

# A model description for cirrus cloud nucleation from homogeneous freezing of sulfate aerosols

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**Abstract.** Classical nucleation theory for homogeneous freezing as well as recent laboratory data are used to formulate an algorithm for ice nucleation from an aqueous sulfuric acid solution droplet. A new parameterized function is derived from recent thermodynamic data to express the variation of sulfuric acid solution composition with temperature and relative humidity. This function is then used to derive critical ice nucleation parameters from recent laboratory data. The critical nucleation parameters are used in a classical nucleation theory to derive the diffusion activation energy of water molecules in a sulfuric acid solution from the measurements. The derived diffusion activation energy of water molecules in a sulfuric acid solution does not agree with the diffusion activation energy calculated from a viscous flow formulation that is commonly used in classical nucleation rate calculations. Our results show that ice nucleation in a sulfate droplet occurs when the interface energy of ice against the sulfate solution is approximately 17 dyn  $\text{cm}^{-1}$ . We calculate that a supersaturation ratio of about 1.3 to 1.5 is required to nucleate ice from an aqueous sulfuric acid solution droplet in the temperature range of about 185 to 240 K. This supersaturation corresponds to a supercooling of a sulfate solution to about 2 to 3 K below the equilibrium condensation point of ice. Simple functions are given for estimating the nucleation point of ice in the upper troposphere. The differences between previous parameterizations and this work are discussed.

## 1. Introduction

Cirrus clouds cover about 35% of the Earth's surface and thus have an important influence on climate through their effect on the radiation budget [Ramanathan *et al.*, 1983; Liou, 1986; Jensen *et al.*, 1994a, b]. Recent studies also indicate that cirrus clouds may play a significant role in the heterogeneous chemistry of the upper troposphere [Borrmann *et al.*, 1996]. One of the most poorly understood aspects of cirrus cloud formation is how such ice particles nucleate in the upper troposphere. There is growing evidence from field observations that the nucleation process occurs by homogeneous freezing of ice in an aqueous  $\text{H}_2\text{SO}_4$  acid solution droplet [Sassen and Dodd, 1989; DeMott *et al.*, 1994; Jensen *et al.*, 1994a; Heymsfield and Miloshevich, 1995]. There are modeling, laboratory, and field studies to support the fact that  $\text{H}_2\text{SO}_4$  acid aerosols can remain supercooled to very low temperatures [Dye *et al.*, 1992; Tabazadeh *et al.*, 1994; Carslaw *et al.*, 1994; Anthony *et al.*, 1995]. Thus when ice saturation is reached in the atmosphere, nucleation of ice particles most likely occurs from an aqueous solution droplet.

Most of the laboratory work over the last 50 years has focused on measuring ice nucleation rates from a pure supercooled water droplet, which can remain liquid to only

about  $-40^\circ\text{C}$  [e.g., Pruppacher and Klett, 1978; Pruppacher, 1995]. On the other hand, cirrus clouds usually nucleate at around  $-80^\circ\text{C}$  to  $-40^\circ\text{C}$  depending on the relative humidity conditions [Jensen *et al.*, 1994a; Heymsfield and Miloshevich, 1995]. Thus the current laboratory data on ice nucleation in supercooled water are not suited to adequately address how cirrus clouds may form in the upper troposphere. Currently, only a few laboratory groups have measured critical ice nucleation parameters in aqueous  $\text{H}_2\text{SO}_4$  acid droplets [Bertram *et al.*, 1996; Imre *et al.*, 1997]. Here we use classical nucleation theory along with the laboratory data of Bertram *et al.* [1996] to parameterize an algorithm for ice nucleation from an aqueous  $\text{H}_2\text{SO}_4$  acid solution droplet.

