Solute effects on the evaporation of ice particles

Jen-Ping Chen¹ and Paul J. Crutzen²

Center for Clouds, Chemistry and Climate, Scripps Institution of Oceanography, University of California, La Jolla

Abstract. The possible influence of trace chemicals, in particular sulfate, nitrate, and ammonia, on the growth and lifetime of ice crystals is studied theoretically, based on the concept of a transition layer on the ice surface. Solutes, which are produced in the gas phase or on the particle surface, can be incorporated into the bulk of the ice crystals during condensational growth and released from the bulk during evaporation. The solute accumulated on the surface of ice particles during evaporation tends to form a layer of concentrated solution, which alters the equilibrium vapor pressure and thus affects the evaporation of ice particles. Our analysis indicates that the evaporation of ice crystals can be retarded significantly by solutes, especially in polluted environments and for low ice particle number concentrations. It is also shown that ice particles in subsaturated air may survive without complete evaporation when the environmental ice-saturation ratio is above a temperature-dependent critical value that can be as low as 91%. Experimental and observational studies are necessary for verification. We also briefly speculate about other conditions in which atmospheric chemical processes may affect surface properties of ice particles.

1. Introduction

The cirrus clouds generated from convective storms, as well as from other weather systems, can significantly increase the Earth's albedo and play an important role in the global radiation budget [e.g., Ackerman *et al.*, 1988; Stephens *et al.*, 1990; Ramanathan and Collins, 1991]. In particular, the cirrus anvils generated from convective storms often extend over hundreds of kilometers into regions of large-scale subsidence motion [Webster and Stephens, 1980; Liou, 1986; Ackerman *et al.*, 1988], where cloud particles normally would not survive evaporation. Various radiative and microphysical mechanisms may contribute to the prolonged lifetime of these cirrus clouds. For instance, the effect of radiative heating may change the vertical stability of cirrus clouds [Detwiler and Ramaswamy, 1990] and thus alter their lifetimes. Also, the evaporation rate of ice particles in these anvil clouds is usually quite low because of their relatively low surface vapor pressure at low temperatures. Ice particles with lower number concentrations can normally grow larger under the same environmental conditions. These larger ice particles evaporate more slowly because of their smaller surface-to-volume ratios. However, at the same time, they may fall a greater distance into drier air below because of their higher fall speeds.

The lifetime of cirrus ice particles may also be important to the glaciation of lower-level clouds. Braham [1967], as well as Braham and Spyers-Duran [1967], observed that cirrus

crystal trails with a concentration of 10^5 to 10^6 m^{-3} can survive a fall of over 5 km in clear air of relative humidities as low as 30%. These falling ice crystals may serve to seed lower-level supercooled clouds and trigger storm development. However, their estimation suggested that the initial sizes required for ice particles to survive the observed fall distance were unrealistic under the given atmospheric conditions. Hall and Pruppacher [1976] performed a more detailed microphysical calculation to investigate the survival distance of ice particles falling from cirrus clouds. They found that a survival distance of greater than 2 km is only possible if the ambient air has a relative humidity > 70%. Thus some nonmicrophysical mechanisms might be necessary for prolonging the lifetime of ice particles in subsaturated air.

Cloud chemistry is often thought to influence cloud microphysical processes only through the activation or nucleation of cloud particles. Therefore it is common to treat chemical reactions as passive processes in cloud studies. Yet some earlier studies have shown that chemistry can greatly influence the microphysics. For instance, the evaporation rate of a liquid or solid can be retarded by the formation of a foreign monolayer on the surface [Langmuir, 1916; Hedestrand, 1924; Langmuir and Langmuir, 1927; Barnes and La Mer, 1962]. Chemical materials can also affect the growth of ice crystals either by changing the evaporation rate [Derjaguin *et al.*, 1966; Davy and Somorjai, 1971; Garrett, 1971] or by altering the structure of ice crystals [Vonnegut, 1948; Hallett and Mason, 1958a; Pitter and Finnegan, 1990]. Thus ice-phase chemistry may be another plausible mechanism that could contribute to the prolonged lifetime of cirrus clouds.

Ice-phase chemical reactions generally do not occur in the bulk phase because of the strong bounding of the ice lattice. However, they can be very active on the surfaces, as well as in the grain boundaries. Also, photochemically produced trace chemicals in the air may deposit on the ice surface. These surface trace chemicals can be incorporated into growing ice particles, possibly with high concentrations. Once the ice

¹ Current affiliation: Department of Atmospheric Sciences, National Taiwan University, Taipei, Taiwan, Republic of China.

² Main affiliation: Max-Planck-Institute for Chemistry, Division of Atmospheric Chemistry, Mainz, Germany.

particles start to evaporate, solute that was originally in the bulk ice will be released to the surface. Nonvolatile trace chemicals, such as sulfate and nitrate, will then accumulate on the surface and form a coating with high solute concentration. The surface vapor pressure of the ice particles can thus be depressed by an amount that is dependent on the solute concentration and thickness of this surface coating.

The physics and chemistry of the ice surface are very complex and not well understood, especially when more than one chemical species are involved. In this study, an idealized model, which is based on the concept of the surface transition layer, is used to present in detail one example of the possible effect of chemistry on the evaporation of ice particles and the lifetime of cirrus clouds. The example involves the deposition and/or production of solutes (e.g., SO_4^{2-} , NO_3^- , and NH_4^+) from the gas phase on the surface transition layer of ice particles, a process that would occur especially over polluted regions of the world. We also briefly mention some other candidate conditions of strong interactions between gas phase and ice surface chemistry.

2. The Transition Layer Model

Since *Faraday* [1859], it has long been recognized that a transition layer exists on the surface of ice crystals [*Weyl*, 1951; *Fletcher*, 1962, 1968, 1973; *Jellinek*, 1967]. *Fletcher* [1962, 1968] and *Lacmann and Stranski* [1972] indicated that the free energy of ice can be reduced if a "liquid-like" layer is formed on the surface. This quasi-liquid layer (also called the transition layer or surface premelting) has thermodynamic properties in between those of water vapor and bulk ice. Although this transition layer does not behave exactly as liquid water and does not have a uniform composition [*Golecki and Jaccard*, 1978], its thermodynamic properties can be described by a water film with a temperature dependent equivalent thickness.

2.1. Thermodynamic Properties of the Transition Layer

Fletcher [1968] described the thickness of the transition layer that is in equilibrium with the bulk ice and vapor phase as a function of temperature:

$$h_{\text{eq}} = a_1 - a_2 \ln \Delta T. \quad (1)$$

Here, a_1 and a_2 are constants, and ΔT is the deviation of temperature T from the thermodynamic melting point T_0 ($\Delta T \equiv T_0 - T$). One can rewrite the above expression as

$$h_{\text{eq}} = h^* \ln \frac{\Delta T^*}{\Delta T}, \quad (2)$$

where $h^* = a_2$ is the characteristic thickness, $\Delta T^* = \exp(a_1/a_2)$, and $T^* (\equiv T_0 - \Delta T^*)$ is the critical temperature at which the thickness of the transition layer becomes zero. *Fletcher* [1973] estimated h^* to be approximately 11 Å and ΔT^* to be around 30 K. *Golecki and Jaccard* [1978] applied the proton backscattering technique to measured the thickness of the layer, which they called the equivalent amorphous layer. Their results gave $h^* \sim 230$ Å and $\Delta T^* \sim 55$ K.

