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ACIDIFICATION OF CLOUD DROPLET DUE TO SO_2(g) ABSORPTION IN PERIOD OF CONDENSATIONAL GROWTH WITH WATER VAPOR

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SYNOPSIS

In order to investigate the acidification process of cloud droplets due to rainout (in cloud scavenging, i.e., mass transfer) of air pollutants, the characteristics of the rainout of SO_2(g) by the growing single cloud droplet are simulated numerically with use of a mathematical model. The mathematical model is constituted from the mass and energy conservation equations, the state equation for ideal gas and the equation of drop-phase chemical reactions. $(NH_4)_2SO_4$ particle is selected for the cloud condensation nucleus (CCN), which is the major aerosol and produced from NH_3(g) and SO_2(g) via gas-phase chemcal reaction in the atmosphere. Time dependent droplet radius, pH value, temperature and concentrations of various chemicals are simulated numerically. The droplet growth is closely connected with the saturation ratio in the atmosphere (S) and the mole ratio of the salt [dissolved CCN, i.e., $(NH_4)_2SO_4$] in the droplet (x_s). And the propulsion for the absorption of SO_2(g) is the concentration difference between the droplet [SO_2(aq)] and the atmosphere [SO_2(g)]. It is confirmed by the numerical simulation that the salt concentration of the droplet (hence, x_s) controls the acidification of the cloud droplet ($[H^+]$) by rainout of SO_2(g) as well as the growth (a) by the condensation of water vapor, although little is known about rainout compared with washout (below cloud scavenging).

INTRODUCTION

Evapo-transpiration of liquid water and condensation of water vapor are indispensable for the transportation of the water and its dissolved substances between the atmosphere and the earth surface, even though the transported amount of the water (precipitation) is only a small part of the surface water over the earth such as oceans, lakes, rivers and so forth. The polluted gaseous and particulate substances emitted into the atmosphere are scavenged by the cloud droplets (rainout) and rain drops (washout) and trasferred from the atmosphere to the surface and subsurface water on the ground through the rainfall. In this way, rainfall plays an important role in transportation of the atmospheric pollutants as well as water itself.

Recently, the study on rainfall hydrology in connection with the water circulation between the atmosphere and the ground has considerably progressed especially in the microscopic teatment as is seen in the analysis of the vertical profile of the rain drop size distribution [Nakagawa et al. (6)]. Such microscopic treatment in rainfall processes is also effective approach for the estimation of the pollutant mass transfer between the atmosphere and the rainwater (below-cloud scavenging). For rainfall volume prediction it is recognized that the cloud process is important as well as the rainfall process. The same is true for rainwater quality prediction, because the in-cloud scavenging considerably contributes to the rainfall quality. For the precise prediction of the rainfall runoff on the ground in early stage as the result of the rainfall event, it is considered that rainfall events should be correlated with the cloud formation due to the condensation of water vapor in the atmosphere. In fact, the study on the rainfall prediction method utilizing the knowledge of convective cloud processes has been started by some advanced researchers in the rainfall hydrology [Oishi et al. (8)].

Two mass transfer processes are considered to control the quality of rainwater. The first is the mass transfer process between cloud droplets and the atmosphere (rainout, i.e., in-cloud scavenging) and the second is the mass transfer process between the rain drops and the atmosphere (washout, i.e., below-cloud scavenging). The unsteady scavenging process of washout (the second process) has been made considerably clear [Shiba et al. (9), (10) and (11)], but that of rainout, which is performed in such various stages of cloud droplet formation (the first process) as generating, growing and equilibrium stages, has not been made clear yet. This is because rainout of pollutants by cloud droplets progresses not only in the grown-up (equilibrium) stage, in which the volume of the cloud droplet can be assumed constant, but also in the generating and growing stages, in which cloud droplets increase their volumes rapidly and the estimation of the mass transfer is difficult. The rate of rainout by cloud droplets is supposed to vary considerably with these three stages in the droplet formation, and the rate is not necessarily in the equilibrium state. Then, it is important to make clear the pollutant mass transfer process in the stages of the generation and the growth of cloud droplets. In these stages the atmospheric water vapor is condensed actively and unstably into cloud droplets. The model equations for rainout should be composed considering the time variations of the rates of the mass transfer and the liquid-phase chemical reaction in addition to the time variation of the droplets volume.