## 2. Model Description

Denoting  $V_d$  (in cubic centimeters) and  $w_s$  as the volume and weight percent of an aqueous sulfate solution droplet, we find the rate of ice nucleation at a given temperature,

$$J(T, w, V_d) = C(T, w_s, V_d) \text{ EXP} \left[ \frac{-\Delta F_g - \Delta F_{act}}{kT} \right] \quad (1)$$

where  $C$  (in particles per second) is the preexponential factor,  $\Delta F_g$  (in ergs) is the free energy for the formation of the ice germ,  $\Delta F_{act}$  (in ergs) is the diffusion activation energy of water molecules across the ice/sulfate solution phase boundary, and  $k$  is the Boltzmann constant. The pre-

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exponential factor is estimated as [Pruppacher and Klett, 1978]

$$C(T, w_s, V_d) \cong 2.1 \times 10^{33} V_d \sqrt{\sigma_{sul/ice}(w_s, T) T} \quad (2)$$

where  $\sigma_{sul/ice}$  is the interface energy between the ice/sulfate solution. For a fixed droplet size the variations of  $C$  with temperature and droplet weight percent have only a negligible effect on the nucleation rate calculations.

The free energy term is given by

$$\Delta F_g(T, w_s) = \frac{4}{3} \pi \sigma_{sul/ice} r_g^2 \quad (3)$$

where  $r_g$ , (in centimeters) is the critical germ radius, defined as [Jensen et al., 1994a]

$$r_g = \frac{2M_w \sigma_{sul/ice}(w_s, T)}{\rho_{ice}(T) \left[ L_m(T) \ln \frac{T_f}{T} + \frac{1}{2} R(T + T_f) \ln a_w(T) \right]} \quad (4)$$

where  $M_w$  is the molecular weight of water (in grams per mole),  $\rho_{ice}$  is the ice density (in grams per cubic centimeter),  $L_m$  is the latent heat of ice melting (in ergs per mole),  $T_f$  is the ice melting temperature (273.15 K),  $R$  is the universal gas constant and  $a_w$  is the water activity. The latent heat and density relations are given in the appendix. The water activity or the ambient relative humidity is calculated by dividing the atmospheric water vapor pressure ( $p_{H_2O}$ ) over the liquid water saturation vapor pressure ( $p_{H_2O}^o$ , see the appendix).

The diffusion activation term is approximated from the viscosity of the sulfate solution by [Pruppacher, 1972]

$$\Delta F_{act} = k \frac{\partial \ln \left( \frac{\eta(T, w_s)}{T} \right)}{\partial \left( \frac{1}{T} \right)} \quad (5)$$

where solution viscosity can be calculated from

$$\eta(T, w_s) = A(w_s) T^n \exp \left[ \frac{B}{T - T_o(w_s)} \right] \quad (6)$$

where  $A$ ,  $B$ ,  $n$ , and  $T_o$  are viscosity parameters. These parameters were recently measured by Williams and Long [1995] for cold aqueous sulfuric acid solutions. Substituting (6) in (5) and differentiating result in

$$\Delta F_{act} = kT \left[ \frac{BT}{(T - T_o(w_s))^2} + 1 - n \right] \quad (7)$$

Traditionally the activation energy of water molecules in supercooled water is calculated from (7) by using the supercooled water viscosity parameters [Pruppacher, 1972; Pruppacher and Klett, 1978]. Here we suggest that using the sulfuric acid viscosity parameters in place of supercooled water in (7) can yield a reasonable value for the diffusion activation energy of single water molecules in solution based on the viscous flow assumption [Pruppacher, 1972]. However, recent studies [Pruppacher, 1995] indicate that the diffusion of water

molecules in supercooled water below 240 K does not agree with a viscous flow formulation as described by Pruppacher [1972]. Basically, below 240 K, water molecules in a supercooled solution form a network of clusters, and the size of such clusters increases with decrease in temperature. A number of spectroscopic studies support the idea of cluster formation in supercooled water [e.g., Bansil et al., 1982; Hare and Soerensen, 1990; Pruppacher, 1995]. From these studies, Pruppacher [1995] recently suggested that the diffusion activation energy of water molecules across the ice/water interface in supercooled water below 240 K should be estimated from the transfer of water clusters across the phase boundary instead of the transfer of single water molecules as formulated previously [Pruppacher, 1972]. Thus if the diffusion of water molecules in a cold aqueous sulfuric acid solution occurs by the transfer of water clusters across the ice/solution interface, then (7) cannot be used to estimate the diffusion activation energy of water molecules in solution. To avoid this problem, here we derive  $\Delta F_{act}$  directly from some recent ice nucleation experiments in sulfuric acid aerosols [Bertram et al., 1996].

