

CHAPTER 8 Compartmental Modeling of Two Phase Systems: Reactions in Gas and Liquid

In many systems, including the atmosphere, reactions occur in more than one phase e.g. gas/air) and liquid (water). We outline here the general approach to modeling such two-phase systems. We consider closed and open systems, equilibrated and nonequilibrated. Later on we extend this to multiphase systems.

In this chapter, we first present the general methodology for treating well mixed two phase systems. Then we show its application to addressing the acid rain problem in the atmosphere.

ChE 505 Chapter 8 Addition

A Guide through Chapter 8

Let us reflect first on what we should have mastered in previous chapters 4 through 7.

Upon introducing the concept of reaction mechanisms and illustrating how to derive rate forms from them, we applied that knowledge, coupled with the assumption of a well-mixed system, to study ozone depletion in the stratosphere and ozone dynamics in polluted urban atmosphere. Considerations of a single phase, gas phase, were sufficient in these situations. We proceeded then in Chapter 5 to formalize the methodology of obtaining rate data from mechanisms (PSSA and RLSA methods were introduced) and we covered various catalytic and noncatalytic reactions including enzyme promoted ones. In Chapter 6 and 7 we focused on the theory of elementary reactions, which are the basic building blocks of any mechanism. We reviewed the kinetic theory of gases, and its use in collision theory, and introduced the classical transition state theory (CTST).

Elementary reactions in gases were considered from the viewpoint of these two theories. In Chapter 7 we extended the CTST to elementary reactions in liquids, and illustrated the effect of dielectric constant, ionic strength and charges in the ions on the prediction of the rate constant. We concluded by explaining the origin and consequences of diffusion-limited reaction on the rate constant of an elementary reaction.

The purpose of Chapter 8 is to introduce the extension of a well-mixed compartmental model to systems (closed and open) that contain two phases – gas and liquid. The general mass balance is presented first for a general species j that can exist in both phases and that can react in each phase. The use of the developed approach is then illustrated in the problem of acid rain. Sulfur dioxide history in the gas and liquid phase is monitored and the dynamics of $S(VI)$ creation and pH of the liquid phase is followed in time.

Section 8.1 introduces the nomenclature to be used. Note by the form of the mass transfer flux N_{gj} that the flux from gas to liquid is defined as positive and that the driving force for this flux is the difference in partial pressure of j in the gas phase p_j , and the partial pressure of j that would be in equilibrium with the liquid phase at concentration C_{jL} . Hence, once equilibrium between gas and liquid is reached the driving force goes to zero and the net transfer of j between gas and liquid becomes zero. The modified Henry's constant H_j^* includes the effect of ionization of the dissolved gas (see Chapter 3), and if there is no ionization, is reduced to the ordinary Henry's constant value H_j .

One should note that in setting the system for use in the sulfur dioxide oxidation problem we introduce the ratio of the volumes of the liquid and gas phase $L = V_L/V_g$. Only when we start neglecting L compared to unity do our equations lose generality and become applicable only to the problems in atmospheric chemistry where typically $10^{-11} < L < 10^{-6}$.

Equations (4) and (4a) present the balance for the gas phase and equations (5) and (5a) for the liquid phase. Both are for a closed system.

Equation (7) represents the dynamics due to reactions of the equilibrated closed system. Method of finding the rates and procedure to be taken with insoluble or nonvolatile species is outlined.

Equations (14a), (14b), (15) are restated as the general ones to be solved for a non-equilibrated closed gas-liquid system.

At that point a procedure is introduced (see additional Hints sub-section) that relies on conservation of the atomic species (which of course cannot be created or consumed by reaction). This procedure is employed in solving the sulfur dioxide oxidation problem and the conservation of sulfur equation for the closed system is presented as eq (18). The gas phase sulfur content is all in oxidation state four form S(IV), i.e. SO_2 , as indicated by eq (19). In the liquid phase sulfur exists in S(VI) form (e.g. various undissociated and dissociated forms of H_2SO_4). The rate of change of S(VI) is given by equation (23) where the oxidation rates are contributed by various species. As these rate forms depend on hydrogen ion concentration the electroneutrality equation (24) must be solved simultaneously to eq (23). Equation (22) representing the overall sulfur conservation as atomic species must be used also simultaneously to update the SO_2 gas phase concentration.

This procedure outlines the algorithm that must be used to solve the dynamics of sulfur dioxide oxidation in a closed system.

The general equations for an open system are shown in eqs. (25a), (25b) (25c).

We consider here only the limiting case when only the gas phase is constantly refreshed while the liquid phase does not have a continuous input and output. This is often used as an extreme model in atmospheric chemistry. The closed system model represents water droplets that travel with the same mass of air and are exposed to the same air all the time. This limiting open system model assumes that air in our compartment, is abundantly and constantly replenished but the droplets of water are the same. If the replenishment rate of gas is very large then the partial pressure of all components in the gas phase is constant and the only equations to be solved are for the reactions in the liquid. Now this becomes a single-phase system (liquid) that is fed by constant composition of the surrounding gas phase. This is the other extreme model that we will solve for the SO_2 problem. The equations to be solved in this case are eqs (23), (23a) with eqs (31) and (32).