According to the survey of the past works, it is no exaggeration to say that no study on the acidification of growing cloud droplets correlates the time variations of the chemical compositions in cloud droplets with the processes of the generation and growth of the cloud droplets. In this study the rainout of growing cloud droplets is treated theoretically and a mathematical model is constructed, based on the physico-chemical considerations. The model is mainly composed of the mass conservation equations for water and chemicals and the heat energy conservation equation. About the physical properties of cloud droplets in the equilibrium state, many studies have been made so far from the point of view of cloud physics. Kelvin's equation [Asai et al. (1)] is one of the representatives of such works. In this study the unsteady phenomena such as growth and acidification of cloud droplets are the matter of primary concerns, which have not been studied sufficiently in the present cloud physics. The cloud condensation neucleus (CCN) is assumed to be $(NH_4)_2SO_4$, which is made from gaseous pollutants NH_3(g) and SO_2(g) and the major aerosol in the atmosphere. The acidification process of the growing cloud droplet due to rainout of SO_2(g) is simulated numerically with the mathematical model.

MATHEMATICAL MODEL OF CLOUD DROPLET ACIDIFICATION IN GROWING STAGE

The mathematical model of the acidification of growing cloud droplets is composed of two main parts. The one is the equation that describes the volume change (due to condensation of the atmospheric water vapor) of the cloud droplet, which is accompanied by the equation of the heat energy. The other is the equation which describes the variations of the concentrations of chemical species in the cloud droplet, and is supported by the equations of chemical reactions of the absorption and dissociation of SO_2(g) in the cloud droplet.

First of all it should be cleared that the cloud droplets treated here are those formed without the ice-phase period in their growth and they are able to become the precipitation called warm rain. Such cloud droplets are usually formed in the maritime air mass produced over the ocean. There are two famous maritime air masses near the Japan Islands. One is Ogasawara air mass formed in summer, the other is Okhotsk air mass formed in the rainy season.

Due to the lack of the sufficient theoretical information to construct the mathematical model, the drop freezing process (ice crystal process) is not treated here, although the process occurs often in the course of cloud formation and can make cold rain and snow. Cold rain and snow formed via the freezing process 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 coastal area. However, winter is considered to be rather dry season in the Pacific side of Japan. The snow is brought about by Siberian cold air mass. Siberian cold air mass is a continental air mass and contains a lot of clay minerals which serve as the ice-forming nuclei. Siberian cold air mass is supplied with much water vapor from Japan Sea on the way to Japan and can make much snowfall on the coastal area.

Another important condition attached to the numerical simulations is that the cloud droplet interactions are not considered here. That is, the processes of droplet growth by condensation of the water vapor are considered exclusively. The processes of growth by collision and coalescence and of collisional breakup are not treated here.

Governing Equations for Cloud Droplet Mass (Condensation of 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 droplet is generated, the flux of water vapor goes on entering into the droplet, since the vapor pressure of the atmosphere (supersaturated) is greater than the pressure over the droplet surface (saturated). This process is a homogeneous nucleation and has been studied well from a thermodynamic point of view [Pruppacher & Klett (7)]. However, supersaturation as high as several hundred percent would be necessary for droplet 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 liquid 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)].

Equations of conservation for mass and heat energy

The governing equations for the cloud droplet formation by the condensation of water vapor are composed of the equations of mass conservation and heat energy conservation [see Shiba et al. (12)]. In lumped form they are given as ordinary differential equations as follows:

$$\frac{dm_\mathrm{w}}{dt} = 4\pi\mathcal{D}_\mathrm{v}a(\rho_\mathrm{ve} - \rho_\mathrm{va}) = j_\mathrm{v} \tag{1}$$

$$\frac{dQ_\mathrm{w}}{dt} = 4\pi k_\mathrm{v}a(T_\mathrm{ve} - T_\mathrm{va}) + L_\mathrm{e}j_\mathrm{v} \tag{2}$$

where, t = time (sec); m_w = mass of droplet (g); Q_w = heat accumulated in droplet (cal); a = radius of droplet (cm); ρ_v = density of water vapor (g/cm^3); $\mathcal{D}_\mathrm{v}$ = diffusion coefficient of water vapor (cm^2/sec); T_v = temperature of water vapor (K); k_v = thermal conductivity of water vapor (cal/sec/cm/K); L_e = latent heat of phase change (cal/g); and j_v = mass flux of water vapor (g/s). The suffixes, w, v, e and a, denote liquid water (i.e., droplet), water vapor, atmosphere and droplet surface, respectively. The similar results are obtained by Pruppacher & Klett (7).

