Effect of liquid-phase oxidation of sulphur dioxide on acidification of growing cloud droplet

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Abstract

Cloud droplets grow by condensation of atmospheric water vapor into themselves, during which they absorb also atmospheric pollutants as SO₂(g) and H₂O₂(g). In order to estimate the contribution of liquid-phase oxidation during growth to cloud droplet acidity, the oxidation of HSO₃⁻ to SO₄²⁻ by H₂O₂(aq) is investigated numerically, using a mathematical model based on physicochemical considerations. The results of the numerical simulations show that: (1) the time variation of [H⁺] behaves as if it attained the equilibrium state, although after a while it breaks the state to increase (i.e., there is a plateau in the curve of [H⁺] vs time); (2) the contribution of the oxidation to the cloud droplet acidity increases with lapse of time; (3) the larger the initial radius of CCN is, the smaller the contribution of the oxidation becomes; and (4) the quasi-equilibrium [H⁺] is reached much faster than the equilibrium droplet radius.

1 Introduction

The chemical substances inhered in rainwater, which are scavenged in the atmosphere, are the important pollution sources of the water on the ground. However, traditional works on the model to estimate quantitatively the rainwater quality (Orel and Seinfeld [1]; Adamowicz [2]; and Shiba [3]) seem to be insufficient, because they lack the scavenging in the early stage of cloud droplet formation (condensational growth with absorption of gaseous pollutants).
The substances contained in rain drops originate from such scavenging processes in the atmosphere as rainout (in-cloud scavenging) and washout (below-cloud scavenging). Rainout should include the scavenging during the stages of generation and growth of cloud droplets. The non-steady generation and growth of cloud droplets condensed on the cloud condensation nuclei [CCN, e.g., (NH$_4$)$_2$SO$_4$, a typical particulate atmospheric pollutant] is governed by mass (water and chemical species) and heat conservation law.

Acidity is an important index of quality of rainwater as is supposed from various acid rain issues. Acid rain causes a lot of damages not only to various ecosystems as lakes, forest, and so on in rural districts but also to human health and architecture in urban districts. The purpose of this study is to investigate the acidification of cloud droplets during the generation and growth by constructing a mathematical model and simulating the acidification numerically by the model, from the viewpoint of the interaction between air and water pollutions.

2 Modeling of cloud droplet acidification

2.1 Chemical framework

2.1.1 Dissociation of sulfur dioxide

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 concentration in droplets reach equilibrium with a given air phase concentration of SO$_2$(g). The sequence of process can be described as follows (Peters [4]):

\[ \text{SO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2(\text{aq}) \quad (\text{H}_1) \]
\[ \text{SO}_2(\text{aq}) \rightleftharpoons \text{HSO}_3^- + \text{H}^+ \quad (K_1) \]
\[ \text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+ \quad (K_2) \]

where, $H_1$ = distribution coefficient (= 30.32); and $K_1$ and $K_2$ = first and second dissociation constants (= $1.74 \times 10^{-2}$M and $6.24 \times 10^{-8}$M at 25 °C, respectively).

2.1.2 Dissociation of hydrogen peroxide

For H$_2$O$_2$(g) the sequence can be described as follows:

\[ \text{H}_2\text{O}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2(\text{aq}) \quad (\text{H}_5) \]
\[ \text{H}_2\text{O}_2(\text{aq}) \rightleftharpoons \text{HO}_2^- + \text{H}^+ + \text{H}_2\text{O} \quad (K_5) \]

where $H_5$ = distribution coefficient (= $1.73 \times 10^7$); and $K_5$ = dissociation constant (= $1.84 \times 10^{-12}$ M at 25 °C).
2.1.3 Oxidation in cloud droplet
Oxidation of HSO$_3^-$ by H$_2$O$_2$(aq) is given by (Martin and Damschen [5]):

$$\text{HSO}_3^- + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{SO}_4^{2-} + \text{H}^+ + 2\text{H}_2\text{O} \quad (k^* = k[\text{H}^+])$$

(6)

where \(k\) = reaction rate constant (\(= 5.2 \times 10^7 \text{ M}^{-2}\text{s}^{-1}\) at 25 °C).