Section 8.2 outlines the story of the sulfur cycle in the atmosphere. The main conclusion to be derived from Section 8.2.1 on atmospheric chemistry of SO_2 is that gas phase reactions are slow (see Table 2 and 3).

Section 8.3.1 introduces the water phase reactions of SO_2 oxidation. Table 6 provides the Henry's constants for soluble gases and Table 7 displays the pertinent dissociation constants. The concepts of electroneutrality and modified Henry's constant are reviewed. The effect of partial pressure of SO_2 , of temperature and pH on solubility of total S(IV) is shown in Figure 2. Figure 3 displays the mole fraction of various dissociated and undissociated forms of H_2SO_3 . Abundance of water in different type of atmosphere is reviewed and its effect on maximum concentration of soluble gases is revealed. Conversion of units and comparison of gas and liquid reactions is shown.

The section on "Reaction Kinetics of Aqueous Sulfur" provides the kinetic rates and their constants for sulfur dioxide oxidation by oxygen, ozone, hydrogen peroxide, etc. and illustrates the mechanism and rates catalyzed by iron, etc. Table 8 lists the rate expressions and rate constants for aqueous oxidation of S(IV). Table 9 lists the important reactions and dissociations of nitrogen oxides and gives the dissociation constant for nitric acid (its Henry's constant is reported in Table 6). The relative magnitude of various oxidation rates is shown in Figure 4.

The section on "Dynamic Behavior" sets up all the equations for the development of a computer algorithm needed to solve the sulfur dioxide oxidation problem.

Since we are considering oxidation of sulfur by ozone and peroxide and the effect of presence of nitric acid we must write the conservation equations for all these species as shown in the rest of Chapter 8.

Now you are armed with the tools to work on your take home Exam 1 which is also listed in the chapter

8.1 Two Phase Systems: Introduction

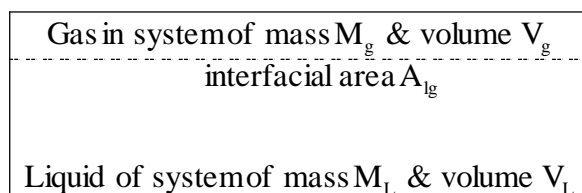
To set up the compartment type model for two phase systems of total mass M and volume V , schematically presented below, we need to make assumptions listed below and keep track of the quantities listed below.

Needed assumptions:

- Each phase is perfectly mixed
- Rate of transport between phases is proportional to a volumetric mass transfer coefficient (mass transfer coefficient times interfacial area per unit volume of the system) and the difference in species concentration in the two phases.

We illustrate this below for a gas liquid system.

1. Closed System



$$V = V_g + V_L$$

$$M = M_g + M_L = \text{const}$$

MUST DIFFERENTIATE MOLAR CONCENTRATION AND REACTIONS IN DIFFERENT PHASES

$$C_{jg} \left(\frac{\text{mol } j}{\text{m}^3 \text{ gas}} \right) = \text{molar concentration of } j \text{ in gas phase}$$

$$C_{jL} \left(\frac{\text{mol } j}{\text{m}^3 \text{ liquid}} \right) = \text{concentration of } j \text{ in liquid phase}$$

$$R_{jg} \left(\frac{\text{mol } j}{\text{m}^3 \text{ gas}} \right) = \text{gas phase reaction rate of } j$$

$$R_{jL} \left(\frac{\text{mol } j}{\text{m}^3 \text{ liquid}} \right) = \text{liquid phase reaction rate of } j$$

$$A_{lg} \left(\text{m}^2 \right) = \text{gas liquid interfacial area } (A_{lg} = a_{lg} V)$$

$$a_{lg} \left(\frac{\text{m}^2}{\text{m}^3} \right) = \text{specific interfacial areas (per unit volume of total system)}$$

$$\varepsilon_g \left(\frac{m^3 \text{ gas}}{m^3 \text{ total}} \right) = \text{gas holdup in the system } (\varepsilon_g = V_g/V)$$

$$\varepsilon_L \left(\frac{m^3 \text{ liquid}}{m^3 \text{ total}} \right) = \text{liquid holdup in the system } (\varepsilon_L = 1 - \varepsilon_g = V_L/V)$$

$$N_{gj} \left(\frac{\text{mol } j}{s} \right) = K_{gj} (p_g - C_{jL}/H_j) = \text{mass transfer flux of } j \text{ from gas to liquid}$$

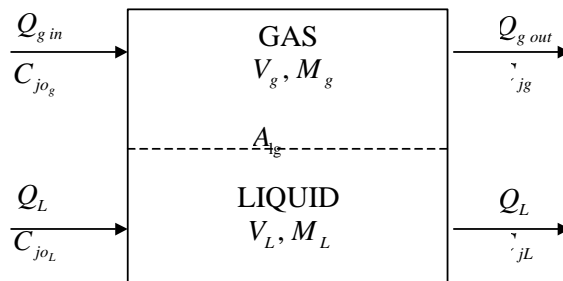
$$K_{gj} \left(\frac{\text{mol } j}{\text{atm } m^2 s} \right) = \text{overall gas-liquid mass transfer coefficient for } j$$

$$p_j (\text{atm}) = \text{partial pressure of } j \text{ in gas phase}$$

$$C_{jL} \left(\frac{\text{mol } j}{m^3 \text{ liquid}} \right) = \text{molar concentration of } j \text{ in liquid phase}$$

$$H_j^* \left(\frac{\text{mol } j}{m^3 \text{ liquid} \times \text{atm}} \right) = \text{Henry's constant (equilibrium gas-liquid partition coefficient) for } j$$

2. Open System



Assume ideal gas

$$p_{jo_g} = C_{jo_g} RT$$

$$p_j = C_{j_g} RT$$

Next we develop first the model equations for closed, then for open system.