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

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

where, ρ_w = density of droplet (g/cm^3); and a_s = radius of solid-phase CCN (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 of water vapor j_v in Eqs. 1 and 2 is given as [Pruppacher & Klett (7)]:

$$j_\mathrm{v} = \frac{4\pi a\mathcal{D}_\mathrm{v}M_\mathrm{w}e_\mathrm{sat.w}(T_\mathrm{e})}{\mathcal{R}_1T_\mathrm{e}}\left\{S(T_\mathrm{e}) - \frac{T_\mathrm{e}}{T_\mathrm{a}}F\right\} \tag{4}$$

$$F = \exp\left\{\frac{L_\mathrm{e}M_\mathrm{w}(T_\mathrm{a} - T_\mathrm{e})}{\mathcal{R}_2T_\mathrm{a}T_\mathrm{e}} + \frac{2M_\mathrm{w}\sigma}{\mathcal{R}_3T_\mathrm{a}\rho_\mathrm{w}a} - x_\mathrm{s}\right\} \tag{5}$$

where, $e_\mathrm{sat.w}$ = equilibrium water vapor pressure (atm); S = saturation ratio of moist air with respect to a plane water surface (–); x_s = mole ratio of salt $(NH_4)_2SO_4$ and its dissociations (NH_4^+ and SO_4^{2-}) to water (–); σ = surface tension of droplet (= 75.7 dyn/cm); M_w = molecular weight of water (= 18 g/mol); $\mathcal{R}_1$ = universal gas constant (= 82 atm/cm^3/mol/K); $\mathcal{R}_2$ = 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:

$$S(T_\mathrm{e}) = \frac{e_\mathrm{e}(T_\mathrm{e})}{e_\mathrm{sat.w}(T_\mathrm{e})} \tag{6}$$

$$x_\mathrm{s} = \frac{\nu n_\mathrm{s}}{n_\mathrm{w}} \tag{7}$$

where, e_e = water vapor pressure of surrounding air (atm); ν = van't Hoff factor (–); n_s = moles of salt (mol); and n_w = moles of water (mol). Van't Hoff factor varies with the chemical composition of CCN. In the aqueous solution, $(NH_4)_2SO_4$ is dissociated almost completely as follows:

$$(\mathrm{NH_4})_2\mathrm{SO_4} \rightleftharpoons 2\mathrm{NH_4^+} + \mathrm{SO_4^{2-}} \tag{8}$$

Eq. 8 shows that two moles of NH_4^+ and one mole of SO_4^{2-} are produced from one mole of $(NH_4)_2SO_4$. Therefore, van't Hoff factor ν for this CCN is 3.

Equilibrium radius of cloud droplet

The equilibrium radius of cloud droplet (a_e) can be estimated from Eq. 4. As in equilibrium state the droplet ceases growing, $j_\mathrm{v} = 0$ in Eq. 4. Furthermore, it is evident that droplet temperature becomes equal to that of the surroundings in the equilibrium state, i.e., $T_\mathrm{a} = T_\mathrm{e}$. Therefore, changing a in Eq. 4 to a_e, the next equation can be taken:

$$\exp\left(\frac{2M_\mathrm{w}\,\sigma}{\mathcal{R}_3\,T_\mathrm{e}\,\rho_\mathrm{w}\,a_\mathrm{e}} - x_\mathrm{s}\right) = S \tag{9}$$

It is not so easy to solve the above equation with respect to a_e, because x_s is also the function of a_e. However, the above equation can be rewritten as follow:

$$a_\mathrm{e} = \frac{2M_\mathrm{w}\sigma}{\mathcal{R}_3 T_\mathrm{e}\rho_\mathrm{w}(x_\mathrm{s} + \ln S)} \tag{10}$$

If $x_\mathrm{s} = 0$ (i.e., without CCN), the process is the homogeneous nucleation and Eq. 10 is reduced to Kelvin's equation [Asai et al. (1)]. As in general $S < 1.01$, 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. 7 into Eq. 9, Köhler equation [Asai et al. (1)] can be taken as:

$$S = 1 + \frac{2M_\mathrm{w}\,\sigma}{\mathcal{R}_3\,T_\mathrm{e}\,\rho_\mathrm{w}\,a_\mathrm{e}} - \frac{3\nu m_\mathrm{s} M_\mathrm{w}}{4\pi M_\mathrm{s}\rho_\mathrm{w} a_\mathrm{e}^3} \tag{11}$$

where, M_s = molecular weight of salt, i.e., $(NH_4)_2SO_4$ (g/mol). If the water vapor pressure over the droplet $e_\mathrm{sat.w}$ (saturated) can be approximated to be equal to that of surroundings e_e (supersaturated for condensation), i.e., $S \approx 1$ (or $\ln S \approx 0$), it is very simple to solve Eq. 11 (or Eq. 10) 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. 7 into Eq. 10 under this approximation, a_e is given as follows:

$$a_\mathrm{e} \approx \left(\frac{3\nu\,\mathcal{R}_3\,T_\mathrm{e}\,m_\mathrm{s}}{8\pi\,\sigma\,M_\mathrm{s}}\right)^{1/2} = \left(\frac{\mathcal{R}_3 T_\mathrm{e}\nu\rho_\mathrm{s}}{2\sigma M_\mathrm{s}}\right)^{\frac{1}{2}} \cdot (a_\mathrm{s0})^{\frac{3}{2}} \tag{12}$$

where, a_s0 = initial radius of cloud 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, i.e., a_s0.