In this study, we adopted the transition layer concept and treated the thermodynamic properties of the quasi-liquid layer

as those of a true liquid. The theoretical model of *Lacmann and Stranski* [1972], which is later modified by *Kuroda and Lacmann* [1982], is used to describe the thermodynamic properties of the transition layer. On the basis of a macroscopic concept of wettability, this model expressed the total free energy of the transition layer as a function of its thickness h [*Kuroda and Lacmann*, 1982]:

$$\Delta f(h) = \sigma_{w/v} + \sigma_{i/w} + \left(\frac{a}{a+h} \right)^n \Delta \sigma_{\infty} + h \frac{kT}{V_m} \ln \frac{e_w}{e_i}, \quad (3)$$

where $\sigma_{w/v}$ and $\sigma_{i/w}$ are the interfacial free energy between water and vapor and between ice and water, respectively, a is the radius of action of the intermolecular forces, n is a constant ($= 2$), $\Delta \sigma_{\infty}$ is the wettability parameter (the interfacial free energy introduced by the transition layer), k is Boltzmann's constant, V_m is the volume of a water molecule ($\sim 27 \text{ Å}^3$), and e_i and e_w are the saturation vapor pressures over pure ice and water, respectively. Based on an estimation for Van der Waals interaction, *Kuroda and Lacmann* [1982] adopted a value of $a = 1.5 \text{ Å}$, which is probably too low for water molecules that have strong hydrogen bond interactions. *Fletcher* [1968] estimated the coherence length (a measure of the decay of molecular ordering) to be approximately 10 Å, which is also about the size of a water cluster [*Nenow*, 1984]. We thus take this coherence length as the parameter a . The estimation of the wettability parameter $\Delta \sigma_{\infty}$ given by *Kuroda and Lacmann* [1982] is roughly 0.031 J m^{-2} at the basal (0001) face and 0.037 J m^{-2} at the prism (10 $\bar{1}$ 0) face. However, they also suggested using the lower values of 0.010 J m^{-2} at the basal face and 0.025 J m^{-2} at the prism face. Here we ignored the variation at different faces and used an intermediate value of $\Delta \sigma_{\infty} = 0.025 \text{ J m}^{-2}$.

The equilibrium thickness of the transition layer, h_{eq} , occurs when the total free energy is the lowest. By taking the derivative of $\Delta f(h)$ with respect to h and setting it to zero, the equilibrium thickness of the transition layer can be derived as

$$h_{\text{eq}} = -a + \left[\frac{na^n \Delta \sigma_{\infty} V_m}{kT \ln(e_w/e_i)} \right]^{1/(n+1)}. \quad (4)$$

Using the values for $\Delta \sigma_{\infty}$ and other parameters given above, this equilibrium thickness is within a factor of 3 of that obtained from *Fletcher's* formula (2) with $\Delta T^* = 40 \text{ K}$ at temperatures between -1°C and -40°C . The critical temperature (where $h_{\text{eq}} = 0$) obtained from (4) is about -43°C . *Kuroda and Lacmann* [1982] also derived the vapor pressure of the quasi-liquid film with an arbitrary thickness h :

$$e(h) = e_w \exp \left[-\frac{\Delta \sigma_{\infty} V_m}{kT} \frac{n}{a} \left(\frac{a}{a+h} \right)^{n+1} \right]. \quad (5)$$

As will be discussed later, this thickness h may be different from the equilibrium thickness h_{eq} because of the existence of solute. For a transition layer of infinite thickness,

$$e(h = \infty) = e_w \quad (6)$$

is simply the vapor pressure over pure water. When the thickness is at its equilibrium value, one has

$$e(h = h_{eq}) = e_w \exp \left[-\frac{\Delta\sigma_{\infty} V_m}{kT} \frac{n}{a} \left(\frac{a}{a + h_{eq}} \right)^{n+1} \right]. \quad (7)$$

Substituting (4) for h_{eq} in (7), one can see that this vapor pressure $e(h = h_{eq})$ is identical to the vapor pressure over pure ice e_i . When the thickness is zero,

$$e(h = 0) = e_w \exp \left[-\frac{\Delta\sigma_{\infty} V_m}{kT} \frac{n}{a} \right] \equiv e_x \quad (8)$$

can be defined as the vapor pressure of bulk ice e_x (i.e., vapor pressure of ice without the transition layer).

By combining (5) and (8), the vapor pressure under the influence of a transition layer with an arbitrary thickness h can be derived as

$$e(h) = (e_x)^{\gamma} (e_w)^{1-\gamma}, \quad (9)$$

where

$$\gamma = \left(\frac{a}{a+h} \right)^{n+1} = \left(\frac{1}{1+h/a} \right)^{n+1}. \quad (10)$$

Equation (9) describes vapor pressure over ice in terms of the contributions from the bulk ice (e_x) and from the quasi-liquid (e_w), each with a geometric weighting factor of γ and $1-\gamma$, respectively. Again, when the thickness is at its equilibrium value, the vapor pressure is simply the normal saturation vapor pressure over ice e_i . So, from (9) one has

$$e(h_{eq}) = e_i = (e_x)^{\gamma_{eq}} (e_w)^{1-\gamma_{eq}}, \quad (11)$$

where

$$\gamma_{eq} = \left(\frac{a}{a+h_{eq}} \right)^{n+1} = \left(\frac{1}{1+h_{eq}/a} \right)^{n+1}. \quad (12)$$

The existence of solutes affects the water activity in the transition layer and thus e_w in (9). Since the effect of solute on the activity of the bulk ice is usually negligible, one can treat e_x as a constant. Equation (9) can then be modified to include the effect of a solute coating:

$$e'(h) = (e_x)^{\gamma} (e'_w)^{1-\gamma} = (e_x)^{\gamma} (e_w a_w)^{1-\gamma}, \quad (13)$$

where the prime denotes the solute effect and $a_w = e'_w / e_w$ is the water activity in the transition layer. Replacing e_x in (13) with that in (11), one has

$$e'(h) = (e_i)^{\gamma/\gamma_{eq}} (e_w)^{1-\gamma/\gamma_{eq}} (a_w)^{1-\gamma}. \quad (14)$$

The parameters e_w , e_i , and γ_{eq} in (14) are parameters for pure water or ice and are functions of temperature only. So, only a_w and γ (a function of h) in (14) remain to be determined. Note that a result very similar to (14) can be derived through a somewhat different theoretical approach (see the Appendix for details).

