

INFLUENCE OF GASEOUS NITRIC ACID ON SULFATE PRODUCTION AND ACIDITY IN RAIN

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Abstract—A physico-chemical subcloud rain model is used to simulate the effect of gaseous HNO_3 and NO_x on pH and SO_4^{2-} production in a 10 mm h^{-1} , 1000-m fall distance rain event. The ambient gases considered in the chemistry were SO_2 , NO , NO_2 , HNO_3 , O_3 , and CO_2 . Raindrops initially at a pH of 5.5 absorbed these gases, and as they fell through a polluted zone, produced SO_4^{2-} and NO_3^- by the oxidation of dissolved SO_2 by O_3 and the dissociation of HNO_3 , which reduced the pH. For the chemical mechanism and the below-cloud washout rain events considered, it was observed that absorption of gaseous HNO_3 controlled the acidification in the initial stages of a rain event, and inhibited the production of SO_4^{2-} ; NO and NO_2 played no direct role in the acidification or formation of NO_3^- or SO_4^{2-} ; pre-acidified raindrops (pH of 4) were further acidified only by absorbing HNO_3 .

NOTATION

| | |
|---------------|---|
| D | Diffusion coefficient, $\text{cm}^2\text{ s}^{-1}$ |
| H | Henry's law constant, dimensionless. Equilibrium ratio of gas phase concentration to liquid phase concentration of same species |
| R | Drop radius (mm) |
| g | Indicates gas phase |
| i | Rate constant subscript, reaction equation number |
| k_g | Gas phase mass transfer coefficient (cm s^{-1}) |
| k_i | Rate constant for i -th reaction |
| s | Indicates a chemical species such as SO_2 , HNO_3 , H^+ , HSO_3^- , etc |
| t | Time |
| u | Fall velocity (m s^{-1}) |
| z | Fall distance (m) |
| l | Indicates liquid phase |
| [] | Molar concentration |
| ν | Kinematic viscosity of air, $0.133\text{ cm}^2\text{ s}^{-1}$ |
| ϕ | Reaction rate |
| ψ | Mass transfer rate |
| μM | $10^{-6}\text{ moles l}^{-1}$ |

INTRODUCTION

It was recognized over a decade ago that the acidity of precipitation was increasing and leading to environmental damage in Sweden (Oden, 1968). Trend analysis of content of precipitation samples indicate that the pH at stations in Sweden and Norway are declining at approximately the same rate (Oden, 1976), suggesting a regional behavior and long-range transport of pollutants from the United Kingdom, western Europe, and eastern Europe. There is no comparable long-term data base for precipitation acidity in the United States.

Using data from 1964–72, Likens and Bormann (1974) have reported for a station in New Hampshire an upward trend for nitrate and hydrogen ion and a downward trend for sulfate; similar trends for sulfate and nitrate were observed in Geneva and Ithaca, New York. Although the period of their acidity observations (9 years in New Hampshire) is not ideal for demonstrating a trend, they did succeed in directing attention to the potential seriousness of this problem which may become more important in the future. An increase in acid precipitation is to be expected because sulfur and nitrogen oxides emissions are projected to increase by 12 and 61%, respectively, over their 1975 values by the year 2000 (Glass, 1978).

The present state of knowledge of acid rain is insufficient to permit a quantitative cause-effect analysis. It is suspected that the increased acidification of precipitation in the northeastern U.S. is being brought about by at least several factors, which include: (a) the path of major storm tracks, which usually pass through the industrialized Tennessee River Valley, the Ohio River Valley, or the north Atlantic states, (b) use of tall stacks to control SO_2 concentrations by dispersion instead of suppression, (c) the use of electrostatic precipitators to selectively remove basic fly ash, but with no reduction of the acid gases SO_2 and NO and (d) the absence of basic mineral dust in the natural environment of the northeastern U.S. The U.S. Environmental Protection Agency has recognized the need for developing regulatory programs to permit the control of acid precipitation (Berry and Bachmann, 1977). Among the research needs to support such an effort is an understanding of the pollutant chemistry leading to rain acidification.

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The acidification of rain is principally due to the

oxidation of SO₂ or N-oxides in cloud droplets and raindrops, the absorption of free gaseous acids by droplets and raindrops, or scavenging of acid aerosol by the falling raindrops. Although the acid aerosol scavenging and in-cloud processes are important, we shall not consider them in our treatment presented here. Instead, we shall focus on the non-photochemistry of the N-oxides, S-oxides, and O₃ in both the gas and aqueous phases, which is an extension of our previous treatment on acid sulfate formation by O₃ and Fe-catalyzed reactions in falling raindrops (Overton *et al.*, 1979).

The chemical composition of rainfall due to sub-cloud scavenging collected at ground level will be calculated by a physical-chemical model employing the gas-phase and aqueous phase reactions for N-oxide and S-oxide species presented below. CO₂ is also included because of its action in buffering liquid water to a pH of 5.6 in the absence of strong acids. The principal oxidant considered is O₃. Due to a lack of information, N-oxide species were not considered to be significant oxidants nor were transition metal ions, but in reality, they may be. Also H₂O₂, which is known to be important (Penkett *et al.*, 1979) is not yet part of our reaction scheme. Initially, before the raindrops begin to fall, we assume that only these reaction gases are important in the polluted atmosphere: SO₂, NO, NO₂, HNO₃, CO₂, and O₃.

The aqueous chemistry of N-oxide species is not well known, and the best current sources of rate constants refer to conditions appropriate for combustion emission control. In some cases the reaction rates for these species were measured at concentrations several orders of magnitude greater than of interest in the free atmosphere. Realizing that the kinetic mechanisms may be different at lower concentrations, we embrace these rate constants reluctantly.

The phenomenon of subcloud scavenging (rain falling through a polluted zone) is modeled, but in-cloud scavenging (formation of rain in the polluted zone) and the effect of in-cloud processes are ignored, although they may be significant.

PHYSICAL MODEL

Our physical model of a rain event, raindrops and mass transfer are described by Overton *et al.* (1979) and repeated here for completeness.

The atmosphere has been divided into two regions, shown in Fig. 1. Raindrops are formed in the upper region in the presence of CO₂ and other compounds which establish the initial pH. The drops enter and fall through a stable polluted region at a constant velocity. In the polluted region are the trace gases CO₂, O₃, SO₂, HNO₃, NO and NO₂. As the drop falls, gases are absorbed, react and produce SO₄²⁻ and NO₃⁻ and other species. A raindrop is taken to be a uniform sphere composed of water and trace quantities of O₃, SO₂, CO₂, HNO₃, NO, NO₂ and their products. The concentrations are assumed to be uniformly distributed at all times throughout the drop, (i.e., no concentration gradients in the drop). The temperature of the raindrops is assumed to be in equilibrium with an isothermal atmosphere at 25°C (a choice dictated by the available chemical rate constant data).

