Effect of drop-phase oxidation on raindrop acidification due to washout of sulfur dioxide

S.Shiba, Y. Hirata

Department of Chemical Engineering, Osaka University, Toyonaka, Osaka 560, Japan

Abstract

For the purpose of investigating the effect of the drop-phase oxidation on acid rain formation by washout of gaseous pollutants, a mathematical model based on physico-chemical consideration has been constructed and the dynamics of the acidification has been simulated numerically with use of the model. The model deals with the below-cloud scavenging of the pollutant gases, considering such factors as: (1) the drop-phase chemistry; and (2) the mass transfer at the interface between the drop and the atmosphere. The results of the model simulation have disclosed that: (1) in the early stage of acidification bisulfate ion HSO$_3^-$ is the major species to acidify the drop; and (2) with lapse of time SO$_4^{2-}$ produced by the drop-phase oxidation increases gradually and eventually dominates the raindrop acidity. It is suggested that such a very high acidity as exceeds the acidity equilibrated with the ambient SO$_2$(g), which is often detected in drizzle and fog, should be reasonably attributed to the increase of SO$_4^{2-}$ in the drops.

1 Introduction

The quality of the rainwater in urbanized area gets worse and worse in these days. This is because urbanization is growing so fast and the atmospheric pollutants emitted from the urban area are increasing explosively. Accordingly the pollutants are increased to deteriorate the water quality. Among such atmospheric pollutants acidic species as sulfur dioxide and nitrogen oxide are important, because they form acid rain. Acid rain has been given considerable attention due to the great impact to the various environments, that is, it has not only human health effects but also a number of other effects, including material corrosion and ecosystem interference such as acidification of lakes and streams and interference with
It is well known that acid rain is caused mainly by such air pollutants as sulfur
dioxide and nitrogen oxide. From the global viewpoint, however, the amount of
the sulfur dioxide emitted to the air is much greater than that of nitrogen oxide.
Then in this study the acid rain due to sulfur dioxide is treated exclusively. Sulfur
dioxide is absorbed by cloud or raindrops to dissociate into anions and cations in
two steps and acidify the drops. However, since the dissociation of \( \text{SO}_2 \) in the
drop is limited to the equilibrium concentration to the ambient \( \text{SO}_2 \), in order
to attain a higher acidity than the equilibrium value, it is necessary that \( \text{SO}_2 \)
dissolved in drops is oxidized to sulfate before the deposition on the ground. The
highly soluble hydrogen peroxide \( \text{H}_2\text{O}_2 \), which results from \( \text{HO}_2 \) by the pho-
tolysis of carbonyl compounds (e.g., \( \text{HCHO} \)) in dry atmosphere (Mason[1]), is
a common chemical species and can work for \( \text{SO}_2 \) oxidation in rain drops. The
model developed here, which treats the concurrent absorption of \( \text{SO}_2 \) and
\( \text{H}_2\text{O}_2 \) and the liquid phase chemical reaction, can well simulate the dynam-
ics of acidification of raindrops in this situation, incorporating the pollutant mass transfer rate between the air and the raindrops.

## 2 Chemical transformation of acidifying gases in rain drop

\( \text{SO}_2 \) is chemically transformed by liquid phase reactions, i.e., dissociation and
oxidation, after incorporation into rain drops. The dissociation process are typi-
cally quite fast and the oxidation process could be considerably slower. If \( \text{SO}_2 \) is
absorbed by raindrops, after the two steps of dissociation, the resulting con-
centration in drops reach equilibrium with a given air phase concentration. For
absorption of \( \text{SO}_2 \) the sequence of process can be described as follows (Liss
and Slinn[2]):