Two Phase Systems: Model Development

The model is based on the mass balance for species j in each compartment (gas and liquid) which in general can be written as:

$$\left(\text{Rate of accumulation of } j \right) = \left(\text{Rate of input of } j \right) - \left(\text{Rate of output of } j \right) + \left(\text{Rate of generation of } j \right)$$

In a closed system the only (rate of input) – (rate of output) is by the exchange mass transfer of j from gas to liquid. Only the open system contains the flow in and out terms. The rate of generation j is the sum of the reaction rates that occur on that compartment and that produce (consume j) multiplied by appropriate stoichiometric coefficients.

1. Closed System

Let us consider the air-water system like in the atmosphere. Then the total volume of the system

$$V = V_g + V_L = (\text{gas volume}) + (\text{liquid volume}) \quad (1)$$

Let $V_L/V_G = L$, and $L \ll 1$ such as is the case in the atmosphere. Then

$$V = V_g (1 + L) \approx V_g. \quad (1a)$$

In addition, a species may be found in the gas phase at concentration C_{jg} and in the liquid at concentration C_{jL} .

When equilibrium is established between the two phases and species j does not dissociate upon dissolution,

$$C_{jL} = \tilde{H}_j C_{jg} = \frac{\tilde{H}_j}{RT} p_j = H_j p_j \quad (2)$$

where p_j (atm) is the partial pressure of j in the gas phase, R is the ideal gas constant while H_j (mol/L atm) and H_j^* (unit less) are the two forms of the Henry's constant.

For a liquid species that undergoes ionization in the liquid phase at equilibrium, we have

$$C_{jL} = \tilde{H}_j^* C_{jg} = \frac{\tilde{H}_j^*}{RT} p_j = H_j^* p_j \quad (2a)$$

and the modified Henry's constant, H_j^* , must be used. H_j^* is a function of pH of the solution and can be readily obtained if the dissociation reactions and their equilibrium constants are known.

In principle we could also consider now the rate of transport between the gas and liquid phase for species j

$$\dot{N}_{g\ell j} \left(\frac{\text{mol } j}{Ls} \right) = (K_{gj} a_{g\ell}) (p_j - C_{jL} / H_j) \quad (3)$$

where

$a_{g\ell} \left(\frac{dm^2}{dm^3} \right)$ - is the interfacial area of the gas-liquid interface per unit volume of the system

$K_{gj} \left(\frac{\text{mol } j}{dm^2 s atm} \right)$ - is the overall mass transfer coefficient for j

$(p_j - C_{jL} / H_j) (atm)$ - is the driving force for transport which goes to zero at equilibrium.

The balance on species j in the gas phase is given by

$$V_g \frac{dC_{jg}}{dt} = R_{jg} V_g - \dot{N}_{gl_s} V; t = 0, C_{jg} = C_{jg^o} \quad (4)$$

$$\frac{dC_{jg}}{dt} = R_{jg} - \dot{N}_{gl_j} (1 + L) \quad (4a)$$

R_{jg} is the reaction rate of production of j in the gas phase.

The balance for species j in the liquid phase yields

$$V_L \left(\frac{dC_{jL}}{dt} \right) = R_{jL} V_L + \dot{N}_{gl_j} V; t = 0, C_{jL} = C_{jL^o} \quad (5)$$

$$L \left(\frac{dC_{jL}}{dt} \right) = R_{jL} L + \dot{N}_{gl_j} (1 + L) \quad (5a)$$

The electroneutrality equation $f([H^*]) = 0$ must be solved in conjunction with the above.

a) Equilibrated System

If we assume that equilibrium is always present between gas and liquid then

$$\dot{N}_{gl_j} = 0 \quad \text{for all } j \quad (6)$$

$$\text{so that } C_{jL} = H_j^* C_j \quad (6a)$$

By adding eq (4a) and (5a) we get

$$\frac{d}{dt} \left[(1 + \tilde{H}_j^* L) C_{jg} \right] = R_{jg} + L R_{jL} \quad t = 0, C_{jg} = C_{jg^o} \quad (7)$$

Now one needs to sort out the reactions in the mechanism proposed for the gas phase:

$$\sum_{j=1}^{S+S'} \nu_{ij}^m A_j = 0; i = 1, 2, \dots, R'_g \quad (8a)$$

Where ν_{ij}^m is the stoichiometric coefficient of j in reaction i occurring in the gas phase; and we have R'_g independent gas reactions.