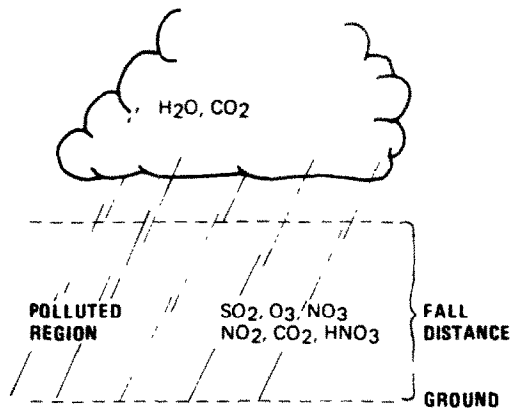


Fig. 1. Environmental model. The raindrops form above and fall through the polluted zone. In the polluted zone, they absorb reactive gases which produce SO₄²⁻ and NO₃⁻.

The rate, per unit fall distance, at which a gaseous species (e.g. O₃, HNO₃, NO, NO₂, SO₂ and CO₂) crosses the gas-water interface of a drop of radius *R* is given by Equation (1):

$$\left. \frac{d[s]}{dz} \right|_{\text{transfer}} = \frac{0.3k_g}{Ru} ([s]_g - H_s[s]_l) \quad (1)$$

The species, *s*, is assumed to be distributed uniformly throughout the drop. The mass transfer coefficient, *k_g*, is obtained from the Frössling correlation (Frössling, 1938).

$$k_g = \frac{10D_s}{R} \left[1 + 0.3 \left(\frac{20Ru}{v} \right)^{1/2} \left(\frac{v}{D_s} \right)^{1.3} \right] \quad (2)$$

where *u* is the fall velocity and *v* is the kinematic viscosity of air. Values of *u* are obtained from a formula by Markowitz (1976):

$$u = 9.58 \{ 1 - \exp[-(R/0.885)^{1.47}] \} \quad (3)$$

Values of *H_s*, Henry's law constant, and *D_s*, gas-phase diffusion coefficient, for molecular species are given in Table 1.

CHEMICAL REACTION WITHIN THE DROP

In Table 2 are the chemical reactions selected for calculating the acidification of falling raindrops. Equations 1-11 are the reversible reactions for the CO₂-SO₂-NO-NO₂-N₂O₃-H₂O₄-HNO₂-HNO₃-water system. The reverse reaction for Equation 10 has not been reported, but due to the expected extremely low concentrations of molecular HNO₃ and HNO₂, we have assumed that it is unimportant. Equations 12-15 are the irreversible oxidation steps for forming NO₃⁻ and SO₄²⁻. There is considerable uncertainty in the rate constants for reactions 6, 7, 10 and 11. For the constants used these reactions were found not to be important and large variations in the constants are not expected to change the importance of these reactions for the conditions chosen. The rate constants for reactions 8 and 9 were chosen to give the correct equilibrium constant since these reactions are, for practical purposes, in equilibrium.

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 non-linear differential equations derived from the kinetic and mass transport

Table 1. Gas phase diffusion coefficients and Henry's law constants

| Species | D^* , $\text{cm}^2 \text{s}^{-1}$ | H | Source of H values |
|------------------------|-------------------------------------|---------|-------------------------------------|
| CO_2 | 0.166 | 1.2 | Perry & Chilton (1973) |
| O_3 | 0.157 | 3.36 | Perry & Chilton (1973) |
| SO_2 | 0.136† | 0.0332 | Hales & Sutter (1973) |
| HNO_3 | 0.136 | 0.46E-6 | Abel & Neusser (1929); McKay (1956) |
| HNO_2 | 0.159 | 0.11E-2 | Komiyama & Inoue (1978) |
| N_2O_4 | 0.113 | 0.25E-1 | Komiyama & Inoue (1978) |
| NO | 0.199 | 21.1 | Komiyama & Inoue (1978) |
| N_2O_3 | 0.125 | 0.16E-2 | Komiyama & Inoue (1978) |
| NO_2 | 0.160 | 1.0 | Andrew & Hanson (1961) |

$$* D_s = \left(\frac{\text{molecular weight of } \text{SO}_2}{\text{molecular weight of species } s} \right)^{1/2} (D_{\text{SO}_2}).$$

† Fish and Durham (1971).

Table 2. Kinetic mechanism of CO_2 - SO_2 - HNO_3 - O_3 -Aqueous phase system used for raindrops*[†]

| | | Source |
|-----|--|--|
| 1. | $\text{H}_2\text{O} \xrightleftharpoons[\frac{1.3\text{E}-3}{1.3\text{E}+11}]{} \text{H}^+ + \text{OH}^-$ | Eigen <i>et al.</i> (1964). |
| 2. | $\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons[\frac{5.6\text{E}+4}{4.3\text{E}-2}]{} \text{HCO}_3^- + \text{H}^+$ | Eigen <i>et al.</i> (1964) |
| 3. | $\text{HCO}_3^- \xrightleftharpoons[\frac{1.4\text{E}+5}{1.0\text{E}-4}]{} \text{CO}_2 + \text{OH}^-$ | Eigen <i>et al.</i> (1964) |
| 4. | $\text{SO}_2 + \text{H}_2\text{O} \xrightleftharpoons[\frac{2.0\text{E}+8}{3.4\text{E}+6}]{} \text{H}^+ + \text{HSO}_3^- (20^\circ\text{C})$ | Eigen <i>et al.</i> (1964) |
| 5. | $\text{HSO}_3^- \xrightleftharpoons[\frac{1.0\text{E}+11}{1.0\text{E}+4}]{} \text{SO}_3^{2-} + \text{H}^+$ | Erickson & Yates (1976), Erickson <i>et al.</i> (1977) |
| 6. | $\text{N}_2\text{O}_3 + \text{H}_2\text{O} \xrightleftharpoons[\frac{1\text{E}+2}{5.3\text{E}+2}]{} 2\text{HNO}_2$ | Grätzel <i>et al.</i> (1970) Schmid & Krenmayr (1967), Kamiyama & Inoue (1978) |
| 7. | $\text{N}_2\text{O}_3 \xrightleftharpoons[\frac{1.0\text{E}+9}{1.66\text{E}+8}]{} \text{NO} + \text{NO}_2$ | Komiyama & Inoue (1978) Grätzel <i>et al.</i> (1970) |
| 8. | $\text{HNO}_3 \xrightleftharpoons[\frac{1.0\text{E}+8}{2.2\text{E}9}]{} \text{H}^+ + \text{NO}_3^-$ | McKay (1956) |
| 9. | $\text{HNO}_2 \xrightleftharpoons[\frac{1.0\text{E}+9}{5.1\text{E}+5}]{} \text{H}^+ + \text{NO}_2^-$ | Schmid <i>et al.</i> (1937) |
| 10. | $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \xrightleftharpoons[\frac{2.0\text{E}+2}{}]{} \text{HNO}_3 + \text{HNO}_2$ | Komiyama & Inoue (1978) Grätzel <i>et al.</i> (1969) |
| 11. | $\text{N}_2\text{O}_4 \xrightleftharpoons[\frac{5.0\text{E}+8}{7.7\text{E}+3}]{} 2\text{NO}_2$ | Grätzel <i>et al.</i> (1969), Komiyama & Inoue (1978) |
| 12. | $\text{O}_3 + \text{NO}_2^- \xrightleftharpoons[\frac{1.6\text{E}+5}{}]{} \text{NO}_3^- (9^\circ\text{C})$ | Penekett (1972) |
| 13. | $\text{O}_3 + \text{SO}_2 \xrightleftharpoons[\frac{5.9\text{E}+2}{}]{} 2\text{H}^+ + \text{SO}_4^{2-}$ | Erickson <i>et al.</i> (1977) |
| 14. | $\text{O}_3 + \text{SO}_3^{2-} \xrightleftharpoons[\frac{2.2\text{E}+9}{}]{} \text{SO}_4^{2-}$ | Erickson <i>et al.</i> (1977) |

