

PRODUCTION OF SULFATE IN RAIN AND RAINDROPS IN POLLUTED ATMOSPHERES

JOHN H. OVERTON, JR. and VINEY P. ANEJA

Environmental Sciences Group, Northrop Services Inc., Research Triangle
Park, NC 27709, U.S.A.

and

JACK L. DURHAM

Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency,
Research Triangle Park, NC 27711, U.S.A.

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Abstract — A physico-chemical model for the accumulation of sulfur species in raindrops is developed in which account is taken of the mass transfer of SO_2 , O_3 , NH_3 and CO_2 into ideal raindrops containing the catalyst Fe(III) . The sulfur accumulation was calculated for the droplets as a function of fall distance. The model predicts the formation of sulfate due to the oxidation of dissolved SO_2 by O_3 and catalytic ions in the presence of NH_3 and CO_2 . The initial pH of a drop was taken as 5.56. The final value depended on drop size, fall distance, and ambient concentrations, but in all cases was between 4.2 and 6.6. Sulfate values also depended on the same conditions and ranged from 2 to $2000 \mu\text{mol l}^{-1}$ for individual drops. For a precipitation rate of 10 mm h^{-1} and a fall distance of 2000 m, the raindrop pH varied from 4.5 to 6.5 and the average sulfate concentration from 3 to $87 \mu\text{mol l}^{-1}$ depending on ambient pollutant concentrations. These results conform to the experimentally measured values of the rain pH (3–9) and sulfate concentration ($20\text{--}150 \mu\text{mol l}^{-1}$), and corresponding air SO_2 concentration (1–10 ppb) as reported in the literature.

NOMENCLATURE

D_{CO_2}	diffusion coefficient for carbon dioxide, $0.166 \text{ cm}^2 \text{ s}^{-1}$
D_{NH_3}	diffusion coefficient for ammonia, $0.234 \text{ cm}^2 \text{ s}^{-1}$
D_{O_3}	diffusion coefficient for ozone, $0.164 \text{ cm}^2 \text{ s}^{-1}$
D_{SO_2}	diffusion coefficient for sulfur dioxide, $0.136 \text{ cm}^2 \text{ s}^{-1}$
H	Henry's law constant, dimensionless. Equilibrium ratio of gas phase concentration to liquid phase concentration of same species
H_{CO_2}	Henry's law constant for molecular carbon dioxide, 1.2.
H_{NH_3}	Henry's law constant for molecular ammonia, 0.00067
H_{O_3}	Henry's law constant for molecular ozone, 7.2
H_{SO_2}	Henry's law constant for molecular sulfur dioxide, 0.0332
K_1, K_2	equilibrium constant for reactions (4) and (5), respectively
R	drop radius
g	indicates gas phase
i	rate constant subscript, reaction equation number
k', k''	chemical reaction rate constant, $\text{l mol}^{-1} \text{ s}^{-1}$
k_g	gas phase mass transfer coefficient, cm s^{-1}
k_{+i}, k_{-i}	forward and backward rate constant for <i>i</i> th reaction
k_i	rate constant for <i>i</i> th reaction
l	liter
m	meter
s	indicates a chemical species such as SO_2 , NH_3 , H^+ , HSO_3^- , etc.
t	time
u	fall velocity, cm s^{-1}
z	fall distance, m
ℓ	indicates liquid phase
[]	molar concentration
v	kinematic viscosity of air, $0.133 \text{ cm}^2 \text{ s}^{-1}$
ϕ	reaction rate
ψ	mass transfer rate.

INTRODUCTION

Raindrops absorb atmospheric gases and thus provide an important mechanism for cleaning the atmosphere. The consequences of this phenomenon have blossomed in a far reaching environmental impact called "acid rainfall". There is evidence that acid rainfall, as a by-product of energy-related activities, is introducing a considerable stress on both rural and urban areas of U.S. and western Europe (Reiquam, 1970). Data obtained on precipitation (Likens, 1976; Engstrom *et al.*, 1971) appear to show that the acidity of the precipitation is associated mainly with the sulfate ion (SO_4^{2-}). For this work we have assumed that is the case; however, nitrate, especially in the form of nitric acid, may be important and should be considered in future work.

Sulfur dioxide (SO_2) can be oxidized in raindrops. The speed at which the reaction takes place varies considerably, owing to various factors such as the presence of catalysts, ammonia (NH_3), ozone (O_3), carbon dioxide (CO_2) and other trace gases in the drop. The product of the oxidation of SO_2 is sulfuric acid (H_2SO_4). An analysis of the interaction between pollutant gases and aerosols that takes place in the atmosphere shows that the sulfur emitted from anthropogenic sources is undoubtedly of fundamental importance so far as the acidity of precipitation is concerned. The relation between sulfur and acid varies, depending on the quantity of basic substances also present in the atmosphere. If these basic substances are not present in sufficient quantities there will be an excess of acid in the atmosphere, observable as acidified precipitation.

The removal of SO_2 or production of SO_4^{2-} by droplets has been considered elsewhere. For example, Scott and Hobbs (1967) modelled sulfate formation in the presence of NH_3 and CO_2 . In their model the concentrations of dissolved chemical species are assumed to be in equilibrium; also, the liquid phase concentrations are in equilibrium with their respective ambient gas phase counterparts. The rate of formation of SO_4^{2-} was assumed to be proportional to the sulfite concentration $[\text{SO}_3^{2-}]$. In the model of Hales *et al.* (1973) only physical absorption by drops was considered. A mass transfer equation (of the type in Equation 1, presented below) was used to represent the removal process; chemical reactions were not considered. The formulations of the chemical and physical aspects of the above approaches were combined by Hill and Adamowicz (1977); however, they did not consider the effects of NH_3 and CO_2 .

We have developed a physico-chemical model to predict SO_4^{2-} formation in raindrops in the presence of SO_2 , O_3 , NH_3 , CO_2 and the catalyst Fe(III). The dependence of reactant and product concentrations on fall distance is determined by initial conditions, ambient concentrations, gas-liquid transfer and chemical reactions that occur within a drop. The equations that describe the oxidation of sulfur-IV to SO_4^{2-} have been taken from the literature, and catalyst oxidation equations have been contrived to approximate published rates. Mathematical formulation of the model leads to a set of non-linear first order differential equations which were numerically solved to obtain the values of dissolved species concentration as a function of fall distance.

Only the phenomenon of washout of gaseous pollutants is considered; no doubt the process of the rain-out of both gaseous and aerosol pollutants are important, but for simplicity these mechanisms of sulfate production in raindrops have been omitted. We have ignored vertical air motion and assumed that the drops are of constant diameter falling at a constant velocity.

PHYSICAL MODEL

The atmosphere has been divided into two regions, shown in Fig. 1. Raindrops are formed in the upper region in the presence of Fe(III) and CO_2 . The drops enter a polluted region and fall through at a constant velocity. In the polluted region are the trace gases CO_2 , O_3 , SO_2 and NH_3 . As the drop falls, gases are absorbed, react and produce SO_4^{2-} . The ambient concentrations of the gases are assumed constant spatially as well as temporally. A raindrop is taken to be a uniform sphere of constant temperature (25°C) and a radius R , composed of water and trace quantities of Fe(III), O_3 , SO_2 , CO_2 , NH_3 and their products uniformly distributed at all times throughout the drop (concentration gradients are neglected).

In all drops the concentration of Fe(III) is con-

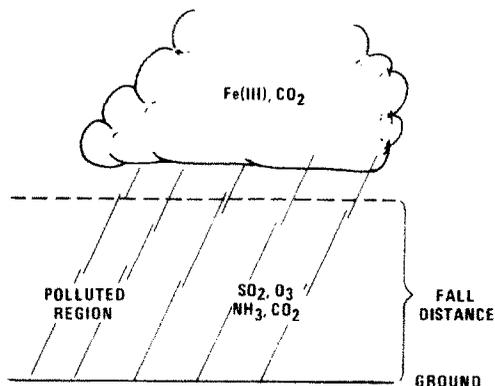


Fig. 1. Environmental model. The raindrop forms above the polluted region; then falls through this region where it absorbs gases which react to produce sulfate.

sidered the same at all times. The initial pH for each drop is that of water in equilibrium with the ambient CO_2 .