The presence of solute in the transition layer may affect $\sigma_{w/v}$, $\sigma_{i/w}$, $\Delta\sigma_{\infty}$, and e_w in (3). For the typical solute

concentration in concern, the effect of solute on $\sigma_{w/v}$ is less than a few percent and tends to be offset by the effect on $\sigma_{i/w}$ in (3). The effect of solute on $\Delta\sigma_{\infty}$ is not well known but is probably less than the uncertainties in $\Delta\sigma_{\infty}$ itself. We will thus focus on the effect of solute on e_w in the fourth term on the right-hand side of (3), which can be expressed as

$$h \frac{kT}{V_m} \ln \frac{e'_w}{e_i} = h \frac{kT}{V_m} \ln \frac{e_w a_w}{e_i} = h \frac{kT}{V_m} \ln \frac{e_w}{e_i} + h \frac{kT}{V_m} \ln a_w. \quad (15)$$

By assuming an ideal solution, the activity of water is written as

$$a_w = \frac{n_w}{n_w + n_s}, \quad (16)$$

where n_w and n_s are the moles of water and equivalents of solute, respectively, in the transition layer. For an ice particle with a surface area A , the number of moles of water in the transition layer is directly proportional to the thickness of the transition layer:

$$n_w \approx h A \rho_w / M_w \equiv h A', \quad (17)$$

where ρ_w is the density of water in the transition layer, M_w is the molecular weight of water, and $A' \equiv A \rho_w / M_w$. Considering a low solute concentration, one has

$$\ln a_w = \ln \frac{n_w}{n_w + n_s} \approx -\frac{n_s}{n_w} \approx -\frac{n_s}{h A'} \approx -\frac{1}{h}, \quad (18)$$

such that the dependence of the last term in (15) on h is canceled. This cancellation reflects the fact that an increase in h leads to a dilution effect and a decrease in the absolute value of $\ln a_w$. Since the equilibrium thickness (4) is obtained from the derivative of (3) with respect to h , it appears that h_{eq} is unaffected by solute of relatively low concentrations.

However, there exists a maximum concentration for a solution to coexist with ice in order to maintain the thermodynamic stability between the two phases. If the solute concentration exceeds this maximum, the ice in contact with the solution will melt to reduce the concentration. This surface melting, which is different from the original surface pre-melting, may cause an increase in the thickness of the transition layer. It is thus assumed here that the thickness of the transition layer (and thus γ) does not deviate from its equilibrium value h_{eq} until the maximum concentration is reached. Once the maximum concentration is reached, the activity of water in the transition layer is maintained at a minimum value of

$$a_{w,\min} = \exp \left[\frac{L_f}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] = \frac{e_i}{e_w}, \quad (19)$$

which is simply the ratio of the saturation vapor pressure of pure ice over that of pure water. Here, the system temperature T can be recognized as the equilibrium freezing point of a solution with a water activity of $a_{w,\min}$ [cf. *Atkins*, 1986 pp. 172-173]. The minimum amount of water that must be maintained in the transition layer can be derived as a function of the solute content:

$$n_{w,\min} = n_s \frac{a_{w,\min}}{1 - a_{w,\min}}. \quad (20)$$

The thickness of the transition layer can thus be expressed as

$$h = \max(h_{eq}, \frac{n_{w,\min}}{A'}). \quad (21)$$

Figure 1 demonstrates the effect of solute on the vapor pressure over ice, according to (14), as a function of temperature and thickness of the solute-saturated transition layer. When the amount of solute is not enough to cause surface melting, the vapor pressure over ice is generally depressed. The maximum possible depression occurs when the activity of water (solute concentration) is at its minimum (maximum), as indicated by the lowest curve ($1 h_{eq}$) in Figure 1. A maximum possible depression of vapor pressure exists between temperatures T_0 and T^* as a result of the opposite temperature dependence of the transition-layer thickness and the equilibrium water activity. The critical saturation ratio over ice, $S_{\min}$, corresponding to the maximum depression has a minimum of about 91% at -20°C .

As surface melting starts to occur because of excess solute, the depression of vapor pressure becomes less significant. The dashed curves in Figure 1 indicate that the surface vapor pressure increases as the thickness of the surface coating increases. Such reversal of the vapor pressure depression indicates that the thickening of the "quasi-liquid" layer is causing the ice particles to become more water-like. By substituting (19) for a_w , (14) can be written as

Figure 1. Ice saturation ratio under the effect of solute coating. The solid curve is the critical saturation ratio $S_{\min}$ and the dashed curves are the saturation ratios at different thickness increments.

$$\frac{e'(h)}{e_i} = \left[\frac{e_w}{e_i} \right]^{\gamma(1-1/\gamma_{eq})}. \quad (22)$$

As shown in Figure 1, this ratio increases with increasing thickness and has a maximum value of unity at $h = \infty$ ($\gamma = 0$). This maximum value also represents the condition of nearly complete evaporation. When the remaining ice mass is less than the factor $n_{w,\min}$, ice particles must melt completely and turn into haze drops, which will continue to evaporate and become more concentrated until their equilibrium vapor pressure reduces to that in the air.

2.2. Chemistry in the Transition Layer

The incorporation of trace chemicals into bulk ice is often thought to be insignificant and is traditionally ignored in cloud studies. Yet some experimental results [e.g., *Sommerfeld and Lamb*, 1986; *Valdez et al.*, 1989] showed that significant amounts of trace gases can be incorporated into vapor-grown ice particles. On the other hand, the production of solute can occur not only in the gas phase but also on the surface of ice particles. However, there are only a limited number of studies done on the ice phase chemical reactions [e.g., *Bales et al.*, 1987; *Mitra et al.*, 1990; *Finnegan et al.*, 1991; *Conklin et al.*, 1993], most of which were done for the formation of sulfate, and no quantitative results for the reaction rates are available. Nevertheless, it is possible to use aqueous phase chemistry to represent the chemistry occurring in the transition layer. *Valdez et al.* [1989] used the analogy of ice growing in a liquid solution to describe the growth of ice with a liquidlike layer and the incorporation of solute from this transition layer to the bulk ice. *Bales et al.* [1987] applied aqueous-phase chemistry in the transition layer for the calculation of mass transfer and reactions of trace chemicals in snow pack. They obtained results in good agreement with laboratory experiments. Hence, at this stage, the transition layer is simply treated as true liquid for chemical calculations. The chemical reactions that occur as a consequence of preferential ion separation and electron transfer during the growth of ice crystals, as discussed by *Finnegan et al.* [1991], are not considered here.

