Condensational growth of cloud droplet on atmospheric $(NH_4)_2SO_4$ particle

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Abstract

In order to investigate the acidification process of cloud drops (i.e., acid rain formation) due to rainout (in cloud scavenging) of gaseous pollutants as SO_2(g) and NO_x(g), the non-steady characteristics of the growth of single cloud droplet by condensation of the atmospheric water vapor is simulated numerically with use of a mathematical model. The mathematical model is constituted by the conservation laws of water mass and heat energy and the state equation of ideal gas. The time variation of droplet heat Q_w is very fast compared with that of droplet mass m_w. Therefore, usually droplet temperature T_a can be treated as in quasi-steady state. The equilibrium droplet size a_e is approximately dependent on the 3/2 power of the initial radius a_{s0} of cloud condensation nucleus $(NH_4)_2SO_4$. Because for large condensation nuclei it takes considerably long time compared with the lifetime of cloud to grow up to its equilibrium radius, the conventional Köhler equation may bring about not a little error in the estimation of cloud drop size.

1 Introduction

Acid rain is formed by rainout (in cloud scavenging) and washout (below cloud scavenging) of such atmospheric pollutants as sulfur dioxide and nitrogen oxide. The scavenging process of washout is considerably made clear (Shiba et al.[1] and [2]), but that of rainout is hardly made clear. One of the

reasons for this is that both the space and the time scales for the process of the washout can be defined easier compared with those of rainout. The acidification of the cloud droplet by rainout occurs not only in the stages of generation and growth of cloud droplets but also in the grown-up stage. The rate of acidification of droplet is supposed to vary with those stages of droplet formation. Therefore, the phenomena in rainout should be evaluated microscopically. The conventional treatment of the scavenging of the atmospheric pollutatnts by a macroscopic scavenging coefficient cannot take account of the time varying rate of droplet acidification in these stages. Then, by the conventional method the quantitative contribution of the rainout to acid rain formation cannot be estimated precisely. The contribution of rainout to acid rain is supposed to be estimated more accurately by accounting the scavenging of the acidic pollutants during the generating and the growing periods of cloud droplet formation in the atmosphere. Judging from the conventional method, this procedure may be seems to be too microscopic to estimate the rainwater quality on the ground. However, we consider that the mechanism of acid rain formation is results of the integration of individual microscopic phenomena and that it is necessary to analyze the cloud droplet formation to investigate acidification of rain water by in cloud scavenging of the atmospheric pollutats. Then, adopting $(NH_4)_2SO_4$ particle as a cloud condensation nuclei, the generation and the growth of a cloud droplet is simulated with use of a mathematical model developed here for this purpose, based on the physico-chemical phenomena.

2 Modeling of cloud droplet formation

2.1 Condensation of atmospheric water vapor

It is well known that in the atmosphere the excess of water vapor over the saturated vapor pressure, which is dependent on the atmospheric temperature, condenses into liquid water and forms droplets. Once a very small water drop is generated, the flux of water vapor flows into the droplet, since the vapor pressure of the atmosphere (supersaturated) is greater than that of over the droplet surface (saturated). This process is a homogeneous nucleation and has been studied well from a thermodynamic point of view (Pruppacher and Klett [3]). The equilibrium radius a_e of the pure water droplet is given by the Kelvin's equation as:

$$a_e = \frac{2M_w\sigma}{\mathcal{R}_3 T \rho_w \ln(e_{pure}/e_{sat.pure})} \tag{1}$$

where, M_w = molecular weight of water (=18 g/mol); σ = surface tension

of water against air (dyn/cm); $\mathcal{R}_3$ = universal gas constant (= 8.314×10^7 erg /mol / ° K); T = temperature (° K); ρ_w = density of water (g/cm^3); e_{pure} = vapor pressure over curved surface of pure water (atm); and $e_{sat.pure}$ = saturated vapor pressure over plane surface of pure water (atm). However, if there exists no cloud condensation nucleus in this process, it is shown using the Kelvin's equation that the atmospheric water vapor requires to be considerably supersaturated ($e_{pure}/e_{sat.pure} > 1$).