This must be repeated for the liquid phase

$$\sum_{j=1}^{S+S'} v_{ijL}^m A_j = 0; i = 1, 2, 3 \dots R'_L \quad (8b)$$

Here v_{ijL}^m is the stoichiometric coefficient of j in reaction i occurring in the liquid phase; and we have R'_L independent liquid phase reactions.

The rate of reaction of j is then found by summing the rate of each reaction multiplied by the stoichiometric coefficient of j in that reaction, as shown by equation (9a) and (9b) for the gas and liquid phase, respectively.

$$R_{jg} = \sum_{i=1}^{R'_g} v_{ijg}^m r_{ig} \quad (9a)$$

and

$$R_{jL} = \sum_{i=1}^{R'_L} v_{ijL}^m r_{iL} \quad (9b)$$

where r_{ig} , r_{iL} is the rate of elementary i -th reaction in the gas and liquid phase, respectively. If we have evaluated complete mechanisms, then each reaction is elementary and its rate law can be written from the law of mass action.

Again, exact and approximate solutions are possible, depending whether we use PSSA or solve the full system of equations.

For the exact solution one must solve equations repeated below as equations (10):

$$\frac{d}{dt} \left[(1 + \tilde{H}_j^* L) C_{jg} \right] = R_{jg} + L R_{jL}, \quad t = 0, \quad C_{jg} = C_{jg0} \quad (10)$$

for all $j = 1, 2, 3, \dots, S, S+1, \dots, S+S'$ which includes intermediates (active centers) as well as S stable species (reactants or products).

For the approximate solution via PSSA one solves S' nonlinear equations for the concentrations of active intermediates

$$R_{jg} = \sum_{i=1}^{R'_g} v_{ijg}^m r_{ig} = 0; i = 1, 2, \dots, R'_g \quad (11a)$$

$$R_{jL} = \sum_{i=1}^{R'_L} v_{ijL}^m r_{iL} = 0; i = 1, 2, \dots, R'_L \quad (11b)$$

Then one solves eq (7) for the stable species $j = 1, 2, 3 \dots S$.

Nota bene: Numerical solutions tend to become inaccurate when one attempts to divide by zero or multiply by infinity.

Hence if the gaseous species is practically insoluble.

$$\tilde{H}_j L \ll 1, \text{ i.e. } H_j RTL \ll 1$$

then for that species only the gas phase reactions should be considered.

$$\frac{dC_{jg}}{dt} = R_{jg} \quad (12)$$

for $j=1,2,\dots,NS$ where NS indicates the total number of insoluble species.

One should pay attention in particular if a highly insoluble species is created by the liquid phase reaction that one does not attempt to calculate its gas phase concentration by $C_{jg} = C_{jL} / \tilde{H}$ as this involves division by a very small number.

If on the other hand the species is highly soluble, i.e. practically nonvolatile,

$\tilde{H}_j L \gg 1, \text{ i.e. } H_j RTL \gg 1$ then only its liquid phase reactions should be accounted for.

$$\frac{dC_{jL}}{dt} = R_{jL} \quad (13)$$

for all j -s of nonvolatile species ($j=1,2,\dots,NU$, where NU is the total number of volatile species). For nonvolatile species one should use only liquid phase concentrations C_{jL} and not attempt to convert them to gas phase concentration $C_{jg} = C_{jL} / \tilde{H}$.

b) Non-equilibrated System

This results in a large and stiff set of differential equations since transport terms must be included in the calculation.

The set of equations to be solved are:

$$\frac{1}{RT} \frac{dp_j}{dt} = R_{jg} - (K_g a_{lg})_j (p_j - C_{jL} / H_j^*) (1 + L) + \frac{Q_g}{V_g} (C_{jin} - \frac{P_j}{RT}) \quad (14a)$$

$$\frac{dC_{jL}}{dt} = R_{jL} + (K_g a_{lg})_j (p_j - C_{jL} / H_j^*) \left(\frac{1 + L}{L} \right) \quad (14b)$$

$$t = 0 \quad p_j = p_{jo}, \quad C_{jL} = C_{jLo} \quad (15)$$

c) Additional Hints

It is sometimes useful in solution of the above problems to work in terms of total concentration of atomic species, say a_i .

In a closed system the total concentration of an atomic species is constant.

$$(a_i)_{tot} = (1 - L)(a_i)_g + L(a_i)_L \quad (16)$$

The atomic species concentration in each phase is found by summing the product of the number of atoms of species i present in species j , α_{ij} and the concentration of species j , over all chemical species j present in that phase ($j = 1, 2 \dots S$).

$$(a_i)_g = \sum_{j=1}^S \alpha_{ij} C_{jg} \quad (17a)$$

$$(a_i)_L = \sum_{j=1}^S \alpha_{ij} C_{jL} \quad (17b)$$

For example for the sulfur dioxide pollution problem the total sulfur concentration must be constant in a closed system.

$$[S]_{tot} = (1 - L)[S]_g + L[S]_L = (1 - L) \frac{P_{SO_2, o}}{RT} \quad (18)$$

The constant sulfur concentration is readily obtained from the initial partial pressure of SO_2 assuming no sulfur is initially present in the liquid.