Although solutes are normally excluded from the crystal structure in a slowly freezing aqueous solution [*Gross*, 1968], the expulsion of solute from the ice will result in a buildup of solute near the advancing ice-liquid interface owing to the finite diffusion rate of solute in the liquid. Thus, as shown in Figure 2, the liquid-phase concentration near the advancing ice-liquid interface (C_2) is higher than that away from the interface (C_1). For an ice-liquid-air interfacial system, C_1 represents the aqueous-phase concentration at the air-liquid interface, and both C_1 and C_2 are determined by the mass-transfer rates at the two interfaces. The concentration of solute in the ice (C_3) is normally a small fraction of that in the interfacial liquid (C_2). The ratio of C_3 to C_2 is called the thermodynamic equilibrium distribution (or partition) coefficient [*Gross*, 1968; *Tiller*, 1991 p. 14]

$$k_0 \equiv \frac{C_3}{C_2}. \quad (23)$$

Note that k_0 is different from the common definition of the distribution coefficient $k \equiv C_3 / C_1$. Normally, $0 < k_0 < k \leq 1$ when ice is advancing, and $0 < k < k_0 < 1$ when ice is

Figure 2. Schematic diagram of the mass transfer of solutes in the transition layer. The reference frame is fixed with respect to the advancing interface ($x = 0$). C is the solute concentration, and h is the thickness of the liquid layer. The arrows indicate the direction of mass transfer at the two boundaries.

retreating. The exact value of k_0 depends on temperature, solute concentration, and chemical species.

The diffusion of solute in the system with the interface moving at a rate of Q can be expressed by the diffusion equation [Smith *et al.*, 1955]

$$D \frac{\partial^2 C}{\partial x^2} + Q \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}, \quad (24)$$

where D is the diffusion coefficient of solute in the liquid, Q is the advancing speed of the ice/liquid interface, C is the concentration in the liquid, x is the distance from the liquid-ice interface, and t is time. For the condensational growth of ice particles, Q is simply the linear growth rate. The solution for (24) is rather complicated and requires initial or boundary conditions [cf. Smith *et al.*, 1955]. Nevertheless, since the emphasis of this study is on the mass transfer of the nonvolatile solutes (e.g., sulfate and nitrate), certain simplifications are possible. Because of the rather short diffusion distance h , the characteristic times of diffusion ($\tau_D = h^2/D$) and growth ($\tau_Q = h/Q$) are usually several orders of magnitude smaller than the time for significant changes in the external or internal sources of solutes. One may thus apply the quasi-steady-state assumption so that

$$D \frac{\partial^2 C}{\partial x^2} + Q \frac{\partial C}{\partial x} = 0. \quad (25)$$

Then the specific relationship among the three characteristic concentrations C_1 , C_2 , and C_3 can be established as follows. By defining $\alpha = Qh/D$, (25) has the following solution:

$$C(x) = a_1 + a_2 \exp(-\frac{Q}{D}x) = a_1 + a_2 \exp(-\alpha \frac{x}{h}), \quad (26)$$

which is subject to the boundary condition that is required by the mass conservation at the ice-liquid interface:

$$\frac{\partial C}{\partial x} = -(1-k_0) \frac{Q}{D} C_2 \quad \text{at } x = 0. \quad (27)$$

One can thus find that $a_1 = C_2 k_0$, $a_2 = C_2 (1-k_0)$, and

$$C(x) = C_2 \left[k_0 + (1-k_0) \exp(-\alpha \frac{x}{h}) \right]. \quad (28)$$

The concentrations C_1 , C_2 , and C_3 can then be derived as

$$C_1 = C(x=h) = \bar{C} \frac{k_0 + (1-k_0) \exp(-\alpha)}{k_0 + \frac{1-k_0}{\alpha} [1-\exp(-\alpha)]} \equiv \bar{C} \cdot A_1, \quad (29)$$

$$C_2 = C(x=0) = \bar{C} \frac{1}{k_0 + \frac{(1-k_0)}{\alpha} [1-\exp(-\alpha)]} \equiv \bar{C} \cdot A_2, \quad (30)$$

$$C_3 = k_0 \cdot C_2 = \bar{C} \frac{k_0}{k_0 + \frac{(1-k_0)}{\alpha} [1-\exp(-\alpha)]} \equiv \bar{C} \cdot A_3, \quad (31)$$

where

$$\bar{C} = \frac{1}{h} \int_0^h C(x) dx = C_2 \left\{ k_0 + \frac{1-k_0}{\alpha} [1-\exp(-\alpha)] \right\} \quad (32)$$

is the mean concentration in the transition layer. Note that the activity of water and the aqueous-phase chemical reaction rates depend on the solute concentration $C(x)$ that is not uniform in the transition layer and should be different at different depths. However, since the linear growth rate Q is typically less than 10^{-7} m s^{-1} for the situations considered here, the absolute value of α is normally much smaller than unity. Then from (29) and (30) one can see that $C_1 \sim C_2 \sim \bar{C}$, which means that the distribution of solute in the transition layer is in fact rather uniform for the situations considered here. Thus, despite the potential for fundamental error, we use the mean concentration $\bar{C}$ for the calculation of the chemical reaction rates and the water activity in the transition layer.

Equations (29) through (31) specify the relative relationship among the various characteristic solute concentrations. The absolute values of these concentrations, however, are subject to external and internal influences. The rate change of the mean concentration can be written as

$$\frac{d\bar{C}}{dt} = \frac{d\bar{C}}{dt} \Big|_{\text{air}} + \frac{d\bar{C}}{dt} \Big|_{\text{ice}} + \frac{d\bar{C}}{dt} \Big|_{\text{liquid}}, \quad (33)$$

where

$$\frac{d\bar{C}}{dt} \Big|_{\text{air}} = \frac{D_a f}{r h R T} \left(P - \frac{C_1}{H^*} \right) = \frac{D_a f}{r h R T} \left(P - \frac{A_1}{H^*} \bar{C} \right) \quad (34)$$

represents the mass exchange with the air [cf. Pandis and Seinfeld, 1989],

$$\frac{d\bar{C}}{dt} \Big|_{\text{ice}} = -\frac{Q}{h} C_3 = -\frac{Q A_3}{h} \bar{C} \quad (35)$$

represents the mass exchange with the bulk ice, and the third term on the right-hand side of (33) is the production due to chemical reactions within the transition layer. In (34), D_a is the diffusivity of the gaseous solute in air, f is the ventilation coefficient of the particle, r is the particle radius, P is the

Figure 3. Height (solid curve) and temperature (dotted curve) profiles for the simulation.

partial pressure of the gaseous solute, and H^* is the modified Henry's law coefficient. Note that the r^2 term that commonly appeared in the denominator of the mass transfer equation (34) should be replaced by rh because only the surface layer is involved. The C_1 term in (34) indicates that the mass exchange with the air is determined by the concentration at the air/liquid interface, whereas the C_3 term in (35) indicates that the mass exchange with the bulk ice is determined by the concentration at the liquid/solid interface. Here, we do not assume all the gaseous nonvolatile solutes produced in the air

are transferred immediately onto the ice particles. Due to the limited amount of liquid and the rather high acidity in the transition layer, as well as the large time constants of mass transfer across the air/liquid interface, significant amounts of the "nonvolatile" solutes may exist in the gas phase. For the conditions considered here, our calculations show that there are 1 ~ 50 parts per trillion by volume (pptv) of H_2SO_4 and HNO_3 that remain in the air. Such amounts of gaseous solutes are much greater than those that exist in the transition layer, except during the later stage of the evaporation process when a very thick layer of solute coating is formed. Thus, the more rigorous treatment (34) is applied.