Table 2 (contd.)

| | Source |
|---|-------------------------------|
| 15. $O_3 + HSO_3^- \xrightarrow{31E+5} H^+ + SO_4^{2-}$ | Erickson <i>et al.</i> (1977) |

* Units are in liters, moles, seconds

† There is considerable uncertainty in the rate constants for the nitrogen species reactions. The values used are, in most cases, compromises between values reported in more than one reference. In some cases forward or backward rate constants are inferred from equilibrium data from one reference (reaction 8 and 9) and/or from a backward or forward constant reported in a second reference at a difference temperature (reactions, 6, 7, 10 and 11).

equations. That is, a set of the following type of equations was integrated,

$$\frac{d}{dz}\{[s]_i(Z, R)\} = \phi_i(Z, R) + \psi_i(Z, R). \quad (4)$$

ϕ , the chemical rate was obtained from the kinetics 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.

In order to simulate the chemistry in a rain event after a given fall distance, we must take into consideration drops of every size that reach the ground. To do this we have used the raindrop size distribution in air developed by Best (1950). This distribution is presented in Fig. 2. 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, $[\bar{s}]$, of a species, s , after a fall distance z is computed as

$$[\bar{s}](z) = \frac{w}{p} \int_0^\infty u(R)\{[s](R, z)\} f(R)dR; \quad (5)$$

$$w = p \int_0^\infty u(R)f(R)dR. \quad (6)$$

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; $f(R)dR$ is the fraction of water in drops of radius between R and $R+dR$.

Time dependence of chemical species as well as vertical

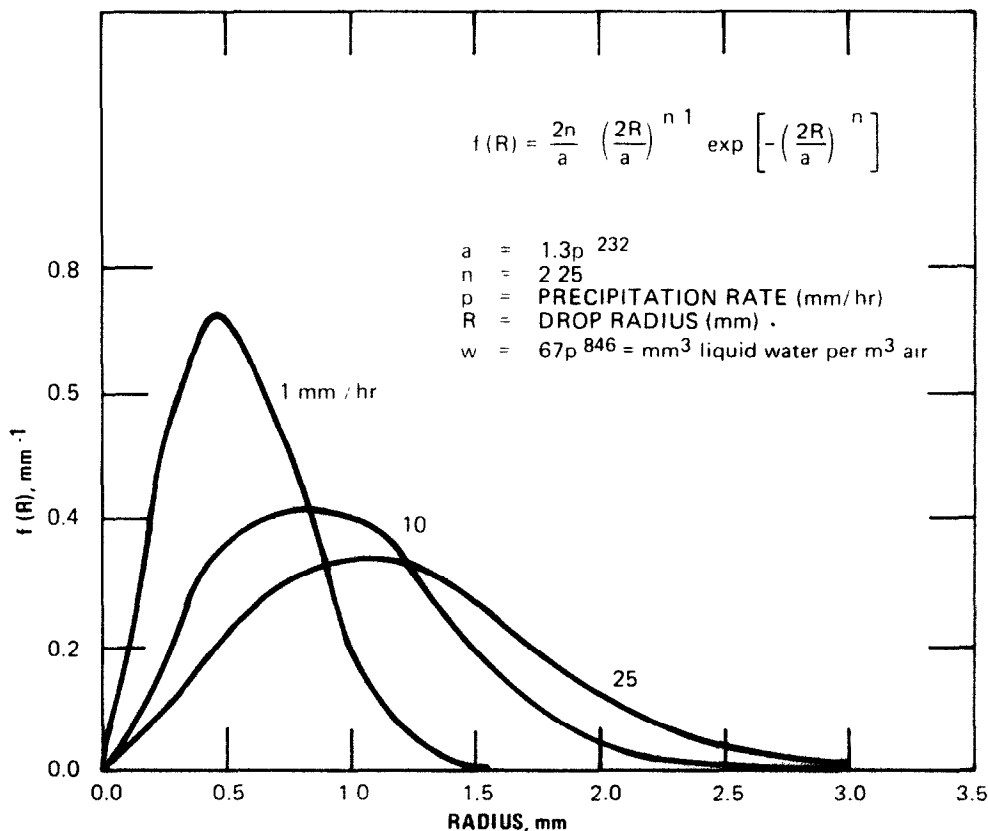


Fig. 2. Raindrop size density (fraction of water) function for various precipitation rates. Calculated curves are shown for precipitation rates $p=1, 10,$ and 25 mm h^{-1} (Source: Best, 1950; and Hill and Adamowicz, 1976).

dependence of ambient gases is obtained in steps. The vertical is divided into zones with ambient concentrations independent of height within each zone. After the calculation for rain reactions the ambient values, held constant in each zone during the calculation, are appropriately modified. They are modified to account for the material gained or lost for the time of the step due to the effect of the rain as well as any effect due to gas phase reactions. Vertical gas phase mixing is not considered. The process is repeated with the net result, as time (number of steps) increases, of variations in height and time of ambient as well as liquid species concentrations. Most of the data presented in this paper, however, are for a few minutes of a 1000 m fall distance. 10 mm h^{-1} rain event in which the ambient concentrations are assumed constant in height and time. Further, the model assumes that the raindrop size distribution is that of an ideal fully developed rain event; that is, the distribution is independent of fall distance and time. Thus 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 $A\pi t[\bar{s}]$. In the collector, continued oxidation by O_3 will not significantly change $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$ or pH. This is due to the low concentration of O_3 in the rainwater that is collected. However, other oxidation pathways (e.g. catalysis by metal ions) may convert the HSO_3^- to SO_4^{2-} , which could significantly alter the measured $[\text{SO}_4^{2-}]$, and perhaps, the pH. The model values of $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, and pH that we present are integrated averages from the beginning of the rain until time t without chemical reactions occurring in the container.

