

# Numerical Simulation on the Rainout-Removal of Sulfur Dioxide and Acidification of Precipitation from Stratiform Clouds<sup>1</sup>

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## ABSTRACT

The rainout-removal of  $\text{SO}_2$  and the acidification of precipitation from stratiform clouds are simulated using a one-dimensional, time-dependent model, parameterized microphysically in which dissolution and dissociation of gaseous  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$ , and oxidation reaction in aqueous phase are taken into account. The effects of dynamic factors, including updraft flow and turbulent transport, and the concentration of gaseous  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  being transported into the clouds on pH value of the precipitation, the conversion rate ( $S'IV_1 - S'VI_1$ ) and the wet deposition rate of  $\text{SO}_2$  are discussed.

## 1. INTRODUCTION

With the development of industrialization and urbanization, more and more anthropogenic pollutants (both gases and particles) are released into the atmosphere that seriously deteriorate the air quality. The wet removal of the trace gases and particles by clouds and precipitation is one of the major self-cleaning processes in the atmosphere. With which however, the multiphase chemical processes make the change of the chemical constituent and the pH value in cloud and rain. So far acid rain has been a public damage in many places in the world. It is necessary to study the law of the wet removal by clouds and precipitation in order to improve air quality and work out the strategy for controlling acid rain.

In current models of pollutant transportation, the product of species concentration and the wet removal rate is often expressed as a term of the wet deposition. Since the thermodynamic and microphysical processes link with the multiphase process very closely, the wet removal process is highly non-linear, and that the wet removal rate would not be a simple constant. Therefore it is an effective way to study such a complicated process using a numerical model based on the observation and experiments.

In recent years, scientists have studied the acidification mechanism and rainout removal process of pollutants by cloudwater and rainwater, and some interesting results have been obtained. Chameides(1984) and Seigneur et al.(1984) investigated the chemistry of cloudwater using zero-dimensional models, which were undoubtedly useful for the study of chemical reaction mechanism but the physical processes were so simple that only the condensation of the cloudwater was taken into account and therefore formation of precipitation could not be simulated. Hobbs et al.(1984, 1986) investigated the effect of nucleation, rainout, washout of

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aerosol and scavenging and oxidation of  $\text{SO}_2$  on constituents of precipitation using two-dimensional models of front cloud system. Chang(1986) discussed the mechanism of forming  $\text{HNO}_3$  in the rain and snow system. We have developed a one-dimensional time-dependent microphysically parameterized model of warm stratiform clouds, with which the removal process of inert gases was discussed (1986). We found that the dissolution scavenging of highly soluble gases is greatly affected by the transport mechanism of the gases into clouds and both updraft flow and turbulent transport play important roles in the removal process.

The major fuel in China is the coal which releases the main pollutant— $\text{SO}_2$  when burning. The precipitation scavenging and acidification processes are the solution of  $\text{SO}_2$  in cloudwater and rainwater and oxidational reaction in aqueous phase takes place successively. Martin(1983) pointed out that when the pH value of water is less than 5, the reaction rate of the  $\text{SO}_2$  dissolved in water and oxidized by  $\text{H}_2\text{O}_2$  is the highest and almost unvariable with pH values in certain range. Based on those consideration, using one-dimensional time-dependent model, the oxidation of  $\text{SO}_2$  in aqueous phase by  $\text{H}_2\text{O}_2$  as well as the relationship between the removal rate of  $\text{SO}_2$  by precipitation and its acidification, and the dynamic factors and concentration of the gases inputted into the clouds are discussed.

## II. PHYSICAL-CHEMICAL MODEL OF THE STRATIFORM CLOUDS

On the basis of given pressure and temperature at the cloud base as well as the given updraft velocity and turbulent transfer coefficient, a one-dimensional, time-dependent model for warm cloud is developed with a hypothesis that a pseudo-adiabatic temperature profile in cloud is held. On the definite thermo-dynamic background, for three water contents, i.e. water vapor ( $Q_v$ ), cloud water ( $Q_c$ ) and rain water ( $Q_r$ ), the parameterized micro-physical processes are considered as condensation of water vapor into cloudwater or rainwater (the rates are written as CONDC and CONDR respectively), autoconversion of cloudwater into rainwater with the primary size (AUTO) and the coalescence of cloudwater into rainwater (COLL). In cloudwater case, a monodisperse distribution with constant concentration of droplets ( $N_c$ ) is assumed. For rain drop, a dual-parameter distribution with a negative power law is adopted. The equations for determining the concentration of the rainwater ( $N_r$ ) and the function expanding the sized spectrum of rain drop ( $F$ ), which trigger the autoconversion process are inputted when the three balanced equations of water contents are given. The balance equation, considering the dynamic factors have the following basic form:

$$\frac{\partial Q_i}{\partial t} + (W - V_i) \frac{\partial Q_i}{\partial z} = K_i \frac{\partial^2 Q_i}{\partial z^2} + \frac{dQ_i}{dt} \Big|_s, \quad (1)$$

where  $Q_i$  represents  $Q_v$ ,  $Q_c$ ,  $Q_r$ ,  $N_r$  and  $F$ , and therefore there are altogether five equations,  $W$  is the updraft velocity,  $V_i$  is the average terminal fall velocity of the drops and take null for both water vapor and cloud water,  $K$  is the coefficient for turbulent transfer,