Governinig Equations for Cloud Droplet Concentration (Acidification of Cloud Droplet)

The governing equations for concetrations of chemical species in cloud droplets are derived from the mass conservation law (i.e., macroscopic mass balance) of chemical species. The equations are ordinary differential equations and are composed of mass transfer between the atmosphere and the cloud droplet, the liquid-phase chemical reactions and the accumulation of chemicals. The form of the equation for the chemical reactions varies with the pollutant gas (e.g., $SO_2(g)$, $HNO_3(g)$, $H_2O_2(g)$ and so forth) absorbed by the cloud droplet. Therefore, first of all, the pollutant absorbed must be specified.

Chemical reactions in cloud droplet

When sulfur dioxide gas $SO_2(g)$ is absorbed into cloud droplets, it is dissociated to produce H^+, HSO_3^- and SO_3^{2-}. Therefore H^+ concentration in droplets is raised (pH value is lowered). After the two steps of dissociation, the resulting concentrations in droplets reach equilibrium with a given air phase concentration of $SO_2(g)$. The sequence of process can be described as follows:

$$\mathrm{SO_2(g) + H_2O \rightleftharpoons SO_2(aq)} \qquad (\mathcal{H}_1) \tag{13}$$

$$\mathrm{SO_2(aq) \rightleftharpoons HSO_3^- + H^+} \qquad (\mathrm{K}_1) \tag{14}$$

$$\mathrm{HSO_3^- \rightleftharpoons SO_3^{2-} + H^+} \qquad (\mathrm{K}_2) \tag{15}$$

where, $\mathcal{H}_1$ = distribution coefficient (= 30.32); and K_1 and K_2 = first and second dissociation constants (= 1.74×10^{-2}M and 6.24×10^{-8}M at 25 °C, respectively). Eqs. 13, 14 and 15 correspond to the absorption of $SO_2(g)$ by cloud droplets, the first step of the dissociation and the second step of the dissociation, respectively. The total concentration of $SO_2(g)$, HSO_3^- and SO_4^{2-} equilibrates with the atmospheric concentration of $SO_2(g)$.

For convenience of expression the concentrations of chemical species produced in cloud droplets and in the atmosphere are defined as follows:

$$(\, C_1, C_2, C_3, C_6, C_{1\mathrm{G}} \,) = (\, [\mathrm{SO_2(aq)}], [\mathrm{HSO_3^-}], [\mathrm{SO_3^{2-}}], [\mathrm{H^+}], [\mathrm{SO_2(g)}] \,) \tag{16}$$

From Eqs. 13 – 15 three equilibrium relations in cloud droplets can be taken. They are represented as:

$$\mathcal{H}_1 \cdot C_{1\mathrm{G}} = C_1 \tag{17}$$

$$\mathrm{K}_1 \cdot C_1 = C_2 \cdot C_6 \tag{18}$$

$$\mathrm{K}_2 \cdot C_2 = C_3 \cdot C_6 \tag{19}$$

The ions in the cloud droplet must satisfy the electroneutrality condition as given by:

$$C_6 = C_2 + 2C_3 + \frac{\mathrm{K_w}}{C_6} + \alpha \tag{20}$$

where, α = constant determined by the initial concentrations of ions in the cloud droplet (mol/l); and K_w = dissociation constant for water (= $10^{-14}M^2$). The value of α for the natural water is supposed to depend mainly on the atmospheric concentration of carbon dioxide gas $CO_2(g)$ ($\alpha = 0$ for pure water).

From the above equation C_6 can be taken as:

$$C_6 = \frac{1}{2}\left\{\left[(C_2 + 2C_3 + \alpha)^2 + 4\mathrm{K_w}\right]^{1/2} + (C_2 + 2C_3 + \alpha)\right\} \tag{21}$$

Once C_6 is obtained by Eq. 21, new equilibrium concentrations easily calculated by Eqs. 18 and 19.