On the other hand, if droplet contains such salt as $(NH_4)_2SO_4$, H_2SO_4, and NaCl, the vapor flux is enhanced to flow toward droplet, since the equilibrium vapor pressure over an aqueous salt solution is less than that over pure water (Raoult's Law) as (Atkins [4]):

$$e = e_{pure} \cdot (1 - x_s) \tag{2}$$

where, e = vapor pressure over an aqueous salt solution (atm); and x_s = ratio of moles of salts to moles of water (–). This means that the higher the salt concentration (x_s) becomes, the more the pressure (e) drops. $(NH_4)_2SO_4$, whose usual size ranges from about 0.1μm to 1.0μm, is a typical secondary atmospheric pollutant produced by the atmospheric chemical reaction of the primary pollutant gases as NH_3(g) and SO_2(g) and is highly soluble in water. $(NH_4)_2SO_4$ is an adequate aerosol for a cloud condensation nucleus.

The equilibrium radius of cloud droplet due to the condensation of water vapor on the nucleus $(NH_4)_2SO_4$ is controlled by both the curveture and the salt effects and is estimated by combining eqn (1) with eqn (2).

2.2 Governing equation of model

There are some usefull works for the modeling of the cloud droplet formation due to the condensation of the atmospheric water vapor (Kulmala et al. [5], Korhonen et al. [6], Vesala et al. [7] and Mattila et al. [8]).

The governing equations for the droplet formation by the condensation are composed of the equation of mass conservation, the equation of heat energy conservation and the equation of gas state. They are given as follows:

$$\frac{dm_w}{dt} = 4\pi \mathcal{D}_v a(\rho_{v\infty} - \rho_{va}) = j_w \tag{3}$$

$$\frac{dQ_w}{dt} = 4\pi k_v a(T_\infty - T_a) + L_e j_w \tag{4}$$

$$e_{vx} = \rho_{vx} \frac{\mathcal{R}_1}{M_w} T_x \tag{5}$$

where, a = radius of droplet (cm); t = time (sec); j_w = mass flux of water vapor (g/s); m_w = mass of droplet (g); $\mathcal{D}_v$ = diffusion coefficient of water

vapor (cm^2/sec); ρ_{vx} = density of water vapor at T_x (g/cm^3); Q_w = heat of droplet (cal); k_v = thermal conductivity of water vapor (cal/sec/cm/ ° K); T_∞ = medium temperature (° K); T_a = surface temperature of droplet (° K); L_e = latent heat of phase change (cal/g); e_{vx} = water vapor pressure at T_x (atm); and $\mathcal{R}_1$ = universal gas constant (= 82 $atm/cm^3/mol/$ ° K).

Considering the effects of the curvature variation, the temperature variation, and the salt concentration variation on the vapor pressure over the drop surface, the mass flux of water vapor j_w can be written as:

$$j_w = \frac{4\pi\, a\, \mathcal{D}_v\, M_w\, e_{sat.w}(T_\infty)}{\mathcal{R}_1 T_\infty}$$

$$\times \left[S(T_\infty) - \frac{T_\infty}{T_a} \exp\left\{ \frac{\mathrm{Le}\, M_w (T_a - T_\infty)}{\mathcal{R}_2\, T_a\, T_\infty} + \frac{2 M_w\, \sigma}{\mathcal{R}_3\, T_a\, \rho_w\, a} - x_s \right\} \right] \quad (6)$$

where, $e_{sat.w}$ = equilibrium water vapor pressure (atm); S = saturation ratio of moist air with respect to a plane water surface (–); and $\mathcal{R}_2$ = universal gas constant (=1.858 cal/mol/ ° K). Saturation ratio S and mole ratio x_s are given as follows:

$$S(T_\infty) = \frac{e_\infty(T_\infty)}{e_{sat.w}(T_\infty)} \quad ; \qquad x_s = \frac{\nu\, n_s}{n_w} \qquad (7), (8)$$

where, e_∞ = water vapor pressure of surrounding air (atm); ν = vant' Hoff factor (–); n_s = moles of salt (mol); and n_w = moles of water (mol). In the aqueous solution $(NH_4)_2SO_4$ is dissociated almost completely as follows:

$$(NH_4)_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-} \qquad (9)$$

Therefore, it can be assumed that one mole of $(NH_4)_2SO_4$ produces two moles of NH_4^+ and one mole of SO_4^{2-} and that $\nu = 3$.