2.1.4 Concentration of chemical species
Unknown concentrations in cloud droplets are defined as follows:

\[
(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8)
= ([\text{SO}_2(\text{aq})], [\text{HSO}_3^-], [\text{SO}_4^{2-}], [\text{SO}_3^{2-}], [\text{H}_2\text{O}_2(\text{aq})], [\text{H}^+], [\text{HO}_2^-], [\text{OH}^-])
\]

(7)

Known concentrations of atmospheric gaseous pollutants are defined as follows:

\[
(C_{1G}, C_{6G}) = ([\text{SO}_2(\text{g})], [\text{H}_2\text{O}_2(\text{g})])
\]

(8)

Because \(C_8\) can be estimated from ionic product as \(C_8 = K_w/C_6\) (\(K_w\): ionic product of water), hereafter \(C_8\) is excluded from unknowns.

2.1.5 Electroneutrality condition on chemical species
Electroneutrality condition, which is said to hold closely in aqueous electrochemical solutions, is adopted in this model. The mathematical model developed here is lumped with respect to space variable (i.e., without advection and diffusion) and \(C_k\) is treated as an uniform concentration in the cloud droplet at any time. Then, electroneutrality is assumed to hold strictly true even in non-steady state.

2.2 Mathematical framework
2.2.1 Governing equation of condensational growth
In the atmosphere the excess water vapor over the saturated vapor pressure condenses into liquid water and forms droplets. This process is a homogeneous nucleation and has been studied well from a thermodynamic point of view (Pruppacher and Klett [6]). If droplet contains such salt as (NH$_4$)$_2$SO$_4$, H$_2$SO$_4$, 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. Particulate (NH$_4$)$_2$SO$_4$, whose usual size ranges from about 0.1\mu m to 1.0\mu m, 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.

There are some useful works for the modeling of the cloud droplet formation due to the condensation of the atmospheric water vapor (Kulmala et al. [7]; Korhonen et al. [8]; and Vesala et al. [9]). The governing equations for the droplet formation by the condensation are composed of the equations of mass conservation.
and heat conservation. Neglecting the heat of chemical reactions, they are given in the lumped forms with respect to space variable as:

\[ \frac{dm_w}{dt} = 4\pi D_v a (\rho_v - \rho_v a) = j_w \]  \tag{9}

\[ \frac{dQ_w}{dt} = 4\pi k_v a (T_a - T_d) + L_a j_w \]  \tag{10}

where, \( a \) = radius of droplet (cm); \( t \) = time (s); \( j_w \) = mass flux of water vapor (g/s); \( m_w \) = mass of droplet (g); \( D_v \) = diffusion coefficient of water vapor (cm\(^2\)/s); \( Q_w \) = heat of droplet (J); \( k_v \) = thermal conductivity of water vapor (J/(s.cm.K)); \( T_a \) = atmospheric temperature (K); \( T_d \) = droplet temperature of (K); \( L_a \) = latent heat of phase change between vapor and liquid (J/g).

### 2.2.1.1 Mass flux of water vapor

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 (Pruppacher and Klett [6]):

\[ j_w = \frac{4\pi a D_v M_w e_{sat.w}(T_a)}{R_1 T_a} \left[S(T_e) - \frac{T_a}{T_d} F \right] \]  \tag{11}

\[ F = \exp \left\{ \frac{L e_{sat.w}(T_d - T_e)}{R_2 T_d} + \frac{2 M_w \sigma}{R_3 T_d \rho_w a} - x_a \right\} \]  \tag{12}

where, \( e_{sat.w} \) = equilibrium water vapor pressure (Pa); \( S \) = saturation ratio of moist air with respect to a plane water surface (\( )\); \( R_1, R_2 \) and \( R_3 \) = universal gas constant (=8.472 m\(^3\)Pa/(mol.K), 7.804 J/(mol.K) and 8.314 \times 10^2 N/(mol.K), respectively); \( \sigma \) = surface tension (N/m); and \( x_a \) = mole ratio of salt (CCN) to solvent water (\( )\).

Saturation ratio \( S \) and mole ratio \( x_a \), which control the mass flux of water vapor and hence the growth of cloud droplets, are given as follows:

\[ S(T_e) = \frac{e_a(T_e)}{e_{sat.w}(T_e)} \]  \tag{13}

\[ x_a = \frac{\nu n_s}{n_w} \]  \tag{14}

where, \( e_a \) = vapor pressure of surrounding air (Pa); \( \nu \) = van’t Hoff factor (\( )\); \( n_s \) = moles of CCN salt (mol); and \( n_w \) = moles of liquid water (mol). As in the aqueous solution \((NH_4)_2SO_4\) is dissociated almost completely, \( \nu \) is assumed to be 3.