$\left. \frac{dQ_i}{dt} \right|_s$  are the source terms or sink terms for microphysical processes. Details of those sym-

bols can be referred to the Reference(1986). In this paper, all the problems being discussed are limited in the cloud (bounded with the top and base of the cloud). The given standard conditions are 293 K for temperature and 900 hPa for pressure at the cloud base, 3 km for cloud depth,  $W = 0.1$  m/s and  $K = 20$  m<sup>2</sup>/s. Calculation starts from vapor saturation of the whole column, afterwards the cloud forms by condensation, 60 min later the rain drop at the middle part of the cloud is firstly forming as the cloud water content increases, at 70 min, appears the rainfall from the cloud base, at 100 min, the highest rain intensity comes, reaching 4.5 mm/h, then decreases and becomes steady gradually. After 200 min, the intensity of the rainfall is about 2.4 mm/h, the three water contents in the cloud are stationary, and the average total water content is 0.46 g/kg. In general those results are similar to the behavior of cloud-rain developing in a warm stratiform cloud. The sensitivity test indicated that the updraft flow was the key factor to control the evolution of cloud and precipitation. On the contrary, the effect of turbulent transfer coefficient was not obvious (1986).

In this paper, these chemical processes, including the dissolution of SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> into cloudwater and rainwater, dissociation and oxidation are taken into account. Given in Table 1 are the equations of dissolution, dissociation and oxidation reaction and their correspondent constants.

Table 1. Equations and Constants of Dissolution, Dissociation and Oxidation Reaction

DISSOLUTION		
$(H_2O_2)_{g} \rightleftharpoons (H_2O_2)_{aq}$	$K_{H_2O_2} = 9.7E4 \cdot \text{EXP}\{6600(1/T-1/298)\}$	M/atm
$(SO_2)_{g} \rightleftharpoons (SO_2)_{aq}$	$K_{SO_2} = 1.23 \cdot \text{EXP}\{3120(1/T-1/298)\}$	M/atm
DISSOCIATION		
$(SO_2)_{aq} \rightleftharpoons HSO_3^- + H^+$	$Eq_1 = 1.7E-2 \cdot \text{EXP}\{2090(1/T-1/298)\}$	M
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	$Eq_2 = 6E-8 \cdot \text{EXP}\{1122(1/T-1/298)\}$	M
CHEMICAL REACTION		
IN AQUEOUS PHASE		
$(S(IV))_{aq} + (H_2O_2)_{aq} \rightleftharpoons SO_4^{2-} + 2H^+$	$K_{SO_4} = 8E4 \cdot \text{EXP}\{-3650(1/T-1/298)\} / (10 \cdot 1 + [H^+])$	

In aqueous phase,  $S(IV)$  includes  $(SO_2)_{aq}$ ,  $HSO_3^-$  and  $SO_3^{2-}$ , and  $S(VI)$ , i.e.  $SO_4^{2-}$ . From Henry's law and dissociation equations, the concentration of  $S(IV)$  can be written as

$$[S(IV)] = P_{SO_2} \cdot K_{SO_2} (1 + Eq_1 / [H^+] + Eq_1 \cdot Eq_2 / [H^+]^2), \quad (2)$$

where  $P_{SO_2}$  is the partial pressure of SO<sub>2</sub>,  $Eq_1$  and  $Eq_2$  are the dissociation constants.  $K_{SO_2}$  is the soluble constant of SO<sub>2</sub> in water. The effective Henry's constant is defined as

$$H_{eff}(SO_2) = K_{SO_2} (1 + Eq_1 / [H^+] + Eq_1 \cdot Eq_2 / [H^+]^2). \quad (3)$$

$G(I)$ ,  $C(I)$  and  $R(I)$  are used to represent the volume mixing ratio of the species  $I$  in gas

phase, cloudwater and rainwater, respectively. The equivalent volume mixing ratio of the species  $I$  is supposed to be the volume mixing ratio of this species  $I$  in gas-phase when it is completely transformed from liquid to gas.