m_w and Q_w are obtained by integrating eqns (3) and (4) simultaneously. Once m_w is obtained as a function of time t, the time varying radius of cloud droplet $a(t)$ can be estimated simply as:

$$a(t) = \left(\frac{3 m_w}{4\pi \rho_w} \right)^{1/3} \qquad (10)$$

In order to compare the rate of time variation of Q_w with that of m_w, the dimensionless times $\hat{t}_m$ and $\hat{t}_Q$ are defined. They characterize the time scales of m_w and Q_w variations, respectively.

$$\hat{t}_m = \frac{t\, D_v}{a^2} \quad ; \qquad \hat{t}_Q = \frac{t\, k_v}{\rho_w\, c_{pw}\, a^2} \qquad (11), (12)$$

where, c_{pw} = specific heat of liquid water at constant pressure (cal/g/ ° K). The ratio of $\hat{t}_Q$ to $\hat{t}_m$ is evaluated as:

$$\frac{\hat{t}_Q}{\hat{t}_m} = \frac{k_v}{D_v \rho_w c_{pw}} = 2.40 \times 10^{-4} \tag{13}$$

This shows that the rate of Q_w is overwhelmingly greater than that of m_w. Therefore, as a matter of fact Q_w is supposed to be in quasi-steady state from considerably early stage compared with m_w. Then, approximating as $dQ_w/dt = 0$, from eqn (4) the next relation can be taken:

$$T_a(t) = T_\infty(t) + \frac{\text{Le}\, j_w}{4\pi\, k_v\, a} \tag{14}$$

In reality the value of $T_a(t)$ computed by rigorous eqn (4) and that by approximated eqn (14) are almost the same.

The equilibrium radius a_e can be obtained from eqn (6). As in equilibrium state the growth of the droplet stops, $j_w = 0$ in eqn (6). And more, it is evident that droplet temperature becomes equal to that of the surroundings in the equilibrium state, i.e., $T_a = T_\infty$. Therefore, from eqn (6), next equation can be taken:

$$\exp\left(\frac{2M_w\,\sigma}{\mathcal{R}_3\, T_\infty\, \rho_w\, a_e} - x_s\right) = S \tag{15}$$

The above equation can be rewritten as follow:

$$a_e = \frac{2M_w\sigma}{\mathcal{R}_3 T_\infty \rho_w (x_s + \ln S)} \tag{16}$$

If $x_s = 0$, eqn (16) reduces to Kelvin's equation [eqn (1)]. Approximating that $\ln S \approx S - 1$ and substituting eqn (8) into eqn (15), Köhler equation can be taken as:

$$S = 1 + \frac{2M_w\,\sigma}{\mathcal{R}_3\, T_\infty\, \rho_w\, a_e} - \frac{3\nu m_s M_w}{4\pi M_s \rho_w a_e^3} \tag{17}$$

It is rather nuisance to solve the above cubic equation with respect to a_e. If the water vapor pressure over the droplet $e_{sat.w}$ (saturated) can be approximated to be equal to that of surroundings e_∞ (supersaturated for condensation), i.e., $S \approx 1$, it is very simple to solve eqn (15) with respect to a_e. As in fact it is said that usually $S < 1.01$, this approximation is not so unreasonable one. Substituting eqn (8) into eqn (15) under this approximation, a_e is given as follows:

$$a_e = \left(\frac{3\nu\, \mathcal{R}_3\, T_\infty\, m_s}{8\pi\, \sigma\, M_s}\right)^{1/2} \tag{18}$$

where, m_s = mass of salt in droplet (g); and M_s = molecular weight of salt [=132 g/mol for $(NH_4)_2SO_4$].