\[
\begin{align*}
\text{SO}_2(g) + \text{H}_2\text{O} &\rightleftharpoons \text{SO}_2(\text{aq}) \quad (\gamma_f) \quad (1) \\
\text{SO}_2(\text{aq}) &\rightleftharpoons \text{HSO}_3^- + \text{H}^+ \quad (K_1) \quad (2) \\
\text{HSO}_3^- &\rightleftharpoons \text{SO}_3^{2-} + \text{H}^+ \quad (K_2) \quad (3)
\end{align*}
\]

where \( \gamma_f = \text{distribution coefficient (}= 30.32); \) and \( K_1 \) and \( K_2 \) = first and second
dissociation constants, respectively (= \( 1.74 \times 10^{-2}\text{M} \) and \( 6.24 \times 10^{-8}\text{M} \)).
Consequently sulfur dioxide exists in raindrops as physically dissolved sulfur diox-
ide, \( \text{SO}_2(\text{aq}) \), and in dissociated form as bisulfite ion, \( \text{HSO}_3^- \), and sulfite ion, \( \text{SO}_3^{2-} \).
These values of coefficient and constants are measured at 25°C. When \( \text{H}_2\text{O}_2 \) is
absorbed, the resulting concentration in drops also reach equilibrium as follows:

\[
\begin{align*}
\text{H}_2\text{O}_2(g) + \text{H}_2\text{O} &\rightleftharpoons \text{H}_2\text{O}_2(\text{aq}) \quad (\gamma_f) \quad (4) \\
\text{H}_2\text{O}_2(\text{aq}) &\rightleftharpoons \text{HO}_2^- + \text{H}^+ + \text{H}_2\text{O} \quad (K_5) \quad (5)
\end{align*}
\]

where \( \gamma_f = \text{distribution coefficient (}= 1.73 \times 10^6); \) and \( K_5 \) = dissociation constant
(\( = 1.84 \times 10^{-12}\text{M} \)). On the time scale of the diffusion process, the equilibrium
can be treated as being instantaneously established.
If \( \text{SO}_2(g) \) and \( \text{H}_2\text{O}_2(g) \) are absorbed concurrently, \( \text{HSO}_3^- \) is oxidized by \( \text{H}_2\text{O}_2(aq) \) to become sulfate ion, \( \text{SO}_4^{2-} \), as follows (Maahs[3]):

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

(6)

where \( k^* = \) reaction rate; and \( k = \) reaction rate constant \((= 5.2 \times 10^7 \text{s}^{-1}\text{M}^{-2})\).

Because hydrogen peroxide is often present in low concentrations compared with those of \( \text{SO}_2(g) \), the conversion rate of \( \text{SO}_2(g) \) to \( \text{SO}_4^{2-} \) may be limited by the concentration of \( \text{H}_2\text{O}_2(g) \). Rain water acidity, which is represented by the concentration of \( \text{H}^+ \) or by \( \text{pH} \), reflects a balance between the concentration of acidic anions and those of basic cations. \( \text{SO}_4^{2-} \) is the acidic anion as well as \( \text{HSO}_3^- \) and \( \text{SO}_3^{2-} \) and is supposed to contribute to rain water acidity.

### 3 Working equations of acidification model

The washout processes of pollutant gases are controlled by such various physical and chemical factors as the drop diameter, falling velocity, inner circulation flow (Levich[4]), gas solubility, liquid phase reactions, diffusion in drop and concentrations of chemical species. In this study, however, the complex interacting washout system is represented by chemical equilibrium relations, oxidation reaction, electro-neutrality condition, and mass balance equations to build a tractable model, providing that rigid spherical raindrops fall through the air of uniform gas concentration with the terminal velocity.