In the gas phase, SO_2 is the only form in which S(IV) exists so that

$$[S]_g = [S(IV)]_g = \frac{P_{SO_2}}{RT} \quad (19)$$

In the liquid phase, various S(IV) forms exist: SO_2H_2O , HSO_3^- , SO_3^{2-} and S(VI) forms SO_3H_2O , HSO_4^- , SO_4^{2-} so that

$$[S] = (S(IV))_L + [S(VI)]_L \quad (20)$$

If we deal with the equilibrated model then

$$[S(IV)]_L = H_{S(IV)}^* p_{SO_2} \quad (21)$$

So that eq (18) can be written as

$$(1-L) \frac{P_{SO_2,0}}{RT} = (1-L) \frac{P_{SO_2}}{RT} + H_{S(IV)}^* L p_{SO_2} + L[S(VI)]_L \quad (22)$$

The rate of change of S(VI) by oxidation in the liquid phase can be written as

$$\left(\frac{d[S(VI)]}{dt} \right) = \sum_{i=1}^N R_{ox,S(VI),i} \quad (23)$$

$$t = 0 \quad [S(VI)] = 0 \quad (23a)$$

Here, $R_{ox,S(VI),i}$ is the i-th oxidation rate form (i.e. with oxygen, with ozone, with peroxide, catalyzed by iron, etc.) and N forms can be included.

In each oxidation rate the liquid phase concentrations can be expressed as $C_{jL} = H_j^* p_j$ in terms of their current partial pressures, p_j , except for the nonvolatile species for which C_{jL} is used directly.

The electroneutrality equation (24)

$$f([H^+]) = 0 \quad (24)$$

must be used and solved at each step to calculate $[H^+]$ and evaluate all modified Henry's constants H_j^* -s which depend on it. Equation (22) can be used at each integration step, as $[S(VI)]$ builds up and $[S(IV)]$ declines, to evaluate and update p_{SO_2} .

For other species that can be found in gas and liquid phase an equation of the type of eq (22) can be written to update the partial pressure p_j of such species. Or equation (7) is solved for all such species.

2. Open System

In an open two phase system inputs and outputs of both phases may be present and must be accounted for. The most general set of equations is obtained by adding such input and output terms to equations (20a, b) to obtain:

$$\frac{1}{RT} \frac{dp_j}{dt} = R_{jg} - (K_g a_{lg})_j (p_j - C_{jL} / H_j^*) (1 + L) + \frac{Q_g}{V_g} \left(C_{jin} - \frac{p_j}{RT} \right) \quad (25a)$$

$$L \frac{dC_{jL}}{dt} = LR_{jL} + (K_g a_{lg})_j (p_j - C_{jL} / H_j^*) \left(\frac{1+L}{L} \right) + \frac{Q_L}{V_L} (C_{jin} - C_{jL}) \quad (25b)$$

$$t = 0 \quad p_j = p_{jo}, \quad C_{jL} = C_{jLo} \quad (25c)$$

For an equilibrated open system we have again (when $Q_L = 0$)

$$C_{jL} = H_j^* p_j \quad (26)$$

and

$$\frac{d}{dt} \left[\left(\frac{1}{RT} + LH_j^* \right) p_j \right] = R_{jg} + LR_{jL} + \frac{Q_g}{V_g RT} (p_{jin} - p_j) \quad (27)$$

$$t = 0, \quad p_j = p_{jo} \quad (27a)$$

In addition, in the air pollution literature it is often assumed that the dominant term in eq (25a) is the last one, i.e. Q_g/V_g is huge so large that

$$C_{jgin} = \frac{p_{jin}}{RT} = \frac{p_j}{RT} \quad (28)$$

This implies that for all gas phase species

$$p_j = p_{jin} = const = p_{jo} \quad (29)$$

The only equations to be solved now are for the species in the liquid phase

$$\frac{dC_{jL}}{dt} = R_{jL} \quad (30)$$

$$t = 0 \quad C_{jL} = C_{jLo} \quad (30a)$$

In this particular case the total concentration of atomic species cannot be assumed constant since the system is open. But the partial pressures of all gaseous species can be taken as constant. This means that in our SO₂ oxidation example

$$[S]_{tot} \neq const$$

but eq (23, 23a) are still valid

$$\frac{d[S(VI)]}{dt} = \sum_{i=1}^N R_{\alpha, S(VI), i} \quad (23)$$

$$t = 0 \quad [S(VI)] = 0 \quad (23a)$$

In the rate forms above, however, one uses now the assigned p_{j0} values and only updates in time the liquid phase concentration of all species C_{jL} and the electroneutrality equation

$$f([H^+]) = 0 \quad (31)$$

so that the proper solubilities can be calculated for gaseous species

$$C_{jL} = H_j^* p_j \quad (32)$$

Eventually as pH falls as $[H^+]$ increases, H_j^* drops off and additional SO_2 is hindered from entering the water phase.