3. Model Setup and Initial Conditions

The theory discussed above is exemplified by a Lagrangian parcel model to simulate the life cycle of ice particles under simplified conditions. The air parcel is assumed to ascend and descend adiabatically according to a sinusoidal function, as shown in Figure 3. The ascending motion occurs during the first hour of simulation; while the descending motion occurs during the second hour. The initial saturation ratio with respect to ice in the air is 94%, a value above the critical saturation ratio S_{min} .

In order to focus on the surface coating theory, simplified microphysics and chemistry are used for the simulations. The ice-nucleation processes are ignored, and it is assumed that ice

Table 1. Gas Phase Chemical Reactions

	Reaction	Rate
1	$O_3 + h\nu \rightarrow O(^1D) + O_2$	$j_1 = 1.5 \times 10^{-5}$
2	$O(^1D) + O_2 (+M) \rightarrow O_3 (+M)$	$k_2 = 3.2 \times 10^{-11} \exp(67/T)$
3	$O(^1D) + H_2O \rightarrow 2HO$	$k_3 = 2.2 \times 10^{-10}$
4	$CH_4 + HO + O_2 \rightarrow CH_3O_2 + H_2O$	$k_4 = 3.9 \times 10^{-12} \exp(-1885/T)$
5	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$k_5 = 4.2 \times 10^{-12} \exp(180/T)$
6	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$k_6 = 7.2 \times 10^{-14} \exp(-1080/T)$
7a	$CH_2O + h\nu \rightarrow CO + H_2$	(70% of reaction 6)
7b	$CH_2O + h\nu + 2O_2 \rightarrow CO + 2HO_2$	(30% of reaction 6)
8	$CO + HO + O_2 \rightarrow CO_2 + HO_2$	$k_8 = 1.5 \times 10^{-13} (1 + 0.6P)$
9	$HO_2 + NO \rightarrow HO + NO_2$	$k_9 = 3.7 \times 10^{-12} \exp(240/T)$
10	$HO_2 + O_3 \rightarrow HO + 2O_2$	$k_{10} = 1.4 \times 10^{-14} \exp(-600/T)$
11	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{11} = 2.2 \times 10^{-13} \exp(600/T) + 1.9 \times 10^{-33} \exp(980/T) M$
12	$H_2O_2 + h\nu \rightarrow 2HO$	$j_{12} = 5 \times 10^{-6}$
13	$H_2O_2 + HO \rightarrow HO_2 + H_2O$	$k_{13} = 2.9 \times 10^{-12} \exp(-160/T)$
14	$HO + SO_2 \xrightarrow{O_3 + H_2O} H_2SO_4 + HO_2$	$k_{14} = 2 \times 10^{-12}$
15	$OH + NO_2 + M \rightarrow HNO_3 + M$	$k_{15} = 6 \times 10^{-11}$
16	$NO + O_3 \rightarrow NO_2 + O_2$	$k_{16} = 1.8 \times 10^{-12} \exp(-1370/T)$
17	$NO_2 + h\nu \rightarrow NO + O$	$j_{17} = 7 \times 10^{-3}$

Note: j is given in s^{-1} , k is in $cm^3 \text{ molecule}^{-1} s^{-1}$, P is pressure in atmospheres, T is in K. M represents N_2 or O_2 or another third molecule. All reactions except (7a) and (7b) are from Atkinson *et al.* [1992].

Table 2. Aqueous Phase Chemical Reactions

	Reaction	Rate
1	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = \exp(-9.731-6710/T)$ ^a
2	$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2 \cdot \text{H}_2\text{O}$	$H_2 = \exp(-11.50+2420/T)$ ^a
3	$\text{CO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$K_3 = \exp(-18.98-1000/T)$ ^a
4	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$K_4 = \exp(-17.86-1760/T)$ ^a
5	$\text{SO}_2(\text{g}) \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	$H_5 = \exp(-10.26+3120/T)$ ^a
6	$\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$K_6 = \exp(-10.97+1960/T)$ ^a
7	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$K_7 = \exp(-21.56+1500/T)$ ^a
8	$\text{H}_2\text{SO}_4(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	$H_8 = \exp(-25.73+17339/T)$ ^b
9	$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	$K_9 = 1000$ ^b
10	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$K_{10} = \exp(-13.71+2720/T)$ ^a
11	$\text{HNO}_3(\text{g}) \rightleftharpoons \text{HNO}_3 \cdot \text{H}_2\text{O}$	$H_{11} = 2.1 \times 10^5$ ^b
12	$\text{HNO}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HNO}_3^-$	$K_{12} = \exp(-26.46+8700/T)$ ^b
13	$\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$	$H_{13} = \exp(-7.086+3400/T)$ ^a
14	$\text{NH}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+$	$K_{14} = \exp(-9.444-450/T)$ ^a
15	$\text{O}_3(\text{g}) \rightleftharpoons \text{O}_3 \cdot \text{H}_2\text{O}$	$H_{15} = \exp(-12.20+2300/T)$ ^a
16	$\text{H}_2\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	$H_{16} = \exp(-10.99+6620/T)$ ^a
17	$\text{S(IV)} + \text{O}_3 \rightarrow \text{S(VI)} + \text{O}_2$	$J_{17a} = 2.4 \times 10^4$; $J_{17b} = \exp(31.37-5530/T)$; $J_{17c} = \exp(38.84-5280/T)$ ^b
18	$\text{S(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{S(VI)} + \text{H}_2\text{O}$	$J_{18} = \exp(34.33-4751/T)$ ^b

K_w is given in M^2 , H is in M atm^{-1} , K is in M , J is in $\text{M}^{-1} \text{s}^{-1}$, and T is in K .

^a Pandis and Seinfeld [1989]. ^b Hoffmann and Calvert [1985].

particles with a specified number concentration of 100 L^{-1} are formed once the ascending air reaches 100% ice saturation. These ice particles then grow by vapor diffusion. The growth habits of ice crystals are ignored, and all ice particles are assumed to be spherical with the same size. During the ascending motion in the first 60 min, the growing ice particles acquire solutes that are produced in the gas phase and in the transition layer, whereas during descending motion after 60 min, ice particles will evaporate and release solutes to the surface as the air becomes subsaturated. A simplified set of photochemical processes in the gas phase and aqueous processes in the transition layer included in the simulations is listed in Tables 1 and 2. The hydronium concentration in the transition layer is calculated according to the electroneutrality requirement.