## 2.1. Aerosol Composition

Commonly, the Gmitro and Vermeulen [1964] vapor pressure relations for sulfuric acid are parameterized into a function in order to calculate the variations of sulfuric acid aerosol composition with relative humidity and temperature [e.g., Steele and Hamill, 1981]. However, recent studies indicate that these parameterizations could underestimate the water activity over a given sulfuric acid solution composition by about 10% [Massucci et al., 1996; Tabazadeh et al., 1997a] since the original vapor pressure relations of Gmitro and Vermeulen [1964] are optimized to obtain better agreement with high-temperature vapor pressure data. Thus we do not recommend using such parameterizations to predict aerosol composition at cold temperatures, which are of interest here. Recently, Clegg and Brimblecombe [1995], using a wide range of thermo-dynamic data in the temperature range of <200 to 328 K, have developed a multicomponent thermodynamic model for aqueous sulfuric acid solutions. We have parameterized the results of the Clegg and Brimblecombe sulfate model in order to express the variations of the aerosol composition with temperature and relative humidity (for more information on this parameterization, see Tabazadeh et al. [1997a]). This relation is given as

$$m_s(a_w, T) = y_1(a_w) + \frac{(T-190)[y_2(a_w) - y_1(a_w)]}{70} \quad (8a)$$

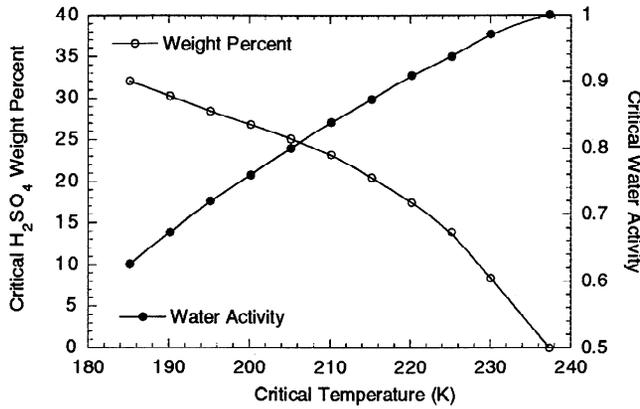
and

$$w_s = \frac{9800m_s}{98m_s + 1000} \quad (8b)$$

Where  $m_s$  is the sulfuric acid molality,  $w_s$  is the sulfuric acid weight percent, and  $y$  functions are given in Table 2 of Tabazadeh et al. [1997a].

## 2.2. Surface Tension

The most important term in the nucleation rate equation is  $\sigma_{sul/ice}$ . The exponential dependence of the nucleation rate on surface tension is magnified, since the surface tension is cubed in the free energy term. Thus slight variations in the value of



**Figure 1.** Variation of the nucleating aerosol composition with temperature measured by *Bertram et al.* [1996]. The critical water activity is calculated from (8) by using the laboratory data as described in the text.

surface tension can cause significant changes in the nucleation rate calculations. Currently, no laboratory data is available on the composition and temperature variations of sulfate/water interface energy. In addition, it is very difficult to determine this type of an interface energy by experimental techniques. The results of numerous experiments show considerable spread for the interface energy of ice in supercooled water ( $\sigma_{wat/ice}$ ) [Pruppacher and Klett, 1978]. For example, at 0°C, *Wood and Walton* [1970] measured  $\sigma_{wat/ice} = 33$  dyn cm<sup>-1</sup>, whereas *Correil et al.* [1971] measured  $\sigma_{wat/ice} = 24$  dyn cm<sup>-1</sup>. This difference would change the calculated nucleation rate of ice germs in liquid water by a factor of  $10^{16}$  at 0°C.