MASS TRANSPORT

The rate, per unit fall distance, at which a gas (here, O_3 , NH_3 , SO_2 and CO_2) crosses the gas-water interface of a drop of radius R is given by Equation (1):

$$\left. \frac{d[s]_l}{dz} \right|_{\text{transfer}} = \frac{3k_g}{Ru} ([s]_g - H_s[s]_l) \quad (1)$$

This gas is assumed to be distributed uniformly throughout the drop. The mass transfer coefficient, k_g , is obtained from the Frössling correlation (Frössling, 1938):

$$k_g = \frac{D_s}{R} \left[1 + 0.3 \left(\frac{2Ru}{v} \right)^{1/2} \left(\frac{v}{D_s} \right)^{1/3} \right] \quad (2)$$

where u is the fall velocity. Values of u are obtained from a formula by Markowitz (1976):

$$u = 958 \cdot \{1 - \exp[-(R/0.0885)^{1.147}]\} \quad (3)$$

(Values of H_s , D_s and v are given along with the notation.)

CHEMICAL REACTION WITHIN THE DROP

In our analysis of the SO_4^{2-} formation rate in atmospheric droplets, we have considered the chemistry of the following in CO_2 saturated water: S(IV)-O_3 , $\text{S(IV)-O}_2\text{-Fe(III)}$, and $\text{S(IV)-O}_3\text{-Fe(III)-O}_2$. The influence of NH_3 on each of these three systems was also considered. Unfortunately, the reaction mechanisms for oxidation in these three systems are not known. However, experimental relationships for the reaction velocities have been reported, and we have selected certain ones for the calculation of the oxidation rates in the droplets.

The chemical kinetic mechanism used is presented in Tables 1 and 2. Reactions 1–7 in Table 1 are the reversible reactions of a $\text{CO}_2\text{--SO}_2\text{--NH}_3\text{--water}$ system. Reactions 8–10 in Table 2 are the equations for SO_4^{2-} production by O_3 oxidation. The last three reactions (11, 12 and 13) in Table 2 are the equations contrived to simulate the catalytic production of SO_4^{2-} .

Experimental rates have been measured for the S(IV)--O_3 aqueous system by Penkett (1972) and

Erickson *et al.* (1977). Penkett's rate constant for S(IV)--O_3 was not resolved in terms of fractional contributions of ozonation of H_2SO_3 , HSO_3^- and SO_3^{2-} . Although substantial differences do exist between the values of Erickson *et al.* (1977) and Penkett (1972) for the ozonation of HSO_3^- , Erickson *et al.* reported the fractional contributions of the three S(IV) species, and for that reason we chose their values of rate constants. These rate constants are presented in Table 2. As can be seen by the large differences in reaction rate constants for the three S(IV) species, a significant pH effect would be expected.

The $\text{S(IV)--O}_2\text{--Fe(III)}$ system has been studied by Reinders and Vles (1925), Neytzell de Wilde and Taverner (1956), Johnstone and Coaghanouer (1958), Karraker (1963), Brimblecombe and Spedding (1974), Barrie and Georgii (1976), and Sutherland and Glines (1977). The reaction mechanism has not yet been established. Although reaction rate data are available, none of the investigators have made extensive pH range studies, except for Reinders and Vles (1925), who report only that Fe(III) 's active range is $4 < \text{pH} < 12$, with an optimum at $8 < \text{pH} < 10$. Neytzell de Wilde and Taverner (1956) made detailed studies over a narrow pH range, and reported that their results indicated that S(IV) oxidation had a second order dependence on $[\text{S(IV)}]$, first order dependence on $[\text{Fe(III)}]$, and inversely proportional to $[\text{H}^+]$. We have re-analyzed their data and discovered that the dependence on $[\text{S(IV)}]$ is first order. In the absence of a unified data set for the pH range of interest, we have assumed that the oxidation rate of S(IV) ($\approx \text{HSO}_3^- + \text{SO}_3^{2-}$) can be expressed as

$$-\text{d}[\text{S(IV)}]/\text{dt} = [\text{Fe(III)}] \{k'[\text{HSO}_3^-] + k''[\text{SO}_3^{2-}]\}. \quad (4a)$$

Assuming chemical equilibrium we can write Equation (4a) as

$$-\text{d}[\text{S(IV)}]/\text{dt} = [\text{Fe(III)}][\text{S(IV)}] \frac{K_1 k' [\text{H}^+] + k'' K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}, \quad (4b)$$

where

$$K_1 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{SO}_2]_f} = 0.017 \quad (5)$$

$$K_2 = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 10^{-7} \quad (6)$$

$$k' \equiv 64.21 \text{ mol}^{-1} \text{ s}^{-1} \quad (7)$$

$$k'' \equiv 47001 \text{ mol}^{-1} \text{ s}^{-1}. \quad (8)$$

The values of k' and k'' were obtained by using the first order rate constant ($1001 \text{ mol}^{-1} \text{ s}^{-1}$) of Brimblecombe and Spedding (1974) at $\text{pH} = 4.9$, and $691 \text{ mol}^{-1} \text{ s}^{-1}$ at $\text{pH} = 4$. The latter rate is ten times that measured at $\text{pH} = 2.6$ by Neytzell de Wilde and Taverner (1956). Sutherland and Glines (1977) reported the rate at pH

Table 1. Kinetic mechanism of $\text{CO}_2\text{--SO}_2\text{--NH}_3\text{--aqueous}$ phase system used for raindrops *, †, ‡

1.	$\text{H}_2\text{O} \xrightleftharpoons[1.3\text{E}+11]{1.3\text{E}-3} \text{H}^+ + \text{OH}^-$
2.	$\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons[5.6\text{E}+4]{4.3\text{E}-2} \text{HCO}_3^- + \text{H}^+$
3.§	$\text{CO}_2 + \text{OH}^- \xrightleftharpoons[1.0\text{E}-4]{1.4\text{E}+4} \text{HCO}_3^-$
4.	$\text{SO}_2 + \text{H}_2\text{O} \xrightleftharpoons[2.0\text{E}+8]{3.4\text{E}+6} \text{H}^+ + \text{HSO}_3^-$
5.	$\text{HSO}_3^- \xrightleftharpoons[1.0\text{E}+11]{1.0\text{E}+4} \text{SO}_3^{2-} + \text{H}^+$
6.	$\text{NH}_3 + \text{H}_2\text{O} \xrightleftharpoons[3.4\text{E}+10]{6.0\text{E}+5} \text{OH}^- + \text{NH}_4^+$
7.§	$\text{NH}_3 + \text{H}^+ \xrightleftharpoons[2.4\text{E}+1]{4.3\text{E}+10} \text{NH}_4^+$

* Units are in liters, moles, seconds.

† The concentration of H_2O has been incorporated into the rate constants where appropriate (i.e. for computations with these rate constants, use a value of unity for the molar concentration of H_2O).

‡ All rate constants, except for 4 and 6, are for 25°C . 4 and 6 are for 20°C ; however, the equilibrium constant for reaction 4 is the same as that reported by Beilke and Lamb (1975) for 25°C . Except for reaction 5 all rate constant values are from Eigen *et al.* (1964). Reaction 5 values are from Erickson and Yates (1976; 1977).

§ Since chemical equilibrium is quickly established, Equations 3 and 7 have little, if any, independent significance, and for all practical purposes may be omitted.

Table 2. Kinetic equations for SO_4^{2-} production in raindrops*

8.	$\text{O}_3 + \text{SO}_2 \xrightarrow{5.9\text{E}+2} 2\text{H}^+ + \text{SO}_4^{2-}$
9.	$\text{O}_3 + \text{SO}_3^{2-} \xrightarrow{2.2\text{E}+9} \text{SO}_4^{2-}$
10.	$\text{O}_3 + \text{HSO}_3^- \xrightarrow{3.1\text{E}+5} \text{H}^+ + \text{SO}_4^{2-}$
11.	$\text{Fe(III)} + \text{HSO}_3^- \xrightarrow{6.42\text{E}+1} \text{H}^+ + \text{SO}_4^{2-} + \text{Fe(II)}$
12.	$\text{Fe(III)} + \text{SO}_3^{2-} \xrightarrow{4.7\text{E}+3} \text{SO}_4^{2-} + \text{Fe(II)}$
13.	$\text{Fe(II)} + \text{O}_2 \xrightarrow{f_{\text{cat}}} \text{Fe(III)}$

* Units are in liters, moles, seconds.