Conservation equations of chemical species in cloud droplet

From a macroscopic mass balance (i.e., conservation) of chemical species i in a cloud droplet, the governing equation in a lumped form for C_i can be taken as follows:

$$\frac{d(V_\mathrm{w} \cdot C_\mathrm{i})}{dt} = A_\mathrm{w} \cdot k_{\mathrm{Gi}} \left(C_{\mathrm{iG}} - \frac{C_\mathrm{i}}{\mathcal{H}_\mathrm{i}} \right) + V_\mathrm{w} \cdot R_\mathrm{i} \tag{22}$$

where, V_w = volume of liquid-phase portion of cloud droplet (cm^3); A_w = surface area of cloud droplet (cm^2); and k_{Gi} = gas-phase mass trasfer coefficient for chemical species i (cm/s). The first term of the right hand side of Eq. 22 represents the mass transfer between the atmosphere and the cloud droplet. The second term represents the source and sink due to the chemical reactions in the cloud droplet. The left hand side of Eq. 22 is the mass accumulated in the cloud droplet.

The expression of the chemical reaction rate R_i varies with the pollutant absorbed by the cloud droplet. As the pollutant gas is assumed to be $SO_2(g)$, R_i's are written as follows:

$$R_1 = -k_{1+}C_1 + k_{1-}C_2C_6 \tag{23}$$

$$R_2 = k_{1+}C_1 - k_{1-}C_2C_6 - k_{2+}C_2 + k_{2-}C_3C_6 \tag{24}$$

$$R_3 = k_{2+}C_2 - k_{2-}C_3C_6 \tag{25}$$

where, k_{i+} and k_{i-} = forward and backward reaction rates, respectively, and satisfy the relation, $K_i = k_{i+}/k_{i-}$.

The initial condition for Eq. 22 simply specifies the uniform concentration of chemical species in the cloud droplet as:

$$C_k = C_{k0} \quad \text{at} \quad t = 0 \tag{26}$$

The concentration of hydrogen ion (i.e., the acidity: $pH = -\log_{10}[H^+]$) of the cloud droplet can be estimated by integrating Eqs. 1, 2 and 22 simultaneously.

NUMERICAL SIMULATION BY MATHEMATICAL MODEL

Using the mathematical model developed here, numerical simulations were performed. The simulations were carried out under the following conditions: initial radius of CCN (a_{s0}) = 10^{-5} cm; atmospheric concentration of $SO_2(g)$ (C_{1G}) = 10 ppb; saturation ratio of moist air (S) = 1.0; ambient temperature (T_e) = 0 ° C; total pressure of atmosphere = 0.692 atm (equivalent to the pressure at the altitude 2.0 km); and initial concentrations of droplet $SO_2(aq)$ (C_{10}), HSO_3^- (C_{20}), SO_3^{2-} (C_{30}) and H^+ (C_{60}) = 0, 0, 0 and 10^{-7} (mol/l), respectively.