Similar to the water balance equations, 10 equations for gaseous  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$ ,  $S(IV)$ ,  $S(VI)$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}^+$  in aqueous phase can be obtained. The source or sink terms in Eq. (1) are written as

$$\begin{aligned}
 \left. \frac{dG(\text{SO}_2)}{dt} \right|_s &= -SCAVC(\text{SO}_2) - SCAVR(\text{SO}_2) \\
 \left. \frac{dG(\text{H}_2\text{O}_2)}{dt} \right|_s &= -SCAVC(\text{H}_2\text{O}_2) - SCAVR(\text{H}_2\text{O}_2) \\
 \left. \frac{dC(SIV)}{dt} \right|_s &= SCAVC(\text{SO}_2) - (COLL + AUTO) \frac{C(SIV)}{Q_c} - S46C \\
 \left. \frac{dC(\text{H}_2\text{O}_2)}{dt} \right|_s &= SCAVC(\text{H}_2\text{O}_2) - (COLL + AUTO) \frac{C(\text{H}_2\text{O}_2)}{Q_c} - S46C \\
 \left. \frac{dC(SVI)}{dt} \right|_s &= -(COLL + AUTO) \frac{C(SVI)}{Q_c} + S46C \\
 \left. \frac{dC(\text{H}^+)}{dt} \right|_s &= SCAVC(\text{H}^+) - (COLL + AUTO) \frac{C(\text{H}^+)}{Q_c} + S46C(\text{H}^+) \\
 \left. \frac{dR(SIV)}{dt} \right|_s &= SCAVR(\text{SO}_2) + (COLL + AUTO) \frac{C(SIV)}{Q_c} - S46R \\
 \left. \frac{dR(\text{H}_2\text{O}_2)}{dt} \right|_s &= SCAVR(\text{H}_2\text{O}_2) + (COLL + AUTO) \frac{C(\text{H}_2\text{O}_2)}{Q_c} - S46R \\
 \left. \frac{dR(SVI)}{dt} \right|_s &= (COLL + AUTO) \frac{C(SVI)}{Q_c} + S46R \\
 \left. \frac{dR(\text{H}^+)}{dt} \right|_s &= SCAVR(\text{H}^+) + (COLL + AUTO) \frac{C(\text{H}^+)}{Q_c} + S46R(\text{H}^+),
 \end{aligned} \tag{4}$$

where  $SCAVC$  and  $SCAVR$  are the scavenging rates of the gases being dissolved into water. According to Fick's diffusion law, with assumptions of steady state and spherical drops, the scavenging rate of the gases by water drop can be expressed by the following formula.

$$\begin{aligned}
 SCAVC(I) &= 4\pi R_c N_c D(I) \left( 1 + \frac{4l}{3R_c \alpha} \right)^{-1} \left( G(I) - \frac{[I]_c}{H_{eff}(I)P} \right) \\
 SCAVR(I) &= 4\pi R_r N_r D(I) F(Re) \left( G(I) - \frac{[I]_r}{H_{eff}(I)P} \right),
 \end{aligned} \tag{5}$$

where  $I$  represents  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$ , respectively, subscript  $c$  and  $r$  represent cloudwater and rainwater,  $R$  and  $N$  are the average radius and concentration of the drops,  $D$  is the

molecular diffusion coefficient. The corrective term of molecular boundary layer in Eq.(5) is given by  $\left(1 + 4l / (3R_c \alpha)\right)^{-1}$  according to recommended formula by Schwartz (1983), where  $l$  is the mean free way of molecules,  $\alpha$  is the accommodation coefficient of gaseous molecular collision on the surface of drops and takes 0.01 being as same as that of Chameides' (1984). The ventilation factor for convective transport of gaseous masses on the surface of spheric drops are considered. The Frossling's formula has  $F(Re) = 1 + 0.23Re^{1/2}$ , where  $Re = 2RV / v_c$  is the Reynolds number for falling drops in the air. In the source and sink terms included also are the transportation of species from cloudwater into rainwater through autoconversion and collision processes. S46C and S46R are included in the term  $S(VI)$ , and formed by oxidation reaction of  $S(IV)$  and  $H_2O_2$  in cloud-rain water.  $H^+$  can be obtained from various processes prescribed. From Martin's paper (1983) we have

$$d[S(IV)] / dt = K_{s46} [H_2O_2] \cdot [(SO_2)_{cu}] = K' \quad (6)$$

therefore,

$$S46C = K_c A Q_c$$

$$S46R = K_r A Q_r$$

where  $K_{s46}$  is the reaction coefficient,  $A$  is a unit exchange coefficient between liquid water content (m / m) and mixing ratio of species (v / v).

The initial conditions are that the saturations of water vapor exist at every levels, mixing ratios of the two gases distribute uniformly at every levels and keep constant at the bounds, the water content of cloud and rain, as well as concentration of constituents are zero. For the boundary conditions, the cloudwater content and its concentration of species are supposed to be zero: the rainwater content and concentration of its constituents at upper bound are zero, but continuous at lower bound. As a matter of fact,  $CO_2$  is added into this model and pH = 5.6 for cloudwater is assumed at initial time. Altogether there are 15 equations including prescribed 5 physical factors and 10 species. Taking 1s and 100m for time and space steps, respectively, the variations of profiles of every factor with time are obtained by solving equations using a finite-difference method with forward time step for the time derivatives and upstream spatial differencing for advection terms. In each case the evolution process of the cloud and rain is calculated for 4h.

