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GROWTH OF CLOUD DROPLET DUE TO CONDENSATION OF WATER VAPOR ON PARTICULATE ATMOSPHEREIC POLLUTANT

by

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SYNOPSIS

Cloud droplet formation is an important process in water cycle between the earth and the atmosphere. In order to investigate the nonsteady growth of cloud droplets due to the condensation of the atmospheric water vapor on $(NH_4)_2SO_4$ particles, a mathematical model has been constructed and the nonsteady growth has been simulated numerically with use of the model. The model is constituted by the conservation laws of water mass and heat energy and the state equation of ideal gas. As the time variation of droplet heat Q_w is very fast compared with that of droplet mass m_w, droplet temperature T_a can be treated as in quasi-steady state. The equilibrium droplet size a_e is dependent on the 3/2 power of the initial radius a_{s0} of $(NH_4)_2SO_4$. The larger a_{s0} is, the more the droplet grows in its equilibrium size a_e. It takes much time for the cloud droplet condensed on large $(NH_4)_2SO_4$ to attain its equilibrium size a_e. It also has been cleared that Kelvin's equation is not always applicable to estimate the cloud droplet size.

INTRODUCTION

Water is indispensable to all living thing to maintain the individual body, because the life usually requires the metabolism, which is composed of the complex biochemical reactions under the existence of water. And also for inanimate nature, mobile water plays an important part in the transportation and chemical reactions of the various matter, since water can fluidize many substances and make the aqueous solution which easily goes everywhere and reacts with another substance. In the global scale, for example, various atmospheric gaseous and particulate substances regardless of naturals or anthropologenics, as aerosol, are absorbed by liquid water and transferred from the atmosphere to the earth through precipitation as rain and snow. Of course, the mass transfer is reversible, i.e., they are released into the air from the rainwater and surface water (river, lake and sea). Although the water vapor content in the atmosphere is very little compared with the other global water, it is condensed to liquid water (as cloud droplet) in the air and precipitated with various matters. Therefore, the cycle of water, i.e., the exchange of water, between the atmosphere and the earth controls also the mass transfer between them.

In connection with the interaction of the atmosphere and the earth, recently the hydrologically microscopic treatise on the rainfall run-off has been developed by the group of Kyoto University considering the variation of size distribution of raindrops with the altitude [Nakagawa et al. (6)]. This suggests that the precise prediction of rainfall run-off on the earth requires the microscopic meteorological information during the stay of hydrometeors in the atmosphere. However, from the viewpoint of the cycle of the aqueous substances (e.g., acidic pollutants as sulfur dioxide and nitrogen oxide) between the atmosphere and the earth through the emission in gas-phase (diffusion) and the scavenging in liquid-phase (rainout and washout), it is supposed that the cloud droplet formation and its growth for the rainout should be considered in addition to the properties of raindrops for the washout. Hence, in this study the nonsteady process of cloud droplet formation and its growth is investigated with use of the microphysics of cloud. Although many theoretical and experimental works about the cloud droplets have been done, most of them are based on the analysis of the equiribrium state typically known as Kelvin's equation [Asai (1)] and only a few of them are the nonsteady analysis. Pollution of rainwater, well known as acid rain, is made by rainout (in-cloud scavenging by cloud droplets) and washout (below-cloud scavenging by rain drops) of such atmospheric pollutants as sulfur dioxide and nitrogen oxide. The nonsteady scavenging process of washout has been considerably made clear [Shiba et al.(8), (9) and (10)], but that of rainout is not made clear. One of the reasons for the nonclearness of rainout process may be due to the fact that by rainout the acidification of the cloud droplets progresses not only in the grown-up stage, in which the treatment of the mass transfer is rather easy, but also in the generation and growing stages, in which it is difficult to take the mass transfer into accout. The rate of acidification of cloud droplets is supposed to vary with these various stages of droplet formation.