= 4 to be ten times that at pH = 2.6. While such a procedure is obviously open to criticism, it is justifiable due to the sparse data available. Although there are no reliable data above pH = 4.9, we assumed that Equation (4a) was valid. Further, we have taken the SO_4^{2-} formation rate to be

$$\frac{d[\text{SO}_4^{2-}]}{dt} = -\frac{d}{dt}[\text{S(IV)}]. \quad (9)$$

The kinetic reactions 11, 12, and 13 in Table 2 are equivalent, as far as rates are concerned, to Equations (4) and (9). (The oxidation of Fe(II) is assumed to be sufficiently fast to assure that [Fe(III)] will remain constant.)

As pH increases from about 2 to 4, the Fe(III) is complexed by OH^- to yield species such as FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}(\text{OH})_3$. The catalytic activities (if any) of these species are not known. In fact, at pHs greater than about 4, $\text{Fe}(\text{OH})_3$ will be present as a colloid (Pourbaix, 1966). While the colloid form does not preclude its acting as a catalyst, unpredictable behavior (due to surface area fluctuations) may occur, as observed by Reinders and Vles (1925) for the $\text{Ni}(\text{OH})_3/\text{Ni}(\text{OH})_2$ system. Due to the absence of data on the relative catalytic effectiveness of Fe^{3+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$, we have assumed for the purpose of these calculations that they are equally effective.

The mixed system $\text{S(IV)}-\text{O}_3-\text{Fe(III)}-\text{O}_2$ has not been studied. For the purpose of these calculations, it has been assumed that its kinetic equations are the same as the "sum" of those of the $\text{S(IV)}-\text{O}_3$ and $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ systems. This approach is likely to be too conservative. Barrie (1975) reported that O_3 and SO_2 are absorbed faster by a manganese dichloride (MnCl_2) solution than by distilled water. However, once again the absence of data for the $\text{S(IV)}-\text{O}_3-\text{Fe(III)}-\text{O}_2$ system requires us to assume that the chemical kinetics are the "sum" of the two separate systems.

The major effect of NH_3 on the three previously mentioned systems is to raise the pH, preventing termination of the reaction due to high hydrogen ion concentrations. The rate of neutralization of the acid droplets by NH_3 is near the gas-collision limit (Robbins and Cadle, 1958). However, the cobalt(III) oxidation of ammonium sulfite proceeds at a rate of one-half that for sodium sulfite; most likely, the ammonium ion complexes the Co(III) and lowers its catalytic effectiveness. The $\text{S(IV)}-\text{Fe(III)}-\text{NH}_3-\text{O}_2$ system has not been studied, and it is not known if ammonium ion retards the oxidation rate. In the mechanism used, the effect of NH_3 is to increase the pH and thus to accelerate the rate of SO_4^{2-} production; no retarding effect due to the ammonium ion-catalyst complexes was considered.

MATHEMATICAL MODEL FORMULATION

The concentration of each chemical species within a

drop of radius R as a function of fall distance, z , was obtained by numerically integrating the coupled nonlinear differential equations derived from the kinetic and mass transport equations. That is, a set of the following type of equations was integrated,

$$\frac{d}{dz}\{[s]_i(Z, R)\} = \phi_s(Z, R) + \psi_s(Z, R).$$

ϕ , the chemical rate was obtained from the kinetic equations in Tables 1 and 2; the mass transfer rate, ψ , (if any) is given in Equation (1). A complete set of the differential equations is given in the Appendix. [Although equilibrium of the species in Table 1 is not assumed, it is quickly reached and maintained and thus justifies Equations (4b), (5) and (6).]

RESULTS AND DISCUSSION

Calculations for the chemical content of drops as a function of fall distance were made for various concentrations of trace species. The specific values used are listed in Table 3. In all cases, except for Fe(III), the initial liquid phase values of $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{CO}_2]$, $[\text{HCO}_3^-]$ are the same. Ambient CO_2 was assumed to have the constant value of 320 ppm. By setting the ambient $[\text{O}_3]$ and/or the $[\text{Fe(III)}]$ equal to one of the values listed, a given oxidizing system could be simulated: e.g. ambient $[\text{O}_3] = 0.0$ and $[\text{Fe(III)}] = 1 \times 10^{-5} \text{ mol l}^{-1}$ is the same as the $\text{S(IV)}-\text{O}_2-\text{Fe(III)}$ system.

We first considered the effects of ambient NH_3 , drop size and fall distance on pH and SO_4^{2-} production, using the $\text{S(IV)}-\text{O}_3-\text{Fe(III)}$ system. The results are illustrated in Figs. 2 and 3.

In Fig. 2 three sets of curves are displayed, each set containing three curves. The sets correspond to the three different values of ambient NH_3 used (0.5 and 20 ppb) and each curve within a set corresponds to a different fall distance (580, 1000 and 2000 m). Each drop had an initial pH = 5.56, which is shown as a dashed line drawn across the graph.

The effect of NH_3 on the pH is apparent: the higher

Table 3. Some basic parameters

Drop radii: 0.02–2.8 mm	
Ambient gas phase values:	
$[\text{SO}_2]$	= 0.01 ppm
$[\text{O}_3]$	= 0, 0.1 ppm
$[\text{NH}_3]$	= 0, 0.005, 0.020 ppm
$[\text{CO}_2]$	= 320 ppm.
Initial liquid phase values:	
$[\text{H}^+]$	= $0.290 \times 10^{-5} \text{ mol l}^{-1}$; pH = 5.56
$[\text{OH}^-]$	= $0.345 \times 10^{-8} \text{ mol l}^{-1}$
$[\text{CO}_2]$	= $0.11 \times 10^{-4} \text{ mol l}^{-1}$
$[\text{HCO}_3^-]$	= $0.29 \times 10^{-5} \text{ mol l}^{-1}$
$[\text{Fe(III)}]$	= 0, $10^{-5} \text{ mol l}^{-1}$

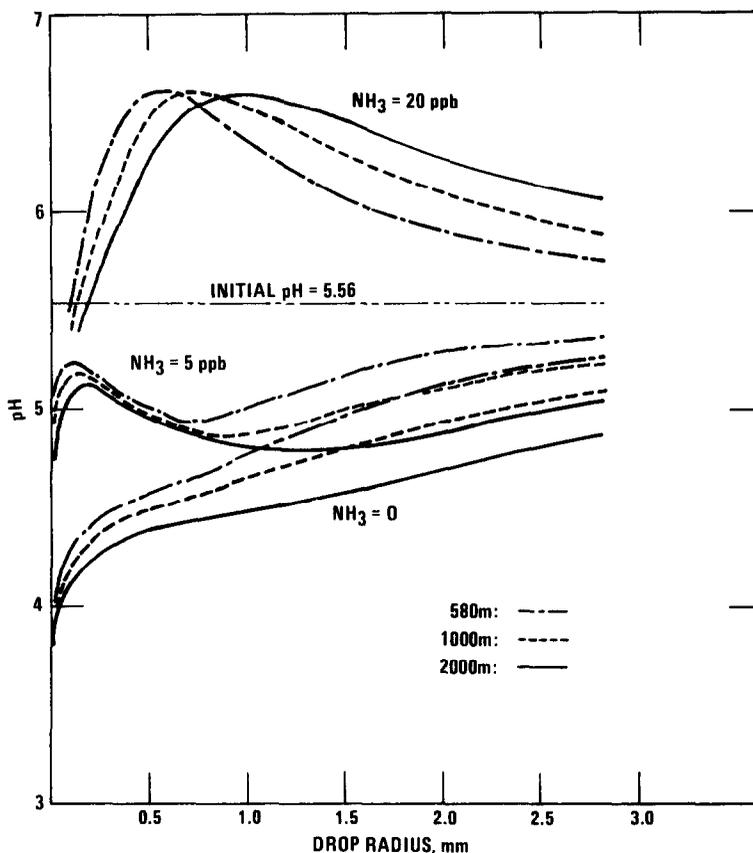


Fig. 2. pH vs drop radius for various fall distances and ambient $[\text{NH}_3]$. Initial liquid phase conditions of the drop: $\text{pH} = 5.5$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$ and $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$. Ambient gas phase values: $[\text{SO}_2]_g = 10 \text{ ppb}$, $[\text{O}_3]_g = 100 \text{ ppb}$, $[\text{NH}_3]_g = 0, 5 \text{ and } 20 \text{ ppb}$ and $[\text{CO}_2]_g = 320 \text{ ppm}$. Fall distances: 580, 1000 and 2000 m.

the ambient $[\text{NH}_3]$, the higher the pH regardless of fall distance or size. Even so, as the drop size increases all curves asymptotically approach the initial pH value of 5.56. The reason for this behavior is an artifact of the mathematical model and becomes clear by observing Equations (1), (2) and (3): as the ideal drop size goes to infinity, the rate of transfer of gases into the drop goes to zero and results in no reactions and changes in internal content.