The assumption of an ideal fully developed rain event is partly justified by the fact that 92% (rain rate = 10 mm h^{-1}) of the initial model drops will have fallen 1000 m in the first 3.7 min of the rain event, and 97% will have fallen the 1000 m in 6.5 min after the first drops hit the ground. Thus the ideal raindrop distribution for a 10 mm h^{-1} rain rate is essentially developed at 1000 m after the first four minutes of the beginning of the rain event at the ground. Therefore we interpret our results as obtained from rain samples collected after the first few minutes of the beginning of the rain event. This interpretation will be reasonable if the ambient concentrations do not change very much during the time of interest. For example, at the end of a 5-min simulation of a 1000 m, 10 mm h^{-1} rain event (initially $[\text{HNO}_3]_g = 10 \text{ ppb}$, $[\text{SO}_2]_g = 20 \text{ ppb}$, $[\text{O}_3]_g = 50 \text{ ppb}$), ambient HNO_3 was reduced by 9% while other significant species, liquid or gas, decreased by less than half this amount.

RESULTS AND DISCUSSIONS

In order to explore the effects of nitric acid and the nitrogen oxides on sulfate formation and acidification in a rain event, we have considered four cases. The first three cases are concerned with effects in the first few minutes of a rain event; whereas the last case presents the results of the simulation of an extended rain event.

Case I. Effect of HNO_3 on acidification and SO_4^{2-} formation

For the first several minutes of a steady-state rain, we have calculated the pH, $[\text{SO}_4^{2-}]$, and $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ for the rainfall collected at ground level. The acidification due to SO_2 (0–20 ppb) oxidation by O_3 in the droplet and the HNO_3 (0–10 ppb) subcloud scavenging are displayed in Fig. 3. The concentration range for HNO_3 is in agreement with recent observations of Spicer (1979). The fall distance was taken to be 1000 m, and the O_3 concentration was

assumed to be 50 ppb. The initial pH was set to 5.56 for the raindrops entering the polluted zone. For case I, the initial concentrations of NO and NO_2 in the polluted zone were set equal to zero in order to first determine the acidification due solely to subcloud scavenging of HNO_3 . That is, only reactions 1–5, 8, and 13–15 in Table 2 were used.

The ability of absorbed HNO_3 to retard the formation of SO_4^{2-} is shown in Fig. 3. In the absence of HNO_3 , the $[\text{SO}_4^{2-}]$ in the collected rainfall is $7 \mu\text{M}$ if the ambient $[\text{SO}_2] = 8 \text{ ppb}$. However, in the presence of $[\text{HNO}_3] = 4 \text{ ppb}$, the rainwater $[\text{SO}_4^{2-}] = 5 \mu\text{M}$, which is a decrease of almost 30%. Note, however, that the presence of the HNO_3 causes the pH to change from 4.70 to 4.50. At $[\text{SO}_2] = 8 \text{ ppm}$, the variation of $[\text{HNO}_3]$ from 0 to 8 ppb results in a pH change from 4.70 to 4.30. Thus HNO_3 reduces pH more than SO_2 alone does and this further reduction of pH retards SO_4^{2-} formation relative to quantities formed in the absence of HNO_3 . Also, for the initial portion of the model steady-state rain, the molar concentration of NO_3^- will dominate that of SO_4^{2-} if $[\text{HNO}_3] \geq 2 \text{ ppb}$ and $[\text{SO}_2] \leq 20 \text{ ppb}$.

For the constraints imposed here, it is expected that for $[\text{SO}_2] \leq 20 \text{ ppb}$ and $[\text{HNO}_3] = 0$, the pH would remain above 4.50; an increase of $[\text{SO}_2]$ to 40 ppb would lower the pH only to about 4.40. However, the subcloud scavenging of HNO_3 at concentrations from 21 to 210 ppb would yield pH's of 4 to 3, respectively, regardless of the SO_2 .

Case II. Effect of NO , NO_2 , HNO_3 on acidification

The conditions for Case II are similar to those for Case I, but the following additions were incorporated: (a) the complete reaction mechanism shown in Tables 2 and 3 were used and (b) the polluted zone was assumed to have initial $[\text{NO}_2] = 10 \text{ ppb}$; the initial concentrations of NO , N_2O_3 , N_2O_4 , and HNO_2 were assumed to be zero.

Thus reactions 11 and 17 were used to transform NO_2 into N_2O_4 , which produced HNO_3 and HNO_2 (reaction 10) in the droplets. The binary reaction of HNO_2 (reaction 6) produced N_2O_3 , which in turn produced NO (reaction 7). Thus, the initial NO_2 (10 ppb) was caused to re-distribute among all the N-oxides and HNO_2 , and to participate in the sink reaction (number 12) leading to NO_3^- .

The influence of these N-oxides and HNO_2 result from the initial NO_2 (10 ppb) on the pH, NO_2^- , NO_3^- , and SO_4^{2-} content of the collected rainwater is compared with Case I in Table 4. It can be seen in this table that NO_2 (10 ppb) and its progeny have no significant influence on the pH, NO_3^- , or SO_4^{2-} content.

That NO_2 has no significant influence can be understood by considering (a) the liquid phase reactions involved in its transformation to NO_3^- and (b) its Henry's law constant which is 1.0. In the water drop, NO_2 quickly comes into equilibrium with the ambient concentration of the gas phase. NO_2 must

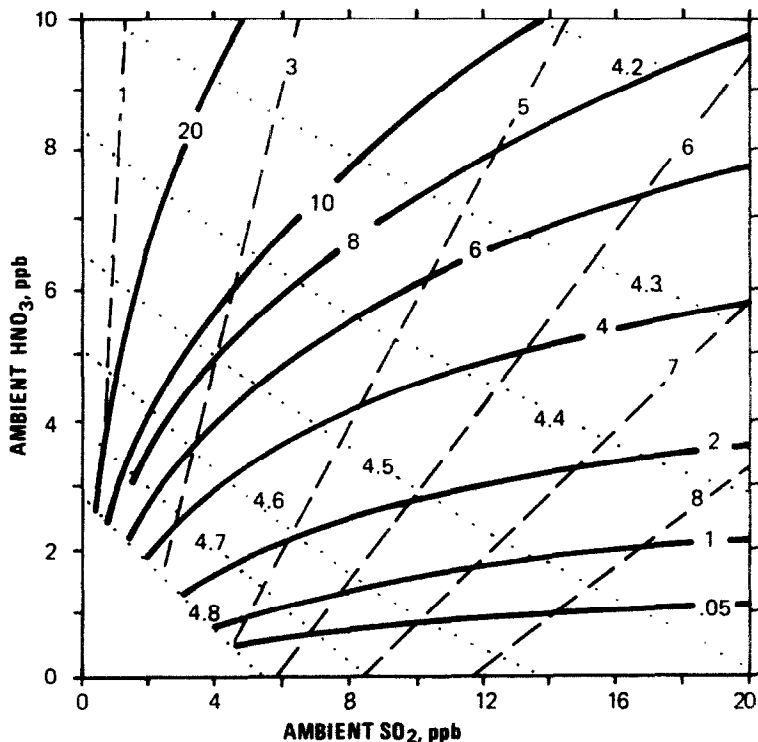


Fig. 3. The effect of ambient SO₂ and HNO₃ on pH, sulfate and nitrate in rain. Plotted are isopleths of pH (.....), SO₄²⁻ (--- micromoles/liter), and the ratio (NO₃⁻/SO₄²⁻) (---) for ambient values of SO₂ and HNO₃. The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.54, ambient [O₃] = 50 ppb, ambient [NO] = [NO₂] = 0. ppb. The absorption of HNO₃ by the falling droplets lowers the pH and retards the formation of SO₄²⁻ due to liquid phase reaction between dissolved O₃ and SO₂ species.