MATHEMATICAL MODEL AND GOVERNING EQUATIONS

The cloud droplets treated here are those which are formed without the occurrence of the ice phase in cloud. Such cloud droplets are usually formed in the maritime air mass (near the Japan Islands, there are the two air mass. One is Ogasawara air mass in summer and another is Okhotsk air mass in the rainy season which appears during transition from spring to summer and during autumn) produced over the ocean and they can make the precipitation called warm rain. Due to the lack of the sufficient theoretical information to construct the mathematical model, the drop freezing process (i.e., ice crystal process), which occurs often in the course of cloud formation, is not treated here, although cold rain and snow formed via the freezing process may also contribute to the mass trasfer between the atmosphere and the earth. It is supposed that especially in winter the great snowfall along the coast of Japan Sea contributes to enhancing the acidic deposition on the coast area (winter is considered to be rather dry season in the Pacific side of Japan). The snow is brought about by Siberian cold air mass (it is a continental air mass and contains clay minerals which serve as the ice-forming nuclei) which is supplied much water vapor from Japan Sea on the way to Japan and can make much snowfall on the coast area.

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 (7)]. However, supersaturation as high as several hundred percent would be necessary for drop formation in homogeneous water vapor, but typically supersaturation remains below 10% and most often even below 1% in the atmosphere. According to Raoult's Law [Atkins (2)], aerosol particles are capable of initiating drop formation at the observed low supersaturation, because they can reduce the drop phase vapor pressure lower than the atmospheric vapor pressure. This process is a heterogeneous nucleation. Such aerosol particles which enable vapor to condense into droplet are called cloud condensation nuclei (CCN). Ammonium sulfate $(NH_4)_2SO_4$ is a well known major CCN, which is formed by the gas phase chemical reaction of $SO_2(g)$ with $NH_3(g)$ [Kim et al. (4)] and is very soluble in water. Owing to oceangoing ships, over the ocean of the northern hemisphere the concentration of $SO_2(g)$ is considerably high to form much of $(NH_4)_2SO_4$ [Corgett et al. (3)]. Another major CCN is sea salt NaCl, but it is supposed that the concentration of $(NH_4)_2SO_4$ is three times as high as that of NaCl [Mason (5)].

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

$$\frac{\partial \rho_{\mathrm{w}}}{\partial t} = \mathcal{D}_{\mathrm{w}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \rho_{\mathrm{w}}}{\partial r}\right) \tag{1}$$

$$\rho_{\mathrm{w}} C_{\mathrm{pw}} \frac{\partial T_{\mathrm{w}}}{\partial t} = k_{\mathrm{w}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial T_{\mathrm{w}}}{\partial r}\right) \tag{2}$$

$$e_{\mathrm{vx}} = \rho_{\mathrm{vx}} \frac{\mathcal{R}_1}{M_{\mathrm{w}}} T_{\mathrm{x}} \tag{3}$$

where, t = time (sec); r = radial coordinate (cm); T_{w} = droplet temperature (°K); T_{a} = surface temperature of droplet (°K); $\mathcal{D}_{\mathrm{v}}$ = diffusion coefficient of water vapor (cm^2/sec); k_{w} = thermal conductivity of water (cal/sec/cm/°K); ρ_{w} and ρ_{vx} = density of water and water vapor at T_{x}, respectively (g/cm^3); C_{pw} = specific heat of water at constant pressure (cal/g/°K); e_{vx} = water vapor pressure at T_{x} (atm); $\mathcal{R}_1$ = universal gas constant (= 82 atm/cm^3/mol/°K); and M_{w} = molecular weight of water (g/mol).

The boundary conditions for the above two partial differential equations (Eqs. 1 and 2) are given at the interface between solid and liquid (i.e., the nucleus and the droplet) ($r = a_\mathrm{s}$) and at the interface between liquid and gas (i.e., the outer surface of the droplet) ($r = a$). At $r = a_\mathrm{s}$ they are given as:

$$-\mathcal{D}_\mathrm{w}\frac{\partial \rho_\mathrm{w}}{\partial r} = 0 \tag{4}$$

$$-k_\mathrm{s}\frac{\partial T_\mathrm{s}}{\partial r} = -k_\mathrm{w}\frac{\partial T_\mathrm{w}}{\partial r} \tag{5}$$

At $r = a$ they are given as:

$$-\mathcal{D}_\mathrm{w}\frac{\partial \rho_\mathrm{w}}{\partial r} = -\mathcal{D}_\mathrm{v}\frac{\partial \rho_\mathrm{v}}{\partial r} \tag{6}$$

$$-k_\mathrm{w}\frac{\partial T_\mathrm{w}}{\partial r} = -k_\mathrm{v}\frac{\partial T_\mathrm{v}}{\partial r} - \frac{\mathrm{L_e} j_\mathrm{w}}{4\pi a^2} \tag{7}$$

where, $\mathrm{L_e}$ = latent heat of phase change (cal/g); and j_w = mass flux of water vapor (g/s).