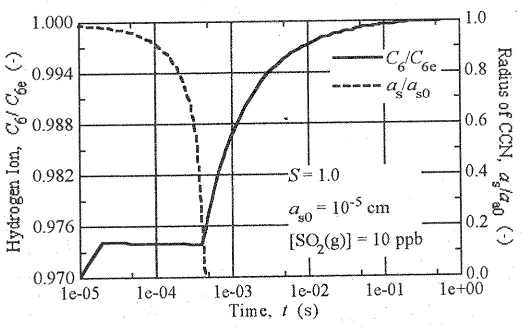

Fig. 1 Time variations of hydrogen ion concentration and decreasing CCN size

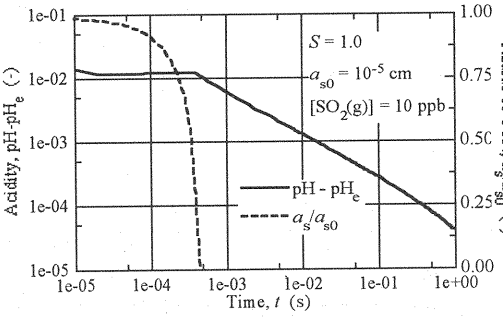

Fig. 2 Time variations of increment of pH and dcreasing CCN size

Shown in Fig. 1 is the time variation of the hydrogen ion concentration in the cloud droplet. The left ordinate is the dimensionless hydrogen ion concentration (C_6/C_{6e}), which is obtained by normalizing the hydrogen ion concentration (C_6) by the equilibrium hydrogen ion concentration (C_{6e}). The right ordinate is the dimensionless radius of solid CCN (a_s/a_{s0}) normalized by the initial radius of CCN (a_{s0}). The abscissa is the lapse of time (in second) from the start of the condensation on CCN (t). The solid curve is for the dimensionless hydrogen concentration C_6/C_{6e} and the broken curve is for the dimensionless radius of CCN a_s/a_{s0}. Therefore, both curves should range from zero to one in their values and it is seen that they do so. The concentration C_i, which is calculated from the mass of the chemical $V_w \cdot C_i$ estimated by Eq. 22, should take some definite positive value even in very early time (in close vicinity of the origin of time). However, it is difficult to calculate the precise value of the concentration C_i in very early time, because the droplet volume V_w is so small that the division of the mass $V_\mathrm{w} \cdot C_\mathrm{i}$ by V_w causes considerable error and oscillation in the estimated C_i. Therefore, in Fig. 1 the ascending short line drawn from the left lower corner does not represent the rigorous concentration, but is drawn tentatively instead of the missing values.

After 5×10^{-4} sec the concentration changes the trend drastically in its value and ultimately approaches to the equilibrium value (i.e., unity). At the time, when the concentration changes to increase, the solid CCN disappears completely as is shown by the broken curve. This suggests that CCN plays an important role in the acidification process of cloud droplets. During the existence of the solid part of CCN in the droplet, the concentration of $(NH_4)_2SO_4$ (to be exact, the total concentratin of $(NH_4)_2SO_4$, NH_4^+ and SO_4^{2-}) is equal to the constant value (saturated concentration), while the concentration of $(NH_4)_2SO_4$ decreases after the disappearance of the solid CCN from the droplet.

When the solid CCN disappeares because of the dissolution into the surrounding condensed liquid water which originates in the condensation of water vapor of the atmosphere, the concentration of $(NH_4)_2SO_4$ in the cloud droplets starts to decrease in its value (i.e., value of x_s) because of the dilution by the condensed liquid water. That is, the propelling power to increase the vapor flux j_v given by Eq. 4 is weaken due to the increase of the liquid volume. While the solid CCN exists in the droplet, the rate of condensation is so large that the condensed liquid water dilutes the concentration of the hydrogen ion, as is seen from the slightly descending solid curve in the region from 2×10^{-5} to 5×10^{-4} sec (Fig. 1). After the disappearance of solid CCN the concentration of hydrogen ion is not decreased at all. On the contrary, it increases drastically as is seen from the jump of the solid curve in Fig. 1. Besides this outstanding feature, it can be seen from the time variation of CCN radius (a_s) that the solid CCN disappeares in so short time as 0.4 or 0.5 ms (broken curve). The hydrogen ion concentration (C_6) also attains more than 98 % of the equilibrium concentration ($C_{6\mathrm{e}}$) in so short time as 1 ms.

The solid curve in Fig. 2 shows the time variation of the acidity (i.e., $[H^+]$) in the cloud droplet in terms of pH value. pH is given by the relation as $\mathrm{pH} = -\log_{10}([\mathrm{H}^+])$. Then, it should be noted that the smaller the pH value becomes, the higher the acidity is. The left ordinate is the difference between pH and $\mathrm{pH_e}$ (equilibrium value of pH), i.e., the quantity which is obtained by adding inverse sign (i.e., multiplying -1) to the common logarithm of the dimensionless hydrogen ion concetration ($C_6/C_{6\mathrm{e}}$). The broken curve represents the dimesionless radius of CCN, which is plotted for reference as in the case of Fig. 1. Before the disappearance of the solid CCN ($2\times10^{-5} < t < 5\times10^{-4}$ sec), pH increases (the acidity decreases) gradually, which is so small to detect at a glance. However, after the disappearance of the solid CCN, pH decreases (the acidity increases) sharply with lapse of time.

