Cirrus Crystal Nucleation by Homogeneous Freezing of Solution Droplets

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ABSTRACT

In recent measurements, liquid water was not detected in cirrus clouds below −40°C and, since there appear to be few ice-forming nuclei in the upper troposphere, ice nucleation evidently takes place by homogeneous freezing of solution droplets. A numerical model consisting of a system of ordinary differential equations is used to study this process in a rising parcel containing a distribution of cloud condensation nuclei (CCN). The model traces the evolution of both the particle population (liquid and solid phases) and the thermodynamic variables in the parcel. Droplet growth rates are calculated in 20 size categories assuming ammonium sulfate nuclei; CCN distributions are taken from aircraft data. Homogeneous nucleation rates are derived by classical methods; adjustments for solution effects are made by considering the water vapor pressure over droplet surfaces.

Results for convective cirrus simulations indicate that if homogeneous freezing is not considered, liquid water should be detected below −40°C; if homogeneous freezing is considered, the rapid growth of ice crystals and concurrent vapor depletion prevent water saturation from being reached. All droplets forming on a given mass CCN freeze almost simultaneously; the homogeneous freezing of most of the entire droplet distribution takes place over a temperature range of less than 1°C. The likelihood of a droplet being frozen is increased by lower temperatures, larger droplet diameter, or lower solution density. Most of the ice crystals produced originate from droplets containing CCN of mass 10⁻¹³ to 10⁻¹⁵ g; the number of ice crystals eventually produced is a function of the temperature, the vertical air velocity, and the CCN distribution.

1. Introduction

Cirrus clouds cover about 35% of the earth’s surface and have an important influence on climate through their effect on the radiation budget (Ramanathan et al. 1983). Cirrus cloud effects on radiative transfer will depend to a large extent upon ice crystal sizes, which in turn might be closely linked to the mechanism by which the crystals are nucleated. This study examines cirrus crystal nucleation at temperatures below about −40°C by freezing of droplets that have grown on cloud condensation nuclei (CCN).

Micrometer-size pure water droplets can supercool to a temperature of about −40°C. Below this point, they freeze homogeneously without the need for ice-forming nuclei (IFN). Schaefer (1962), from observations at Yellowstone Park, showed that liquid droplets existed at temperatures as low as −38°C but not below, in agreement with many laboratory studies (Bigg 1953; Mossop 1955; Hagen et al. 1981). Heymsfield (1977), and Sassen and Dodd (1988), reported water droplets down to −36° and −37°C, respectively, but not below. Heymsfield and Miloshevich (1989) used a Rosemount icing detector with a minimumetectable liquid water content (LWC) of 0.002 g m⁻³ (depending upon droplet size) to identify regions of liquid water (LW) in cold clouds, using the NCAR King Air during the First ISCCP Research Experiment (FIRE). Although the icing detector had a detection threshold of about 0.002 g m⁻³, about an order of magnitude lower than in previous studies in LW clouds, LW was not detected at temperatures below −34.9°C (Table 1). Data collected on the NCAR Sabreliner during FIRE with an icing probe having a detection threshold of about 0.005 g m⁻³ also failed to detect any LW below −35.3°C (Table 1). Persistent liquid phase clouds almost devoid of ice particles were sampled at temperatures from −30 to −35°C. Evidently, relatively few IFN were active in these clouds, in agreement with the more general findings of Heymsfield (1977) and Rangno and Hobbs (1986) that ice crystal concentrations are unexpectedly low at cold temperatures in the upper troposphere.

Liquid water should have been detectable with the icing probes at temperatures below −40°C if it had been present. To illustrate this, Fig. 1 shows the level at which LW would have been detectable in a parcel rising 500 m from ice saturation at −40°C. Depths of convectively unstable layers during FIRE and in earlier studies (e.g., Heymsfield 1975) often exceeded 500 m. At levels above 450 m, droplet sizes should be large.

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TABLE 1. Summary of time (sec) in liquid water and in cloud during FIRE.

<table>
<thead>
<tr>
<th></th>
<th>$T$ (°C)</th>
<th>-20 to -25</th>
<th>-25 to -30</th>
<th>-30 to -35</th>
<th>-35 to -40</th>
<th>-40 to -45</th>
<th>&lt; -45</th>
</tr>
</thead>
<tbody>
<tr>
<td>King Air</td>
<td>in LW</td>
<td>96</td>
<td>780</td>
<td>114</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>in cloud</td>
<td>6616</td>
<td>11 104</td>
<td>9189</td>
<td>6319</td>
<td>5201</td>
<td>967</td>
</tr>
<tr>
<td>Sabreliner</td>
<td>in LW</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>in cloud</td>
<td>904</td>
<td>2312</td>
<td>5281</td>
<td>8998</td>
<td>11 306</td>
<td>23 054</td>
</tr>
</tbody>
</table>

* Minimum detectable LWC = 0.002 g m$^{-3}$.
** Ice particle concentration from 2D-C and 2D-P probes >0.1 L$^{-1}$.
*** Minimum detectable LWC = 0.005 g m$^{-3}$ based on “calibration” of probe using data from field experiment reported in Sassen and Dodd (1988) (K. Sassen, personal communication).

... enough, and liquid water content high enough, for detection with the icing detector. The height at which LW becomes detectable will be affected by the CCN composition and mass distribution and updraft velocity, as discussed later.