Integrating Eqs. 1 and 2 with respect to r and inserting the boundary conditions into the resulting equations, the simultaneous ordinary differential equations are obtained as follows:

$$\frac{\mathrm{d}m_\mathrm{w}}{\mathrm{d}t} = 4\pi\mathcal{D}_\mathrm{v} a(\rho_{\mathrm{v}\infty} - \rho_\mathrm{va}) = j_\mathrm{w} \tag{8}$$

$$\frac{\mathrm{d}Q_\mathrm{w}}{\mathrm{d}t} = 4\pi k_\mathrm{v} a(T_\infty - T_\mathrm{a}) + \mathrm{L_e} j_\mathrm{w} \tag{9}$$

where, T_∞ = temperature of the atmosphere (° K); m_w = mass of droplet (g); and Q_w = heat of droplet (cal).

Once m_w is known, the droplet radius a is easily obtained by:

$$m_\mathrm{w} = \rho_\mathrm{w}\frac{4\pi}{3}(a^3 - a_\mathrm{s}^3) \tag{10}$$

where, a_s = radius of nucleus (cm), which is reduced by aquatic dissolution with lapse of time and should be estimated using the solubility and the droplet volume at every time step of the integration. Mass flux j_w in Eqs. 7, 8 and 9 is given as [Pruppacher & Klett (7)]:

$$j_\mathrm{w} = \frac{4\pi\ a\ \mathcal{D}_\mathrm{v}\ M_\mathrm{w}\ e_\mathrm{sat.w}(T_\infty)}{\mathcal{R}_1 T_\infty}\left[S(T_\infty) - \frac{T_\infty}{T_\mathrm{a}}\ F\right] \tag{11}$$

$$F = \exp\left\{\frac{\mathrm{Le}\ M_\mathrm{w}(T_\mathrm{a} - T_\infty)}{\mathcal{R}_2\ T_\mathrm{a}\ T_\infty} + \frac{2M_\mathrm{w}\ \sigma}{\mathcal{R}_3\ T_\mathrm{a}\ \rho_\mathrm{w}\ a} - x_\mathrm{s}\right\} \tag{12}$$

where, $e_\mathrm{sat.w}$ = equilibrium water vapor pressure (atm); S = saturation ratio of moist air with respect to a plane water surface (–); σ = surface tension of droplet (= 75.7 dyn/cm); $\mathcal{R}_2$ = universal gas constant (=1.858 cal/mol/ ° K); and $\mathcal{R}_3$ = universal gas constant (= 8.314×10^7 erg/mol/ ° K). Saturation ratio S and mole ratio x_s are given as follows:

$$S(T_\infty) = \frac{e_\infty(T_\infty)}{e_\mathrm{sat.w}(T_\infty)} \quad ; \qquad x_\mathrm{s} = \frac{\nu\ n_\mathrm{s}}{n_\mathrm{w}} \tag{13),(14}$$

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 $(\mathrm{NH_4})_2\mathrm{SO_4}$ is dissociated almost completely as follows:

$$(\mathrm{NH_4})_2\mathrm{SO_4} \rightleftharpoons 2\mathrm{NH_4^+} + \mathrm{SO_4^{2-}} \tag{15}$$

Therefore, it can be assumed that one mole of $(\mathrm{NH_4})_2\mathrm{SO_4}$ produces two moles of $\mathrm{NH_4^+}$ and one mole of $\mathrm{SO_4^{2-}}$ and that ν = 3. In order to compare the rate of time variation of Q_w with that of m_w, the dimensionless times $\hat{t}_\mathrm{m}$ and $\hat{t}_\mathrm{Q}$ are defined from Eqs. 8 and 9 as follows:

$$\hat{t}_\mathrm{m} = \frac{t\ \mathcal{D}_\mathrm{v}}{a^2} \quad ; \qquad \hat{t}_\mathrm{Q} = \frac{t\ k_\mathrm{v}}{\rho_\mathrm{w} C_\mathrm{pw}\ a^2} \tag{16),(17}$$