Initial radius of condensation nucleus is decided from eqn (19). Then, if $S \sim 1$, the relationship between the initial radius of nucleus and the equilibrium radius of droplet can be given as:

$$\frac{4\pi\rho_s\, a_{s0}^3}{3} = m_s \quad ; \qquad a_e = \left(\frac{\mathcal{R}_3 T_\infty \nu \rho_s}{2\sigma M_s}\right)^{\frac{1}{2}} \cdot a_{s0}^{\frac{3}{2}} \qquad (19), (20)$$

where, a_{s0} = initial radius of condensation nucleus (cm). It can be seen that the equilibrium radius of droplet a_e is approximately proportional to the 3/2 power of initial radius of nucleus a_{s0}.

3 Numerical simulation of condensation

Integrating the governing equations [eqns (3) and (4)], the time variations of the radius and the temperature of cloud droplet due to the condensation of water vapor in the atmosphere can be simulated numerically. The variation of the radius is considerably large, but that of the temperature (in ° K) from the initial value is very small. Then, the dimensionless radius $\hat{a}(t)$ and the temperature increment $\Delta T_a(t)$ are defined as follows:

$$\hat{a}(t) = \frac{a}{a_e} \quad ; \qquad \Delta T_a(t) = T_a - T_\infty \qquad (21), (22)$$

Although usually the equilibrium radius a_e is approximated value, $\hat{a}$ is expected to asymptote approximately to unity, because the saturation ratio S is close to unity. As in this study it is assumed that $S = 1$ for simplicity, the asymptotic value is exactly unity.

The physical properties used in this simulation are tabulated in Tables 1 and 2. As the variation of drop temperature T_a is small, these values are assumed to be constant in the simulation and are those at 0 ° C.

Table 1. Values of Physical Properties at 0 ° C (1)

$\mathcal{D}_v$ (cm^2/s)	k_v (cal/s/cm/° K)	ρ_s (g/cm^3)	ρ_w (g/cm^3)	σ (dyn/cm)
0.251	6×10^{-5}	1.769	1.0	75.7

$\mathcal{R}_1$ (atm/cm^3/mol/° K)	$\mathcal{R}_2$ (cal/mol/° K)	$\mathcal{R}_3$ (erg/mol/° K)	Le (cal/g)	c_{pw} (cal/g/ ° K)
82.0	1.858	8.314×10^7	597.3	1.0

Table 2. Values of Physical Properties at 0 ° C (2)

e_∞ (atm)	T_∞ (° K)	S (—)	M_s (g/mol)	M_w (g/mol)	Solubility of $(NH_4)_2SO_4$ (g-salt/100g-solution)
0.922	273.15	1.0	132	18	41.22

Numerical simulations were done about two initial radii a_{s0} of condensation nucleus $(NH_4)_2SO_4$, i.e., 0.1 μm (10^{-5} cm) and 1 μm (10^{-4} cm). Time variation of the dimensionless radius of cloud droplet $\hat{a}$ and that of the increment of droplet temperature ΔT_a are shown in Figure 1. Solid curves are for $\hat{a}$ and broken curves are for ΔT_a.