8.2 THE SULFUR PROBLEM

The major sulfur components in the environment are

- carbonyl sulfide, $CO S$
- carbondisulfide, CS_2
- dimethyl sulfide, $(CH_3)_2 S$
- hydrogen sulfide, $H_2 S$
- sulfur dioxide, SO_2
- sulfate ion, SO_4^{2-}
- elemental sulfur, S_8

The global sulfur cycle is depicted in Figure 1. Table 1 presents estimates from various sources (clearly there is great uncertainty). Nevertheless the anthropogenic emissions of SO_2 are an appreciable fraction of the total flux to the atmosphere.

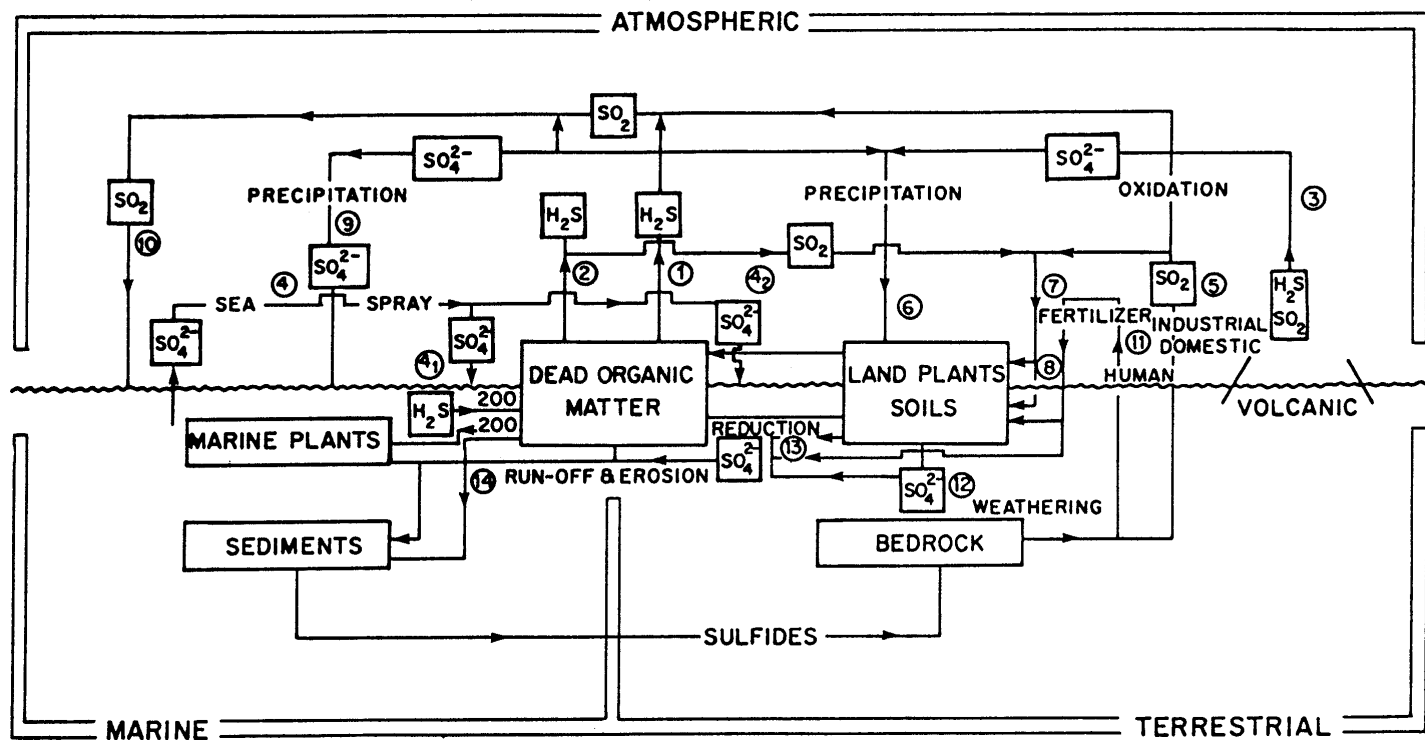
Most abundant are $CO S$, CS_2 , $(CH_3)_2 S$ and $H_2 S$. In the troposphere $[CO S] \approx 500 \pm 50 \text{ ppt}$ indicating a long life time. $[CS_2] \approx 15$ to 30 ppt in surface nonurban air and 100 to 200 ppt in polluted urban air. $[CS_2]$ decays rapidly with altitude indicating short life time. $(CH_3)_2 S$ is most abundant in seawater about $1 \times 10^{-7} \text{ (g/L)}$. It is produced by algae and bacteria. $H_2 S$ sources are anearobic processes in sulfur rich soils. Concentration levels are not well known.