$\hat{t}_\mathrm{m}$ and $\hat{t}_\mathrm{Q}$ characterize the time scales of m_w and Q_w variations, respectively. From the above two equations the ratio of $\widehat{t}_{\mathrm{Q}}$ to $\widehat{t}_{\mathrm{m}}$ is evaluated as:

$$\frac{\widehat{t}_{\mathrm{Q}}}{\widehat{t}_{\mathrm{m}}} = \frac{k_{\mathrm{v}}}{\mathcal{D}_{\mathrm{v}}\, \rho_{\mathrm{w}}\, C_{\mathrm{pw}}} = 2.40 \times 10^{-4} \tag{18}$$

This small value ($\ll 1$) shows that the rate of time variation of Q_{w} is overwhelmingly greater (more rapid) than that of m_{w}. Therefore, as a matter of fact it is supposed that Q_{w} attains the quasi-steady state at considerably early stage compared with m_{w}. Then, approximating as $\mathrm{d}Q_{\mathrm{w}}/\mathrm{d}t = 0$, from Eq. 9 the next relation can be taken:

$$T_{\mathrm{a}}(t) \approx T_{\infty}(t) + \frac{\mathrm{L_e}\, j_{\mathrm{w}}}{4\pi\, k_{\mathrm{v}}\, a} \tag{19}$$

In fact, except for very early stage, $T_{\mathrm{a}}(t)$ values by Eq. 9 are almost equal to those by Eq. 19.

The equilibrium radius of cloud droplet a_{e} can be estimated from Eq. 11. As in equilibrium state the droplet ceases from growing, $j_{\mathrm{w}} = 0$ in Eq. 11. And more, it is evident that droplet temperature becomes equal to that of the surroundings in the equilibrium state, i.e., $T_{\mathrm{a}} = T_{\infty}$. Therefore, from Eq. 11, the next equation can be taken:

$$\exp\left(\frac{2M_{\mathrm{w}}\, \sigma}{\mathcal{R}_3\, T_{\infty}\, \rho_{\mathrm{w}}\, a_{\mathrm{e}}} - x_{\mathrm{s}}\right) = S \tag{20}$$

where, $\mathcal{R}_3$ = universal gas constant (=8.314×10^{7} erg/mol/°K). It is not so easy to solve the above equation with respect to a_{e}, because x_{s} is the function of a_{e}. However, the above equation can be rewritten as follow:

$$a_{\mathrm{e}} = \frac{2M_{\mathrm{w}}\sigma}{\mathcal{R}_3\, T_{\infty}\, \rho_{\mathrm{w}}(x_{\mathrm{s}} + \ln S)} \tag{21}$$

If $x_{\mathrm{s}} = 0$ (i.e., without CCN), the process is the homogeneous nucleation and Eq. 21 is reduced to Kelvin's equation [Asai et al. (1)]. As most often $S < 1.01$, it can be approximated that $\ln S \approx \Delta S$, denoting $S = 1 + \Delta S$. Then, approximating that $\ln S \approx S - 1$ and substituting Eq. 14 into Eq. 20, Köhler equation [Asai et al. (1)] can be taken as:

$$S = 1 + \frac{2M_{\mathrm{w}}\, \sigma}{\mathcal{R}_3\, T_{\infty}\, \rho_{\mathrm{w}}\, a_{\mathrm{e}}} - \frac{3\nu m_{\mathrm{s}} M_{\mathrm{w}}}{4\pi M_{\mathrm{s}} \rho_{\mathrm{w}}\, a_{\mathrm{e}}^3} \tag{22}$$