### III. RESULTS AND DISCUSSION

Under the condition of prescribed "STANDARD CASE", with given different initial and boundary values of the gaseous  $SO_2$  and  $H_2O_2$  and changing some other parameters, numerical experiments have been done and some results are obtained.

#### 1. The Time Variation of the Concentration of the Constituents in Rainwater at the Cloud Base

1 ppbv is taken as the initial and boundary values for  $SO_2$  and  $H_2O_2$  in light pollution condition. Given in Fig.1 are the variations of concentrations and pH values in rainwater at the cloud base with time. 70 min later, the precipitation appears at the cloud base, while the

pH value and concentration of  $S(IV)$  are minimum, then increase and keep steady, but the curves of  $H^+$ ,  $S(VI)$  and  $H_2O_2$  inversely correlate with the curves of  $S(IV)$  and pH. It is easy to understand why the maximum and minimum values occur at the beginning of the rainfall at the cloud base. In the first 70 min, the time is long enough to dissolve  $SO_2$  and  $H_2O_2$  into cloudwater and to form  $SO_4^{2-}$ , then convert into  $S(VI)$  in rainwater through autoconversion and collision processes. The time is coincident with Chameides's, i.e. about 1 hour for the transformation time of  $SO_2$ . Afterwards, steady distribution is gradually formed due to the results of flux balance between gas inputted by updraft and turbulence and precipitation outputted from the cloud base. There is not enough time to transform  $S(IV)$  in cloud-rain water into  $S(VI)$  which will be seen in Fig.2.

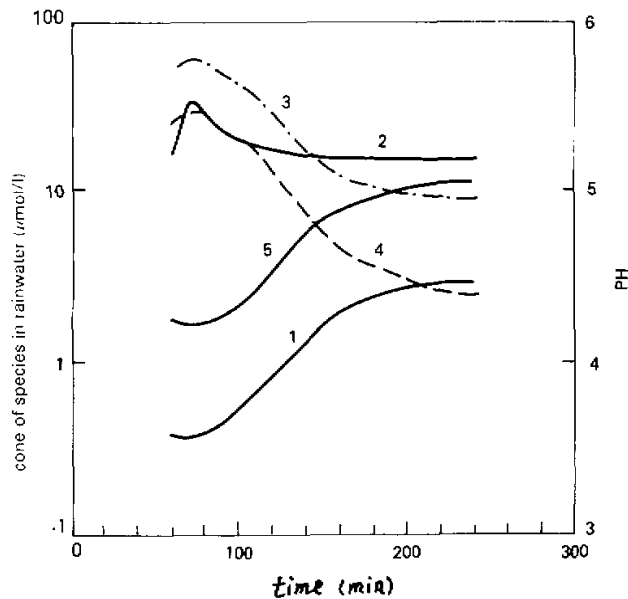


Fig.1. The concentration of species and the pH value in rainwater at the cloud base (1:  $S(IV)$ , 2:  $H_2O_2$ , 3:  $H^+$ , 4:  $S(VI)$ , 5: pH).

The variation of pH value with time in Fig.1 may be used to explain the phenomena observed in some places that the maximum of acidity in the rain samples occurs at the beginning, then decreases gradually. Besides, it is interesting that although the inputted gaseous concentration of  $SO_2$  and  $H_2O_2$  is lower, the concentration of  $H_2O_2$  in rainwater is as high as  $30 \mu\text{mol/l}$ , and finally keeps at  $20 \mu\text{mol/l}$ , which approximates to that observed by Zika et al. (1981) in Florida and Bahama.

## 2. The Concentration Profiles of Species in Cloudwater and Rainwater

In Fig.2, the profiles of species concentration in cloudwater and rainwater at 70 and 240

min are drawn. From these curves, one can see that in both cloudwater and rainwater, the concentrations of all  $S(VI)$ ,  $H_2O_2$  and  $H^+$  at 70 min are higher than the values at 240 min and the value of  $S(IV)$  at 70 min is one order lower than that at 240 min. In addition, the concentration of  $S(IV)$  at 240 min is much higher than the value of  $S(VI)$ . All of these show that the dissolution of the gases in water and oxidation in aqueous phase at 70 min is more complete than that at 240 min.