Table 3. Gas phase reactions*

| | | | | |
|-----|-------------------------------|-------------------------------------|----------------------------------|--------------------------------|
| 16. | N ₂ O ₃ | $\frac{1.04E+4}{1.3E+6}$ | NO + NO ₂ (30°C) | Vlastaras & Winkler (1967) |
| 17. | N ₂ O ₄ | $\frac{6.4E+4}{1.0+7}$ | 2NO ₂ | Gray & Yoffe (1955) |
| 18. | NO + O ₃ | $\frac{5.6E+6}{\rightleftharpoons}$ | NO ₂ + O ₂ | Demerjian <i>et al.</i> (1974) |

* Units are in liters, moles, seconds.

Table 4. Effect of N-oxides on acidification

| Air* | | pH | Water† | | |
|------------------------|------------------------|------|-----------------------------------|-----------------------------------|------------------------------------|
| NO ₂ ‡(ppb) | HNO ₃ (ppb) | | NO ₂ ⁻ (μM) | NO ₃ ⁻ (μM) | SO ₄ ²⁻ (μM) |
| 0 | 0 | 4.51 | 0 | 0 | 9.62 |
| 10 | 0 | 4.51 | <10 ⁻⁴ | <10 ⁻³ | 9.62 |
| 0 | 10 | 4.17 | 0 | 47.8 | 5.80 |
| 10 | 10 | 4.17 | <10 ⁻⁴ | 47.8 | 5.80 |

* [SO₂] = 20 ppb, [O₃] = 100 ppb.

† Initial pH = 5.54.

‡ Initially, the sole N-oxide species.

then react with itself (reaction II) in order to produce products that can lead to NO_3^- . This reaction is an inefficient process compared to that of SO_2 and its chemical mechanistic analogue, HNO_2 . In these cases the species rapidly dissociates into products that are immediately oxidized by O_3 . HNO_3 , of course, dissociates directly into H^+ and NO_3^- . Thus in view of the chemical kinetics of HNO_2 and HNO_3 and their Henry's law constants of much less than 1.0, we can understand why these species have a much greater effect on pH and on NO_3^- production than does NO_2 .

Case III. Effect of acidification prior to entering polluted zone

Raindrops may be acidified prior to entering the polluted zone, perhaps due to formation from strongly acidic cloud condensation nuclei. Here we assume that occurs, and that the raindrops have an initial pH = 4 and $[\text{SO}_4^{2-}] = 50 \mu\text{M}$ prior to entering the polluted zone. The calculated values for selected gas phase concentrations of HNO_3 and SO_2 are presented in Table 5.

Table 5. Effect of pre-acidification

| Air | | pH | Water* | |
|----------------------------|---------------------------|------|------------------------------|---------------------------------|
| $\text{HNO}_3(\text{ppb})$ | $\text{SO}_2(\text{ppb})$ | | $\text{NO}_3^-(\mu\text{M})$ | $\text{SO}_4^{2-}(\mu\text{M})$ |
| 0 | 0 | 4.00 | 0 | 50.0 |
| 0 | 20 | 3.97 | 0 | 50.8 |
| 10 | 0 | 3.83 | 47.8 | 50.0 |
| 10 | 20 | 3.83 | 47.8 | 50.7 |

* Raindrops entering polluted zone have pH = 4, $[\text{SO}_4^{2-}] = 50 \mu\text{M}$

If the $[\text{SO}_2] = 20 \text{ ppb}$ in the polluted zone, the change in pH and $[\text{SO}_4^{2-}]$ for the collected rainwater is insignificant. The falling rain is already too acidic to support the reactions between dissolved O_3 and $\text{HSO}_3^-/\text{SO}_3^{2-}$. However, the presence of HNO_3 leads to further acidification independently of the $[\text{SO}_2]$.

Case IV. Effect of HNO_3 on SO_4^{2-} and NO_3^- production and pH in an extended rain event

Figure 4 presents the variation of SO_4^{2-} , NO_3^- , pH and ambient HNO_3 as a function of time resulting from the simulation of a 1000-m, 10-mm h^{-1} rain event over a period of one hour. The initial values of pH, ambient O_3 , SO_2 and HNO_3 are 55, 50 ppb, 20 ppb, and 5 ppb respectively. Liquid phase values are for simulated cumulative quantities (which are essentially the same as the instantaneous quantities in this example) collected at the ground from the beginning of the rain event to the time of interest, whereas HNO_3 values are instantaneous. The most noticeable feature of the figure is the rapid decrease in NO_3^- (41% in 1 h) and HNO_3 (70% in 1 h) as compared to a slight increase in pH and SO_4^{2-} . The rapid decrease in ambient HNO_3 is to be expected because of its very low Henry's law constant and extensive dissociation. As the ambient values of HNO_3 decrease, and consequently the drop

values decrease, the NO_3^- produced in the drops also decreases since the production of NO_3^- is directly related to the liquid phase HNO_3 concentration (see above and Table 2, Equation 8). The decrease in nitrate is also accompanied by a decrease in hydrogen ion concentration in the falling rain, which increases the rate of the oxidation of SO_2 to SO_4^{2-} . This increase, with the given conditions, is sufficient to offset the effects of the reduction of ambient SO_2 ($\sim 4\% \text{ h}^{-1}$ in this simulation) and O_3 ($< 2\% \text{ h}^{-1}$ in this simulation) and to slightly increase the production of sulfate.

The results of the simulation, presented in Fig. 4 could have been inferred by considering Fig. 3: for approximately constant O_3 and SO_2 concentrations, a lowering of ambient HNO_3 increases pH, sulfate and reduces NO_3^- in drops reaching the ground. More generally by tracing changes in HNO_3 and SO_2 in Fig. 3 an idea as to the sequential properties of the rain event can be obtained.

For the chemical mechanisms used in the model we can expect a more rapid decrease in time of ambient HNO_3 than SO_2 . Thus the qualitative results of the simulated 60-min subcloud scavenging rain event are expected to be valid for general conditions other than the ones used. That is, in general, we can expect a rapid decrease in time of NO_3^- relative to changes in SO_4^{2-} and pH. Of course if the rain continues long enough, SO_4^{2-} concentrations will decrease as a result of the loss of ambient SO_2 .