It is rather nuisance to solve the above cubic equation with respect to a_{e}, though it is feasible. If the water vapor pressure over the droplet $e_{\mathrm{sat.w}}$ (saturated) can be approximated to be equal to that of surroundings e_{∞} (supersaturated for condensation), i.e., $S \approx 1$ (or $\ln S \approx 0$), it is very simple to solve Eq. 22 (or Eq. 21) with respect to a_{e}. As in fact it is said that usually $S < 1.01$, this approximation is not so unreasonable one. Substituting Eq. 14 into Eq. 21 under this approximation, a_{e} is given as follows:

$$a_{\mathrm{e}} = \left(\frac{3\nu\, \mathcal{R}_3\, T_{\infty}\, m_{\mathrm{s}}}{8\pi\, \sigma\, M_{\mathrm{s}}}\right)^{\frac{1}{2}} = \left(\frac{\mathcal{R}_3\, T_{\infty} \nu \rho_{\mathrm{s}}}{2\sigma\, M_{\mathrm{s}}}\right)^{\frac{1}{2}} \times a_{\mathrm{s0}}^{\frac{3}{2}} \tag{23}$$

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

NUMERICAL SIMULATION OF CLOUD DROPLET GROWTH

Integrating Eqs. 1 and 2 with respect to r to obtain the spatially-lumped governing equations (Eqs. 8 and 9), the time variations of the droplet radius a and the droplet temperature T_{a} can be simulated numerically. The variation of the droplet radius is considerably large, but that of the temperature (in °K) from the initial value is very small. Then, in order to demonstrate the variations clearly, the dimensionless radius $\widehat{a}(t)$ and the temperature increment $\Delta T_{\mathrm{a}}(t)$ are defined as follows:

$$\widehat{a}(t) = \frac{a}{a_{\mathrm{e}}} \quad ; \qquad \Delta T_{\mathrm{a}}(t) = T_{\mathrm{a}} - T_{\infty} \qquad \text{(24),(25)}$$

Although usually the equilibrium radius a_{e} is approximated value, $\widehat{a}$ 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 of $\widehat{a}(t)$ is exactly unity. It is evident that the value of $\Delta T_{\mathrm{a}}(t)$ approaches zero ultimately.

The physical properties used in this simulation are tabulated in Tables 1 and 2. As the variation of droplet temperature T_{a} is small, these values of physical properties are assumed to be constant in the numerical simulations and the values at 0 ° C are used.

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

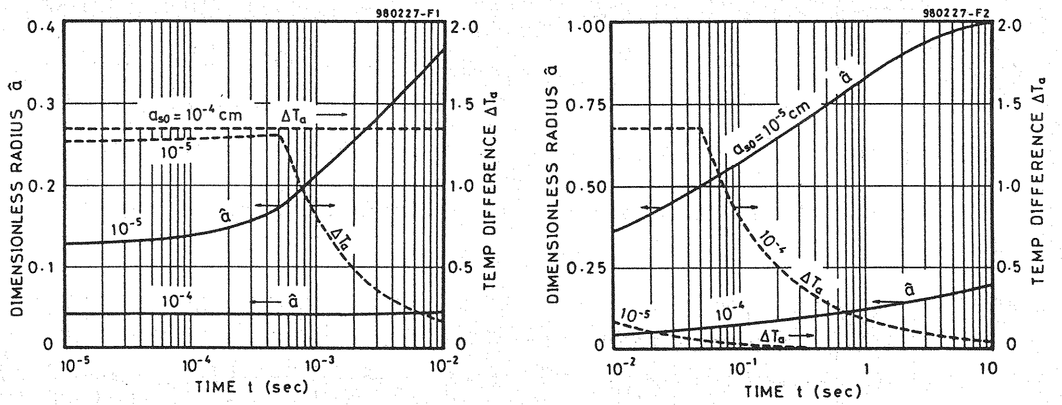
$\mathcal{D}_{\mathrm{v}}$ (cm^2/s)	k_{v} (cal/s/cm/° K)	ρ_{s} (g/cm^3)	ρ_{w} (g/cm^3)	σ (dyn/cm)
0.251	6×10^{-5}	1.769	1.0	75.7

$\mathcal{R}_1$ (atm/cm^3/mol/° K)	$\mathcal{R}_2$ (cal/mol/° K)	$\mathcal{R}_3$ (erg/mol/° K)	L_e (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

With use of the mathematical model 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 $\widehat{a}(t)$ and that of the increment of droplet temperature $\Delta T_{\mathrm{a}}(t)$ are shown in Fig. 1. Solid curves are for $\widehat{a}(t)$ and broken curves are for $\Delta T_{\mathrm{a}}(t)$.