The apparent dearth of IFN and the absence of LW at temperatures below -40°C suggest that ice nucleation takes place by homogeneous freezing of droplets. The absence of LW below -40°C is consistent with the study of Ludlum (1956) and the hypothesis and numerical study of Heymsfield (1973) that cirrus crystals are nucleated by solution droplets that freeze without IFN at this and lower temperatures. However, the solute in the droplets acts to depress the freezing point below that for the homogeneous freezing of pure droplets. Sassen and Dodd (1988) reported evidence for this effect in cirrus using aircraft and lidar data. The present study develops a framework for examining the growth and homogeneous freezing of solution droplets rising in air parcels, and the ice crystal concentrations and maximum relative humidity attained, based on Heymsfield’s (1973) treatment of this problem. Uncertainties in parameters used to derive theoretical homogeneous freezing rates and in applying the results to the atmosphere are discussed, as are recommendations for further research.

2. Model development

The model consists of a system of ordinary differential equations that describes both the micro properties of the droplets, and the macro properties of the rising air parcel. The model is set up as an initial value problem, and the values for each of the parameters after time $t = 0$ s are found using a Runge-Kutta solver with a fourth-order Adams-Moulton predictor. Small step sizes were chosen (about 0.01 s) to eliminate instabilities in any of the solutions (primarily those for droplet growth).

A schematic depiction of the process modeled is presented in Fig. 1. The calculations begin with a CCN distribution in a rising parcel of air at a saturation ratio at which the CCN first dissolve into solution by absorbing water vapor from the air (deliquesce), a temperature between -37 and -50°C, and a pressure ranging from 320 to 270 mb, depending upon the temperature. The vertical air velocity is held constant throughout the calculations. As the parcel lifts, the droplets grow by vapor diffusion. Some of the droplets freeze; the frozen droplets then grow as ice crystals. The saturation ratio with respect to water, $s$, of the parcel can exceed 1.0, some droplets grow large enough to be activated, and a liquid water cloud is produced. A point is reached at which the ice crystals (which grow much faster than the solution droplets) deplete the vapor faster than it is being supplied. The resulting saturation ratio decrease causes the remaining solution droplets to begin to evaporate, and prevents most of them from freezing.

Fig. 1. Schematic illustration of the evolution of solution droplets in a parcel at cirrus altitudes rising from ice saturation at $T_0 = -40°C$. Relative humidity is with respect to water.

1Activated droplets are those which continue to grow after the maximum saturation ratio is reached in a parcel as long as $s > 1.0$. 
The model assumes that all ice crystals are produced by homogeneous freezing, no preexisting ice crystals are introduced into the rising parcel, and ice crystals do not sediment in the updrafts. These points are reviewed in sensitivity studies in section 4. The model also ignores random variations in local droplet concentrations.

a. Homogeneous freezing rates of solution droplets

The Gibb’s free energy of formation of an ice embryo in a solution droplet, \(\Delta G\), is expressed by classical theory (Byers 1965) as

\[
\Delta G = -\frac{4}{3} \pi r_g^3 \alpha N_i k T_i \ln(p_l/p_v) + 4 \pi r_g^2 \beta \sigma_d.
\]

In this, and in all following equations, the subscript \(l\) will refer to liquid, and \(s\) to solid water. (All symbols are defined in the Appendix.) In previous studies of homogeneous freezing of droplets, the equilibrium vapor pressure of the solution droplet, \(p'_l\), was taken to be the saturation vapor pressure over a flat, pure water surface, \(p_v\). Solute and curvature effects to \(p'_l\) could safely be neglected when relatively large, pure water droplets were concerned. In this study, a large range of droplet sizes and molalities are considered, so these effects on \(p'_l\) are included. In discussions that follow, \(p'_l\) is replaced by \(s'p_l\), where the term \(s'\) is virtually equivalent to the environmental saturation ratio with respect to water at most times since the droplets are usually at equilibrium with their environment. The "critical" size of the ice embryo, that is, the size above which the ice embryo will grow spontaneously to freeze the droplet, is found by setting \(\partial \Delta G/\partial r_g = 0\); the resulting critical free energy is

\[
\Delta G^* = \frac{16 \pi \sigma_d^2}{3} \left[ N_i k T_i \ln(s'p_l/p_v) \right]^{-2}. \tag{2}
\]

It is useful to separate \(\Delta G^*\) into components for a pure water droplet, \(\Delta G^{(0)*}\), and for the solution effect; this involves an expansion of

\[
\left( 1 + \frac{\ln s'}{\ln(p_l/p_v)} \right)^{-2},
\]

for small \(\ln s'/\ln(p_l/p_v)\), which is terminated with a high degree of accuracy at \(n = 5\) terms. This gives

\[
\Delta G^* \approx \Delta G^{(0)*} \times \left[ 1 + \sum_{n=2}^{5} (-1)^{(n-1)} n \left( \frac{\ln s'}{\ln(p_l/p_v)} \right)^{(n-1)} \right]. \tag{3}
\]

The nucleation rate \(J_H\), which is the number of ice embryos passing the critical radius per second per unit volume, can be expressed as

\[
J_H = \frac{N_i k T_i}{h} [e^{-\Delta G^{(0)*}/kT_i}e^{-\Delta G^*/kT_i}], \tag{4}
\]

where \(N_i\) is the number of water molecules per unit volume of the liquid. The droplet temperature, \(T_i\), is approximated by \(T\), since during growth the two are within \(10^{-2}\) °C. By employing Eq. (3), the nucleation rate can be expressed in terms of the rate for pure water droplets \(J_H^{(0)}\) as

\[
J_H \approx J_H^{(0)} \frac{N_i}{N_i^{(0)}} \exp \left\{ \frac{-\Delta G^*/(kT)}{kT} \times \left[ \sum_{n=2}^{5} (-1)^{(n-1)} n \left( \frac{\ln s'/\ln(p_l/p_v)}{(n-1)} \right) \right] \right\}. \tag{5}
\]

The preexponent term in Eq. (5) accounts for the nucleation rate of pure water droplets since, in general, \(N_i/N_i^{(0)}\) is very close to 1.0, and the exponents account for the solution effect.