SUMMARY

The results of model simulations have been presented that describe the effect of ambient gases on sulfate and nitrate production and acidity in rain. The model is limited in that it attempts only to describe the subcloud scavenging of select ambient gases (SO_2 , HNO_3 , O_3 , NO_2 and CO_2) and includes only one path by which SO_2 is transformed to SO_4^{2-} (oxidation by O_3). Thus, important processes such as incloud scavenging, subcloud scavenging of aerosols and SO_2 oxidation by steps other than reaction with O_3 (e.g., H_2O_2 and catalysts) are ignored. In addition, NH_3 has been excluded from the ambient gases; its effect would be to raise the pH and to counter the effects of HNO_3 . Other features not included in the model are in-cloud processes, atmospheric dynamics, temperature variations, and drop dynamics. For example, drops can be retained in polluted regions for longer than their 'fall time' (as calculated from the terminal velocity). As the ambient gases are absorbed by the drops at rates that depended on height, gas phase concentration gradients are formed; however, vertical mixing of gases was not considered. Temperature changes could play an important role as rate constants and solubility constants depend on temperature. What can be expected for rain events occurring at different temperatures is not clear due to the complicated nature of the equations describing the process as well as due to the lack of information

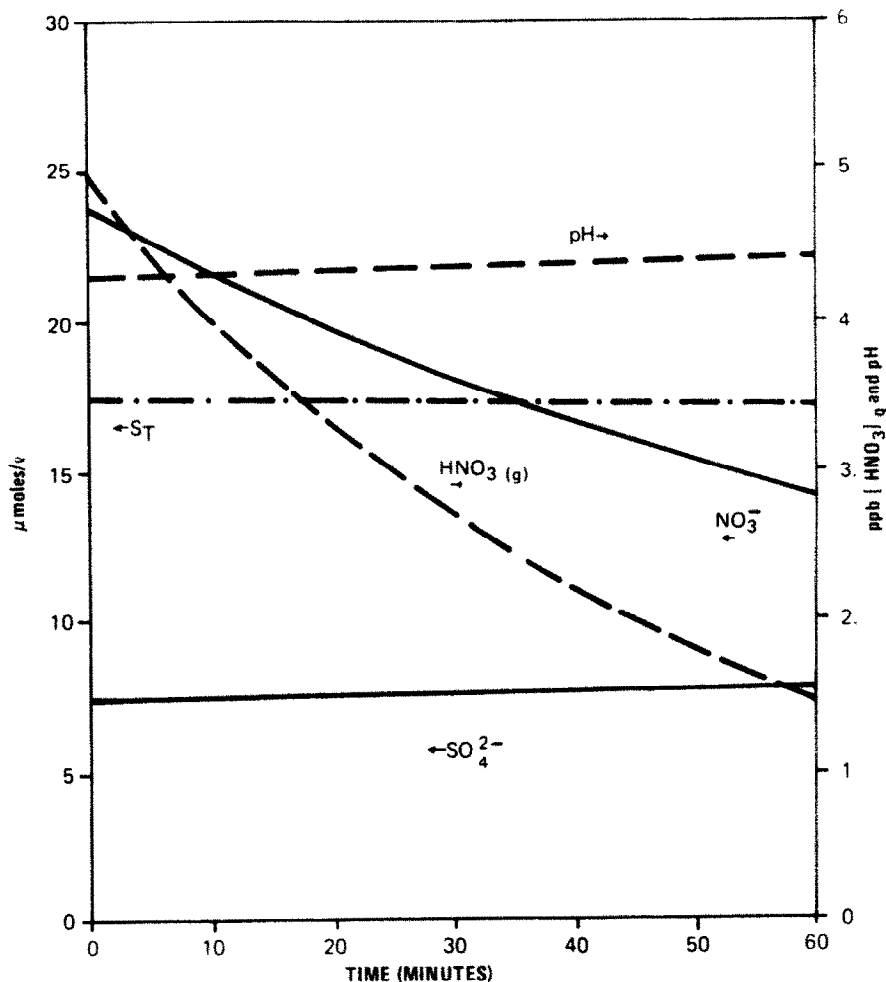


Fig. 4. Variations of SO_4^{2-} , NO_3^- , S_T (total sulfur), and pH of cumulative (\sim instantaneous values) collected rain water and ambient $\text{HNO}_{3(g)}$ as a function of time during a 1000-m, 10-mm h^{-1} , 60-minute simulated subcloud scavenging rain event. Reactions in the collector are assumed not to occur. Initial conditions: pH = 5.5 ambient gas phase value: $[\text{O}_3] = 50$ ppb, $[\text{SO}_2] = 20$ ppb, $[\text{HNO}_3] = 5$ ppb, $[\text{NO}] = [\text{NO}_2] = 0$ ppb (liquid phase values are for quantities collected from the beginning of the event, Time = 0, to the time of interest). Note the rapid decline in $[\text{NO}_3^-]$ compared to the slight rise in $[\text{SO}_4^{2-}]$ and pH. If the rain should stop at 60 min, and all of the HSO_3^- were oxidized in the collector then $[\text{SO}_4^{2-}] = 17 \mu\text{M}$, and pH = 4.3.

on the temperature dependence of many of the relevant physical and chemical parameters. The model also ignores the realities of raindrops: they are not rigid spheres; they evaporate, breakup and collide with each other, etc. We have also not considered the effects of internal currents and concentration gradients.

The model is limited in that it considers only a few of the major processes that are involved in a rain event and therefore it must be considered inadequate as a realistic rain model. Nevertheless by limiting the model, the effects of some important processes and conditions that do occur in rain events could be easily studied without being obscured by the effects of many processes.

CONCLUSIONS

As a result of this investigation of the effect of HNO_3 on the production of acidity, NO_3^- and SO_4^{2-} , with O_3 as the only oxidizing agent, we have concluded that:

- (1) The subcloud scavenging of HNO_3 may control acidification in the initial stages of a rain event and may have a greater control over final pH than gaseous SO_2 .
- (2) Gaseous HNO_3 inhibits the production of sulfate in rain by lowering the pH.
- (3) The oxides of nitrogen, NO and NO_2 , play no role in acidification, nitrate and sulfate production in a subcloud scavenging rain event.

(4) Precipitation (incloud scavenging) can have a greater control over final acidity than the subcloud scavenging of HNO_3 or SO_2 . In this case sulfate production is reduced, but nitrate production is independent of the initial pH.

(5) Gaseous HNO_3 is more rapidly removed from the atmosphere as compared to SO_2 and O_3 .

(6) In a subcloud scavenging rain event, as the event progresses, nitrate concentrations decrease much more rapidly than sulfate values. In the present simulation cumulative NO_3^- decreases by 42% in one hour, whereas SO_4^{2-} , as well as pH slightly increased.

