change in vapor concentration and that a condensation freezing process is involved. Cloud droplet concentration is not involved in the mechanism since nucleation does not vary with changes in cloud droplet concentration. The increase in water vapor concentration at a particular temperature increases the effectivity as well as the rate of nucleation. At -16°C, a factor of 5 increase in effectivity was observed

Developing clouds usually contain some areas of supersaturation with respect to liquid water. When supersaturations are large enough and temperatures are sufficiently low, the ice phase may quickly be initiated by the introduction of 2AgI·NaI aerosol. Past laboratory determined effectivities have been incomplete since all such determinations were made only when cloud chamber conditions were held at water saturation. Rates, mechanisms, and effectivities are generally altered as transient supersaturations are induced. All characteristics of ice crystal formation by 2AgI·NaI aerosol must be understood before such material can be used effectively in weather modification experimentation.

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REFERENCES

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-NH_4I. J. Appl. Met., 12, 1012-1017.

DeMott, P.J., 1982: A characterization of mixed silver iodide-silver chloride ice nuclei. Master's Thesis, Department of Atmospheric Science, Colorado State University, 124 pp.

_____, W.G. Finnegan, and L.O. Grant, 1983: An application of chemical kinetic theory and methodology to characterize the ice nucleating properties of aerosols used for weather modification. J. Appl. Met., accepted.

Gagin, A., and J. Neumann, 1974: Rain stimulation and cloud physics in Israel, in Weather and Climate Modification, W.N. Hess, ed., John Wiley & Sons, New York, 454-494.

_____ and _____, 1981: The second Israeli randomized cloud seeding experiment. Evaluation of the results. J. Appl. Met., 20, 1301-1311.

Garvey, D.M., 1975: Testing of cloud seeding materials at the cloud simulation and aerosol laboratory, 1971-1973. J. Appl. Met., 14, 883-890.

Grant, L.O., and P.W. Mielke, Jr., 1967: A randomized cloud seeding experiment at Climax, Colorado, 1960-1965. Proceedings of the Fifth Berkeley Symposium on Mathematical Statistics and Probability, Vol. 5, University of California Press, 115-131.

Maron, S.H., and C.F. Prutton, 1965: Principles of Physical Chemistry. MacMillan Company, New York, p. 2.

Mielke, P.W., Jr., G.W. Brier, L.O. Grant, G.J. Mulvey, and P. Rosenzweig, 1981: A statistical reanalysis of the replicated Climax I and II wintertime orographic cloud seeding experiments. J. Appl. Met., 20, 643-659.

Moore, W.J., 1972: Physical Chemistry. Prentice Hall, Inc., Englewood Cliffs, N.J., 324-347, pp. 281-282.

Pruppacher, H.R., and J.D. Klett, 1980: Microphysics of Clouds and Precipitation. D Reidel Publishing Co., Dordrecht, Holland, 90-97.

Reiss, H., 1982: Common problems in nucleation and growth, chemical kinetics, and catalysis, in Heterogeneous Atmospheric Chemistry, Davis Schryer, ed., Geophysical Monograph Series, 26, 2-5

St. Amand, P., W.G. Finnegan, and L. Burkardt, 1971: Understanding of the use of simple and complex ice nuclei generated from pyrotechnics and acetone burners. J. Wea. Mod., 3,31-48.