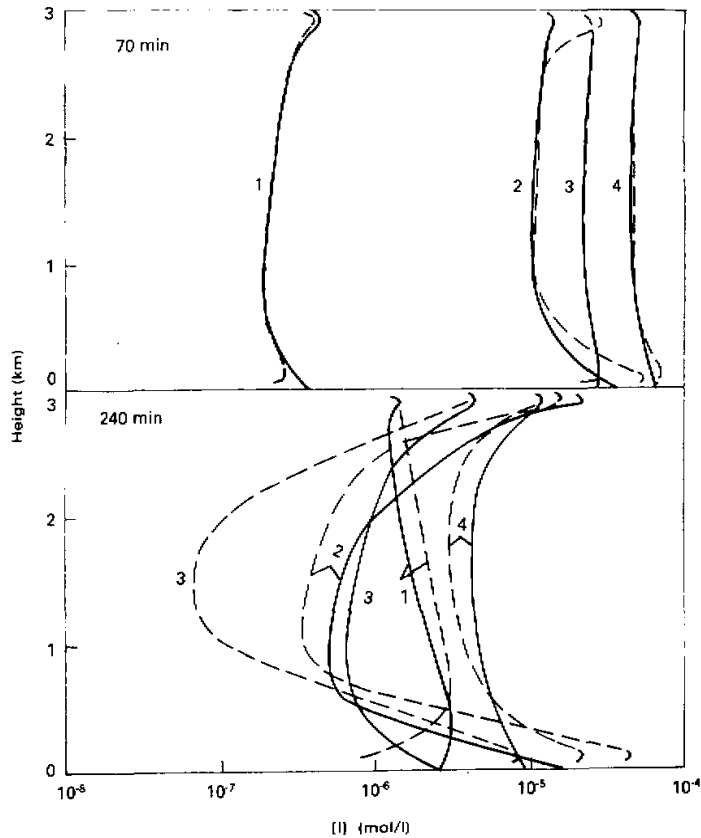


Fig.2. The concentration profiles of species in cloudwater and rainwater. solid line: rainwater, dash line: cloudwater. 1:  $S(IV)$ , 2:  $H_2O_2$ , 3:  $S(VI)$ , 4:  $H^+$ .

The curves of species concentration both in cloudwater and rainwater are almost overlapped each other at 70 min, but great differences between the two curves occur at 240 min. It means that the micro-structure and microphysics of cloud and precipitation affect the removal and aciditative processes. It seems to be not reasonable that someone uses the removal rate and pH value of cloudwater as the values of precipitation.

3. *The Effects of Updraft Flow, Turbulent Transport and the Concentration of Input Gases on the pH Value, the Conversion Rate of S(IV) to S(VI) and the Wet Deposition Rate of SO<sub>2</sub>*

To discuss the effects of input parameters on various quantities in precipitation, a series of numerical tests and a comparative study of the results at 240 min have been done, in which various parameters are taken as 0.1, 0.05 m/s for updraft velocity, 20, 40 m<sup>2</sup>/s for turbulent transport coefficient, 1, 10 ppbv for gaseous H<sub>2</sub>O<sub>2</sub> and 0.1 to 100 ppbv for SO<sub>2</sub>.

(1) *The relationship of species concentration in rainwater at the cloud base with the parameters*

Examples for four different values of parameters are listed in table 2. The results of sensitivity tests are given in Qin's paper(1986) which pointed out that the effects of the turbulent transport coefficient on forming time and intensity of precipitation are not very strong but the updraft velocity plays a dominant role in precipitation that the weaker the updraft velocity is, the smaller the intensity of rain and the later the time of forming rain would be. In comparison of example 2 with 1, it can be seen that the smaller the intensity of rain is, the higher the concentration of the whole sulfur, the lower of H<sub>2</sub>O<sub>2</sub> and the smaller value of pH in rainwater would be, that is consistent with the general facts observed.

**Table 2.** Relationship of Concentration of Species in Rainwater at Cloud Base at 240 min with Parameters

Input value of parameters and rain intensity of cloud base

No.		1	2	3	4
$w$	m/s	0.10	0.05	0.10	0.10
$k$	m <sup>2</sup> /s	20.0	20.0	40.0	20.0
GSO <sub>2</sub>	ppbv	1.0	1.0	1.0	1.0
GH <sub>2</sub> O <sub>2</sub>	ppbv	1.0	1.0	1.0	10.0
$I$	mm/h	2.4	1.1	2.3	2.4

Concentration of species and pH value in rainwater at cloud base (mol/l)

S(IV)	2.78	1.31	2.11	0.71
S(VI)	2.51	8.27	4.27	13.9
H <sub>2</sub> O <sub>2</sub>	15.6	21.9	18.9	170.4
pH	5.04	4.72	4.93	4.52

In comparison of examples 3 and 4 with example 1, it can be seen that the increases of values of turbulent transport coefficient  $K$  make increase of concentration of the whole  $S$  in rainwater, and  $S(IV)$ , but decrease of the pH value. The major cause is due to the more H<sub>2</sub>O<sub>2</sub> dissolution into water that will be discussed later. As the input concentration of gaseous H<sub>2</sub>O<sub>2</sub> increases one order, more H<sub>2</sub>O<sub>2</sub> would dissolve into rainwater and the conversion rate from  $S(IV)$  to  $S(VI)$  would be very high that makes increase of the concen-



tration of the total  $S$  and  $H^+$  in rainwater.