Comparison of the results of the simulations to experimental values (Raynor *et al.*, 1979 and Robertson *et al.*, 1980) indicate that the quantitative results presented fall within the range of measured values; however this does not prove the model to be useful in simulating the results of specific rain events. Before this can be done more information that is usually obtained about a rain event is necessary. For example, we need to know the fall distance, ambient concentrations, drop size distribution and rain rate as a function of time, temperature, type of rain event (subcloud, incloud scavenging, or combination of both) and raindrop initial conditions. This, of course, is not a complete list of the conditions of a rain event; nevertheless such information in addition to rain species concentrations would be very helpful in validating a rain model.

Simulations, not discussed in this paper, indicate that, qualitatively, the conclusions presented here hold for substantially decreased rain rates (which is equivalent to a reduction in average drop size). These simulations also show that the processes we have taken into account do not have the capacity to lower pH below ~ 3.5 . Since there is evidence of pH's as low as ~ 2.2 (Likens and Bormann, 1974) we conclude that our present model has deficiencies. Our next step will be to include H_2O_2 in model calculations.

As a final word, we would like to reiterate that this exercise has been to theoretically investigate the effects of a limited set of possible processes that may occur in a rain event, namely the effect of gaseous nitric acid on sulfate and nitrate production and acidity in a rain event. With respect to this a better understanding of the chemistry of rain has been obtained.

REFERENCES

- Abel E. and Neusser E. (1929) Über den Dampfdruck der salpitrigen saure. *Monatshfte fuer Chemie* **54**, 855-873.
- Andrew S. P. S. and Hanson D. (1961) The dynamics of nitrous gas absorption. *Chem. Engng Sci.* **14**, 105-114.
- Berry M. A. and Bachmann J. D. (1977) Developing regulatory programs for the control of acid precipitation. *Wat. Air, Soil Pollut.* **8**, 95-103.
- Best A. C. (1950) The size distribution of raindrops. *Q. Jl Roy. Met. Soc.* **76**, 16-36.
- Demerjian K. L. Kerr J. A. and Calvert J. G. (1974) *Advances in Environmental Science and Technology* Eds. J. N. Pitts and R. L. Metcalf Vol. 4 John Wiley & Sons, Inc.
- Drozdova V. M. and Makhońko E. P. (1970) Content of trace elements in precipitation. *J. geophys. Res.* **75**, 3610-3612.
- Eigen M., Kruse W., Maass G. and DeMaeyer L. (1964) Rate constants of protolytic reactions in aqueous solution. *Progress in Reaction Kinetics*, (Ed. G. Porter) Vol. 2, pp. 287-318. MacMillan, NY.
- Erickson R. E. and Yates L. M. (1976) Reaction kinetics of ozone with sulfur compounds. U.S. Environmental Protection Agency. Report No. EPA-600/3-76-089 (69 pages).
- Erickson R. E., Yates L. M., Clard R. L. and McEwen C. M. (1977) The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. *Atmospheric Environment* **11**, 813-817.
- Fish B. R. and Durham J. L. (1971) Diffusion coefficient of SO_2 in air. *Envir. Lett.* **2**, 13-21.
- Frössling N. (1938) The evaporation of falling drops. *Gerlands Beits. Geophys.* **52**, 170-216.
- Glass N. R. (Ed.) (1978) Environmental effects of increased coal utilization: ecological effects of gaseous emissions from coal combustion. EPA-600/7-78-108, U.S. Environmental Protection Agency, Research Triangle Park, NC. 50 pp.
- Grätzel Von M., Henglein A., Lilie J. and Beck G. (1969) Pulsradiolytische untersuchung einiger elementarprozesse der oxydation und reduktion des nitritions. *Berichte der Bunsengesellschaft fuer Physikealesch Chemie* **73**(7), 646-653.
- Grätzel, Von, M., Taniguchi S. and Henglein A. (1970) Pulsradiolytisch utersuchung der NO-oxydation und des gleichgewichts N_2O_3 $\text{NO} + \text{NO}_2$ in wässreger lösung. *Berichte der Bunsengesellschaft fuer Physikealische Chemie* **74**(5), 488-492.
- Gray P. and Yoffe A. D. (1955) The reactivity and structure of nitrogen dioxide. *Chem. Rev.* **55**, 1069-1154.
- Hales J. M. and Sutter S. L. (1973) Solubility of sulfur dioxide in water at low concentrations. *Atmospheric Environment* **2**, 997-1001.
- Hales J. M., Wolf M. A. and Dana M. T. (1973) A linear model for predicting the washout of pollutant gases from industrial plumes. *AIChE J.* **19**, 292-297.
- Komiyama H. and Inoue H. (1978) Reaction and transport of nitrogen oxides in nitrous acid solutions. *J. Chem. Eng Japan* **11**(1).
- Likens E. and Bormann F. H. (1974) Acid rain: A serious regional environmental problem. *Science* **184**, 1176-1179.
- McKay H. A. C. (1956) The activity coefficient of nitric acid, a partially ionized 1:1-electrolyte. *Trans. Faraday Soc.* **52**, 1568-1573.
- Markowitz A. H. (1976) Raindrop size distribution expressions. *J. appl. Met.* **15**, 1029-1031.
- Oden S. (1968) The acidification of air and precipitation and its consequences on the natural environment Swedish Nat. Sci. Res. Council, Ecology Committee. Bull. 1.
- Oden S. (1976) The acidity problem—an outline of concepts. In: *Proc. First International symposium on Acid Precipitation and the Forest Ecology*, May 12-15, 1975, Columbus, OH. USDA Forest Service General Technical Report NE-23, pp. 1-30.
- Overton J. H., Aneja V. P. and Durham J. L. (1979) Production of sulfate in rain and raindrops in polluted atmospheres. *Atmospheric Environment* **13**, 355-367.
- Penkett S. A. (1972) Oxidation of SO_2 and other atmospheric gases by ozone in aqueous solution. *Nature* **240**, 105-6.
- Penkett S. A., Jones M. R., Brice K. A. and Eggleton A. E. J. (1979) The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rainwater. *Atmospheric Environment* **13**, 123-137.
- Perry R. H. and Chilton C. H. (Ed.) (1973) *Chemical Engineer Handbook*, 5th Edition. McGraw-Hill Book Company.
- Raynor G. S. and Hayes J. V. (1979) Analytical summary of experimental data from two years of hourly sequential precipitation samples at Brookhaven National Laboratory

- BNL-51058, UC-11, Brookhaven National Laboratory, Upton, NY. 91 pp.
- Robertson J. K., Dolzine T. W. Graham R. C. (1980) Chemistry of precipitation from sequentially sampled storms. EPA-600/4-80-004, U.S. Environmental Protection Agency, Research Triangle Park, NC. 117 pp.
- Schmid, H. and P. Krenmayr. (1967) Der aktivitätskoeffizient der salpetrigen säure und die gleichgewichtskonstante der distickstofftrioxidbildung. *Monatsheft fuer Chemie* **98**(2), 417-422.
- Schmid H., Marchgraber R. and Dunkl F. (1937) A study of the thermodynamics of intermediate reactions with the aid of electrolytic conductivity measurements. *Z. Electrochem.* **43**, 337-340.
- Spicer C. W. (1979) Measurement of gaseous HNO_3 by electrochemistry and chemiluminescence, in *Current Methods to Measure Atmospheric Nitric Acid and Nitric Acid Artifacts*, (Ed. Stevens, R. K.) pp. 27-35, U.S. Environmental Protection Agency, EPA-600/2-79-051, Research Triangle Park, NC.
- Vlastaras A. S. and Winkler C. A. (1967) Reaction of active nitrogen with oxygen. *Can. J. Chem.* **45**, 2837-2840.