The development given by Eqs. (1) to (5) describing the depression of the homogeneous nucleation temperature by the solute differs from the use of bulk water freezing point depression (Raoult’s law) in two ways. Raoult’s law accounts for vapor pressure lowering due only to the presence of the solute and does not account for vapor pressure increases due to droplet curvature (Kelvin’s effect). Furthermore, Raoult’s law assumes the liquid solution is ideal while solutions containing typical CCN deviate by as much as 50% in freezing point depression from ideality (e.g., Low 1969).

Researchers working on the homogeneous nucleation problem agree on the rapid increase in the nucleation rate between -30 and -40°C. However, values of \(J_H^{(0)}\) as a function of temperature are still uncertain. The chief difficulty lies in assigning accurate values for \(\sigma_d\). Most determinations of \(\sigma_d\) have been made by fitting theoretical curves of the freezing rate (proportional to \(J_H^{(0)}\)) through experimental data showing the freezing temperatures of an ensemble of pure water droplets; \(J_H^{(0)}\) and \(\sigma_d\) can then be obtained.

Eadie (1971) calculated values for \(\sigma_d\) and \(J_H^{(0)}\) on the basis of a statistical thermodynamic model of liquid water. This model predicted the thermodynamic properties of liquid water satisfactorily. Since Eadie’s theoretical values of \(J_H^{(0)}\) between -34 and -37°C also compare favorably with recent estimates of \(J_H^{(0)}\) based on in-cloud and lidar measurements by Sassen and Dodd (1988) for the same temperatures (Fig. 2), it seems appropriate to use Eadie’s temperature-dependent values here. Also shown in the figure are values for \(J_H^{(0)}\) from Pruppacher and Klett (1978), hereafter PK, and Hagen et al. (1981), which do not fit the Sassen and Dodd estimates nearly as well as Eadie’s theory.

Given values for \(J_H^{(0)}\) from above, the fraction of droplets \(df\) frozen per time step \(dt\) can then be estimated from

\[
df = (1 - f)V_i(t)J_H(t)dt, \tag{6}
\]

where the droplet volume \(V_i\) is computed on the basis
of the mass of the soluble nuclei, and the droplet density and radius.

b. Change in vapor density and temperature in the parcel

In a rising parcel, the time rate of change of the saturation ratio can be written as (Heymsfield 1973, 1975):

$$\frac{ds}{dt} = \phi_1 w - \phi_2 \frac{dX_l}{dt} - \phi_3 \frac{dX_s}{dt},$$

(7)

where $w$ is the vertical air velocity, $X_l$ and $X_s$ are the liquid and ice mixing ratios, and

$$\phi_1 = s \left( \frac{L_v}{R_v T^2 c_p} - \frac{1}{R_d T} \right),$$

(8)

$$\phi_2 = s \left( \frac{L_v^2}{R_v T^2 c_p} + \frac{PR_v}{s_p R_d} \right),$$

(9)

$$\phi_3 = s \left( \frac{L_v L_s}{R_v T^2 c_p} + \frac{PR_s}{s_p R_d} \right).$$

(10)

The three terms represent vapor supply to the updraft, vapor depletion by droplet growth, and vapor depletion by ice crystal growth, respectively. A fourth term, accounting for fallout of ice crystals from the parcel (Heymsfield 1973), is not used because ice particle terminal velocities are small in comparison with the vertical velocities employed in the calculations. Depletion of liquid water by riming on ice crystals will be negligible for the conditions considered here and is thus not included. Entrainment is not considered for simplicity.

Ice crystals that fall or are entrained into an updraft developing in an existing cirrus layer reduce $ds/dt$. Their effect can be taken into account in Eq. (7) by subtracting a term $\phi_3 (dX_p/dt)$. Equivalently, their effect can be viewed as reducing the vapor supplied by the updraft by an amount $w^*$, where $w^* = (\phi_3 / \phi_1) (dX_p/dt)$. The effects of preexisting ice crystals are examined in sensitivity studies.

The time rate of change of temperature is computed on the basis of dry adiabatic ascent and latent heat released due to vapor condensation onto water droplets and deposition onto ice crystals:

$$\frac{dT}{dt} = - \frac{gL_v}{c_p} X_l \frac{dX_l}{dt} + \frac{L_s}{c_p} X_s \frac{dX_s}{dt}. $$

(11)

A term accounting for the latent heat released by droplet freezing is ignored in Eqs. (8) and (11) as it is very small relative to the other terms.

c. Cloud condensation nuclei

As a parcel lifts and cools, solution droplets form on CCN (Fig. 1). The CCN composition and size distribution control the relative humidity (RH) for deliquescence and the resulting evolution of the solution droplet size spectrum. Assuming that the CCN at cirrus levels are ammonium sulfate, consistent with the experiments of Twomey (1971), deliquescence occurs at about 82% RH.