(2) *The relationship between pH value of rainwater and parameters*

Given in Fig.3 are the 4 lines of pH value v.s. concentration of gaseous  $SO_2$ , in which line 1 represents the standard case:  $W=0.1$  m/s,  $K=20$  m<sup>2</sup>/s and the input concentration of gaseous  $H_2O_2$  is 1 ppbv; line 2 represents case 2:  $W=0.05$  m/s and others are equal to the values adopted in case 1; line 3 represents case 3:  $K=40$  m<sup>2</sup>/s; and line 4 represents case 4:  $G(H_2O_2)=10$  ppbv.

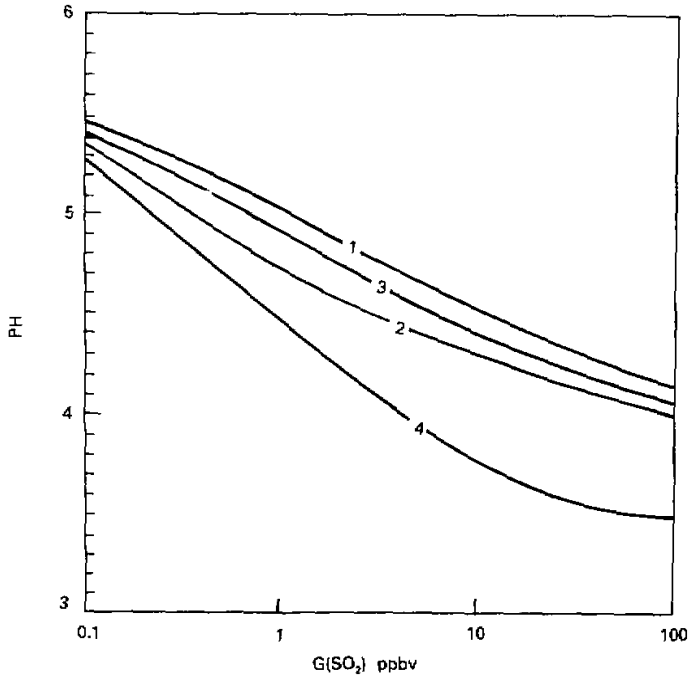


Fig.3. The variation of pH value of rainwater with the concentration of gaseous  $SO_2$ . 1: standard case, 2:  $W=0.05$  m/s, 3:  $K=40$  m<sup>2</sup>/s, 4:  $G(H_2O_2)=10$  ppbv.

Fig.3 shows that the pH values decrease with the increase of concentration of gaseous  $SO_2$ . It is easy to understand since the higher concentration of gaseous  $SO_2$ , the more  $S$  dissolved into rainwater, the smaller the pH value of rainwater would be. The lines in Fig.3 display that the rainout removal of  $SO_2$  and acidification of rainwater are non-linear. When the concentration of gaseous  $SO_2$  is either near 1 ppbv or very high, the variation of pH value is not sharp, but in the middle of the curves, the variations of pH value are very great. For example, when the concentration of  $SO_2$  decreases from 100 ppbv to 10 ppbv, the con-

centrations of  $H^+$  in rainwater only decrease by a factor of 0.5 in case 1, and larger than 0.5 in case 4. In the contrary, when concentrations of  $SO_2$  decrease from 10 to 1 ppbv, the concentrations of  $H^+$  in rainwater for cases 1 and 4 decrease by a factor of 0.33 and 0.2 respectively.

In comparison of cases 2, 3 and 4 with case 1, one can see that the pH value of rainwater reduces either due to the decrease of updraft velocity or the enhancement of turbulent transport coefficient and input concentration of gaseous  $H_2O_2$ , but this decrease is not proportional to the variations of those parameters and the maximum decrease is related to the input concentration of gaseous  $SO_2$ . In case 2, the updraft velocity is only half of the value of case 1, the pH values decrease in the range of 0.1 to 0.3. For  $SO_2 = 1$  ppbv, the pH value reduces to 0.3, i.e. the concentration  $H^+$  is double of that in case 1. The pH values in case 3 are about 0.1 less than the values along curve 1. The pH values for curve 4 are the smallest and the greatest decrease appears at the end of high concentration of gaseous  $SO_2$  where the pH value is 0.7 less than that in case 1. It means the  $H^+$  concentration in rainwater is factors 4 higher. The range from which the greatest decrease of pH value takes place is consistent with that from which the maximum conversion rate of  $S(IV)$  to  $S(VI)$  appears, which will be described in the following paragraph.