APPENDIX I

Presented here is the set of differential equations used for the chemical kinetics in the aqueous droplets. The equations are the mathematical formulation of the reactions in Table 2. 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.

$$\begin{aligned} u \frac{d[\text{H}^+]}{dz} &= -k_{-1}[\text{H}^+][\text{OH}^-] + k_{+1} \\ &\quad + k_{+2}[\text{CO}_2] - k_{-2}[\text{H}^+][\text{HCO}_3^-] \\ &\quad + k_{+4}[\text{SO}_2] - k_{-4}[\text{H}^+][\text{HSO}_3^-] \\ &\quad + k_{+5}[\text{HSO}_3^-] - k_{-5}[\text{H}^+][\text{SO}_3^{2-}] \\ &\quad + k_{+8}[\text{HNO}_3] - k_{-8}[\text{H}^+][\text{NO}_3^-] \\ &\quad + k_{+9}[\text{HNO}_2] - k_{-9}[\text{H}^+][\text{NO}_2^-] \\ &\quad + 2 \cdot k_{13}[\text{O}_3][\text{SO}_2] + k_{15}[\text{O}_3][\text{HSO}_3^-] \\ u \frac{d[\text{OH}^-]}{dz} &= k_{+1} - k_{-1}[\text{H}^+][\text{OH}^-] \\ &\quad - k_{-3}[\text{CO}_2][\text{OH}^-] + k_{+3}[\text{HCO}_3^-] \\ u \frac{d[\text{CO}_2]}{dz} &= -k_{+2}[\text{CO}_2] + k_{-2}[\text{H}^+][\text{HCO}_3^-] \\ &\quad - k_{-3}[\text{CO}_2][\text{OH}^-] + k_{+3}[\text{HCO}_3^-] \\ &\quad + \frac{3k_g}{R}([\text{CO}_2]_g - H[\text{CO}_2]) \\ u \frac{d[\text{HCO}_3^-]}{dz} &= +k_{+2}[\text{CO}_2] - k_{-2}[\text{HCO}_3^-][\text{H}^+] \\ &\quad + k_{-3}[\text{CO}_2][\text{OH}^-] - k_{+3}[\text{HCO}_3^-] \\ u \frac{d[\text{SO}_2]}{dz} &= -k_{+4}[\text{SO}_2] + k_{-4}[\text{H}^+][\text{HSO}_3^-] \end{aligned}$$

$$\begin{aligned} &\quad - k_{13}[\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^-] \\ &\quad - k_{-5}[\text{HSO}_3^-] + k_{+5}[\text{SO}_3^{2-}][\text{H}^+] \\ &\quad - k_{13}[\text{O}_3][\text{HSO}_3^-] \\ u \frac{d[\text{SO}_3^{2-}]}{dz} &= k_{+5}[\text{HSO}_3^-][\text{H}^+] - k_{-5}[\text{SO}_3^{2-}][\text{H}^+] \\ &\quad - k_{14}[\text{O}_3][\text{SO}_3^{2-}] \\ u \frac{d[\text{N}_2\text{O}_3]}{dz} &= -(k_{+6} + k_{+7})[\text{N}_2\text{O}_3] \\ &\quad + k_{-6}[\text{HNO}_2]^2 + k_{-7}[\text{NO}][\text{NO}_2] \\ &\quad + \frac{3k_g}{R}([\text{N}_2\text{O}_3]_g - H[\text{N}_2\text{O}_3]) \\ u \frac{d[\text{HNO}_2]}{dz} &= -k_{-6}[\text{HNO}_2]^2 - k_{+6}\text{HNO}_2 \\ &\quad + k_{10}[\text{N}_2\text{O}_4] + \frac{3k_g}{R}([\text{HNO}_2]_g \\ &\quad - H[\text{HNO}_2]) \\ u \frac{d[\text{NO}]}{dz} &= k_{+7}[\text{N}_2\text{O}_3] - k_{-7}[\text{NO}][\text{NO}_2] \\ &\quad + \frac{3k_g}{R}([\text{NO}]_g - H[\text{NO}]) \\ u \frac{d[\text{NO}_2]}{dz} &= k_{+7}[\text{N}_2\text{O}_3] - k_{-7}[\text{NO}][\text{NO}_2] \\ &\quad - k_{-11}[\text{NO}]^2 + k_{+11}[\text{N}_2\text{O}_4] + \frac{3k_g}{R}([\text{NO}_2]_g \\ &\quad - H[\text{NO}_2]) \\ u \frac{d[\text{HNO}_3]}{dz} &= -k_{+8}[\text{HNO}_3] + k_{-8}[\text{H}^+][\text{NO}_3^-] \\ &\quad + k_{10}[\text{N}_2\text{O}_4] + \frac{3k_g}{R}([\text{HNO}_3]_g - H[\text{HNO}_3]) \\ u \frac{d[\text{N}_2\text{O}_4]}{dz} &= -k_{+11}[\text{N}_2\text{O}_4] - k_{-11}[\text{NO}_2]^2 \\ &\quad - k_{10}[\text{N}_2\text{O}_4] + \frac{3k_g}{R}([\text{N}_2\text{O}_4]_g - H[\text{N}_2\text{O}_4]) \\ u \frac{d[\text{NO}_3^-]}{dz} &= k_{+8}[\text{HNO}_3] - k_{-8}[\text{H}^+][\text{NO}_3^-] \\ &\quad + k_{12}[\text{O}_3][\text{NO}_2^-] \\ u \frac{d[\text{NO}_2^-]}{dz} &= k_{+9}[\text{HNO}_2] - k_{-9}[\text{H}^+][\text{NO}_2^-] \\ &\quad - k_{12}[\text{O}_3][\text{NO}_2^-] \\ u \frac{d[\text{O}_3]}{dz} &= -[\text{O}_3](k_{12}[\text{NO}_2^-] + k_{13}[\text{SO}_2] \\ &\quad + k_{14}[\text{SO}_3^{2-}] + k_{15}[\text{HSO}_3^-]) \\ &\quad + \frac{3k_g}{R}([\text{O}_3]_g - H[\text{O}_3]) \\ u \frac{d[\text{SO}_3^{2-}]}{dz} &= [\text{O}_3](k_{13}[\text{SO}_2] + k_{14}[\text{SO}_3^{2-}] \\ &\quad + k_{15}[\text{HSO}_3^-]) \end{aligned}$$