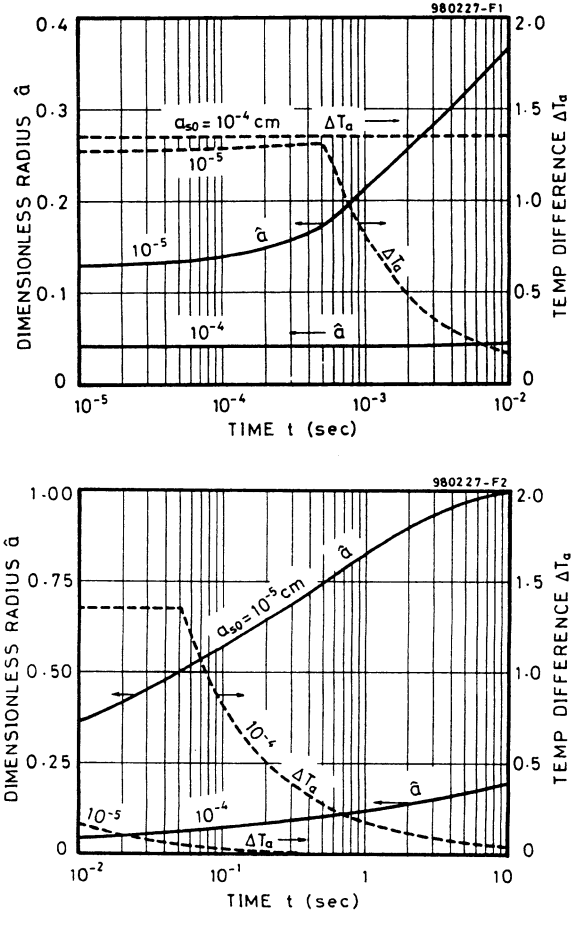

Figure 1. Time Variations of Dimensionless Radius of Droplet $\hat{a}$ and Temperature Increment ΔT_a
(Upper Fig.: $t = 10^{-5} \sim 10^{-2}$ sec and Lower Fig.: $t = 10^{-2} \sim 10$ sec).

From the solid curves of Fig 1 for the initial radius of nucleus $a_{s0} = 10^{-5}$ cm it can be seen that $\hat{a}$ (i.e., cloud droplet size) is greatly increased after about $t = 10^{-4}$ sec and the increase continues until about $t = 1$ sec. Then, the increase is gradually weakened and ultimately the droplet attains its equilibrium size a_e at $t \sim 25$ sec. The droplet growth on larger condensation nucleus ($a_{s0} = 10^{-4}$ cm) is extraordinarily slow compared with the growth on smaller condensation nucleus, and the equilibrium state is attained at $t \sim 2.5 \times 10^5$ sec ($\sim$ 70 hr), although its equilibrium size is much larger. Therefore, for the droplets condensed on large nuclei such phenomena occur in next stage as collision, coalescence, evaporation, and raining may take place before the droplets get their equilibrium size. In Table 3 these equilibrium droplet sizes are tabulated with the time required to reach the equilibrium state. The numerical results show that the mass flux of water vapor condensed on $(NH_4)_2SO_4$ (i.e., j_w) increases monotonously from the begining of the condensation until it gets the maximum value. At the time j_w gets the maximum solid-phase $(NH_4)_2SO_4$ disappears and j_w starts to diminishe gradually to zero. When j_w gets the maximum value, the increment of droplet temperature ΔT_a also obtains the maximum. This is because j_w is the driving force of the increase not only for droplet mass but also for droplet heat, as can be seen from eqns (3) and (4).

The temperature increment ΔT_a is not so large as seen from the broken curves in Figure 1. Their values are about 1.30 °C for smaller nucleus and 1.35 °C for larger one, respectively. This suggests that the larger the nucleus is, the higher the droplet temperature becomes. The maximum values of ΔT_a for smaller nucleus and larger one (i.e., $a_{s0} = 10^{-5}$ cm and $a_{s0} = 10^{-4}$ cm) are realized at the time $t = 5 \times 10^{-4}$ sec and $t = 5 \times 10^{-2}$ sec, respectively. These times are very short and it is hard to simulate numerically the time variations of droplet temperatures in very early stage. Anyway the temperature decrease from its maximum is drastically rapid especially in smaller nucleus. So the measuring of the time variation of droplet temperature supposed to be considerably difficult.

Table 3. Equilibrium Droplet Radius a_e and Maximum Increment of Droplet Temperature $\Delta T_{a.max}$

a_{s0} (cm)	a_e (cm)	$t_{0.99e}$ (sec)	$\Delta T_{a.max}$ (°C)	$t_{\Delta Ta.max}$ (sec)
10^{-5}	7.765×10^{-5}	~ 25	1.30	$\sim 5 \times 10^{-4}$
10^{-4}	2.456×10^{-3}	$\sim 2.5 \times 10^5$	1.35	$\sim 5 \times 10^{-2}$

$t_{0.99e}$ = time required to attain 99 % of the equilibrium value a_e

$t_{\Delta Ta.max}$ = time when the maximum value of ΔT_a is realized.