Except for having a minimum pH for radii less than 0.1 mm, the three sets of curves behave differently. In the case in which $[\text{NH}_3] = 0$, for drops with radii greater than 0.1 mm, the pH increases with drop size, but in all cases remains below the initial pH = 5.56. For $[\text{NH}_3] = 20 \text{ ppb}$ the pH of drops with radii greater than 0.1 mm has a maximum value of about 6.6 in the range 0.4–1.0 mm; then pH decreases with respect to increasing drop size. For $[\text{NH}_3] = 5 \text{ ppb}$ the drops have a maximum pH of 5.1–5.3 for radii of about 0.1 mm, and a minimum in pH of 4.8–5.0 for radii in the range of 0.4–1.6 mm.

In all cases as the drop size approaches zero the pH decreases; it decreases to a low of 3.8 for $[\text{NH}_3] = 0$ and radius of 0.02 mm. This drop size is unreasonable

for rain; extending the size below 0.2 mm was carried out to explore the system's behavior for $[\text{NH}_3] = 5 \text{ ppb}$ as the radius becomes very small. A complete explanation as to the behavior of the system with $[\text{NH}_3] = 5 \text{ ppb}$ is not offered; however, qualitatively there are several factors which should be considered:

(1) The smaller the drop the longer the fall time for a given fall distance. For example, a 0.1 mm drop takes about eleven times as long to fall the same distance as a 1.5 mm drop. For 2000 m this translates into 44 and 4.2 min, respectively, of reaction time. In accordance with the kinetic mechanism used, the longer the reaction time the greater the hydrogen ion concentration, i.e. lower pH. The effect of reaction time is most apparent for the smallest drops.

(2) The smaller the drop radius the larger the effective mass transfer coefficient. (The effect of the radius getting very large has already been discussed.) The variation of transfer coefficient with radius could lead to the case of mass transfer controlled reactions for the large drops and chemically controlled rates for the small drops.

(3) The addition of NH_3 is expected to raise the pH, as it does.

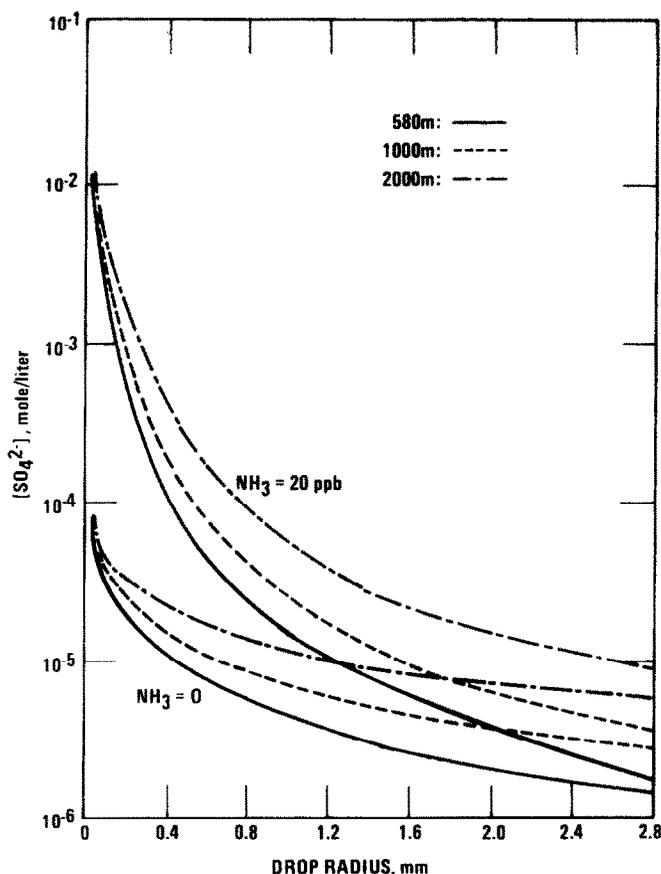


Fig. 3. $[\text{SO}_4^{2-}]$ vs drop radius for various fall distances and ambient $[\text{NH}_3]$. Initial liquid phase conditions of the drop: $\text{pH} = 5.56$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$ and $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$. Ambient gas phase values: $[\text{SO}_2]_g = 10 \text{ ppb}$, $[\text{O}_3]_g = 100 \text{ ppb}$, $[\text{NH}_3] = 0$ and 20 ppb and $[\text{CO}_2]_g = 320 \text{ ppm}$. Fall distances: 580, 1000 and 2000 m.

(4) The reaction system is non-linear which further complicates any interpretation.

In Fig. 3 the effects of drop size, fall distance and two values of ambient $[\text{NH}_3]$ on the production of SO_4^{2-} are displayed. (The set of curves that would correspond to $[\text{NH}_3] = 5 \text{ ppb}$ lie between the $[\text{NH}_3] = 0 \text{ ppb}$ and $[\text{NH}_3] = 20 \text{ ppb}$ sets of curves, are monotonically decreasing, and are omitted for clarity.) Ammonia has the effect of increasing the concentration of SO_4^{2-} . A drop, 0.2 mm radius, that falls between 600 and 2000 m in the absence of NH_3 contains about $20 \mu\text{mol l}^{-1}$ of SO_4^{2-} . With the ambient $[\text{NH}_3] = 20 \text{ ppb}$, the SO_4^{2-} concentration is 50 times as much ($\sim 2000 \mu\text{mol l}^{-1}$). In general the longer the reaction, the greater the sulfate concentration. Thus, the concentration is greater with smaller size or greater fall distance.

In order to simulate the production of SO_4^{2-} or the pH of rain after a given fall distance, we must take into consideration drops of every size that fall. To do this we have used the raindrop size distribution in air developed by Best (1950). This distribution is presented in Fig. 4. It depends only on the precipitation

rate. To obtain the size distribution at ground level, the air size distribution must be multiplied by the fall velocity (Best, 1950).

The average ground level concentration, $\overline{[s]}$, of a species, s , after a fall distance z is computed as

$$\overline{[s]}(z) = \frac{w}{p} \int_0^\infty u(R) \{[s](R, z)\} f(R) dR;$$

$$w = p \int_0^\infty u(R) f(R) dR,$$

where w is the ratio of the volume of rain water in air to the volume of air containing the water; p is the precipitation rate which is taken to be 10 mm h^{-1} for this work; f is the raindrop size density function. The average concentration has the following meaning: if A is the area of a container perpendicular to falling rain and t is the time spent in collecting the rain, then the total amount of species s collected is $A \cdot p \cdot t \cdot \overline{[s]}$. (No reactions are assumed to occur in the container.)