### (3) *The conversion rate of $S(IV)$ to $S(VI)$ in rainwater*

The ratio of  $S(VI)$  to the total sulfur  $S(IV)+S(VI)$  in rainwater,  $C$ , is defined as a measure that  $S(IV)$  dissolved in rainwater is oxidated into  $S(VI)$ . The relationship between proportional coefficient  $c$  and input concentration of gaseous  $SO_2$  is given in Fig.4, and from which we can find that by decreasing updraft velocity, enhancing turbulent transport or by increasing input concentration of  $H_2O_2$ , the rate of conversion from  $S(IV)$  to  $S(VI)$  may be raised and therefore can make the pH value decrease. This is consistent with the results in Fig.3.

One can also see in Fig.4 that the maximum conversion rate does not take place at the minimum input value of  $SO_2$ , but in a suitable range of input value of  $SO_2$ , which is relative to the turbulent transport. In Qin's paper (1986), the relationship between the turbulent transport and high soluble gases was described.  $H_2O_2$  is a high soluble gas with a solubility coefficient being about  $10^5$  mol/l · atm. Following the evolution of clouds and rain, the concentration of  $H_2O_2$  in the middle part of the clouds would be very low owing to the depletions of dissolution, oxidation and fallout of rain. The concentrations at both bounds are supposed to be constant so that a large concentration gradient inside the cloud can be formed and  $H_2O_2$  is transported into the cloud through turbulence. This maximum concentration gradient does not take place in the case of minimum input concentration of  $SO_2$ , and when the concentration of  $SO_2$  is too high, the relative value of  $H_2O_2$  would be too low, therefore, the maximum conversion rate should be in the suitable range of  $SO_2$  concentration.

In this paper only the removal processes in clouds are discussed, therefore it is difficult to keep constant concentration of  $H_2O_2$  at the cloud base owing to the removal of  $H_2O_2$  below the cloud. Kumar(1982) pointed out that the concentration of  $H_2O_2$  below the cloud base would exponentially decrease with time. The prescribed results are only suitable to a steady-state condition in which gaseous  $H_2O_2$  could be compensated.

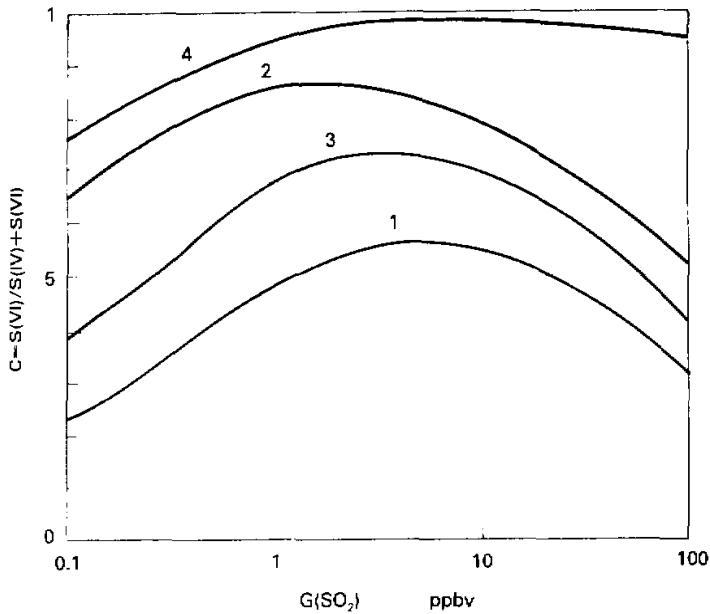


Fig.4. The variation of conversion rate of  $S(VI)/S(V)+S(VI)$  with the input concentration of  $SO_2$  (The parameters here are the same as that in Fig.3).

(4) *The removal rate of  $SO_2$  by the precipitating cloud system*

As a measure of the removal rate of  $SO_2$  by the cloud system, the wet deposition velocity of  $SO_2$ ,  $V_{wd}$  is defined as the ratio of the fallout flux of the total sulfur,  $S(V)+S(VI)$  in the precipitation from the cloud base to the concentration of gaseous  $SO_2$  at the cloud base.

$$V_{wd} = \frac{(R(S(V)) + R(S(VI))) \cdot (V - W)}{G(SO_2)} \quad (7)$$

In Fig.5, the relationship between  $V_{wd}$  and the input  $SO_2$  concentration is given. The curves in Fig.5, display that the maximum removal rates occur at the ends of lower concentration of  $SO_2$  and the rates reduce with the increase of gaseous  $SO_2$  concentration. In comparison of curve 1 with 2, it can be found that the removal rates of  $SO_2$  decrease when updraft flow weakens. From curve 3, the rate increases when turbulent transport enhances, that makes enhancing the conversion from  $S(V)$  to  $S(VI)$  but this increment of wet removal is not very large. From curve 4 we find that the increase of  $H_2O_2$  can also enhance the wet removal because the enhancement of conversion makes more  $SO_2$  to be dissolved into water and oxidized.