The values used for the parameters k_o and D in (29) through (31) are based on laboratory experiments. Values of the partition coefficient k_o are typically between 10^{-4} and 10^{-2} [cf. Gross, 1968; Cobb and Gross, 1969; Gross et al., 1987]. A low value of 10^{-4} is used for sulfate and nitrate; an intermediate value of 10^{-3} is used for all other solutes. The diffusion coefficient of solute in the transition layer is not well known. Valdez et al. [1989] suggested that it should be between those for bulk water, which is around $10^{-9} \text{ m}^2 \text{ s}^{-1}$ [cf. Gross, 1968; Mills and Lobo, 1989], and bulk solids, which is around $10^{-15} \text{ m}^2 \text{ s}^{-1}$ [cf. Itagaki, 1967; Jaccard, 1972; Barnaal and

Slotfeldt-Ellinsen, 1983]. In this study, $D = 10^{-12} \text{ m}^2 \text{ s}^{-1}$ is used. The initial conditions and various parameters used in the simulation are listed in Table 3.

4. Model Results

Figure 4 shows the evolution of the particle size with (solid curve) and without (dashed curve) the solute effect. The particle size is only slightly affected by the solute during the initial growth. A maximum radius of $106 \mu\text{m}$ is reached after 1 hour of simulation. During evaporation, the effect of the solute is not significant until the ice particles shrink to about $60 \mu\text{m}$ in radius and lose a large portion (~80%) of their maximum mass. The retardation of evaporation is evident, as the two curves in Figure 4 depart from each other. Figure 5 shows the evolution of the ice saturation ratio in the air S_∞ (solid curve) and over the ice particle S_i (dashed curve). The saturation ratio in the air is controlled by the balance between the updraft speed and the particle growth rate such that the maximum and minimum S_∞ coincide with the maximum updraft and downdraft speeds, respectively. The saturation ratio over the ice particles remains close to unity for most of the time until the final stage of evaporation. As a significant amount of solute is accumulated on the particle surface, S_i decreases significantly and eventually approaches that in the air at about 135 min simulation time. At this instance, a layer of

Table 3. Initial Values and Key Parameters

Parameter	Value
Cloud base temperature, °C	-20
Cloud base pressure, mbar	600
Initial ice saturation ratio in the air, %	94
Maximum/minimum updraft speed, m s ⁻¹	± 0.5
Ice particle number concentration, L ⁻¹	100
Diffusion coefficient of all solute in the transition layer, m ² s ⁻¹	10 ⁻¹²
Distribution coefficient k_0	
SO ₄ ²⁻ and NO ₃ ⁻	10 ⁻⁴
others	10 ⁻³
Initial mixing ratio	
H ₂ SO ₄ , ppbv	0.001
SO ₂ , ppbv	5
NH ₃ , ppbv	0.01
HNO ₃ , ppbv	0.01
CO ₂ , ppmv	350
H ₂ O ₂ , ppbv	0.5
O ₃ , ppbv	10
CH ₄ , ppmv	1.7
CO, ppmv	0.1
NO + NO ₂ , ppbv	1
HO + HO ₂ , ppbv	0.04

Note that pptv indicates parts per billion by volume and ppmv is parts per million by volume.

concentrated solution is formed on the surface of the particles in such a way that they can remain in equilibrium with an under-saturated environment. Then the evaporation of ice particles is terminated. Note that, as shown in Figure 5, the final value of S_∞ is somewhat lower than the initial value, because a portion of the original water vapor is locked up in the remaining ice particles. The equilibrium radius (r_{eq}) of the solute-coated ice particles is about 34 μm , equivalent to 3.3% of the maximum mass. Additional simulations indicate that r_{eq} is larger for lower number concentrations and for a dirtier environment, because in each case the particles collect more solutes.

Figure 6 shows the solute concentration of various chemical species in the transition layer. The concentrations of sulfate, nitrate, and ammonium decrease with time during the growth stage, because the mass growth rate of ice particles increases with the particle size. So the rate of consumption (mass transfer to the bulk ice) increases while the rate of production (surface oxidation and mass transfer from the gas phase) remains relatively unchanged. The decrease of ammonium concentration is more rapid because of the lack of gas-phase production. The concentrations of these solutes in the bulk

Figure 4. Evolution of the size of an ice particle. The solid curve is for the growth of ice with solute effect and the dashed curve is for that without solute effect.

ice are about 3 to 4 orders of magnitude lower than those in the transition layer. Note that for the given conditions, the sulfate production in the transition layer is at least 1 order of magnitude less than that in the gas phase. However, it can be higher for different ambient conditions (e.g., high SO₂ and H₂O₂ concentrations) or when additional surface chemical reactions are considered. The concentrations of sulfate and ammonium increase steadily during the evaporation stage due to the release of these solutes from the bulk ice. The concentration of nitrate, however, decreases after a brief increase. This is because sulfate is a stronger acid that tends to drive out the weaker acid, nitrate, from the solution. Overall, the transition layer exhibits rather high solute concentrations, especially during the evaporation stage. Such solute concentrations are several orders of magnitude higher than that typical in cloud drops and are very similar to those in the haze drops.

If the final air saturation ratio is below the critical saturation ratio S_{min} , ice particles will continue to evaporate, since the equilibrium saturation ratio over the ice particles cannot drop below S_{min} . According to Figure 1, the surface saturation ratio has to increase after it reaches S_{min} when more solute is released to the surface. For comparison, another

Figure 5. Evolution of ice saturation ratio in the air (solid curve) and over the ice particles (dashed curve).

Figure 6. Evolution of solute concentrations in the transition layer.

simulation is done by having an initial S_{∞} of 85%. As shown in Figure 7, the evaporation process toward the end is retarded but not terminated. In this case, ice particles evaporate almost completely, with their residual turning into haze drops. Nevertheless, the particle lifetime has been prolonged for about 6 min compared to that without the solute effect.

5. Discussion

In this study, the model used to describe the effect of solute on the growth of ice particles is quite idealized. The actual physical and chemical processes are much more complicated. For instance, all the ice particles were assumed to be spherical, and yet real ice particles exhibit distinct habits [Nakaya, 1954; Hallett and Mason, 1958b; Kobayashi, 1961]. The linear growth rate Q at the prism faces is different from that at the basal faces of the ice crystals. Furthermore, the thickness of the transition layer is different at different crystal faces [Beaglehole and Nason, 1980; Kuroda and Lacmann, 1982]. Thus the effect of solute can be expected to be dependent on the crystal habits. Also, the size of ice particles in real cloud is not monodispersed as assumed. Competitions might exist between particles of different sizes and shapes, which may

Figure 7. Same as Figure 4, except the initial ice saturation ratio in air is 85%.

result in a selected survival of a few particles in the whole population. These secondary effects need to be further investigated.

In our idealized scenario, it is assumed that no other particles were present. However, the air in the troposphere usually contains a high concentration of aerosol particles. These particles may compete with the ice particles for the solutes produced in the gas phase. Moreover, in mixed-phase clouds, liquid drops may provide the majority of the total surface area and absorb most of the solutes such that the amount of solute available to the ice particles is limited.