Figure 5 illustrates the effects of NH_3 and fall distance on pH and SO_4^{2-} production for a rain event when $[\text{O}_3] = 0 \text{ ppb}$. (Taking $[\text{O}_3] = 0$ is equivalent to

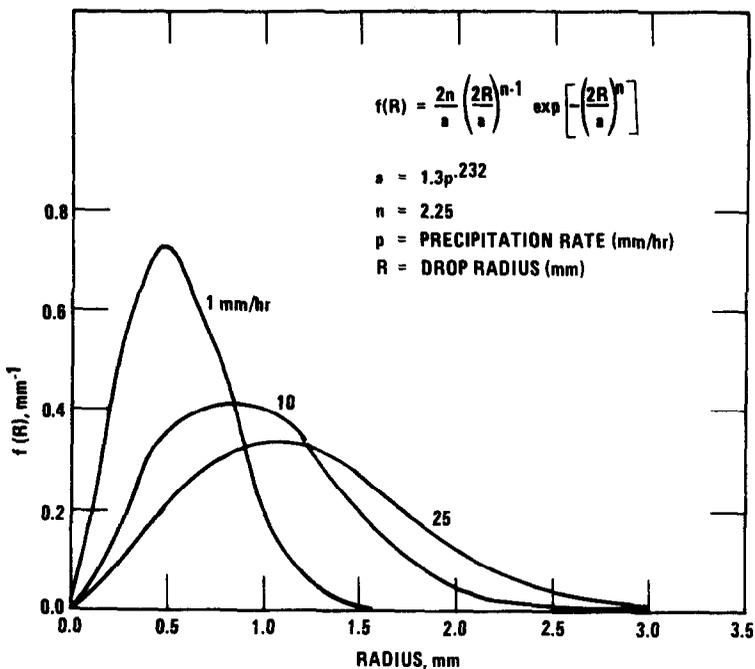


Fig. 4. Raindrop size density function for various precipitation rates. Calculated curves are shown for precipitation rates $p = 1, 10$ and 25 mm h^{-1} . (Source: Best, 1950; and Hill and Adamowicz, 1977.)

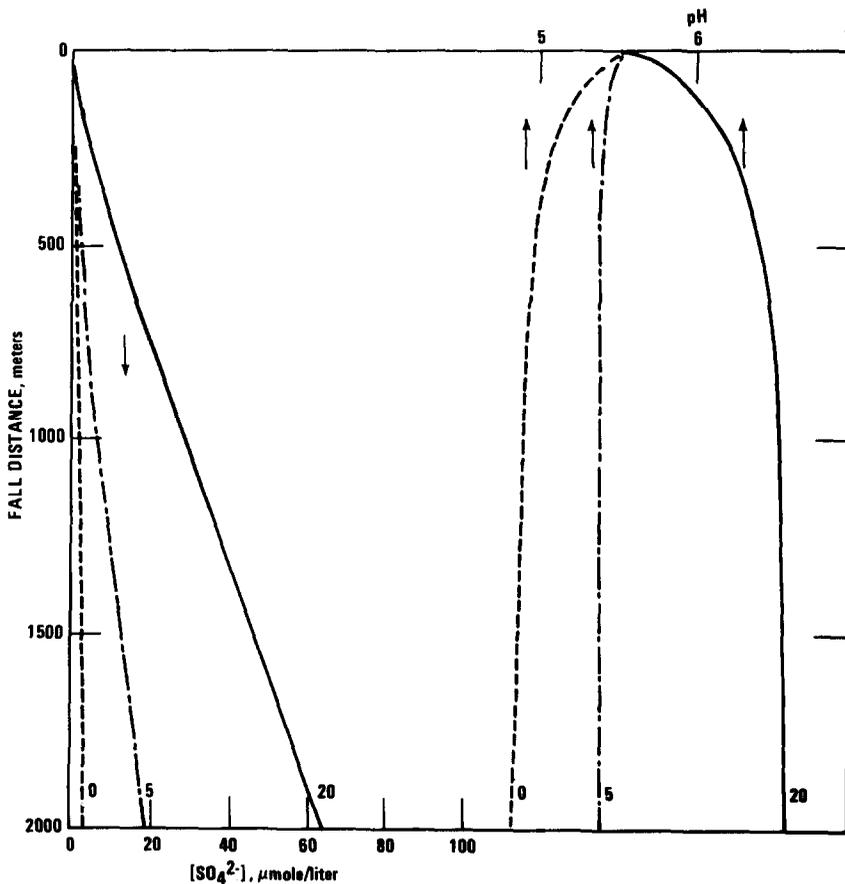


Fig. 5. pH and $[\text{SO}_4^{2-}]$ vs fall distance for various ambient $[\text{NH}_3]$, and a precipitation rate of 10 mm h^{-1} . Initial liquid phase conditions of the drop: $\text{pH} = 5.56$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$ and $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$. Ambient gas phase values: $[\text{SO}_2]_g = 10 \text{ ppb}$, $[\text{O}_3]_g = 0 \text{ ppb}$, $[\text{NH}_3]_g = 0, 5$ and 20 ppb , and $[\text{CO}_2]_g = 320 \text{ ppb}$.

using only the S(IV)-O₂-Fe(III) oxidation system.) Displayed are two sets of three curves. One set is for pH, the other is for sulfate; the curves within a set correspond to three values of ambient NH₃ (0, 5 and 20 ppb).

At a fall distance of zero, the initial value of pH is 5.56 and either increases or decreases depending on the ambient NH₃. After a 2000-m fall, the pH reaches about 4.8 or 6.6 for [NH₃] = 0 or [NH₃] = 20 ppb, respectively. Little change occurs for the [NH₃] = 5 ppb case or for any of the three curves after about a 500-m fall. Initially, the sulfate production rate is high and then becomes approximately constant after a fall of 500 m. The effect of NH₃ is to increase the concentration of SO₄²⁻; e.g. 3 μmol l⁻¹ and 18 μmol l⁻¹ for [NH₃] = 0 ppb and 5 ppb, respectively, after a 2000-m fall.

The S(IV)-O₃ and S(IV)-O₃-Fe(III) oxidizing systems gave the same results. These are illustrated in Fig. 6 and are similar to those of Fig. 5. Greater concentrations of sulfate are produced for these two systems than in the S(IV)-Fe(III)([O₃] = 0) system

(Fig. 5). At 2000 m the concentration is (O₃ and/or O₃-Fe(III) system) 12 and 35 μmol l⁻¹ for 0 and 5 ppb of NH₃, respectively. These are 2 and 4 times larger than for the same respective values of [NH₃] when [O₃] = 0. For our model calculations, oxidation of S(IV) in droplets by Fe(III) present at a concentration of 10⁻⁵ mol l⁻¹ is insignificant compared to that by the simultaneous presence of O₃ at a concentration of 100 ppb. The same qualitative shifts in Fig. 6 for pH are observed as in Fig. 5. However, the pHs are lower after a 2000-m fall; the largest change (comparing Figs. 5 and 6) is observed for the NH₃ = 5 ppb case.

Figures 7, 8 and 9 illustrate the effect of the three oxidizing systems on pH and sulfate production for given ambient ammonia values as a function of fall distance. (Only two distinct curves are shown on the graphs as the S(IV)-O₃-Fe(III) and S(IV)-O₃ systems gave the same results.)

In general, for the particular initial conditions and ambient concentrations chosen, the S(IV)-O₃ and S(IV)-O₃-Fe(III) oxidizing systems produced greater sulfate concentrations and lower pHs than did the