The application of the Antonoff's rule of surface tension is another procedure that is commonly used to determine the interface energy between two condensed liquid phases [Adamson, 1990]. This rule states that the interfacial energy between two mutually saturated liquids is given by the absolute difference of their respective surface tensions against vapor (air). Antonoff's rule has successfully been applied to calculate the interface energy for the ice/water system and is given as [Pruppacher and Klett, 1978]

$$\sigma_{wat/ice} \approx |\sigma_{wat/air} - \sigma_{ice/air}| = 28.5 + 0.25(T - 273.15) \quad (9)$$

where  $\sigma_{wat/air}$  ( $= 76.1 - 0.155(T - 273.15)$ ) is the water/air interface energy and  $\sigma_{ice/air}$  is the ice/air interface energy ( $\sim 105$  dyn cm<sup>-1</sup>). Similarly, we could use Antonoff's rule to obtain the surface tension of an ice germ in an aqueous sulfuric acid solution as

$$\sigma_{sul/ice}(w, T) \approx |\sigma_{sul/air}(T, w) - \sigma_{ice/air}| \quad (10)$$

where  $\sigma_{sul/ice}$  is the interface energy of a sulfate solution against air. The data of *Sabinina and Terpugov* [1935] can be fitted to obtain the surface tension as a linear function of temperature and composition (see the appendix). Note that these data were obtained for a sulfuric acid weight percent range between 40% and 60%. At a fixed temperature the surface tension data are linear in composition. Thus we have used a linear extrapolation to estimate the surface tension beyond the range of the data. It is important to note that in the atmosphere, ice nucleates out of sulfuric acid solution, which contains less than 35% sulfuric acid by weight [Bertram et al., 1996]. This composition is beyond the range of surface

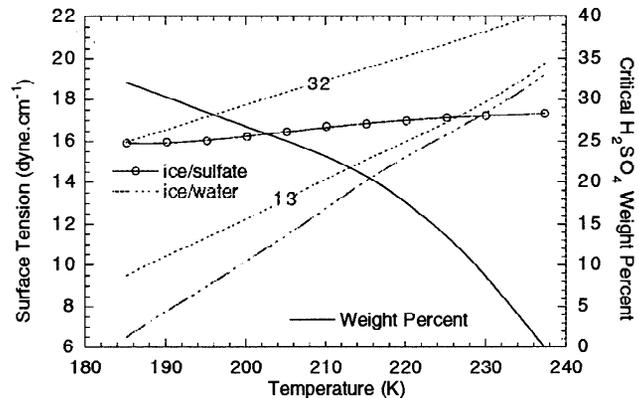
tension data that we used to derive the relation given in the appendix. In addition, the applicability of Antonoff's rule to this system has not been tested in the laboratory. For these reasons our calculated  $\sigma_{sul/ice}$  from (10) are only preliminary, and future laboratory experiments are needed for a more accurate determination of this value.