The source of solutes in the ice particles can also be important. In the situations considered so far in this study, the ice particles are assumed to form on nuclei that do not contain any solute. However, ice particles in cirrus clouds may originate from frozen cloud drops [Heymsfield and Sabin, 1989] that contain an ample amount of solutes, which may become available during evaporation. Whether the solute contained in the frozen drops is enough to form a stable surface coating depends on solute concentration in the bulk ice. Since the freezing of cloud drops is a rather fast process, all nonvolatile solutes tend to be trapped within the bulk ice during freezing. The solute concentration in the frozen drops then would be similar to that in the original cloud drops, which is typically 10 to 100 μM (but can be several orders of magnitude lower or higher). Figure 8 shows the equilibrium radius that an frozen drop (initially 20 μm in radius) will reach by evaporation in air with humidity exactly at $S_{\min}$. It ranges from a few microns to more than 10 microns for the typical solute concentrations. Thus frozen drops can be quite self-sufficient in providing solute for the formation of the solute coating.

As indicated by Stephens *et al.* [1990], as well as Heymsfield and Miloshevich [1991], small ice particles with effective radii less than about 20 μm are very effective in scattering the shortwave radiation. So the formation of a solute coating may have indirect effect on the global radiation

Figure 8. The equilibrium radius that an ice particle initially 20 μm in radius will reach by evaporation in air with humidity $S_{\min}$. The values are calculated for various bulk solute concentrations and temperatures. Note: for an ammonium-sulfate solution drop 20 μm in radius, the concentrations 1000, 100, 10, 1, 0.1, and 0.01 μM correspond to dry particle radii of about 0.84, 0.39, 0.18, 0.084, 0.039, and 0.018 μm , respectively.

budget by means of stabilizing the vapor-grown ice crystals or frozen drops in subsaturated environment and prolonging their lifetime. Since these ice particles are still large enough to have appreciable fall speeds, solutes may also enhance the dehydration of the atmosphere by keeping water molecules in the condensed phase.

Great uncertainties also exist in the properties of solutes in the transition layer. For instance, the parameters D and k_0 are different for each chemical species. Chemical fractionation of the solutes might occur during the growth of the ice particles. Furthermore, the existence of solutes might change the thermodynamic properties of the transition layer [Jellinek, 1967; Ocampo and Klinger, 1983], but the actual effect is not well known, especially when there is a mixture of solutes. Also, the uncertainties in the parameters a and $\Delta\sigma_\infty$ in (3) may affect the critical saturation ratios shown in Figure 1.

The transition layer model actually breaks down at low temperatures where the thickness of the transition layer becomes zero. Yet, as shown by Conklin *et al.* [1993], the chemistry on the ice can still be active at lower temperatures. Orem and Adamson [1969] showed that the adsorption behavior of *n*-alkanes on ice at temperatures above -35°C is similar to the adsorption on liquid water, marked by abnormally high adsorption heats. The adsorption process can still occur at temperatures below -35°C , but the behavior changed drastically to that characteristic of low adsorption energies. Thus, at low temperatures, the thermodynamic model used here must be abandoned. Instead, the processes of physisorption or chemisorption should be considered.

Some observations of long-lived, mountain leewave-induced stratospheric ice particles in subsaturated air by Deshler *et al.* [1994] over Scandinavia have been explained by Peter *et al.* [1994] to be due to the formation of a nitric acid trihydrate (NAT) coating after the evaporation of some 300 monolayers of H_2O from the surface. The equilibrium vapor pressure of water over NAT being much lower than over ice, the ice particle will stop evaporating if $T_{\text{ice}} < T < T_{\text{NAT}}$, where T_{ice} and T_{NAT} are the "frost point" of ice and NAT, respectively. When $T > T_{\text{NAT}}$, they will evaporate but at a slower rate than pure ice. We do not expect such conditions to exist in the troposphere, because the temperatures are too high. However, the temperature stability regime of solid sulfuric acid tetrahydrate (SAT) could be favorable for the formation of a SAT coating at higher temperatures, up to -50° to -60°C [Luo *et al.*, 1994; Peter *et al.*, 1994], provided that SAT nucleation can occur, which may, however, require substantial supercooling [Dye *et al.*, 1992] and possibly restricting this phenomenon to the equatorial tropopause region and high-latitude lower stratosphere in winter. Even if SAT formation could not occur to a significant degree in the troposphere, the formation or deposition of sulfuric acid on the surface of ice particles may still affect their surface properties.

Finally, a significant influence of atmospheric chemistry on ice particle physics may involve organic compounds, which may behave very differently from those soluble chemicals mentioned so far in this study. It has been demonstrated by Derjaguin *et al.* [1966] and Garrett [1971] that certain organic chemicals may reduce the rate of evaporation of water drops by more than 1 order of magnitude. This leads to the question of whether retardation of evaporation by deposition of partially oxidized organic gases could occur on ice particles, especially at low temperatures in the upper troposphere. It is well known that, favored by high

temperatures, forests produce copious amounts of isoprene, terpenes, and other hydrocarbons [e.g., Fehsenfeld *et al.*, 1992; Singh and Zimmerman, 1992], a substantial fraction of which are subject to oxidation by OH and O_3 in the boundary layer, producing a large variety of partially oxidized organics, such as ketones, aldehydes, carboxylic acids, peroxides, nitrates, peroxy-acids, and alcohols, as shown by Madronich and Calvert [1990] for the Amazon case. Interactions between the primary and partially oxidized hydrocarbons and ice particles maximize when heavy convection takes place over forested regions in the tropics and during summer at midlatitudes. Intense photochemical processes are also expected near the upper boundaries of the anvil clouds, which can have a lifetime of several hours [e.g., Heymsfield, 1975; Sassen *et al.*, 1989]. Assuming a typical ice crystal number density of 10^5 m^{-3} and an equivalent radius of $50\text{ }\mu\text{m}$, the average time between collisions for a gas molecule with the cirrus particles is about 10 s, much shorter than the timescales of photochemical reactions for these organic gases, which can be of the order of hours or more [Fehsenfeld *et al.*, 1992]. To form a complete monolayer on these ice particles, about 1 ppb of adequate organic gases are necessary to condense out from the gas phase, whereas just 1 part per trillion (ppt) is needed if the equivalent particle size reduces to $5\text{ }\mu\text{m}$ by evaporation. Madronich and Calvert [1990] have shown that the concentration of the partially oxidized organics within the boundary layer may reach several orders of magnitude higher values than 1 ppt. The partially oxidized organics are not likely to cause surface melting and can be more effective in retarding the evaporation of ice particles than the soluble chemicals. After evaporation of the ice particles, organic aerosol particles may be left behind. The interactions of the organic gases with the cirrus particle surfaces therefore might lead to interesting heterogeneous chemistry and surface effects.