For the standard case, the wet deposition velocity decreases from about 20 to 1.2 cm / s,

when the input concentration of gaseous  $\text{SO}_2$  increases from 0.1 to 100 ppbv. If the velocity is divided by 3 km. the cloud depth, the mean removal rate obtained would be from 24% / h to 1.4% / h. these values are less than the values in a closure system which is about 100% / h.

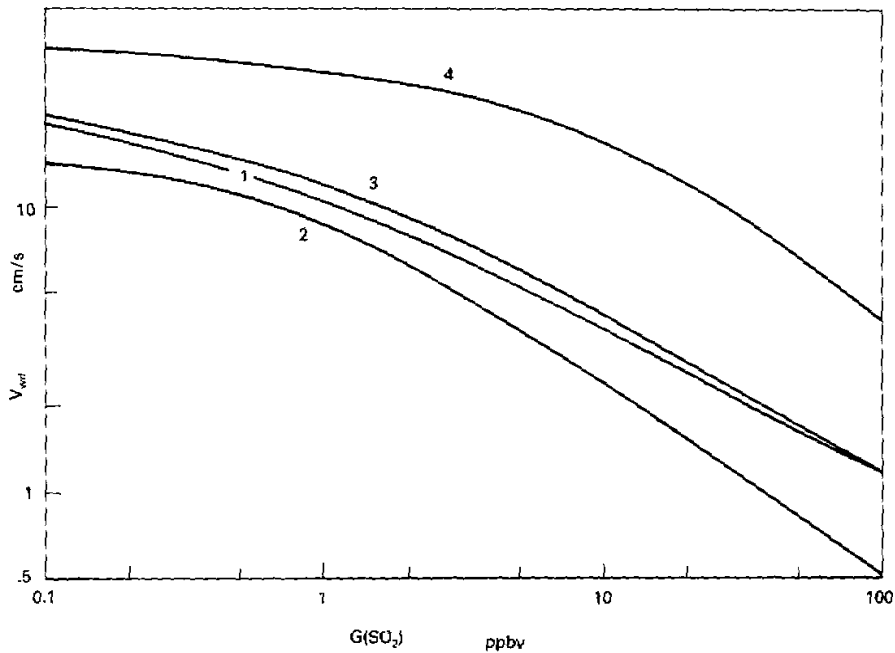


Fig.5. The variation of the removal deposition velocity of gaseous  $\text{SO}_2$  with  $\text{SO}_2$  input concentration. (The parameters here are the same as that in Fig.3).

#### IV. CONCLUSION

In this paper, the mechanism of the removal of  $\text{SO}_2$  by precipitation in a stratiform cloud and the acidity of the precipitation are investigated with a simple one-dimensional time-dependent model. The results are consistent with those observed and can be used to interpret some facts. From prescribed results, following conclusions can be obtained.

(1) The effects of the precipitation in a stratiform cloud on the removal of  $\text{SO}_2$  and precipitation acidity are non-linear processes and the relationships between these processes and the dynamic factor, microphysics and input concentration of the gases are complicated.

(2) The updraft flow in clouds controls the evolution of the cloud and precipitation, rain intensity and water content, the removal of  $\text{SO}_2$  as well as the concentration and acidity of species on rainwater. The weaker updraft velocity is, the less the water content of rain, the weaker the intensity of precipitation and the smaller removal rate of  $\text{SO}_2$  would be, but the larger the concentration of total sulfur in rainwater and the higher acidity would be.

(3) The turbulent diffusion can affect the transport of gases from the bounds into clouds.

Stronger turbulent coefficient may help transporting  $\text{H}_2\text{O}_2$  into clouds that makes increasing the conversion rate from  $S(IV)$  to  $S(VI)$ . Therefore, it can enhance the removal of  $\text{SO}_2$  and the acidity of the rainwater. However, there is a shortage of data for turbulent transport coefficient which varies with cloud, so that the uncertainty would exist significantly.

(4) The gaseous  $\text{H}_2\text{O}_2$  is high soluble and strong oxidant. The concentration of  $\text{H}_2\text{O}_2$  in rainwater can exist if there is a suitable concentration of gaseous  $\text{H}_2\text{O}_2$  transported into clouds.  $\text{H}_2\text{O}_2$  could convert  $S(IV)$  into  $S(VI)$  in water and enhance the wet removal and acidity of the rainwater. So far very few observational data for both gaseous  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$  in the water have been obtained. Therefore much attention should be paid on observation.

(5) The model in this paper is very simple in both physics and chemistry. Here only the processes in clouds are discussed but the processes outside, especially the process of washout removal under the clouds not only affect the concentration of species in rain water falling down on the ground, but also affect indirectly the concentration of species transported into the clouds from the cloud base. As a matter of fact, there are some other gases such as  $\text{O}_3$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ , hydrocarbon and aerosols that can participate chemical reaction processes in cloud-precipitation system. It is necessary to improve this model for advanced research.

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