### 2.3. Parameterization of Activation Energy

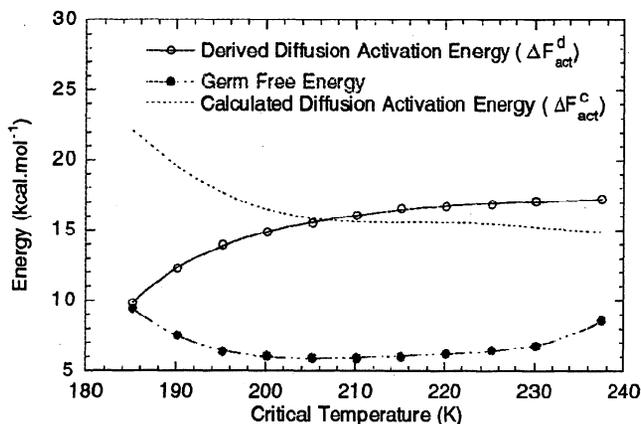
*Bertram et al.* [1996] measured the ice nucleation freezing curve in aqueous sulfuric acid solutions. Figure 1 illustrates the critical composition and temperature at which ice formed in a 0.2  $\mu$ m sulfuric acid solution droplet in the laboratory. From the critical composition and temperature we first iterated (8) to obtain the critical water activity. Using these critical values in the nucleation rate equations (1)-(4) and estimating  $\sigma_{sul/ice}$  from (10), we then varied  $\Delta F_{act}$  until the calculated nucleation rate was unity. We assume that these data represent the case  $J=1$  (particle<sup>-1</sup> s<sup>-1</sup>) in equation (1), however, the results are not too sensitive to the variations in  $J$  to within 2 orders of magnitude. The derived activation energy values ( $\Delta F_{act}$ ) were then fitted into a polynomial function of temperature which is given in the appendix. A similar procedure was used by *Jensen et al.* [1994a] to derive  $\Delta F_{act}$  from ice nucleation experiments [Hagen et al., 1981; DeMott and Rogers, 1990] by assuming  $\sigma_{sul/ice} \sim \sigma_{wat/ice}$  and then varying  $\Delta F_{act}$  in (1) until the calculated nucleation rate agreed with the observed one. The only difference between this parameterization and the old one is that we estimate  $\sigma_{sul/ice}$  from (10) instead of (9) (see Figure 2) and we use more recent laboratory data to parameterize the diffusion activation energy term.

## 3. Results and Discussion

Figure 2 illustrates the temperature and compositional variations of the surface tension for the ice/sulfate solution interface calculated from (10). In the temperature range of 180 to 240 K this interface energy varies only slightly ( $\sim 1$  dyn cm<sup>-1</sup>), whereas the estimated surface tension of the ice/water system would change by about 12 dyn cm<sup>-1</sup>. We attribute this difference to the fact that the critical composition of the sulfate solution varies from 0% to 30% (H<sub>2</sub>SO<sub>4</sub> by weight) in



**Figure 2.** Variation of the surface tension with temperature calculated from (10) by using the solution compositions shown in Figure 1. The ice/water surface tension is calculated from (9). The dotted lines show the change of surface tension with temperature for two fixed aqueous sulfuric acid solution compositions (13% and 32%).



**Figure 3.** Variation of the germ free energy and the diffusion activation energy with temperature. The diffusion activation energy is derived from *Bertram et al.* [1996] data by using (1) through (4) as described in the text. The dashed lines show the calculated diffusion activation energy from (7) based on a viscous flow formulation.

this temperature range. The dotted lines in Figure 2 show the calculated ice/sulfate solution surface tension for two fixed solution compositions (13% and 32%). For these cases the slope of the surface tension change with temperature is closer to that of the supercooled water. The slope gets steeper and closer to that of pure water as the solution becomes more dilute in  $\text{H}_2\text{SO}_4$ .

It is interesting that the ice/sulfate solution surface tension remains roughly constant, 16 to 17  $\text{dyn cm}^{-1}$ , in this 60 K temperature range. This consistency occurs since two compensating effects nearly cancel each other out. First, for a fixed solution composition the interface energy declines with temperature decrease as shown in Figure 2. Second, at a fixed temperature the interface energy is higher for a more concentrated solution.

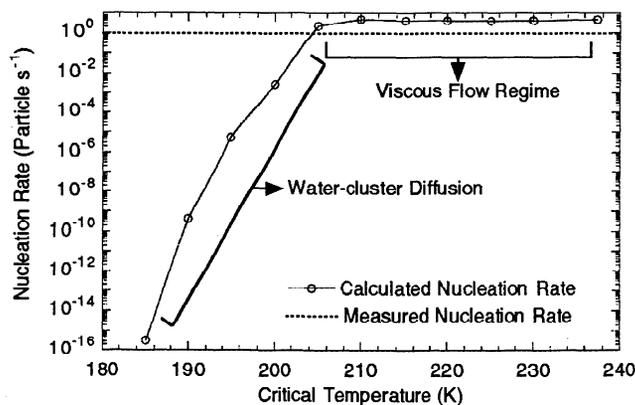
The variations of the germ free energy and the diffusion activation energy with temperature are illustrated in Figure 3. The  $\Delta F_{act}^d$  was derived from the ice nucleation data of *Bertram et al.* [1996] as described above. The  $\Delta F_{act}^c$  calculated from (7) based on a viscous flow assumption is also shown in Figure 3. In the temperature range of about 205 to 240 K the calculated  $\Delta F_{act}^c$  is smaller than the values derived from data by a maximum of about 2  $\text{kcal mol}^{-1}$ . The lower activation energy would result in a slightly higher nucleation rate for  $T > 205$  K as shown in Figure 4. Note that the nucleation rate obtained by using the derived  $\Delta F_{act}^d$  would be unity for all the points shown in Figure 4, since this criterion was used to parameterize the experimental data. Thus in the temperature range of 205 to 240 K the diffusion of water molecules in solution is roughly consistent with the viscous flow formulation since the nucleation rates calculated by using (7) are different from the measured values by at most a factor of 10. This difference can be overcome by only a slight change in the critical nucleation temperature ( $<0.3$  K).