The notations used to represent concentrations of chemical species in drops and in the air are:

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

(7)

\[
(C'_{1G}, C'_{5G}) = ([\text{SO}_2(g)], [\text{H}_2\text{O}_2(g)])
\]

(8)

From eqns (1)-(5) three equilibrium relations held in raindrops can be taken as

\[
K_1 \cdot C_1 = C_2 \cdot C_6
\]

(9)

\[
K_2 \cdot C_2 = C_3 \cdot C_6
\]

(10)

\[
K_5 \cdot C_5 = C_7 \cdot C_6
\]

(11)

The charge neutrality condition for anions and cations in drops is

\[
C_6 - C_2 - 2C_3 - 2C_4 - C_7 - K_W/C_6 = \alpha
\]

(12)

where \( K_W = \) dissociation constant for water \((= 10^{-14}\text{M}^2)\); and \( \alpha = \) constant estimated by initial concentrations of ions in drops. Although the concentration of chemical species in raindrops can be estimated by the diffusion model described by partial differential equations (Shiba[5]; Shiba and Hirata[6]), it is considerably time-consuming task to compute the time variation of the concentrations in.
raindrops especially for small drops whose travelling time is long. Therefore, to make the computation time shorter in this study the model is constructed by simple ordinary differential equations as shown below.

With use of the macroscopic mass balance of \( C_i \) in a raindrop the governing equation for chemical species can be taken as follows:

\[
\frac{d(V \cdot C_i)}{dt} = V \cdot R_i + S \cdot k_{G1} \left( \frac{C_{iG}}{\gamma_i} - C_i \right) \tag{13}
\]

\[C_i = C_{i0} \quad \text{at} \quad t = 0 \tag{14}\]

where \( t \) = time; \( V \) = volume of drop (= \( \pi D^3 / 6 \)); \( S \) = surface area of drop (= \( \pi D^2 \)); \( k_{G1} \) = gas phase mass transfer coefficient; \( \gamma_i \) = distribution coefficient; \( D \) = drop diameter; and \( R_i \) = reaction terms given as follows:

\[R_1 = -k_{1+}C_1 + k_{1-C}C_2C_6 \tag{15}\]

\[R_2 = k_{1+}C_1 - k_{1-C}C_2C_6 - k_{2+}C_2 + k_{2-C}C_6 - kC_6C_2C_5 \tag{16}\]

\[R_3 = k_{2+}C_2 - k_{2-C}C_6 \tag{17}\]

\[R_4 = kC_6C_2C_5 \tag{18}\]

\[R_5 = -k_{5+}C_5 + k_{5-C}C_7C_6 - kC_6C_2C_5 \tag{19}\]

\[R_6 = k_{1+}C_1 - k_{1-C}C_2C_6 + k_{2+}C_2 - k_{2-C}C_5C_6 + k_{5+}C_5 - k_{5-C}C_7C_6 + kC_6C_2C_5 \tag{20}\]

\[R_7 = k_{5+}C_5 - k_{5-C}C_7C_6 \tag{21}\]

As in most acid rain \( C_6 \) ranges from \( 10^{-6} \text{M} \) (pH 6) to \( 10^{-3} \text{M} \) (pH 3), it can be assumed that \( C_2 \) is much greater than both of \( C_1 \) and \( C_5 \) and that \( C_5 \) is much higher than \( C_7 \). Making use of these assumptions the governing equations can be reduced to simple dimensionless forms as

\[
\frac{d\tilde{C}_i}{d\tilde{t}} = \tilde{R}_i + \tilde{T}_i \quad (i = 2, 4 \text{ and } 5) \tag{22}\]

\[\tilde{C}_i = \tilde{C}_{i0} \quad \text{at} \quad \tilde{t} = 0 \quad (i = 2, 4 \text{ and } 5) \tag{23}\]

where \( \tilde{R}_i \) = reaction terms and \( \tilde{T}_i \) = mass transfer terms. \( \tilde{R}_i \) and \( \tilde{T}_i \) are given by