### 2.2.1.2 Radius of cloud droplet

Inserting \( j_w = 0 \) and \( T_d = T_a \) into eqn (11), the equilibrium radius \( a_e \) can be obtained as eqn (15) without any integration (e.g., \( a_e = 0.777 \mu m \) for \( 0.1 \mu m \) CCN). Once \( m_w \) is obtained as a function of time \( t \) by integrating eqns (9) and (10) simultaneously, the time varying radius of cloud...
droplet $a(t)$ can be easily estimated. $a_s$ and $a(t)$ are given by:

$$a_s = \frac{2M_w \sigma}{R_3 T_a \rho_w (x_a + \ln S)} ; \quad a(t) = \left( \frac{3m_w(t)}{4\pi \rho_w} + a_s^3 \right)^{1/3} \quad (15), (16)$$

where $a_s$ = solid CCN radius (cm).

### 2.2.2 Governing equation of acidification

During the growth, cloud droplets absorb also such atmospheric gaseous pollutants as $\text{SO}_2(g)$ and $\text{H}_2\text{O}_2(g)$. In consequence of the pollutant absorption, drop-phase chemical reactions occur and the cloud droplet are acidified.

Macroscopic mass conservation of chemical species is given as follows as:

$$\frac{dm_k}{dt} = V_w R_k + 4\pi a^2 k_{Gk} \left( C_{kG} - \frac{C_k}{H_k} \right) \quad (17)$$

where $m_k$ = mass of chemical species (mol); $R_k$ = rate of chemical reaction (mol/s); $V_w$ = cloud droplet volume (cm$^3$); $k_{Gk}$ = mass transfer coefficient (cm/s); $C_{kG}$ = atmospheric concentration (M); $C_k$ = droplet concentration (M); and $H_k$ = distribution coefficient ($\cdot$). The first term of right hand side is source-sink term ($10^{-3}$ mol/s) and the second one is mass-transfer term ($10^{-3}$ mol/s).

#### 2.2.2.1 Mass transfer coefficient

For the estimation of $k_{Gk}$ the relationship between $k_{Gk}$ and Sherwood Number $Sh_{kG}$ can be used. The relation is given as (Clift et al. [10]):

$$Sh_{kG} = \frac{2a k_{Gk}}{D_{kg}} = 2 + 0.6 Re_{kg}^{1/2} \cdot Sc_{kG}^{1/3} \quad (18)$$

$$Re_{kg} = \frac{2ua}{\nu_{kg}} ; \quad Sc_{kG} = \frac{\nu_{kg}}{D_{kg}} \quad (19), (20)$$

where $D_{kg}$ = gas phase diffusion coefficient (cm$^2$/s); $Re_{kg}$ = Reynolds Number of cloud droplet ($\cdot$); $Sc_{kG}$ = Schmidt Number ($\cdot$); $\nu_{kg}$ = kinematic viscosity (cm$^2$/s); and $u$ = velocity of cloud droplet (cm/s). Therefore, gas phase mass transfer coefficient $k_{Gk}$ is easily estimated, inserting $Re_{kg}$, $Sh_{kG}$, $D_{kg}$ and $a$ into eqn (18).

#### 2.2.2.2 Liquid-phase chemical reaction

From the liquid-phase chemical reactions described by eqns (2), (3), (5) and (6) the reaction rates, $R_k$, are given as:

$$R_1 = -k_{1+} C_1 + k_{1-} C_2 C_6 \quad (21)$$

$$R_2 = k_{1+} C_1 - k_{1-} C_2 C_6 - k_{2+} C_2 + k_{2-} C_3 C_6 - k C_2 C_5 C_6 \quad (22)$$

$$R_3 = -k_{2+} C_2 + k_{2-} C_3 C_6 \quad (23)$$

$$R_4 = k C_2 C_5 C_6 \quad (24)$$
\[ R_5 = -k_{5+}C_5 + k_{5-}C_6C_7 - kC_2C_5C_6 \quad (25) \]
\[ R_6 = k_{1+}C_1 - k_{1-}C_2C_6 - k_{2+}C_2 + k_{2-}C_3C_6 + k_{5+}C_5 - k_{5-}C_6C_7 + kC_2C_5C_6 \quad (26) \]
\[ R_7 = k_{5+}C_5 - k_{5-}C_6C_7 \quad (27) \]

where \( k_{k\pm} \) = forward and backward reaction rate constant.