(a): $t = 10^{-5} \sim 10^{-2}$ sec

(b): $t = 10^{-2} \sim 10$ sec

Fig. 1 Time Variations of Dimensionless Radius of Droplet $\widehat{a}$ and Temperature Increment ΔT_{a}

From the solid curve for the small nucleus (the initial radius $a_{s0} = 10^{-5}$ cm) in Fig. 1, it can be seen that $\widehat{a}$ (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, in case of the cloud formation by the droplets condensed on large nuclei, such phenomena as collision, coalescence and raining caused by the droplets may take place before the droplets get their equilibrium size. In Table 3 these equilibrium droplet sizes are tabulated along with the time required to reach the equilibrium state.

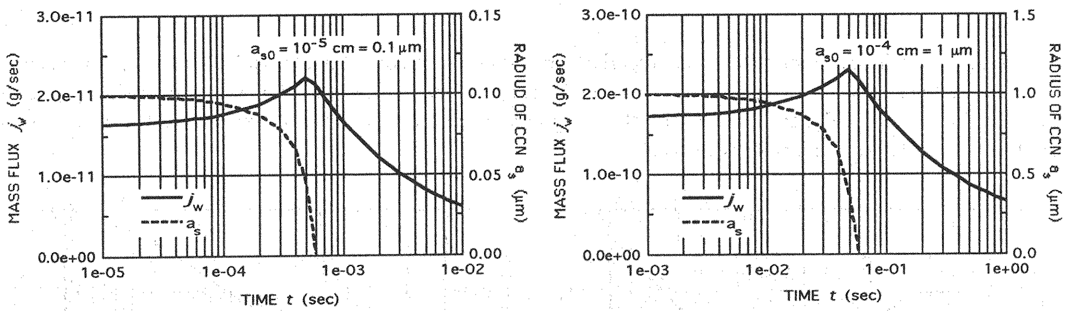
Fig. 2 shows the time variations of the mass flux j_{w} and the CCN radius a_{s}. The solid curve is for j_{w} and the broken one is for a_{s}. The numerical results show that the mass flux of water vapor condensed on $(NH_4)_2SO_4$

(i.e., j_w) increases monotonously from the begining of the condensation until it gets the maximum value. As is seen from these curves in Fig. 2, at the time j_w gets the maximum, solid-phase $(NH_4)_2SO_4$ disappears and j_w starts to diminish gradually to zero. In Fig. 3 the time variation of j_w is compared with that of ΔT_a. The solid curve is for j_w and the broken one is for ΔT_a. 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 Eqs. 8 and 9.

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

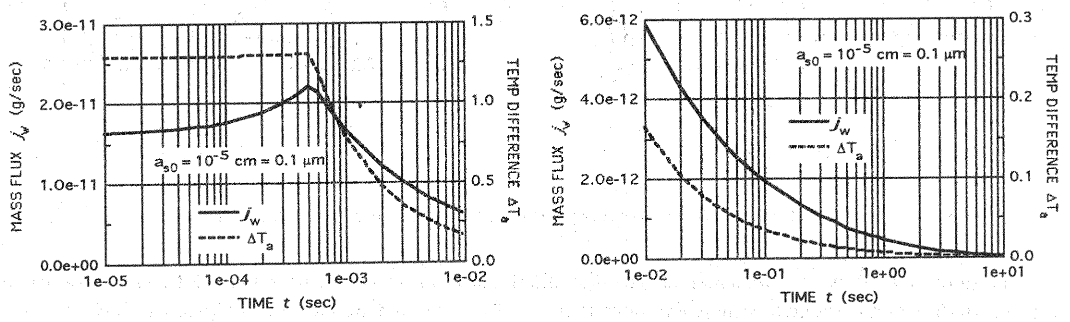
a_{s0} (cm)	a_e (cm)	$t_{0.99e}$ (sec)	$\Delta T_{a.max}$ (°C)	$t_{\Delta Ta.max}$ (sec)
10^{-5}	7.765×10^{-5}	$\sim 2.5 \times 10^1$	1.30	$\sim 5 \times 10^{-4}$
10^{-4}	2.456×10^{-3}	$\sim 2.5 \times 10^5$	1.35	$\sim 5 \times 10^{-2}$

$t_{0.99e}$ = 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.