\[\begin{align*}
(\tilde{R}_2, \tilde{R}_4, \tilde{R}_5) &= (\tilde{k}_{1+}\tilde{C}_6\tilde{C}_2\tilde{C}_5, \tilde{k}_{1+}\tilde{C}_6\tilde{C}_2\tilde{C}_5, -\tilde{k}_{1+}\tilde{C}_6\tilde{C}_2\tilde{C}_5) \\
(\tilde{T}_2, \tilde{T}_4, \tilde{T}_5) &= \left[ 3\beta_1 \left( \frac{\gamma_{i1}\tilde{C}_{1G} - \tilde{C}_{6i1}}{K_1} \tilde{C}_2 \right), 0, 3\beta_5\beta_5 \left( \frac{\gamma_{i5}\tilde{C}_{5G} - \tilde{C}_5}{} \right) \right]
\end{align*}\tag{24}\]

where \( \tilde{C}_{6i1} \) = value of \( \tilde{C}_6 \) at the drop surface.

The dimensionless variables and constants used in the above equations can be written as

\[\tilde{C}_i = \frac{C_i}{\gamma_{i1}C_{1G}} \tag{26}\]
where $Bi_i$ is the Biot Number for species $i$ and it controls the mass transfer rate of gas between raindrops and the air. Biot Number can be estimated by

$$Bi_i = \frac{k_{Gi} D}{2 \nu_i \delta_i}$$  \hspace{1cm} (29)

$$Sh_{IG} = 2 + 0.6 \frac{Re_G^{1/2}}{Sc_{IG}}$$ \hspace{1cm} (34)

$$Re_G = \frac{u D}{\nu_G}$$ \hspace{1cm} (35)

$$Sc_{IG} = \frac{\nu_G}{\delta_{IG}}$$ \hspace{1cm} (36)

where $Sh_{IG}$ = Sherwood Number; $Re_G$ = Reynolds Number; $Sc_{IG}$ = Schmidt Number; $\nu_G$ = kinematic viscosity of gas; and $u$ = falling velocity of raindrop. $u$ in cm/s is given by

$$u(D) = 958 \left[ 1 - \exp \left( -(D/0.177)^{1.147} \right) \right]$$ \hspace{1cm} (37)

From the above relations $Bi_1$ for $SO_2(g)$ and $Bi_5$ for $H_2O_2(g)$ are formulated as functions of $Re_G$ as

$$Bi_1 = 217.4 + 72.97 Re_G^{1/2}$$ \hspace{1cm} (38)

$$Bi_5 = 3.557 \times 10^{-3} + 1.060 \times 10^{-3} Re_G^{1/2}$$ \hspace{1cm} (39)

Figure 1 shows the relationships between Biot Number and drop diameter. $Bi_1$ is about $10^4$ or $10^5$ times as much as $Bi_5$. This is the reason why the mass transfer rate between the air and drops of $SO_2(g)$ is much greater than that of $H_2O_2(g)$.

Once $\tilde{C}_2$, $\tilde{C}_4$ and $\tilde{C}_5$ are known, the remainders $\tilde{C}_1$, $\tilde{C}_3$, $\tilde{C}_6$ and $\tilde{C}_7$ are easily calculated from the charge neutrality condition and the equilibrium relations. They are given as follows:

$$\tilde{C}_6 = \frac{1}{2} \left( \tilde{C}_2 + 2 \tilde{C}_4 + \tilde{\alpha} + \sqrt{(\tilde{C}_2 + 2 \tilde{C}_4 + \tilde{\alpha})^2 + 4(2K_2 \tilde{C}_2 + K_5 \tilde{C}_5 + K_W)} \right)$$ \hspace{1cm} (40)
The computational algorithm of the concentrations in the raindrop at every time step is summarized as: 1) With the appropriate time increment and old known values of $C_i$’s integrate the governing eqn (22) to obtain new $\tilde{C}_2$, $\tilde{C}_4$ and $\tilde{C}_5$; 2) Substituting thus obtained new $\tilde{C}_2$, $\tilde{C}_4$ and $\tilde{C}_5$ into eqn (40), compute $\tilde{C}_6$; and 3) Using these new $\tilde{C}_2$, $\tilde{C}_4$, $\tilde{C}_5$ and $\tilde{C}_6$, calculate $\tilde{C}_1$, $\tilde{C}_3$ and $\tilde{C}_7$ by eqn (41).