CCN size spectra were obtained as follows. From aircraft, Heymsfield (1973) collected air in Mylar bags in cloud-free conditions at altitudes from 7 to 8 km and temperatures from −27 to −39°C over Greenville, Illinois, during February 1972. The bags were returned to the ground within an hour. Immediately thereafter, a thermal diffusion chamber was used to measure the CCN activity spectrum (Fitzgerald 1972) over the range 0.3% to 2% supersaturation with respect to water. The spectra were adjusted to account for differences in the surface tension of water and temperature between the measurements taken at +20°C and typical −40°C cirrus conditions. Decay in the concentration of CCN occurring during storage of the air sample in the Mylar bag was not taken into account, but this would have decreased the concentration by less than 10% (Fitzgerald 1972) for the sizes considered in the measurement. Figure 3 shows data points and curve fits of the form $N = CS_f^p$, where $N$ is the CCN concentration that is activated when a supersaturation with respect to water $S_f$ (%) is achieved.

The measured CCN spectrum can be used to derive
the ammonium sulfate mass concentration spectrum. The Kohler equations (PK) describe the variation of the equilibrium vapor pressure over an aqueous solution drop as a function of drop size, supersaturation, and salt mass. The supersaturation (%) needed to activate a droplet containing a given or higher mass of ammonium sulfate can be found from

\[ S_f = 100 \left( \frac{4A^3}{27B} \right)^{0.5}, \tag{12} \]

where

\[ A = \frac{2\sigma_{la}}{R e T \rho_w}, \quad B = \frac{3\nu m M_0}{4\pi M \rho_l}. \]

In this equation, \( \sigma_{la} \) is the surface tension of water against air, \( \nu \) the total number of ions into which a salt molecule dissociates, \( \rho_l \) the solution density, and \( m \) the mass of the solute. An empirical relationship (PK) is used to include the effects of solution molality on \( \sigma_{la} \). Equation (12) is used to derive the solute masses shown on the upper axis of Fig. 3 at \(-40^\circ\). CCN concentrations were not measured for masses \( \geq 10^{-15} \) g, although it is important to estimate their magnitude since freezing probability is dependent upon droplet volume, which in turn depends directly upon droplet mass. Recent balloon measurements of dry aerosol sizes in the upper troposphere indicate that nuclei are present in concentrations of 0.1 to 1.0 cm\(^{-3}\) with diameters of about 0.25 \(\mu\)m, and in concentrations of \(10^{-4}\) to \(10^{-5}\) cm\(^{-3}\) with diameters of about 2 \(\mu\)m (J. Rosen, personal communication). Assuming that the nuclei are spherical with density 1.25 g cm\(^{-3}\), the former sizes correspond to an ammonium sulfate mass of \(8 \times 10^{-14} \) g and the latter to one of \(5 \times 10^{-12} \) g. An estimate of the CCN concentrations roughly agreeing with the balloon measurements is given by extrapolation of curve I in Fig. 3. The implication of the extrapolation is that the spectral slope \( K \) is greater than perhaps 1.5 at masses exceeding about \(10^{-15} \) g. In this study, unless otherwise noted, a CCN spectrum is used which approximates curve I in Fig. 3:

\[ N = 200 S_i^{1.5}. \tag{13} \]

Equation (13) is converted to an \( N \) versus \( m \) equation by use of Eq. (12). Values for \( N \) are derived in 20 mass categories, whose centers are equally spaced on a logarithmic scale, over a mass range from a maximum, \( m_{\text{max}} \), \(10^{-12} \) g, to a minimum, \( m_{\text{min}} \), of \(5 \times 10^{-18} \) g. Concentrations used in the model are found by taking differences in \( N \) between successive mass categories; the concentration for category \( m_{\text{max}} \) is given directly by the values from Eqs. (12) and (13).

d. Liquid and ice mixing ratios

Two methods are used to compute LWC and its time derivative. The first method assumes that the droplets are always in equilibrium with the environment, and cannot be used if any of the droplets are activated. The equilibrium diameter of a solution droplet can be found from (PK):

\[ s = \exp \left[ -\frac{4\sigma_{la}}{R e T d_1 \rho_w} - \frac{\nu \Phi_i m M_0}{4\pi M \rho_l} \right], \tag{14} \]

where \( d_1 \) is the diameter of the solution droplet\(^2 \) and \( \Phi_i \) is the osmotic coefficient of the solution. Values of \( \nu \Phi_i \) are taken from Low (1969) for ammonium sulfate solutions at +25\(^\circ\)C, and the dependence of \( \rho_l \) on concentration of ammonium sulfate in the nuclei is taken from Weast (1985), also for +25\(^\circ\)C. Given values for \( s \) and \( m \) in Eq. (14), the droplet diameter is solved for numerically. The LWC is found by computing the growth of a population of droplets, and the growth rate is found from the difference in LWC between successive time steps.

The second method holds for both equilibrium and nonequilibrium conditions. The time rate of change of a droplet's diameter can be found directly from

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\(^{2}\) Nucleation researchers formulate equations in terms of droplet radius while aerosol and cloud researchers measure a particle's physical diameter. Since this study bridges these disciplines both particle radius and diameter are used.
The time rate of change of the ice mixing ratio is found by converting Eq. (16) into a mass growth rate, and considering the growth rate of all ice crystals.