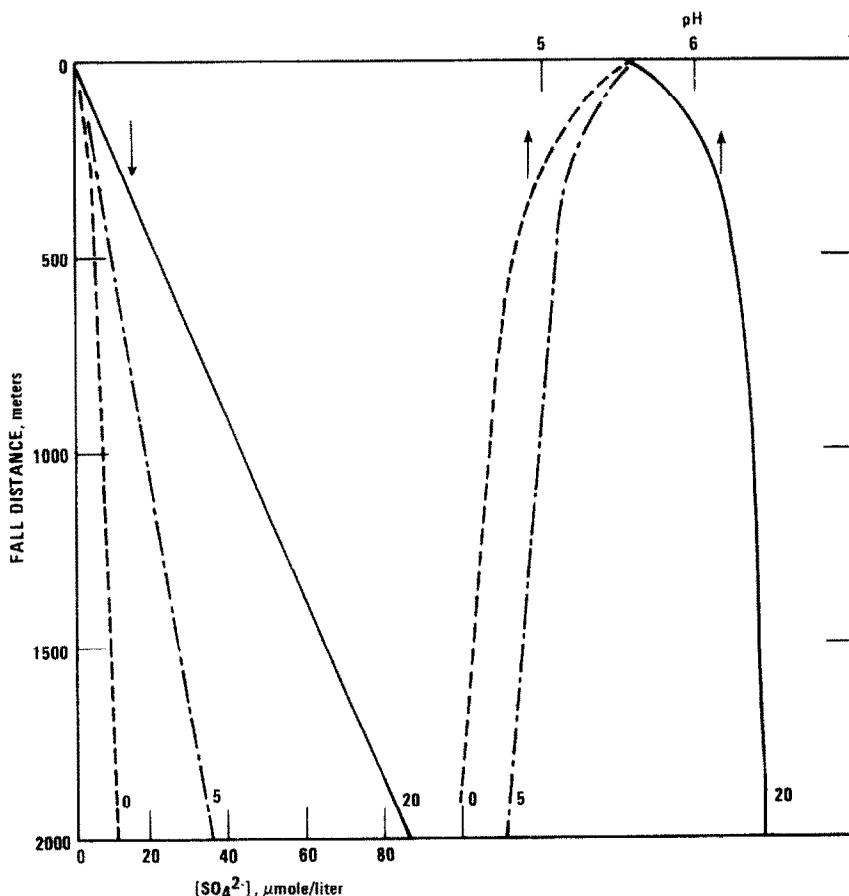


Fig. 6. pH and [SO₄²⁻] vs fall distance for various ambient [NH₃] and a precipitation rate of 10 mm h⁻¹. Initial liquid phase conditions of the drop: pH = 5.56, [CO₂]_l = 0.11 × 10⁻⁴ mol l⁻¹, [HCO₃⁻]_l = 0.29 × 10⁻⁵ mol l⁻¹ and [Fe(III)] = 0 and 10⁻⁵ mol l⁻¹. Ambient gas phase values: [SO₂]_g = 10 ppb, [O₃]_g = 100 ppb, [NH₃]_g = 0, 5 and 20 ppb and [CO₂]_g = 320 ppb. For the conditions considered, the results are indistinguishable for the two iron concentrations.

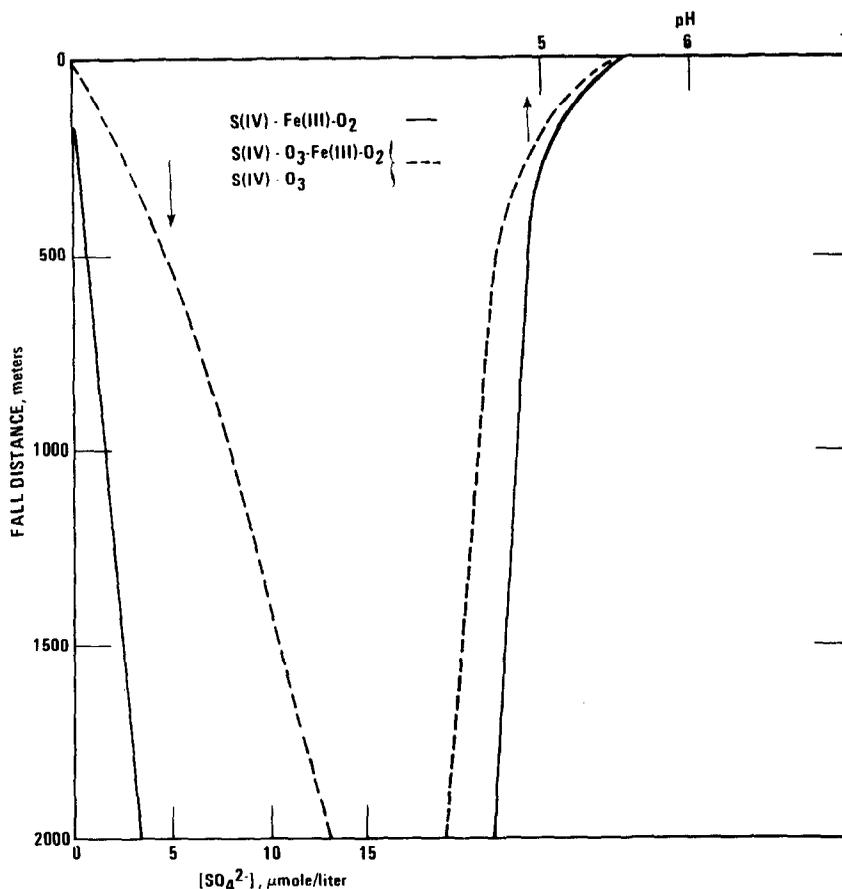


Fig. 7. pH and $[\text{SO}_4^{2-}]$ vs fall distance for various reaction systems with $[\text{NH}_3]_0 = 0$ ppb. The reaction systems considered are: (a) $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$, (b) $\text{S(IV)}-\text{O}_3-\text{Fe(III)}-\text{O}_2$ and (c) $\text{S(IV)}-\text{O}_3$. For the conditions considered, the latter two systems are indistinguishable. Initial liquid phase conditions of the drop: $\text{pH} = 5.56$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$ for system (a) and (b) and $[\text{Fe(III)}] = 0 \text{ mol l}^{-1}$ for system (c). Ambient gas phase values: $[\text{SO}_2]_g = 10$ ppb, $[\text{O}_3]_g = 0$ ppb for system (a), $[\text{O}_3]_g = 100$ ppb for system (b) and (c), $[\text{NH}_3]_g = 0$ ppb and $[\text{CO}_2]_g = 320$ ppm. After a 2000-m fall, the $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system's pH is 0.3 higher than that for the other two systems, and its $[\text{SO}_4^{2-}]$ is about 75% lower.

$\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system. As the ambient value of $[\text{NH}_3]$ increases, the relative differences in the production of sulfate decreases: after a 2000-m fall ~ 3 times as much sulfate is produced by the $\text{S(IV)}-\text{O}_3-\text{Fe(III)}$ or $\text{S(IV)}-\text{O}_3$ systems as by the $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system for $[\text{NH}_3] = 0$. Whereas for the $[\text{NH}_3] = 20$ ppb case, the ratio is only 1.3. On the other hand, the relative values of pH increase then decrease as the ambient value of NH_3 increases: the pHs of the systems graphed (Figs. 7, 8, 9) differ by 0.3, 0.55 and 0.1 for $[\text{NH}_3] = 0, 5$ and 20 ppb, respectively.

A tabular summary of Figs. 7-9 is presented in Table 4. From this table an idea as to the effect of oxidizing system, ambient $[\text{NH}_3]$ and fall distance on pH and sulfate production can be obtained.

Using Table 4 we can draw the following conclusions for the model:

(a) For the $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system

(1) sulfate production is $[\text{NH}_3]$ and fall dis-

tance dependent. At 1000 m, five times as much sulfate is produced for $[\text{NH}_3] = 5$ ppb as for the $[\text{NH}_3] = 0$ ppb case. Sulfate production is approximately proportional to fall distance.

(2) pH increases as the ambient $[\text{NH}_3]$ increases; but it is not very sensitive to fall distance after 500 m.

(b) The $\text{S(IV)}-\text{O}_3$ system

(1) behaves, with respect to fall distance and ambient $[\text{NH}_3]$, like the $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system. However, the effect of NH_3 on sulfate production is less dramatic - at 1000 m the $[\text{SO}_4^{2-}]$ concentration is only two times as large for $[\text{NH}_3] = 5$ ppb as for $[\text{NH}_3] = 0$ ppb.

(2) Has a pH behavior similar to the $\text{S(IV)}-\text{Fe(III)}-\text{O}_2$ system: increasing with increasing $[\text{NH}_3]$ and insensitive to fall distance after 500 m.