\[ (\tilde{C}_1, \tilde{C}_3, \tilde{C}_7) = (\tilde{C}_6 \tilde{C}_2 / \tilde{K}_1, \tilde{K}_2 \tilde{C}_2 / \tilde{C}_6, \tilde{K}_5 \tilde{C}_5 / \tilde{C}_6) \]  

**Figure 1:** Variation of Biot Number with $D$ ($B_{i1}$: SO$_2$(g); and $B_{i5}$: H$_2$O$_2$(g)).

### 4 Acidification of raindrop

The acidification process of raindrops has been simulated for various drop diameters, the cloud bottom height being fixed at 500 m. The initial concentrations in the raindrops are: $C_2 = 10^{-7}$M; $C_4 = 10^{-10}$M; $C_5 = 10^{-6}$M; and $C_6 = 2.5 \times 10^{-6}$M (pH = 5.6). The relationships between drop acidity in pH and drop diameter $D$ in cm are depicted in Figures 2 and 3.

In Figure 2 the curves are shown parametrically in H$_2$O$_2$(g) concentration and SO$_2$(g) concentration is fixed at 50 ppb. As is supposed, the smaller the drop size is, the lower the pH value becomes, that is, the higher the acidity becomes. Also the higher H$_2$O$_2$(g) concentration is, the smaller pH value becomes. However, in the range of small size ($D < 0.2$ cm) the manner of the curves of pH variations with drop size is greatly different from curve to curve depending on their H$_2$O$_2$(g) concentrations. For large size ($D > 0.3$ cm) all of the curves take almost same
manner of the variation, that is, pH is nearly independent on H$_2$O$_2$(g) concentration. This means that the sensitivity of pH to H$_2$O$_2$(g) concentration is much higher in small size region ($D < 0.2$ cm) than in large one ($D > 0.3$ cm). The sensitivity of [H$^+$] to $D$ is much greater than that impressed visually from the pH figure (Figure 2), because pH value is the logarithm of inverse of [H$^+$] to base 10.

The curve for 0.1 ppb of H$_2$O$_2$(g) has a plateau of pH value of about 4.45. The plateau spreads out to a width from 0.05 cm to 0.15 cm. The value of H$^+$ (i.e., $C_6$) for this plateau may correspond to the quasi-equilibrium concentration equilibrated approximately to the ambient SO$_2$(g), because H$_2$O$_2$(g) concentration is low to neglect the oxidation effect on H$^+$ production in this size region. About other curves there cannot be seen such plateau like this and their pH values drop dramatically with decrease in size. The high acidity observed often in drizzle ($D \leq 0.05$ cm) supports these sudden falls of curves in pH.

The higher H$_2$O$_2$(g) concentration is, the more remarkable the decrease in pH becomes. This is because the production rate of SO$_4^{2-}$ (i.e., $C_4$) by the oxidation is intensified with increase in both the concentrations of H$_2$O$_2$(aq) (i.e., $C_5$) and H$^+$ (i.e., $C_6$). Since from eqn (40) $C_6$ is increased with growth of $C_4$ and since from eqn (6) the production rate of $C_4$ is catalysed by increase in $C_6$, $C_6$ in raindrops is auto-multiplied during the fall in the air.

The curves in Figure 3 are shown parametrically in SO$_2$(g) concentration but H$_2$O$_2$(g) is fixed at 0.1 ppb. As is supposed from Figure 2 all these curves have plateaus and the acidities attain the quasi-equilibrium state, since H$_2$O$_2$(g) concentration is low enough to neglect the effect of the oxidation in this size region. pH values, however, decrease abruptly in small size drop ($D < 0.05$ cm) to show clearly the oxidation effect. The sensitivity of pH to the variation of parameter [i.e., SO$_2$(g) concentration] seems to be not so clear. It, however, may be seen that the sensitivity is rather higher in large size ($D > 0.1$ cm) than in small size ($D < 0.05$ cm). The variation of the sensitivity is not so drastic and in contrast with Figure 2 the sensitivity varies rather in reverse manner to Figure 2 with respect to the drop size.