### 2.2.3 Initial conditions

Initial conditions for the governing equations [eqns (9), (10) and (17)] are given as:
\[ m_w(0) = 0; \quad Q_w(0) = 0; \quad m_k(0) = 0 \quad (28), (29), (30) \]

Once \( m_k(t) \) is obtained, \( C_k(t) \) is estimated as \( C_k = m_k/V_w \).

### 3 Numerical simulation

Numerical simulations were carried out under the conditions that: initial CCN radius \( \langle a_{60} \rangle = 0.1, 0.2 \) and 0.3 \( \mu \text{m} \); saturation ratio \( (S) = 1.0 \); \( \text{SO}_2(g) \) concentration \( (C_{1G}) = 10 \text{ ppb} \); \( \text{H}_2\text{O}_2(g) \) concentration \( (C_{5G}) = 0.1 \text{ ppb} \); and velocity of cloud droplet \( (u) = 0 \) (i.e., stationary cloud droplet).

#### 3.1 Practical procedure

##### 3.1.1 Estimation of mole ratio of dissolved CCN

At every time step, mole ratio \( x_a \) is estimated as follows: (1) calculate \( n_a \) from dissolved \( \text{(NH}_4\text{)}_2\text{SO}_4 \), which is equilibrium with condensed liquid water \( m_w \) and calculated from the solubility; (2) calculate \( n_w \) from condensed \( m_w \); and (3) obtain \( x_a = \nu n_a/m_w \).

##### 3.1.2 Estimation of concentrations

In the practical calculation procedure adopted here, the unknown constants \( k_{1\pm} \) (i.e., reaction term \( R_k \)) are eliminated from the governing equations. This makes a new set of differential equations about reduced number of new dependent variables (virtual concentrations). The new dependent variables are:
\[ C_{N1} = C_1 + C_2 + C_3; \quad C_{N2} = C_4; \quad C_{N3} = C_5 \mp C_7 \quad (31), (32), (33) \]

Seven governing equation for \( C_k \) are reduced to three for \( C_{Nk} \). From the estimated virtual concentrations \( C_{N1}, C_{N2} \) and \( C_{N3} \), the real concentrations \( C_k \) can be obtained at every time step of the numerical integration, using the equations from the dissociation reactions and the electroneutrality. The dissociation equations are:
\[ K_1 C_1 = C_2 C_6; \quad K_2 C_2 = C_3 C_6; \quad K_5 C_5 = C_7 C_6 \quad (34), (35), (36) \]
The electroneutrality in the form solved with respect to \( C_6 \), is represented as:

\[
C_6 = C_2 + 2C_3 + 2C_4 + C_7 + \frac{K_w}{C_6} + \alpha \quad (37)
\]

where \( K_w \) = dissociation constant for water \( (= 10^{-14} \text{M}^2) \); and \( \alpha \) = constant determined by the initial concentrations of ions \( (\text{M}) \).

The differential form of the electroneutrality, which is equivalent to eqn (37) in the case of lumped model [eqn (17)], is given by:

\[
\sum_{k=1}^{7} z_k \frac{dC_k}{dt} = 0 \quad (38)
\]

where \( z_k \) = charge number of species \( k \) \((-\)). The above differential form is directly derived from the governing equations [eqn (17)] for \( m_k \) (i.e., \( C_k \)) and is not independent of the governing equations (linear dependent). Then, any one of the governing equations must be dropped (in this case, the equation for \( C_6 \) is selected), if the equation for the electroneutrality, eqn (37), is adopted.

### 3.2 Time variation of hydrogen ion concentration

In Figures 1 \((t = 10^{-4} \sim 10^{-1} \text{ s})\) and 2 \((t = 10^{-1} \sim 10^2 \text{ s})\), time variations of dimensionless \([\text{H}^+]\), \( \tilde{C}_6 \) \((= C_6/C_{6e})\), and dimensionless cloud droplet radius, \( \tilde{a} \) \((= a/a_0)\), are demonstrated. \( \tilde{C}_6 \) and \( \tilde{a} \) are normalized by the equilibrium values, \( \hat{C}_{6e} \) and \( \hat{a}_0 \), respectively.