(a): $a_{s0} = 10^{-5}\text{cm} = 0.1\mu\text{m}$ (b): $a_{s0} = 10^{-4}\text{cm} = 1\mu\text{m}$

Fig. 2 Time Variations of Mass Flux j_w and CCN Radius a_s



(a): $t = 10^{-5} \sim 10^{-2}$ sec (b): $t = 10^{-2} \sim 10$ sec

Fig. 3 Time Variations of Mass Flux j_w and Temperature Increment ΔT_a

The temperature increment ΔT_a is not so large as seen from the broken curves in Fig. 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 for 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 is supposed to be considerably difficult, because the measuring apparatus must possess incredibly quick response to the time variation.

The time variations of radius of solid salt (a_s) within droplet are shown by the broken curve in Fig. 2 [(a): $a_{s0} = 10^{-5}\mathrm{cm} = 0.1\mu\mathrm{m}$ and (b): $a_{s0} = 10^{-4}\mathrm{cm} = 1\mu\mathrm{m}$]. The initial radius ($a_{s0}$) of small condensation nucleus and the large one are 10^{-5} cm and 10^{-4} cm, respectively. It takes about 6×10^{-4} sec for the solid portion of the small nucleus to disappear completely ($a_s = 0$) from the droplet. The large nucleus ($a_{s0} = 10^{-4}$ cm) dissolves completely in about 6×10^{-2} sec. These times required for disappearance of solid salt are nearly equal to the times when ΔT_a becomes maximum, i.e., $t_{\Delta T\mathrm{a.max}}$ (see Table 3). ΔT_a shown in Figs. 1 and 3 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 time solid $(NH_4)_2SO_4$ exists within 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_∞.

CONCLUSIONS

From the numerical simulation of the generation and growth process of cloud droplet due to the condensation of the atmospheric water vapor on $(NH_4)_2SO_4$, it is supposed that the transfers of the water mass and the heat energy 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 former is very fast and in fact the temperature can be approximated to be in quasi-steady state;
2. The larger the initial size of the condensation nucleus a_{s0} is, the larger the equilibrium size of the cloud droplet a_e becomes;
3. If the saturation ratio of the atmospheric vapor pressure is close to unity (i.e., $S \approx 1$), the equilibrium size of cloud droplet 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) and then there may exist error in the estimation of nonsteady droplet radius by the Köhler equation; and
5. When the solid nucleus disappears and the liquid-phase salt concentration begins to decrease, the droplet temperature also starts to decrease.

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APPENDIX-NOTATION

The following symbols are used in this paper;

a = radius of cloud droplet;
a_e = equilibrium radius of cloud droplet;
a_s = radius of condensation nucleus [$(NH_4)_2SO_4$];
a_{s0} = initial radius of condensation nucleus;
$\hat{a}$ = dimensionless raius of cloud droplet;
C_{pw} = specific heat of water at constant pressure;
$\mathcal{D}_v$ = diffusion coefficient of water vapor;
e_{vx} = water vapor pressure at T_x;
$e_{sat.w}$ = equilibrium water vapor pressure;
e_∞ = water vapor pressure of surrounding air;
j_w = mass flux of water vapor;
k_w = thermal conductivity of water;
L_e = latent heat of phase change;
m_s = mass of salt;
m_w = mass of droplet;
M_s = molecular weight of salt;
M_w = molecular weight of water;
n_s = moles of salt;
n_w = moles of water;
Q_w = heat of droplet;
r = radial coordinate;
$\mathcal{R}_1$ = universal gas constant (= 82 atm/cm^3/mol/° K);
$\mathcal{R}_2$ = universal gas constant (= 1.858 cal/mol/° K);
$\mathcal{R}_3$ = universal gas constnat (= 8.314 erg/mol/° K);
S = saturation ratio of moist air with respect to a plane water surface;
t = time;
$t_{0.99e}$ = 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;
T_a = surface temperature of droplet;
T_w = droplet temperature;
T_∞ = temperature of the atmosphere;
ΔT_a = temperature increment;
ν = vant' Hoff factor;

ρ_w = density of water;
ρ_{vx} = density of water vapor at T_x; and
σ = surface tension of cloud droplet.

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