In Figure 4 variations of $C_2$, $C_4$, $C_6$ and $2C_4/(C_2 + 2C_3)$ with drop size are shown. It is apparent that both SO$_4^{2-}$ concentration (i.e., $C_4$) and H$^+$ concentration (i.e., $C_6$) increase suddenly with decrease in drop size especially in drizzle size ($D \leq 0.05$ cm). It should be noted that the increase in H$^+$ concentration enhance the production of SO$_4^{2-}$ and vice versa. Without oxidation the major contributor to the acidification of raindrops is HSO$_3^-$ (i.e., $C_2$) produced by dissociation reaction. This is true also in the early stage of acidification in which the effect of oxidation is small. The value of $2C_4/(C_2 + 2C_3)$ shows which of S(VI) (i.e., SO$_2^{4-}$) and S(IV) (i.e., HSO$_3^-$ and SO$_4^{2-}$) is the major contributor to drop acidification. At $D = 0.1$ cm the ratio is about 0.12 ($\ll 1.0$) and the contribution of HSO$_3^-$ (i.e., $C_2$) is overwhelmingly great ($C_2 \gg C_3$), but at $D = 0.02$ cm the ratio becomes about 4.4 and the contribution of SO$_4^{2-}$ (i.e., $C_4$) grows to be very important.
Figure 2: Relations between raindrop acidity pH and diameter $D$.

Figure 3: Relations between raindrop acidity pH and diameter $D$. 
5 Conclusions

With use of the mathematical model developed in this study the following conclusions may be drawn from the simulations:

1. Comparing the Biot Number of SO$_2$(g) with that of H$_2$O$_2$(g) (Figure 1), it has been proved that the nonsteady mass transfer rate of SO$_2$(g) is much greater than the rate of H$_2$O$_2$(g), though H$_2$O$_2$(g) is said to be more soluble than SO$_2$(g) in equilibrium state.

2. Then the conventional prediction of acidity based on the equilibrium concentration is supposed to be inadequate to nonsteady problems and then inadequate to the problems which is dependent on travelling time $t$. The same is true to the problems which is dependent on drop size $D$, because the independent variable $D$ can be transformed to travelling time $t$ via falling velocity $u(D)$ with use of the relationship between $t$ and $D$ as: $t = (\text{cloud bottom hight}) / u(D)$.

3. The effect of H$_2$O$_2$(g) concentration on raindrop pH, in other words the sensitivity of pH to H$_2$O$_2$(g) concentration, is greater in small size drops than in large ones (Figure 2). On the other hand the effect of SO$_2$(g) concentration on raindrop pH is greater rather in large size drops than in small size drops, although this is not so clear (Figure 3).
4. In small size drops especially in drizzle size the contribution of SO$_4^{2-}$ (i.e., oxidation of HSO$_3^-$) to the acid rain formation becomes more and more important with lapse of time (Figure 4). As well as small drops, drops falling long distance also produce significant amount of SO$_4^{2-}$ to contribute to the acidification, since the residence time (i.e., reaction time) in the air becomes long enough to produce SO$_4^{2-}$.

5. Under the existence of the oxidant like H$_2$O$_2$(g), washout of 50 ppb SO$_2$(g) in about 500 m fall by 0.1 cm drops can raise the drop acidity up to pH 4.5 from pH 5.6 of natural cloud water. This means that the acid rain of pH 4.5 experienced in Japan may be easily formed even if there is no long-distance transport of acidic pollutants from outside of Japan.

References