(c) The $\text{S(IV)}-\text{Fe(III)}-\text{O}_3$ system for $[\text{Fe(III)}] =$

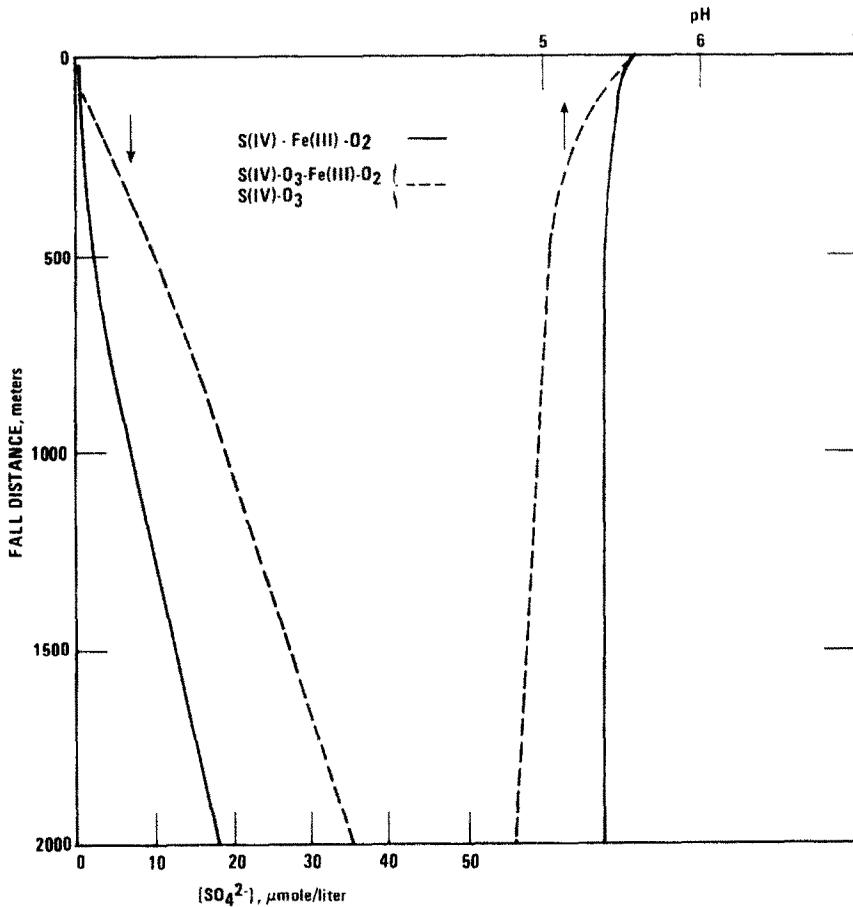


Fig. 8. pH and $[\text{SO}_4^{2-}]$ vs fall distance for various reaction systems with $[\text{NH}_3]_g = 5$ ppb. The reaction systems considered are: (a) S(IV)-Fe(III)-O_2 , (b) $\text{S(IV)-O}_3\text{-Fe(III)-O}_2$, and (c) S(IV)-O_3 . For the conditions considered, the latter two systems are indistinguishable. Initial liquid phase conditions of the drop: $\text{pH} = 5.56$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$ for system (a) and (b), and $[\text{Fe(III)}] = 0 \text{ mol l}^{-1}$ for system (c). Ambient gas phase values: $[\text{SO}_2]_g = 10$ ppb, $[\text{O}_3]_g = 0$ ppb for system (a), $[\text{O}_3]_g = 100$ ppb for system (b) and (c), $[\text{NH}_3]_g = 20$ ppb, and $[\text{CO}_2]_g = 320$ ppm. After a 2000-m fall, the S(IV)-Fe(III)-O_2 system's pH is 0.5 higher than that for the other two systems, and its $[\text{SO}_4^{2-}]$ is about 50% lower.

Table 4. Summary of Figs. 7-9. Effect of oxidizing system, ambient NH_3 and fall Distance on pH and sulfate production

		Oxidizing system					
		S(IV)-O ₃ -Fe(III) S(IV)-O ₃			S(IV)-Fe(III)-O ₂		
		Ambient NH ₃ (ppb)			Ambient NH ₃ (ppb)		
		0	5	20	0	5	20
	Fall distance (m)						
pH	500	5.0	5.1	6.2	4.8	5.4	6.4
	1000	4.9	4.9	6.3	4.6	5.4	6.5
	2000	4.8	4.8	6.4	4.5	5.35	6.55
Sulfate ($\mu\text{mol l}^{-1}$)	500	4.4	9.0	22.0	0.6	2.5	12.0
	1000	8.0	19.0	43.0	1.5	7.0	30.0
	2000	13.2	35.0	87.0	3.2	18.0	65.0

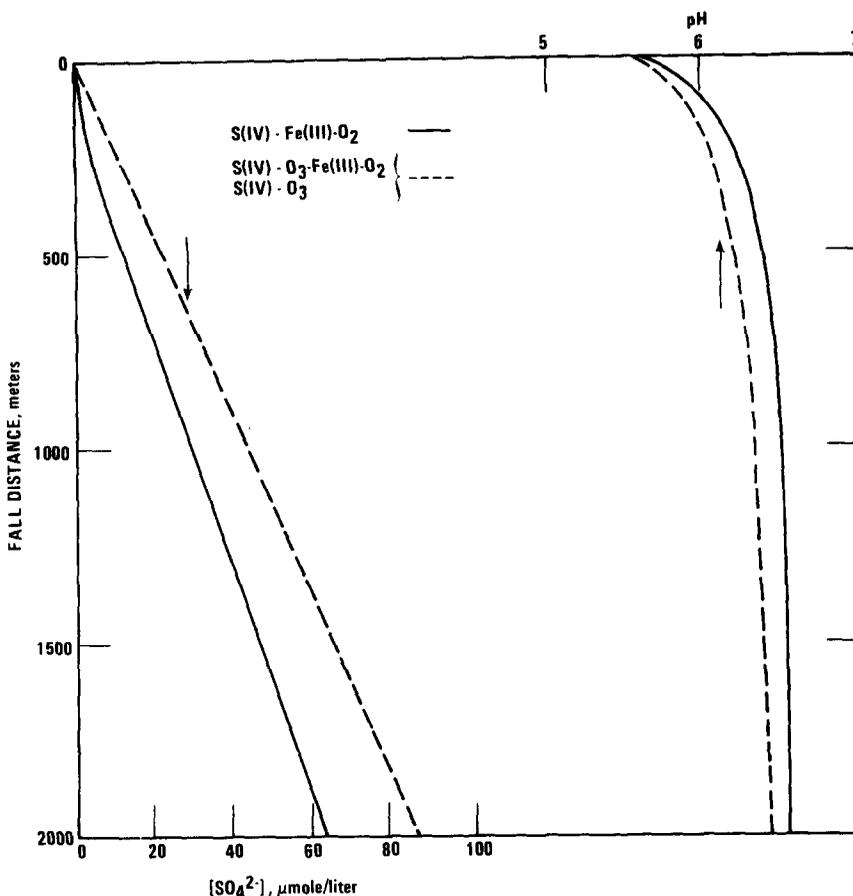


Fig. 9. pH and $[\text{SO}_4^{2-}]$ vs fall distance for various reaction systems and $[\text{NH}_3]_g = 20$ ppb. The reaction systems considered are: (a) S(IV)-Fe(III)-O_2 , (b) $\text{S(IV)-O}_3\text{-Fe(III)-O}_2$ and (c) S(IV)-O_3 . For the conditions considered, the latter two systems are indistinguishable. Initial liquid phase conditions of the drop: $\text{pH} = 5.56$, $[\text{CO}_2]_l = 0.11 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{HCO}_3^-] = 0.29 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{Fe(III)}] = 10^{-5} \text{ mol l}^{-1}$ for system (a) and (b), and $[\text{Fe(III)}] = 0 \text{ mol l}^{-1}$ for system (c). Ambient gas phase values: $[\text{SO}_2]_g = 10$ ppb, $[\text{O}_3]_g = 0$ ppb for system (a), $[\text{O}_3]_g = 100$ ppb for system (b) and (c), $[\text{NH}_3]_g = 5$ ppb, and $[\text{CO}_2]_g = 320$ ppm. After a 2000-m fall, the S(IV)-Fe(III)-O_2 system's pH is 0.10 higher than that for the other two systems, and its $[\text{SO}_4^{2-}]$ is about 20% lower.

$10^{-5} \text{ mol l}^{-1}$ and $[\text{O}_3] = 100$ ppb give the same results as the S(IV)-O_3 system ($[\text{O}_3] = 100$ ppb and $[\text{Fe(III)}] = 0$).