3. Model results

Figures 4a–d show plots of various parameters related to the conceptual view of a convective cirrus layer, for an updraft velocity of \( w = 100 \) cm s\(^{-1} \) and a temperature at the start of deliquescence, \( T_0 \), of \(-40^\circ\)C. Two cases are considered: in one case homogeneous freezing takes place as discussed previously, and in the other, freezing is prevented. If freezing is prevented, LW should be detectable with the icing probes 495 m above the \(-40^\circ\)C level (Fig. 4a), based on a probe calibration equation that takes into account collection efficiency as a function of droplet size (Heymsfield and Miloshevich 1989). The mean droplet diameter reaches about 3 \( \mu \)m at this time (Fig. 4c). The saturation ratio reaches a maximum, \( s_{sr} \), of 1.05 (Fig. 4b), much higher than for cumuliform clouds at warmer temperatures with similar \( w \) and CCN spectra (PK); term 2 on the right-hand side of Eq. (7) decreases relative to term 1 with decreasing temperature. The concentration of activated droplets reaches 126 cm\(^{-3} \) similar to those reported between \(-34 \) and \(-37^\circ\)C by Sassen and Dodd (1988). When ice is included, water saturation is not achieved (Fig. 4b). The concentration of ice crystals produced (Fig. 4d) is unexpectedly high. Ice crystals continue to form after \( s_{sr} \) is reached, but within a short time (about 20 s), \( s \) decreases rapidly, droplets begin to evaporate, and freezing ceases. It is found that during this period of evaporation, \( T_i \) is about \( 10^{-5} \) \( ^\circ\)C lower than \( T \), and thus evaporative cooling will have an insignificant effect on droplet freezing probability. The largest crystals (Fig. 4c), those produced at the first time step of the model run, grow to about 60 \( \mu \)m. They have terminal velocities of about 12 cm s\(^{-1} \) (based on drag coefficients for rigid spheres in PK), but most have less than \( \frac{1}{2} \) of this value; they grow at an average rate of 0.25 \( \mu \)m s\(^{-1} \), about ten times faster than the droplets.

The concentration of ice crystals produced in the parcel decreases by roughly a factor of ten if the unmodified diffusion and heat conduction coefficients are used to calculate the ice crystal growth rates. The larger crystals deplete the water vapor at a disproportionately higher rate than the smaller ones, preventing the smaller droplets from freezing.

Model runs with \( T_0 \) between \(-35 \) and \(-40^\circ\)C have been conducted with \( w = 100 \) cm s\(^{-1} \). Water saturation is not reached at air temperatures below \(-39^\circ\)C. The absence of LW below \(-40^\circ\)C in the FIRE measurements supports the idea that droplets homogeneously froze, at least in the several cases where isolated convective cells were sampled.

Appreciable homogeneous freezing of solution droplets occurs with only small decreases in tempera-
ture following deliquescence. This is illustrated from curves of the saturation ratio and temperature at which 10% of the droplets containing a given $m$ are frozen (Fig. 5a). (In order to examine the dependences on $m$, these curves were derived by not allowing ice crystals to deplete the vapor.) Freezing of solution droplets occurs over a very narrow temperature range, almost independent of $m$; at $-48$°C, only 100–185 m of uplift is required to freeze droplets containing all $m$. Freezing occurs at progressively lower saturation ratios as the temperature is lowered. Changes in solution droplet diameter and density are modest during the uplift (Fig. 5b); the temperature dependence of freezing in Fig. 5a is therefore attributable to the increase in nucleation rate with decreasing temperature.

The freezing behavior of solution droplets containing a given mass CCN as they are growing and cooling in a parcel is illustrated from curves of $s$ versus $f$ (fraction frozen) for several $m$ and $T_0$ in Fig. 6 (solid curves); these curves were also derived assuming no vapor depletion by ice particles. Freezing rates increase rapidly when a particular $s$ is reached and most of the freezing occurs in a narrow temperature range (see right ordinate) for droplets containing a given $m$. The curves are similar in shape, the displacement between them depending upon $J_{nf}^{(0)}(T)$ and droplet size.

Sensitivity studies (dotted lines, Fig. 6) show changes due to simplified treatment of the solution effect. Comparison of curves I and II indicates that droplets forming on CCN with high $m$ are not in equilibrium at temperatures where $s$ is close to or exceeds 1.0, $T_0 \geq -42$°C. For example, at the time that $f$ becomes
begins to become appreciable $s_{\infty}$ (concentration $\geq 1$ L$^{-1}$, which is 1 to 10% of that reported for crystals $> 100 \mu$m in cirrus clouds); the difference between the peak saturation ratio and $s_{\infty}$, $\Delta s$; and the concentration of ice crystals produced in the parcel, $n_c$. Vertical velocities were set at 25 cm s$^{-1}$ or higher where crystal terminal velocities were small relative to the updrafts. Here, $s_{\infty}$ is almost independent of updraft velocity and decreases almost linearly with $T_0$ (Fig. 7a). The $s_{\infty}$ curves should have almost zero slope until very low values of $w$ are reached, as indicated by the dashed, estimated curves in the figure. The $\Delta s$ increases roughly as $w^{0.45}$ (Fig. 7b), and decreases slightly with decreasing $T$. The $\Delta s$ at the time that $f$ becomes 0.01, 0.1 and 1.0 in the various mass categories (Fig. 7c, open symbols) is dependent upon $m$ but nearly independent of $w$ and $T$. (Data are not shown for the $-44^\circ$C runs because they are similar to those for $-40^\circ$ and $-48^\circ$C, nor are they shown for any of the runs where $f$ did not reach 1.0 in any mass class.) A similar plot of data for the model runs that did not include ice depletion (solid symbols) is similar to those that included ice depletion. Curves fit through the data with no depletion are shown.