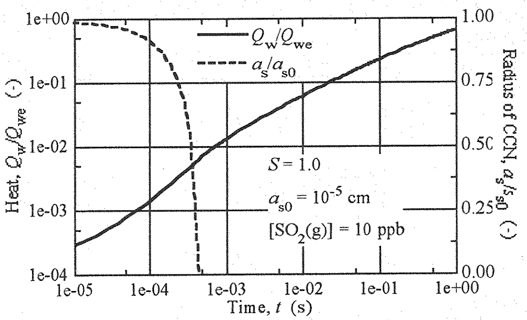

Fig. 3 Time variations of heat accumulation and decreasing CCN size

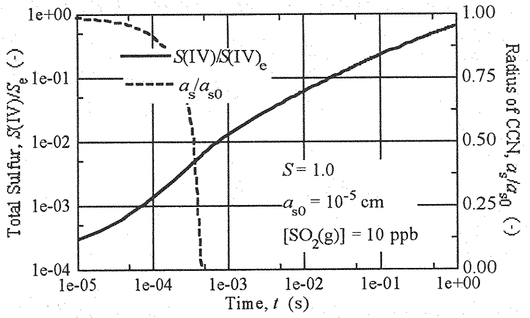

Fig. 4 Time variations of total sulfur and dcreasing CCN size

The time variation of the heat accumulated in the cloud droplet is shown in Fig. 3 by the solid curve. The curve represents the dimensionless heat $Q_\mathrm{w}/Q_\mathrm{we}$ normalized by dividing Q_w with Q_we. During the whole range shown in this figure the dimensionless heat accumulation increases almost linearly. No remarkable change is seen in this increasing trend. Moreover the rate of time variation of the heat accumulation is slow as 1.2 % in 1 ms, compared with the rate of time variation of the hydrogen ion concentration (98 % in 1 ms).

The solid curve in Fig. 4 demonstrates the time variation of the absorption of $SO_2(g)$. In this figure the absorption is estimated by the total amount of $[SO_2(aq)]$, $[HSO_3^-]$ and $[SO_3^{2-}]$ in the cloud droplet. This quantity is denoted as S(IV) and called as ’total sulfur’. The left ordinate is the dimensionless total sulfur, S(IV)/S(IV)$_e$, in which S(IV)$_e$ is the equilibrium total sulfur. The solid curve in Fig. 4 [S(IV)/S(IV)$_e$] is almost the same as the solid curve in Fig. 3 (Q_w/Q_{we}). This coincidence is expected, because it is due to the similarity between the heat transfer (Q_w/Q_{we}) and the mass transfer [S(IV)/S(IV)$_e$]. This coincidence is supposed to support the validity of the results of the simulation using the mathematical model developed here. It is because the relation between the simulation rerult of Fig. 3 and that of Fig. 4 satisfy the similarity which must be realized in the correct calculations.

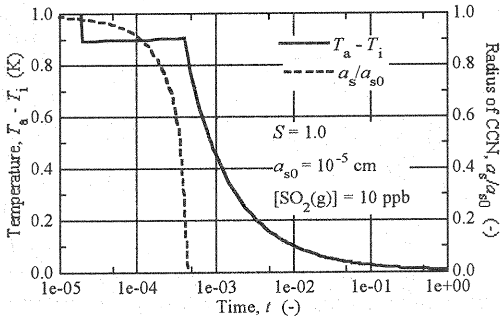

Fig. 5 Time variations of droplet temperature and decreasing CCN size

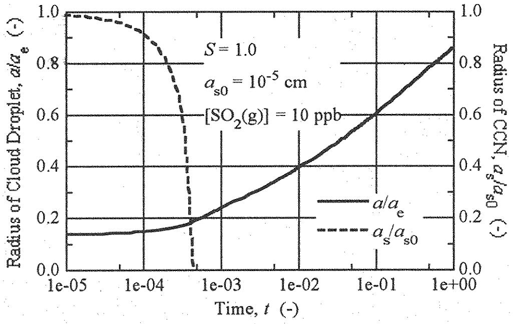

Fig. 6 Time variations of droplet radius and dcreasing CCN size.

The solid curve in Fig. 5 shows the time variation of the temperature of the cloud droplet. The temperature is represented by the difference from the ambient temperature (T_e), i.e., $T_a - T_e$. Immediately after the start of the growth, it is considered that T_e rises to some value almost instantaneouly. However, the rise is not shown here, because in the vicinity of the origin of the time the numerical calculation of the pricise temperature is very difficult. And then, during the existence of solid CCN ($2 \times 10^{-5} < t < 5 \times 10^{-4}$ sec) it increases slowly by a very small amount. However, after the disappearance of the solid CCN, the temperature decreases rapidly. When the solid CCN disappears, the liquid-phase salt concentration [total concentration of $(NH_4)_2SO_4$ and its dissociations NH_4^+ and SO_4^{2-}] begins to decrease. Then the droplet temperature also starts to decrease. The manner of the increase and decrease of the temperature may be interpreted in similar way as is done in the case of the hydrogen ion concentration.