6. Conclusions

A transition layer model is developed to study the effects of trace chemicals on the evaporation of ice crystals. This chemical effect can generally be divided into two stages: (1) the incorporation of solutes into the bulk (internal) ice during growth and (2) the accumulation of solutes on the ice surface during evaporation. The intake of solute into the bulk ice is demonstrated by calculating their mass transfer between air and the transition layer, as well as between the transition layer and the bulk ice. Solute that is released from the bulk ice during evaporation tends to accumulate on the surface of the ice particles and form a highly concentrated solute coating. With excessive solute, surface melting may occur such as to increase the thickness of the transition layer. This solute coating alters the surface vapor pressure and thus affects the evaporation of ice particles. A theory is derived to separate the contribution of vapor pressure from the bulk ice and from the transition layer. The effect of solute in the transition layer on the vapor pressure is then determined through the consideration of transition layer energetics. The theory predicts that the vapor pressure of ice particles with a solute coating may be significantly reduced. Ice particles may survive in subsaturated air without evaporation when the relative humidity (with respect to ice) in the air is above a critical saturation ratio. This critical saturation ratio is temperature dependent and can be as low as 91%.

Model simulations showed that with a sufficient amount of solute released from the bulk ice during evaporation, a layer of solute with rather high concentration can be formed on the surface of the ice particles. Such solute coating enables the ice particles to stay in equilibrium with the environment by reducing the water activity of the ice surface. The equilibrium size of the ice particles is determined by the accumulated amount of solute in the outer layers of the particles, and is larger for a lower particle number concentration and a dirtier environment. When the environmental saturation ratio is below the critical saturation ratio, ice particles become thermodynamically unstable and will evaporate completely, but at a slower rate than that of pure ice. Photochemical reactions in the gas phase and heterogeneous reactions on the ice surface can both be important sources of solute for the uptake by the ice particles.

Using an idealized transition layer model, the possible effect of trace chemicals on the growth of ice particles was demonstrated. Chemical processes may play a significant role in prolonging the lifetime of cirrus clouds, possibly exerting an indirect impact on the climate, as well as enabling cirrus ice particles to survive a greater fall distance and to trigger the glaciation of lower-level supercooled clouds. However, there still exist great uncertainties in our understanding of the ice-phase chemical processes. Also, atmospheric conditions that are important to the solute effects, such as the trace gas concentrations and the temperatures where the ice particles are formed, have very large global variation and can be significantly different from the scenarios included in this study. Further studies of the interplay between atmospheric chemistry and ice particle surface properties, as indicated in this paper, are of great interest.

Appendix: A Second Theoretical Analysis of the Vapor Pressure Over Ice

The vapor pressure over ice is controlled by the intermolecular energies and is directly related to the enthalpy (latent heat) of sublimation L_s , which is composed of the hydrogen-bond energy $E_{\text{H-bond}}$ (two for each water molecule) and other intermolecular energies E_{other} [Eisenberg and Kauzmann, 1969 p. 139]:

$$L_s = 2E_{\text{H-bond}} + E_{\text{other}}. \quad (\text{A1})$$

The energy introduced by the transition layer E_{TL} constitutes part of E_{other} so that

$$L_s = 2E_{\text{H-bond}} + E'_{\text{other}} + E_{\text{TL}} \equiv E_x + E_{\text{TL}}. \quad (\text{A2})$$

Here, the enthalpy of sublimation is separated into the part contributed by the bulk ice, E_x , and the part contributed by the transition layer, E_{TL} , which can be expressed in terms of the latent heat of freezing L_f :

$$E_{\text{TL}} \equiv -\xi_{\text{eq}} L_f, \quad (\text{A3})$$

where ξ_{eq} is a function of temperature and the equilibrium thickness h_{eq} in (2). Estimation of this transition layer free energy has been done by Fletcher [1962, 1968]. Since L_s is the sum of the latent heat of evaporation L_v and latent heat of freezing L_f , we have

$$L_s = E_x - \xi_{\text{eq}} L_f = E_x - \xi_{\text{eq}} (L_s - L_v), \quad (\text{A4})$$

which can be rearranged into

$$L_s = \frac{1}{1 + \xi_{\text{eq}}} E_x + \frac{\xi_{\text{eq}}}{1 + \xi_{\text{eq}}} L_v \equiv \lambda_{\text{eq}} E_x + (1 - \lambda_{\text{eq}}) L_v, \quad (\text{A5})$$

where

$$\lambda_{\text{eq}} \equiv 1/(1 + \xi_{\text{eq}}). \quad (\text{A6})$$

Applying the Clausius-Clapeyron equations, it can be determined that

$$\begin{aligned} d \ln e_i &= \frac{L_s}{RT^2} dT = \lambda_{\text{eq}} \frac{E_x}{RT^2} dT + (1 - \lambda_{\text{eq}}) \frac{L_v}{RT^2} dT \\ &= \lambda_{\text{eq}} d \ln e_x + (1 - \lambda_{\text{eq}}) d \ln e_w. \end{aligned} \quad (\text{A7})$$

Here, R is the universal gas constant, e_x is the vapor pressure over the bulk ice, and

$$d \ln e_x \equiv \frac{E_x}{RT^2} dT. \quad (\text{A8})$$

Expressed in its integral form, (A7) can be written in a form very similar to (11):

$$e_i = (e_x)^{\lambda_{\text{eq}}} (e_w)^{1 - \lambda_{\text{eq}}}. \quad (\text{A9})$$

Note that the expression of λ_{eq} in (A6) is similar to γ_{eq} in (12), except for the exponent. Using the various parameters given by Fletcher [1962, 1968], we estimated that ξ_{eq} in (A6) is within a factor of two of the parameter h_{eq}/a in (12) for $-38^\circ\text{C} < T < -2^\circ\text{C}$.

Considering the situation when the system is disturbed from equilibrium, (A4) can be expressed as

$$L(h) = E_x - \xi L_f = E_x - \xi (L_s - L_v), \quad (\text{A10})$$

from which we have

$$e(h) = (e_x)^\lambda (e_w)^{1 - \lambda}. \quad (\text{A11})$$

Here, ξ and λ are the nonequilibrium values of ξ_{eq} and λ_{eq} , respectively. Following the same approach of (11) to (14), one derives

$$e'(h) = (e_x)^{\lambda/\lambda_{\text{eq}}} (e_w)^{1 - \lambda/\lambda_{\text{eq}}} (a_w)^{1 - \lambda}, \quad (\text{A12})$$

which is very similar to (14), with the parameters λ and λ_{eq} replacing γ and γ_{eq} .

Acknowledgments. This research was supported in part under NSF grant ATM-8920119. The support of the computing facilities at the National Center for Atmospheric Research is also acknowledged. The comments and suggestions of the anonymous reviewers are greatly appreciated.

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Jen-Ping Chen, Department of Atmospheric Sciences, National Taiwan University, Taipei, Taiwan, Republic of China.

Paul J. Crutzen, Max-Planck-Institute for Chemistry, Division of Atmospheric Chemistry, Mainz, Germany.

(Received July 20, 1993; revised April 29, 1994;
accepted May 17, 1994)