For small nucleus the time variation of radius of solid salt (a_s) in droplet is shown in Figure 2. The initial radius of condensation nucleus (a_{s0}) is 10^{-5} cm. It takes about 6×10^{-4} sec for the solid-phase nucleus to disappear completely ($a_s = 0$) in the droplet. The large nucleus ($a_{s0} = 10^{-4}$ cm) dissolves completely in about 6×10^{-2} sec (the curve for the nucleus is not shown in Figure 2). These times required for disappearance of solid salt are nearly equal to the times when ΔT_a becomes maximum, i.e., $t_{\Delta Ta.max}$ (see Table 3). ΔT_a shown in Figure 1 rises monotonously until the maximum, although its increase is very gradual. It can be seen from the inspection of numerical results that the temperature continues to rise during the solid $(NH_4)_2SO_4$ exists in the droplet. In this period $(NH_4)_2SO_4$ concentration in liquid-phase remains constant to the saturated concentration, because there is the solid-phase $(NH_4)_2SO_4$ in the droplet. The begining of the temperature decrease corresponds to the complete vanishment of solid-phase $(NH_4)_2SO_4$ from the droplet. It also corresponds to the start of the decrease in liquid-phase $(NH_4)_2SO_4$ concentration due to dilution by condensation of liquid water. The decrease of ΔT_a, which starts after the vanishiment of solid $(NH_4)_2SO_4$, is very rapid compared with the increase. Ultimately the droplet temperature T_a is lowered to the atmospheric temperature T_∞.

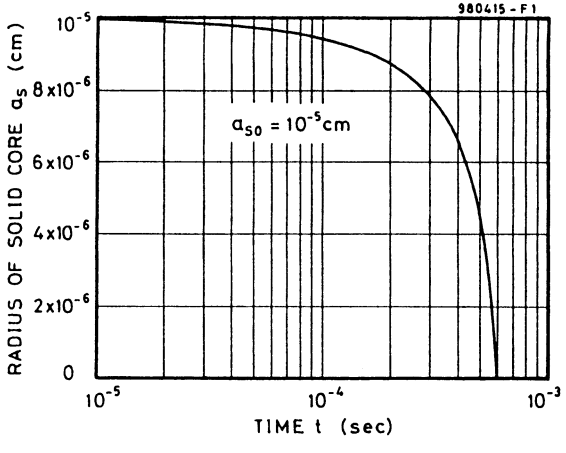

Figure 2. Time Variation of Radius of Solid $(NH_4)_2SO_4$ in Droplet

4 Conclusions

From the numerical simulation of the generation and growth process of cloud droplet due to the condensation of atmospheric water vapor on $(NH_4)_2SO_4$, it is supposed that the trasfers of the water mass and the heat enery into droplets are greatly dependent on the salt concentration of droplets.

It may be concluded that:
(1) Comparing the rate of temperature variation with that of mass variation of droplet, the rate of temperature variation is very fast and in fact the temperature can be approximated to be in quasi-steady state;
(2) The larger the initial condensation nucleus a_{s0} is, the larger the equilibrium droplet radius a_e becomes;
(3) If the saturation ratio of the atmospheric vapor pressure is close to unity (i.e., $S \sim 1$), a_e is approximately proportional to the 3/2 power of a_{s0};
(4) For large nucleus (e.g., $a_{s0} = 10^{-4}$ cm), the time to get to the equilibrium state is considerably long (about 70 hr for 10^{-4} cm) and then there may exist error in the estimation of droplet radius by the Köhler equation; and
(5) When the solid portion of salt originated from the condensation nucleus disappears and the liquid-phase salt concentration begins to dcrease from the saturation, the droplet temperature also starts to dcrease.

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