The concentration of ice crystals, $n_c$, varies approximately as $w^2$ (Fig. 7d). This concentration increases with decreasing temperature; term 3 on the right-hand side of Eq. (7) decreases relative to term 1 as the temperature decreases. The ratio of the ice crystal concentration at the time that the maximum saturation ratio is reached in the parcel to $n_c$ (dashed lines) ranges from 0.57 to 0.67, with a mean of 0.61.

The above model runs provide insight into which CCN masses contribute most to the ice crystals produced. It is noted from Fig. 8a that the higher the CCN mass the higher the probability that the droplets in that mass category will freeze. The higher-mass CCN con-

**Fig. 5.** (a) Saturation ratio at which 10% of the population of solution droplets growing on a given mass of ammonium sulfate CCN freeze after being lifted from 82% RH at initial temperatures indicated along the curves. Difference in temperature corresponding to $s$ is shown on right ordinate from run at $T_0 = -44^\circ$C. (b) $s$ vs solution droplet diameter for various $m$ when $T_0 = -44^\circ$C. Solution densities at various points along curves are shown.

1.0, the equilibrium diameter (method 1) for curve II calculations is 4.5 $\mu$m while the model (time-dependent) diameter (method 2) is 2.9 $\mu$m. Freezing probability is related to droplet volume (or diameter) and solution density. Consequently, if the equilibrium diameter is used, homogeneous freezing occurs at too high a $T$ and too low an $s$. The error increases with increasing $s$ and hence with $T_0$. Comparison of curves III and IV illustrates the effect of droplet curvature on homogeneous freezing rates. When curvature is not considered (bulk freezing given by Raoult’s law), the vapor pressure over the solution droplet is too low, and homogeneous freezing occurs at too low a $T$ and too high an $s$. The discrepancy increases with decreasing droplet diameter but is almost independent of $T$.

A series of model runs was used to examine the effects of differing vertical velocity and $T$ on the following parameters: the saturation ratio at which ice nucleation

**Fig. 6.** Saturation ratio vs fraction of droplets containing indicated $m$ that are homogeneously frozen, for indicated conditions. Right ordinate, as in Fig. 5a.
Fig. 7. (a) Saturation ratio at which concentration of solution droplets frozen exceeds 1 L⁻¹, for different $T_0$. (b) $\Delta s$ vs $w$ for different $T_0$. Curve fits to the data are shown. (c) $\Delta s$ at the time that $f$ becomes 0.01, 0.1 and 1.0 in the various mass categories. Open symbols: model runs as in (a) and (b). Solid symbols: model runs with no vapor depletion by ice. Curves fit through the latter data are shown. (Note that the fits are in terms of air temperature.) Triangles, $-40^\circ$C; circles, $-48^\circ$C. (d) Number of ice crystals produced. Least squares curves fit to the data are shown. Dashed lines: ratio of number of crystals produced at $s_{10}$ to $n_i$.

Contribute relatively more to $n_i$ as $w$ decreases and $T$ increases. Figure 8b shows that the contributions to $n_i$ depend in a systematic and expected way upon $T$ and $w$, the greatest contributions coming from nuclei with masses from $10^{-13}$ to $10^{-15}$ g.

Model runs were used to examine the dependence of the parameters shown in Fig. 7 on $C$ and $K$ of the CCN spectrum. In these calculations the CCN concentration in the largest mass bin is set to 0; otherwise, concentrations in this bin would usually greatly exceed the previously reported observations. Table 2 shows the results for $T = -44^\circ$C and $w = 100$ cm s⁻¹. With increasing $C$ and $K$, $s_{10}$ is almost constant, $s_{1f}$ decreases slightly, and $n_i$ increases significantly. These runs with varying $C$ and $K$ conform well to the curves showing $s$ vs $m$ as a function of $f$ in Fig. 7c.

4. Discussion

Cirrus particles that originate at temperatures above $-40^\circ$C are predominantly polycrystals (e.g., bullet rosettes), those that originate below $-50^\circ$C are single crystals (columns), and those that originate between $-40$ and $-50^\circ$C are a mixture of the two types (Heymsfield and Platt 1984). Furthermore, in the temperature range $-40$ to $-50^\circ$C, polycrystals are more prevalent in isolated convective cirrus than in cirrostratus. Polycrystals are thought to originate from droplets that freeze above some critical size, and single crystals to originate either from those that freeze below this size or from sublimation on IFN. Laboratory experiments indicate that this critical size decreases as the temperature decreases from $-4$ to $-30^\circ$C (Pitter
Fig. 8. (a) Fraction of droplets in given m category (shown at centerpoint with dot) at the time that f = 1.0 (no further ice crystals are produced in that mass category) in a parcel for several model runs. (b) Cumulative ice crystal concentration produced by all CCN masses ≥ to indicated value, normalized by the total ice crystal concentration.

Fig. 9. Maximum droplet diameter grown in various mass categories plotted against temperature, based on model runs using regular CCN spectrum.

Table 2. Model runs with different values of C, K. w = 100 cm s\(^{-1}\), \(T_0 = -44^\circ\text{C}\).