- (d) The $\text{S(IV)-O}_3\text{-Fe(III)}$ or S(IV)-O_3 system produced more sulfate than the S(IV)-Fe(III) system: e.g. at 1000 m and $[\text{NH}_3] = 5$ ppb, the concentration of the first two systems was over twice the third system (19 and $7 \mu\text{mol l}^{-1}$, respectively). Except for the $[\text{NH}_3] = 0$ case, the S(IV)-Fe(III) system had the higher pHs.
- (e) In all cases pH fell between 4.5 and 6.55. The most sulfate produced was $87 \mu\text{mol l}^{-1}$ for the longest fall distance, 2000 m, and highest $[\text{NH}_3]$ value, 20 ppb.

CONCLUSIONS

A model has been presented that describes the production of sulfate and the variation of pH in rain

and raindrops as a function of fall distance, drop size, a catalyst (Fe(III)) and ambient CO_2 , SO_2 , O_3 , and NH_3 . The model is an idealization of a rather limited physico-chemical system and is far from complete. For example, the model does not allow for the effects of nitrogen oxide gases which may effect the acidity of the rain. Also, the mechanism by which sulfate in the present model is produced is not unique; catalysts, other than Fe(III) , could be present. Further, one cannot expect a catalyst, such as Fe , to be uniformly distributed among the raindrops; thus drops of the same size could have significantly different amounts of sulfate, as well as vary in pH. Drops also absorb gases while they are forming and they are not always formed in the absence of pollutants as assumed here; in general we may expect for a given rain event a wide range of "initial" conditions for drops.

Atmospheric dynamics have also not been considered. Drops can be retained in polluted regions for

longer than their "fall time" (as calculated from terminal velocity). The ambient concentration profiles are dependent on height as well as time. In fact, we can expect rain to remove ambient pollutants and decrease the ambient concentrations as the rain proceeds; this effect was not considered in the model.

We have not considered the influence of temperature on sulfate formation in droplets. However, the aspect of temperature influence has been investigated by others for reactions of dissolved sulfur dioxide in solution and atmospheric aerosols. Neytzell de Wilde and Taverner (1958) have experimentally measured the reaction rate of dissolved sulfur dioxide in the presence of Fe(III) at 1.5, 15 and 20°C; the rate increased with temperature. Also, Erickson *et al.* (1977) observed for the dissolved sulfur dioxide-ozone reaction in water an increase in rate constants as temperature increased. However, the temperature dependence of solubility and equilibrium constants for the dissolved species may offset the above positive dependence, as suggested by Freiberg (1974) for aerosols in a power plant plume.

Even though the model is limited, it does give useful insight into the effect of chemical reactions and fall distance on the production of sulfate in rain and raindrops, and may be considered as a basis for a more complex model.

Because of the above limitations in the model, comparisons of the model to actual situations may not be valid, and indeed could be misleading. Nevertheless, experimental data are available and as comparison is inevitable, we give some ranges of pH and sulfate values found in the literature. For individual raindrops, pHs less than two to greater than eight have been reported (Esmen and Fergus, 1976). For rain events, reported average pH values range from 3 to about 9 (Likens, 1976; Jacobson *et al.*, 1976; Semonin, 1976). Average sulfate values have been found as high as 150 $\mu\text{mol l}^{-1}$ and as low as 20 $\mu\text{mol l}^{-1}$ with a weighted mean of 32 $\mu\text{mol l}^{-1}$ for corresponding $[\text{SO}_2]$ in air of 10–1 ppb with a weighted mean of 2 ppb (Semb, 1976). Comparison of the above ranges of experimental values with those in Table 4 indicate that the model results are not unreasonable.

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APPENDIX

Presented here is the set of differential equations used for the chemical kinetics in the aqueous droplets. All concentrations are for the liquid phase, unless denoted with a subscript "g" (gas phase). The value of the mass transfer coefficient, k_g , and Henry's law constant, H , depend on the species.

$$u \frac{d[\text{H}^+]}{dz} = -k_{-1}[\text{H}^+][\text{OH}^-] + k_{+1} + k_{+2}[\text{CO}_2] \\ - k_{-2}[\text{H}^+][\text{HCO}_3^-] + k_{+4}[\text{SO}_2] \\ - k_{-4}[\text{H}^+][\text{HSO}_3^-] + k_{+5}[\text{HSO}_3^-] \\ - k_{-5}[\text{H}^+][\text{SO}_3^{2-}] - k_{+7}[\text{H}^+][\text{NH}_3] \\ + k_{-7}[\text{NH}_4^+] + 2 \cdot k_8[\text{O}_3][\text{SO}_2] \\ + k_{10}[\text{O}_3][\text{HSO}_3^-] \\ + k_{11}[\text{Fe(III)}][\text{HSO}_3^-]$$

$$u \frac{d[\text{OH}^-]}{dz} = k_{+1} - k_{-1}[\text{H}^+][\text{OH}^-] \\ - k_{+3}[\text{CO}_2][\text{OH}^-] \\ + k_{-3}[\text{HCO}_3^-] + k_{+6}[\text{NH}_3] \\ - k_{-6}[\text{OH}^-][\text{NH}_4^+]$$

$$u \frac{d[\text{CO}_2]}{dz} = -k_{+2}[\text{CO}_2] + k_{-2}[\text{H}^+][\text{HCO}_3^-] \\ - k_{+3}[\text{CO}_2][\text{OH}^-] + k_{-3}[\text{HCO}_3^-] \\ + \frac{3k_g}{R}([\text{CO}_2]_g - H[\text{CO}_2])$$

$$u \frac{d[\text{HCO}_3^-]}{dz} = +k_{+2}[\text{CO}_2] - k_{-2}[\text{HCO}_3^-][\text{H}^+] \\ + k_{+3}[\text{CO}_2][\text{OH}^-] - k_{-3}[\text{HCO}_3^-]$$

$$u \frac{d[\text{SO}_2]}{dz} = -k_{+4}[\text{SO}_2] + k_{-4}[\text{H}^+][\text{HSO}_3^-] \\ - k_8[\text{O}_3][\text{SO}_2] + \frac{3k_g}{R}([\text{SO}_2]_g \\ - H[\text{SO}_2])$$

$$u \frac{d[\text{HSO}_3^-]}{dz} = k_{+4}[\text{SO}_2] - k_{-4}[\text{H}^+][\text{HSO}_3^-] \\ - k_{-5}[\text{HSO}_3^-] + k_{+5}[\text{SO}_3^{2-}][\text{H}^+] \\ - k_{10}[\text{O}_3][\text{HSO}_3^-] \\ - k_{11}[\text{Fe(III)}][\text{HSO}_3^-]$$

$$u \frac{d[\text{SO}_3^{2-}]}{dz} = k_{+5}[\text{HSO}_3^-] - k_{-5}[\text{SO}_3^{2-}][\text{H}^+] \\ - k_9[\text{O}_3][\text{SO}_3^{2-}] - k_{12}[\text{Fe(III)}][\text{SO}_3^{2-}]$$

$$u \frac{d[\text{NH}_3]}{dz} = -k_{+6}[\text{NH}_3] + k_{-6}[\text{OH}^-][\text{NH}_4^+] \\ - k_{+7}[\text{NH}_3][\text{H}^+] + k_{-7}[\text{NH}_4^+] \\ + \frac{3k_g}{R}([\text{NH}_3]_g - H[\text{NH}_3])$$

$$u \frac{d[\text{NH}_4^+]}{dz} = k_{+6}[\text{NH}_3] - k_{-6}[\text{OH}^-][\text{NH}_4^+] \\ + k_{+7}[\text{NH}_3][\text{H}^+] - k_{-7}[\text{NH}_4^+]$$

$$u \frac{d[\text{O}_3]}{dz} = -[\text{O}_3](k_8[\text{SO}_2] + k_9[\text{SO}_3^{2-}] \\ + k_{10}[\text{HSO}_3^-]) + \frac{3k_g}{R}([\text{O}_3]_g - H[\text{O}_3])$$

$$u \frac{d[\text{Fe(III)}]}{dz} = 0$$

$$u \frac{d[\text{SO}_4^{2-}]}{dz} = [\text{O}_3](k_8[\text{SO}_2] + k_9[\text{SO}_3^{2-}] \\ + k_{10}[\text{HSO}_3^-]) \\ - [\text{Fe(III)}](k_{11}[\text{HSO}_3^-] + k_{12}[\text{SO}_3^{2-}]).$$