However, below 205 K the derived  $\Delta F_{act}^d$  deviates dramatically from the values calculated from (7). The exponential increase in the calculated  $\Delta F_{act}^c$  results in a drastic drop in the nucleation rate, as shown in Figure 4. To match the results of the ice nucleation data [*Bertram et al.*, 1996], a rapid decrease in the activation energy must occur at  $\sim 205$  K. Recently, *Pruppacher* [1995] has shown that in pure supercooled water,  $\Delta F_{act}$  has a maximum at  $\sim 240$  K and below

this temperature  $\Delta F_{act}$  decreases with temperature decrease. He attributed this behavior to the formation of a network of clusters in supercooled water below 240 K. The energy for the diffusion of water clusters to the ice germ would decrease with temperature decrease, since the size of such clusters would grow larger at lower temperatures. The decrease in the diffusion activation energy occurs in a water cluster regime, since the diffusion activation energy per water molecule in the cluster is lower than that of single water molecules in the solution. Here we suggest that a similar phenomenon may also occur in aqueous sulfuric acid solutions at  $\sim 205$  K, causing the rapid lowering of  $\Delta F_{act}^d$  with temperature decrease. It is important to emphasize that our results are only preliminary and future laboratory studies are desirable to investigate whether water cluster formation could also occur in aqueous  $\text{H}_2\text{SO}_4$  acid solutions similar to what is observed in pure supercooled water below 240 K [e.g., *Bansil et al.*, 1989; *Hare and Soerensen*, 1990; *Pruppacher*, 1995].

#### 4. Atmospheric Applications

Homogeneous freezing of ice in  $\text{H}_2\text{SO}_4$  acid solution droplets has been suggested to be an important process in the formation of cirrus clouds [*Sassen and Dodd*, 1989; *DeMott et al.*, 1994; *Jensen et al.*, 1994a, b; *Heymsfield and Miloshevich*, 1995]. Two factors commonly of interest are the ice supersaturation when nucleation occurs and the extent to which a sulfate solution can be supercooled before ice nucleation is possible in the atmosphere. The ice supersaturation is defined as the ratio of the ambient water vapor pressure over the ice saturation vapor pressure when  $J=1$  ( $\text{particle}^{-1} \text{s}^{-1}$ ) (see the appendix). The supercooling is defined as the critical nucleation temperature minus the temperature of ice which has a vapor pressure equal to the ambient water vapor pressure. Figure 5 illustrates the variation of the ice supersaturation and the extent of supercooling in the sulfate solution as a function of critical temperature. For example, at 230 K the ice supersaturation is about 1.46 when  $J=1$  ( $\text{particle}^{-1} \text{s}^{-1}$ ), which corresponds to a sulfate solution that is supercooled by about 3 K below the ice point. The ice supersaturation has a maximum at around 210. Thus in this temperature range, ice nucleation from a sulfate solution is slightly more difficult than that at



**Figure 4.** Variation of the nucleation rate with temperature using the calculated diffusion activation energy values from (7). In the viscous flow regime the calculated nucleation rate agrees reasonably well with the measured nucleation values. In the water cluster diffusion regime the calculated nucleation rate based on a viscous flow formulation deviates dramatically from the measured values.