<table>
<thead>
<tr>
<th>C</th>
<th>K</th>
<th>(n_t) (cm(^{-3}))</th>
<th>(s_{nf})</th>
<th>(s_{nf})</th>
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<tr>
<td>0.5</td>
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<td>25</td>
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<tr>
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<td>0.927</td>
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<tr>
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<td>2.0</td>
<td>0.919</td>
<td>0.919</td>
<td>0.923</td>
</tr>
<tr>
<td>100</td>
<td>2.0</td>
<td>0.915</td>
<td>0.915</td>
<td>0.923</td>
</tr>
<tr>
<td>200</td>
<td>2.0</td>
<td>0.915</td>
<td>0.915</td>
<td>0.919</td>
</tr>
</tbody>
</table>

and Pruppacher 1973). Figure 9, compiled from runs with \(w = 100 \text{ cm s}^{-1}\), shows that maximum droplet diameters with \(w = 100 \text{ cm s}^{-1}\) increase rapidly at temperatures above about \(-42^\circ\text{C}\); a similar tendency is noted with lower \(w\). If the critical diameter at temperatures from about \(-37\) to \(-50^\circ\text{C}\) is above 1 or 2 \(\mu\text{m}\) (reasonable in view of the laboratory experiments), the habit dependence on temperature can be explained by homogeneous freezing.

The high concentrations of ice particles produced in model runs having the highest \(C\) and \(K\) are comparable to particle concentrations measured in the upper portions of a cirrus convective cell at \(-42^\circ\text{C}\) by Rangno and Hobbs (1986), although their particles could have been liquid. The high ice concentrations will rapidly deplete the vapor available for their growth; they will not grow to sizes much larger than 100 \(\mu\text{m}\). Such sizes are much smaller than average sizes found in isolated cirrus convective cells (Heymsfield 1975). Particles that are larger, but orders of magnitude fewer in concentra-
of large particles in cirrus (Kajikawa and Heymsfield 1989), especially when high ice concentrations are produced.

Our treatment has focused on the initial development of ice crystals in convective cirrus by homogeneous freezing. The importance of this nucleation process will be diminished if some ice crystals are nucleated by ice-forming nuclei (although their concentrations are probably quite low) or introduced into parcels by entrainment and sedimentation. The hydrometeor data of Heymsfield (1977) collected through deep ice clouds can be used in the model to study the effects of vapor depletion in parcels by the growth of ice particles. Ice concentrations of 10 and 100 L\(^{-1}\) bounding typical measurements reported for cirrus are initialized with a diameter of 90 \(\mu\)m in a parcel with \(w = 100\) cm s\(^{-1}\), \(T_0 = -44^\circ\text{C}\), and \(s = 0.82\). Particles grow larger than in the regular model runs and hence their density is modified, according to Heymsfield (1975). As the diameter increases from 100 to 200 \(\mu\)m, \(\rho_s\) decreases from 0.7 to 0.084 g cm\(^{-3}\) by a power law.Above 200 \(\mu\)m, \(\rho_s\) retains the value 0.084 g cm\(^{-3}\). Compared to the normal model runs with the same initial conditions, the run with an initial concentration of 10 L\(^{-1}\) leads to a reduction in \(n_i\) of 30\%, and, with 100 L\(^{-1}\), homogeneous freezing does not occur. Intermediate concentrations, a larger mean ice particle size, and a lower vertical velocity will also prevent the process from occurring.

Heymsfield (1977), using in-situ measurements, also reported the mass growth rate of ice crystal populations (assuming water saturation) as a function of temperature in terms of the vertical velocity needed to sustain this growth. This term is equivalent to \(w^*\) discussed earlier, representing the (hypothetical) reduction in vertical velocity of a parcel due to the growth of a preexisting ice particle population.\(^3\) In the temperature range \(-35^\circ\text{C}\) to \(-45^\circ\text{C}\), values of \(w^*\) were equally distributed over the range 0 to 60 cm s\(^{-1}\). This indicates that in deep ice clouds with typical vertical velocities of 1 to 20 cm s\(^{-1}\) (Heymsfield 1977), (a) homogeneous freezing will occur only in strong updrafts associated with convection or waves, or at cloud top by radiative cooling reducing the temperature and increasing the saturation ratio above \(s_m\); and (b) since \(n_i\) is roughly proportional to \(w^*\), the concentrations of ice crystals produced are significantly lower than situations without preexisting ice crystals.

5. Summary and conclusions

This study develops a numerical model for examining the nucleation of ice crystals in isolated cirrus convective cells, employing equations for describing homogeneous freezing of solution droplets, the growth of ice crystals and droplets, and the supply and deple-
personal communication). Pruppacher and Neiburger (1963) found that water drop solutions supercool by an amount exceeding that expected from bulk water freezing point depression. As a sensitivity study, calculations were made where $\sigma_d$ increased linearly with solute concentration to 1.5 times its nominal value at a concentration of 40%. The results showed that homogenous freezing rates are essentially unchanged, because solute concentrations are so low at the time of freezing that the $\sigma_d$ is essentially the pure water value. Surface tension values for the ice water interface derived from theoretical values for pure water droplets and freezing rates based on these data agree well with laboratory and field data.

- The relative humidity threshold for deliquescence of ammonium sulfate nuclei, and the macroscopic properties of the solution droplets (e.g., density), have not been reported for the temperatures or pressures considered here. Measurements of the relative humidity for deliquescence of ammonium sulfate range from 79 to 82% for $T = +10$ to $+108^\circ C$ with no apparent temperature dependence (Obrien 1948); thus the assumption of deliquescence occurring at 82% is reasonable. Deviations in the macroscopic properties of the droplets from their reported values at $+25^\circ C$ are not expected to be large (Harned and Owen 1958) or to affect the calculations presented in this paper in a significant way.