TABLE 1: Estimates of annual fluxes (Tg yr^{-1}) of environmental sulfur^a

Source of Sulfur	Flux Number in Figure	Eriksson (1960, 1963)	Robinson and Robbins (1968, 1970)	Kellogg et al. (1972)	Friend (1973)	Granat et al. (1976)
Biological decay (land)	1	110	68	90	58	5
Biological decay (ocean)	2	170	30		48	27
Volcanic activity	3	—	—	1.5	2	3
Sea spray (total)	4	45	44	47	44	44
To ocean	4 ₁	(40)	—	(43)	(40)	(40)
To land	4 ₂	(5)	—	(4)	(4)	(4)
Anthropogenic	5	40	70	50	65	65
Precipitation (land)	6	65	70	86	86	43
Dry deposition	7	100	20	10	20	28
Absorption (vegetation)	8	75	26	15	15	
Precipitation and deposition (ocean)	9,10	200	96	72	96	73
Total sulfur involved in atmospheric balance		365	212	183	217	144
Atmospheric balance						
Land → sea		-10	+26	+5	+8	+18
Sea → land		5	4	4	4	17
Fertilizer	11	10	11	—	26	—
Rock weathering	12	15	14	—	42	—
Pedosphere → river runoff	13	55	48	—	89	—
Total river runoff	14	80	73	—	136	122

^aSource: as cited in each column and, in part, Friend (1973, Table 4). Moss (1978).

FIGURE 1: The global sulfur cycle, showing the major reservoirs, pathways, and forms of occurrence of sulfur. Figures enclosed in circles refer to the individual fluxes and correspond to figures in column 2, Table 1.2. Flux between marine plants and dead organic matter estimated as 200 Tg yr⁻¹. (Moss, 1978).



8.2.1 Atmospheric Chemistry of SO_2

Thermodynamically the tendency to react is high



so that $\left. \frac{[SO_3]}{[SO_2]} \right|_{eq} = 8 \times 10^{11}$ in air at 1 atm and 25°C.



Reaction (2) is in humid atmosphere instantaneous for all practical purposes. However, reaction (1) cannot proceed at atmospheric conditions without a catalyst. Such catalyst may be present in aerosols but the rates at 25°C are still very slow.



The above photoexcitation of SO_2 is effective only at $\lambda < 218$ nm and hence does not occur to a great extent. Moreover quenching with N_2 , O_2 and H_2O occurs 45.7%, 41.7% and 12.2% of the time making this reaction (3) a negligible source of SO_3 in the atmosphere. Other possible reactions include those with

- electronically excited O_2 , reactive molecules and free radicals (e.g. O_3 , NO_3 , OH^* , HO_2^*)
- other peroxyalkyl ($CH_3C(O)O_2$) and acyl peroxy radicals.

Possible reactions are summarized in Table 2 and their relative importance in Table 3. By far the most important gas phase reaction is the one with hydroxyl radical.



The $HOSO_2^*$ ultimately leads to H_2SO_4 . Recent evidence suggests that the $[OH^*]$ concentration in the photo-oxidizing mixtures of HNO_2 , NO , NO_2 is insensitive to even large addition of SO_2 . Hence, reaction (4) is slow compared to reactions in that cycle and is the rate determining step for H_2SO_4 formation.

For a value of the rate constant reported in Table 2 with $[OH^*] = 10^7$ (molecules/cm³) we get an estimate that SO_2 would be converted at a rate of 3.96%/hr or 95%/day. However, using an improved estimate of the daily average $[OH^*] = 1.7 \times 10^6$ (molecules/cm³) we get 0.67%/hr conversion rate or 16.1%/day. Clearly, the main uncertainty is in estimating the (OH^*) concentration.

The reactions of reduced sulfur species are reported in Table 4. Here a lower estimate of $[OH^*] = 10^6$ molecules/cm³ is used as these processes tend to occur in a cleaner atmosphere.

TABLE 2: Rate constants for potentially important reactions of ground state SO₂ and SO₃ molecules in the lower atmosphere^a

Reaction	$k, {}^b \text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$
$\text{O}_2({}^1\Delta_g) + \text{SO}_2 \rightarrow \text{SO}_4$ (biradical; cyclic) $\text{O}_2({}^1\Delta_g) + \text{SO}_2 \rightarrow \text{SO}_3 + \text{O}$ $\text{O}_2({}^1\Delta_g) + \text{SO}_2 \rightarrow \text{O}_2({}^3\Sigma_g^-) + \text{SO}_2$	3.9×10^{-20}
$\text{O}_2({}^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_4$ (biradical; cyclic) $\text{O}_2({}^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_3 + \text{O}$ $\text{O}_2({}^1\Sigma_g^+) + \text{SO}_2 \rightarrow \text{SO}_2 + \text{O}_2({}^1\Delta_g)$	6.6×10^{-16}
$\text{O} + \text{SO}_2(+M) \rightarrow \text{SO}_3(+M)$	5.7×10^{-14}
$\text{O}_3 + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}_3$	$< 8 \times 10^{-24}$
$\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$	8.8×10^{-30}
$\text{NO}_3 + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3$	$< 7 \times 10^{-21}$
$\text{N}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{N}_2\text{O}_4 + \text{SO}_3$	$< 4 \times 10^{-23}$
$\text{HO}_2 + \text{SO}_2 \rightarrow \text{OH} + \text{SO}_3$	$< 1 \times 10^{-18}$
$\text{HO}_2 + \text{SO}_2(+M) \rightarrow \text{HO}_2\text{SO}_2(+M)$	
$\text{CH}_3\text{O}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{O} + \text{SO}_3$	$< 1 \times 10^{-18}$
$(\text{CH}_3)_3\text{CO}_2 + \text{SO}_2 \rightarrow (\text{CH}_3)_3\text{CO} + \text{SO}_3$	$< 7.3 \times 10^{-19}$
$(\text{CH}_3)_3\text{CO}_2 + \text{SO}_2 \rightarrow (\text{CH}_3)_3\text{CO}_2\text{SO}_2$	
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{CO}_2 + \text{SO}_3$	$< 7 \times 10^{-19}$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{SO}_2$	
$\text{OH} + \text{SO}_2(+M) \rightarrow \text{HOSO}_2(+M)$	1.1×10^{-12}
$\text{CH}_3\text{O} + \text{SO}_2(+M) \rightarrow \text{CH}_3\text{OSO}_2(+M)$	5.5×10^{-13}
$\text{RCHO} + \text{SO}_2 \xrightarrow{a} \text{RCHO} + \text{SO}_3$	
$\text{RCHO} + \text{H}_2\text{O} \xrightarrow{b} \text{RCOOH} + \text{H}_2\text{O}$	$k_a/k_b = 6 \times 10^{-5}$
	(R = CH ₃)
$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	9.1×10^{-13}