The time variation of the cloud droplet radius (a) is shown in Fig. 6 by the solid curve. It is represented by the dimensionless radius, a/a_e (the left ordinate), which is normalized by the equilibrium radius (a_e). According to the simility between the mass transfer of chemical species and the heat trasfer, it is supposed that the variation of radius (a/a_e) coincides with the variations of the cube root of the quantities ($\{Q_w/Q_{we}\}^{1/3}$ and $\{S(IV)/S(IV)_e\}^{1/3}$) plotted in Fig. 3 for the heat accumulated and Fig. 4 for the total sulfur absorbed. It is because the cube root of the cloud droplet volume, i.e., $V_w^{1/3}$, hence that of mass and heat, is proportional to the radius a. In reality, as is supposed the normalized radius (Fig. 6) coincides with the cube root of the normalized mass (Fig. 4) and that of the normalized heat (Fig. 3), i.e., $a/a_e = \{S(IV)/S(IV)_e\}^{1/3}$ and $a/a_e = \{Q_w/Q_{we}\}^{1/3}$ to show the validity of the numerical simulations.

CONCLUSIONS

A mathematical model has been developed, based on the consideration of the physico-chemical mass and heat transfer. Using the mathematical model, the acidification process of the growing cloud droplet has been investigated for the absorption of SO_2(g) by condensed water on $(NH_4)_2SO_4$ particle. From the results of the numerical simulation, it is concluded that:

1. The time variations of the hydrogen ion concentration (C_6) and that of the cloud droplet temperature (T_a) exhibit drastical change in their trends, comparing the variations before and after of the disappearance of the solid CCN. In other words, the concentration of the dissolved CCN plays an important role in the time variations of the hydrogen ion concentration and the cloud droplet temperature;
2. On the other hand, the time variations of the heat accumulation (Q_w) and the absorption of SO_2(g) [S(IV)]

increase in the same manner and the time variations are almost linear during the growth, regardless of the disappearance of the solid CCN;

3. The time required to attain the equilibrium concentration of the hydrogen ion is considerably short (in 1 ms, 99 % of the equilibrium value is obtained), compared with the time required to obtain the equilibrium radius of the cloud droplet (in 1 ms, 23 % of the equilibrium value is obtained); and
4. The similarity between the heat trasfer (accumulation of the heat) and the mass transfer [condensation of the atmospheric water vapor and the absorption of $SO_2(g)$] is confirmed by the numerical simulation using the mathematical model developed here.

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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 cloud condensation nucleus (CCN) [solid $(NH_4)_2SO_4$];
a_{s0} = initial radius of cloud condensation nucleus;
A_w = surface area of cloud droplet;
C_i = concentration of chemical species i in cloud droplet;
C_{i0} = initial concentration of chemical species i in cloud droplet;
C_{ie} = equilibrium concentration of chemical species i in cloud droplet;

C_{iG} = concentration of chemical species i in the atmosphere;
$\mathcal{D}_{\mathrm{v}}$ = diffusion coefficient of water vapor;
e_{e} = water vapor pressure of surrounding air;
$e_{\mathrm{sat.w}}$ = saturated water vapor pressure;
e_{vx} = water vapor pressure at T_{x};
F = function defined by Eq. 5;
$\mathcal{H}_1$ = distribution coefficient of $SO_2(g)$;
j_{v} = mass flux of water vapor;
k_{Gi} = gas-phase mass transfer coefficient of chemical species i;
k_{v} = thermal conductivity of vapor;
$k_{\mathrm{i+}}$ = forward reaction rate constant;
$k_{\mathrm{i-}}$ = backward reaction rate constant;
$\mathrm{K_i}$ = dissociation constant of chemical species i;
$\mathrm{K_w}$ = dissociation constant of water;
L_{e} = latent heat of phase change;
m_{s} = mass of salt;
m_{w} = mass of droplet (pure water);
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 accumulated in cloud droplet;
Q_{we} = equilibrium heat accumulated in cloud droplet;
R_{i} = rate of chemical reaction of chemical species i;
$\mathcal{R}_1$ = 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;
$S(\mathrm{IV})$ = total sulfur define by $S(\mathrm{IV}) = [SO_2(aq)] + [HSO_3^-] + [SO_4^{2-}]$;
$S(\mathrm{IV})_{\mathrm{e}}$ = equilibrium total sulfur;
t = time;
T_{a} = droplet temperature;
T_{e} = ambient temperature;
T_{va} = temperature of water vapor at droplet surface;
T_{ve} = temperature of water vapor in surroundings;
V_{w} = volume of liquid portion of cloud droplet;
x_{s} = mole ratio defined by Eq. 7;
α = constant in electroneutrality condition (defined by Eq. 20);
ν = van't Hoff factor;
π = ratio of circumference of circle to diameter;
ρ_{va} = density of water vapor at droplet surface;
ρ_{ve} = density of water vapor in surroundings;
ρ_{w} = density of water; and
σ = surface tension of cloud droplet.

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