- The CCN mass spectrum above $10^{-15} \, g$, from which most of the ice crystals form in low vertical velocity situations, is unknown, as is the purity of ammonium sulfate CCN. Some of the CCN might be solid sulfuric acid particles, whose freezing properties following deliquescence might depend to a large extent upon the water-sulfuric acid composition.

The uncertainties in the model input parameters discussed above indicate a need for laboratory measurements to study the homogeneous freezing process, and for airborne and laboratory measurements to quantify the CCN distribution and the composition of the nuclei at masses greater than $10^{-15} \, g$. Aircraft measurements of relative humidity, size spectra, and liquid water content at temperatures between $-37$ and $-50^\circ C$ in well-definable cloud conditions, (e.g., mountain wave clouds), and determinations of CCN spectra, composition, and range of masses in clear air at cirrus altitudes, are needed for further study of this problem. Only with this information can we be certain about quantitative predictions of ice formation in cirrus.

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**APPENDIX**

**Definition of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A, B$</td>
<td>coefficients in Kohler equation</td>
</tr>
<tr>
<td>$C$</td>
<td>coefficient in CCN spectrum equation</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity of dry air</td>
</tr>
<tr>
<td>$d_1, d_4$</td>
<td>diameter of solution droplet, ice crystal</td>
</tr>
<tr>
<td>$F_s$</td>
<td>ice crystal ventilation coefficient</td>
</tr>
<tr>
<td>$f$</td>
<td>fraction of droplets frozen that contain a given mass of solute</td>
</tr>
<tr>
<td>$G'_w, G'_s$</td>
<td>coefficients in growth rate equation for droplets, ice crystals</td>
</tr>
<tr>
<td>$\Delta G, \Delta G^{(0)*}$</td>
<td>free energy of formation of an ice embryo in a solution droplet, critical free energy of an ice embryo in a solution droplet, pure water droplet</td>
</tr>
<tr>
<td>$\Delta g$</td>
<td>activation energy for self-diffusion in the liquid</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration constant</td>
</tr>
<tr>
<td>$J_H, J_{H(0)}$</td>
<td>nucleation rate of an ice embryo in a solution droplet, pure water droplet; these terms represent the number of ice embryos passing the critical radius per second per cubic centimeter</td>
</tr>
<tr>
<td>$K$</td>
<td>exponent in CCN spectrum equation</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$L_a, L_s$</td>
<td>latent heats of vaporization, sublimation</td>
</tr>
<tr>
<td>$M_0, M$</td>
<td>the molecular weights of water and solute, respectively</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of solute</td>
</tr>
<tr>
<td>$m_{\text{max}}, m_{\text{min}}$</td>
<td>maximum, minimum masses used to specify CCN distribution</td>
</tr>
<tr>
<td>$N_i, N_i^{(0)}, N_s$</td>
<td>number of water molecules per unit volume of solution drop, pure water drop, ice embryo</td>
</tr>
<tr>
<td>$n_s$</td>
<td>ice crystal concentration produced in a parcel</td>
</tr>
<tr>
<td>$P, P_i, P_s, P_i'$</td>
<td>atmospheric pressure, saturation vapor pressures over liquid and ice surfaces, over solution droplet ideal gas constants to water vapor, dry air</td>
</tr>
<tr>
<td>$R_v, R_d$</td>
<td>is the radius of a sphere containing an ice embryo</td>
</tr>
<tr>
<td>$S_i, S_s$</td>
<td>supersaturation with respect to water (%) , ice (fractional)</td>
</tr>
<tr>
<td>$s, s'$</td>
<td>saturation ratio</td>
</tr>
<tr>
<td>$s_i, s_t$</td>
<td>vapor pressure over a solution droplet divided by $p_i$</td>
</tr>
<tr>
<td>$s_0, s_{sf}$</td>
<td>saturation ratio when ice concentration reaches 1 liter$^{-1}$, maximum saturation ratio reached in parcel</td>
</tr>
<tr>
<td>$\Delta s$</td>
<td>Difference between $s$ and $s_0$</td>
</tr>
<tr>
<td>$T, T_i$</td>
<td>air and solution droplet temperature ($^\circ K$)</td>
</tr>
<tr>
<td>$T_0$</td>
<td>initial temperature, e.g., where the model is initialized and CCN start to deliquesce at 82% RH</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
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</table>
$V_{l}$
droplet volume

$w, w^*$
vertical velocity of air, hypothetical vertical velocity equal to the rate of vapor depletion by ice particles sedimenting or entrained into the updraft

$X_l, X_5, X_ip$
mixing ratio of liquid water, ice crystals nucleated in updraft, ice crystals sedimenting or entrained into updraft

term in droplet growth rate equation accounting for curvature and solution effects

$\alpha$
parameter to adjust ice embryo volume to an equivalent diameter sphere

$\beta$
parameter to adjust ice embryo surface area to an equivalent diameter sphere

term in the droplet growth equation

$\gamma$
osmotic coefficient of the solution

$\phi_1, \phi_2, \phi_3$
terms describing vapor supply to the updraft, vapor depletion by droplet growth, vapor depletion by ice crystal growth

$\rho_l, \rho_w, \rho_a$
solution density, density of pure water, density of air

$\sigma_{sl}, \sigma_{ia}$
surface tension of ice against water, water against air

$\nu$
total number of ions into which a salt molecule dissociates

$\zeta = \beta^3/\alpha^2$
shape parameter for ice embryo

REFERENCES