Thick solid curves represent the case with oxidation reaction and thick broken curves the case without oxidation, respectively. In the early stage (Figure 1) both cases take almost the same values till get to the equilibrium values \((\hat{C}_6 = 1)\). This means that the effect of oxidation on the cloud droplet acidity is small in this stage. After the arrival at the equilibrium level the level is maintained for a while \((t = 10^{-1} \sim 1 \text{ s})\), i.e., \( \hat{C}_6 \) with oxidation gets to the quasi-equilibrium state (Figure 2). However, in the oxidation case the acidity \((\hat{C}_6)\) gets out the equilibrium plateau and gradually increases at first with a little increment but intensifies the increments more and more to get to the so high value of 1.65 at \( t = 100 \text{ s} \). It is proved that the oxidation effect on the acidity increases with lapse of time and that it enables to bring about very high acidification of cloud droplet (very low pH).

Thin dotted curves represent the time variations of cloud droplet radius (i.e., \( \tilde{a} \)). \( \tilde{a}(t) \) is increased from the CCN radius (start of the droplet generation) and it increases up to about 0.37 at \( t = 0.01 \text{ s} \). At \( t \sim 25 \text{ s} \) the droplet size attains its equilibrium size \((a_0 = 7.77 \times 10^{-5} \text{ cm})\) given by eqn (15). However, the increase of \( \hat{C}_6(t) \) is more rapid than that of \( \tilde{a}(t) \). And at \( t = 0.01 \text{ s} \) \( \hat{C}_6(t) \) gets so high value of 0.998 compared with 0.37 of \( \tilde{a}(t) \). This means that the acidification of cloud droplet is very fast and that in effect it is accomplished instantaneously.
1.7 Variation of radius of cloud droplet and hydrogen ion concentration (1).

Figure 1: Variation of radius of cloud droplet and hydrogen ion concentration (1).

1.7 Variation of radius of cloud droplet and hydrogen ion concentration (2).

Figure 2: Variation of radius of cloud droplet and hydrogen ion concentration (2).

3.3 Contribution of oxidation to cloud droplet acidity

SO$_4^{2-}$ produced by the droplet-phase oxidation increases [H$^+$] and then it raises the droplet acidity. To measure the contribution of SO$_4^{2-}$ (i.e., oxidation reaction) to the droplet acidity, an index, $E_{ox}$, is defined as:

$$E_{ox} = \frac{2C_4}{C_2 + 2C_3 + 2C_4}$$

The denominator of the above quantity corresponds to total acidity due to HSO$_5^-$, SO$_3^{2-}$ and SO$_4^{2-}$, and the numerator corresponds to acidity due to SO$_4^{2-}$. Then this quantity gives the fractional contribution of SO$_4^{2-}$ to the cloud droplet acidity.

Figures 3 ($t = 10^{-3} \sim 10^{-1}$ s) and 4 ($t = 1 \sim 100$ s) show the time variation of
Figure 3: Contribution of oxidation to cloud droplet acidity (1).

Figure 4: Contribution of oxidation to cloud droplet acidity (2).

The contribution of $SO_4^{2-}$ to the cloud droplet acidity. The curves are plotted parametrically in the initial CCN radius $a_{90}$. For any size of CCN the contribution of oxidation (i.e., $SO_4^{2-}$) increases with lapse of time. This can be guessed from the fact that the oxidation reaction is irreversible and with lapse of time the produced $SO_4^{2-}$ is accumulated more and more in the cloud droplet. However, the smaller CCN size is, the larger the contribution becomes. This is because the production of $SO_4^{2-}$ per unit volume of cloud droplet, which is proportional to the quantity $S_w/V_w$, becomes larger in the smaller size droplet.

The contribution is less than 10 % during about 10 s from the start of the growth (Figure 3). However, it exceeds more than 50 % after lapse of 100 s (Figure 4). This results show that the importance of the droplet-phase oxidation for the acidification of cloud droplets increases with lapse of time (for long life cloud).
4 Conclusions

The results of the numerical simulations show that: (1) the time variation of $[\text{H}^+]$ behaves as if it attained the equilibrium state, although after a while it breaks the state to increase (quasi-equilibrium state, i.e., there is a plateau in the curve of $[\text{H}^+]$ vs time); (2) the contribution of the oxidation to the cloud droplet acidity increases with lapse of time; (3) the smaller the initial radius of CCN, the larger the contribution of the oxidation becomes; and (4) the quasi-equilibrium $[\text{H}^+]$ is reached much faster than the equilibrium droplet radius.

References