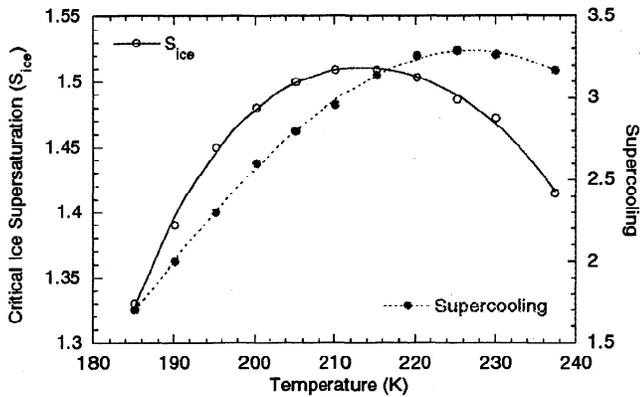


Figure 5. Variation of the critical ice supersaturation and the extent of supercooling with temperature.

higher or lower temperatures. The supercooling curve shows that sulfate in the solution can result in the supercooling of the droplet by about 2 to 3 K below the ice point of the solution.

Figure 6 compares the results of this study against previous parameterizations [Jensen et al., 1994a; Heymsfield and Miloshevich, 1995]. We predict a higher critical ice supersaturation for all temperatures, whereas previous parameterizations show a continual decrease in the critical ice supersaturation with temperature decrease. We attribute these differences to the fact that the ice/water surface tension was used in the previous studies instead of the ice/sulfate solution surface tension (see also Figure 2). Also shown in Figure 6 is another parameterization of ice supersaturation ratio as a function of temperature given by Sassen and Dodd [1989], which is based on in situ observations of cirrus clouds (for temperatures above -50°C). Thus our parameterization agrees well with the ice supersaturations inferred from the field observations.

For convenience we fitted the critical nucleation parameters into simple polynomial functions, which are given in Table 1. These polynomials vary only as a function of the ambient water vapor pressure. The results given in Table 1 are applicable only if the aerosol is aqueous H<sub>2</sub>SO<sub>4</sub>. Replacing H<sub>2</sub>SO<sub>4</sub> by a different electrolyte such as HNO<sub>3</sub> [Tabazadeh et al., 1997b] or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> should to some extent alter the critical values given in Table 1 and the appendix. The difference mainly arises because the surface tension of the ice germ against an aqueous HNO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution is different from that of aqueous H<sub>2</sub>SO<sub>4</sub>. At this point, because laboratory data are lacking, we suggest using the results of Table 1 to estimate the ice nucleation point in the upper troposphere.

5. Conclusions

In this paper we used recent laboratory data and classical nucleation theory to outline an algorithm for ice nucleation from an aqueous H<sub>2</sub>SO<sub>4</sub> solution droplet. Overall we find that ice nucleation from a sulfate solution occurs when the ice/sulfate solution interface energy is ~17 dyn cm<sup>-2</sup>. We also derived simple relations that would allow for a direct calculation of critical nucleation parameters in the upper troposphere from the ambient water vapor concentration. It is important to note that in the stratosphere, ice nucleates out of

a solution that is mainly composed of aqueous HNO<sub>3</sub> [Tabazadeh et al., 1997b]. Thus care should be exercised when the results of this study are applied to the stratosphere. To improve our results, more laboratory data on ice nucleation from different solute solutions are highly desirable. In addition, measurements of the surface tension of aqueous solute solutions against air at cold temperatures are needed since the current values are all above the frost point. Finally, we plan to compare the results of this study against observations of cirrus clouds during recent aircraft campaigns to investigate whether cirrus cloud formation in the upper troposphere agrees with nucleation of ice particles from a sulfuric acid solution droplet.

Appendix: Ice Nucleation Functions

Latent heat of melting ( $\Delta T = T - T_f$ ).

$$L_m(T) = 10^{-18} [19.04 + 0.05793\Delta T - 1.9907 \times 10^{-4} \Delta T^2]$$

Ice density ( $\Delta T = T - T_f$ ).

$$\rho_{ice}(T) = 0.916 - 8.75 \times 10^{-5} \Delta T - 1.667 \times 10^{-7} \Delta T^2$$

Water saturation vapor pressure (in millibars, see Tabazadeh et al., [1997a]).

$$\ln P_{H_2O}^o = 18.452406985 - 3505.1578807 / T - 330918.55082 / T^2 + 12725068.262 / T^3$$

Ice saturation vapor pressure (in millibars, fitted to the data of Buck et al. [1972]).

$$\ln P_{ice}^o = 24.313 - 6146.8 / T$$

Sulfate solution/air interface energy (in dyn cm<sup>-1</sup>, fitted to the data of Sabinina and Terpugov, [1935]).

$$\sigma_{sul/air} = 142.35 - 0.96525w_s - T(0.22954 - 0.0033948w_s)$$

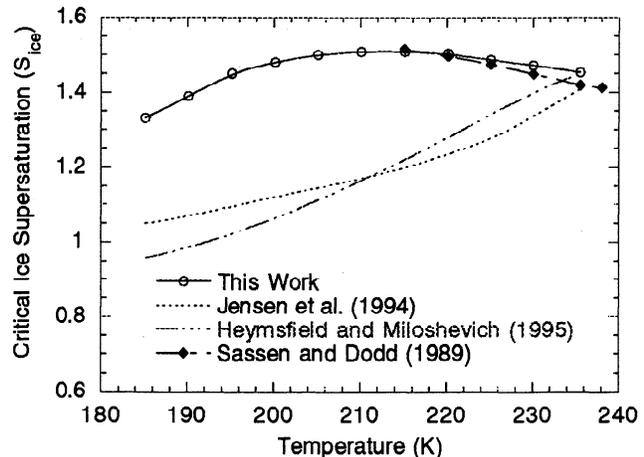


Figure 6. A comparison in the variation of critical ice supersaturation with temperature between this work and the previous studies (see text for more detail).

**Table 1.** Critical Ice Nucleation Parameters,  $X_c = a_0 + a_1 \ln P + a_2 (\ln P)^2 + a_3 (\ln P)^3 + a_4 (\ln P)^4 + a_5 (\ln P)^5$ 

$X_c$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$
$T_c, K$	2.5040e+2	1.1480e+1	8.6941e-1	9.5801e-2	7.8849e-3	2.7712e-4
$w_s$	-1.9088e+1	-1.8112e+1	-2.1913e+0	4.8128e-2	3.0381e-2	1.6617e-3
$a_w$	1.0119e+0	-2.1855e-2	-3.2418e-2	-6.6310e-3	-6.4073e-4	-2.3609e-5
$S_{ice}$	1.1963e+0	-2.8092e-1	-1.0803e-1	-2.2122e-2	-2.3131e-3	-9.1171e-5
$\Delta T, K$	2.5622e-0	-7.6651e-1	-2.7031e-1	-3.9865e-2	-3.4327e-3	-1.2659e-4

Here,  $P$  is the atmospheric water vapor pressure in millibars,  $T_c$  is the critical temperature,  $S_{ice}$  is the critical ice supersaturation and,  $\Delta T$  is the critical supercooling. Read 2.5040e+2 as  $2.5040 \times 10^2$ . Note that these critical values are derived for a 0.2  $\mu\text{m}$  aqueous sulfuric acid solution droplet.

Diffusion activation energy  $\times 10^{13}$  (in ergs, derived from the Bertram *et al.* [1996] ice nucleation data).

$$\Delta F_{act} = 1.1992475202 \times 10^4 - 5.2298196745 \times 10^2 T + 8.232842046 \times 10^0 T^2 - 6.4173902638 \times 10^{-2} T^3 + 2.6889968134 \times 10^{-4} T^4 - 5.8279763451 \times 10^{-7} T^5 + 5.1479983159 \times 10^{-10} T^6$$

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