^aCalvert and Stockwell (1984).
^bThe rate constants are all expressed as second order reactions for 1 atm of air at 298 K.

TABLE 3: Estimated relative contributions to SO₂ oxidation by gas-phase reactions $\text{SO}_2 + X \xrightarrow{k}$

SO ₂ Oxidation by Gas-Phase Reactions $\text{SO}_2 + X \xrightarrow{k}$			
X	[X], molecule cm ⁻³	k, cm ³ molecule ⁻¹ sec ⁻¹	k[X], sec ⁻¹
O	10 ⁶	5.7×10^{-14}	5.7×10^{-8}
OH·	10 ⁷	1.1×10^{-12}	1.1×10^{-5}
HO ₂ ·	10 ⁹	$< 1 \times 10^{-18}$	$< 10^{-9}$
CH ₃ O ₂ ·	10 ⁹	$< 1 \times 10^{-18}$	$< 10^{-9}$

TABLE 4: Reactions of reduced sulfur species: RSH alkane thiols, RSR' sulfides, RSSR' disulfides.

Species	Reaction ^{a, b}	Rate Constant at 298 K cm ³ molecule ⁻¹ sec ⁻¹ ^a	Mean Lifetime Based on [OH] = 10 ⁶ molecules cm ⁻³
Hydrogen sulfide	$\text{H}_2\text{S} + \text{OH}\cdot \rightarrow \text{H}_2\text{O} + \text{HS}\cdot$	5.3×10^{-12}	53 hr
Methyl sulfide	$\text{CH}_3\text{SH} + \text{OH}\cdot \rightarrow \text{CH}_3\text{S}\cdot + \text{H}_2\text{O}$	$21\text{--}90 \times 10^{-12}$	13–3 hr
Dimethyl sulfide	$\text{CH}_3\text{SCH}_3 + \text{OH}\cdot \rightarrow \text{CH}_3\text{SCH}_2\cdot + \text{H}_2\text{O}$ $\rightarrow \text{CH}_3\cdot + \text{CH}_3\text{SOH}$	9.1×10^{-12}	31 hr
Carbon disulfide	$\text{CS}_2 + \text{OH}\cdot \rightarrow \text{Products}$	$\leq 1.5 \times 10^{-15}$	$\geq 1.8 \times 10^5$ hr
Methyl disulfide	$\text{CH}_3\text{SSCH}_3 + \text{OH}\cdot \rightarrow \text{CH}_3\text{SSCH}_2\cdot + \text{H}_2\text{O}$ $\rightarrow \text{CH}_3\text{SOH} + \text{CH}_3\text{S}\cdot$	2.2×10^{-10}	1.2 hr
Carbonyl sulfide	$\text{COS} + \text{OH}\cdot \rightarrow \text{Products}$	$\leq 9 \times 10^{-15}$	$\geq 0.3 \times 10^5$ hr

^aBaulch et al. (1982).^bGrosjean (1984).

8.3 HETEROGENEOUS REACTIONS IN THE ATMOSPHERE

The atmosphere in addition to gases contains liquid (aqueous) droplets and particulate matter (aerosols). In addition to the homogeneous gas phase reactions discussed thus far, heterogeneous reactions can occur in the droplets or on the surfaces of droplets and of particulate matter. These types of reactions will cause us to examine a few additional concepts such as

- phase equilibria
- interphase transport
- intraphase diffusion and reaction.

The particles in the atmosphere vary in size from less than 1 μm (aerosols), 1-100 μm water droplets in fog and clouds, and hydrometeors of 0.1 to 3 mm diameter. Precipitation results from hydrometeors reaching the earth's surface.

Let us consider now reactions in such aqueous droplets.

8.3.1 Aqueous-Atmospheric Reactions - SO₂

Oxidation

These reactions are oxidative in nature and involve neutral free radicals, free radical ions, ions, nonradical nonionic species such as H₂O₂ and O₃.

The best known set of atmospheric aqueous reactions is related to SO₂ oxidation that results in acid rain. SO₂ rises in power plant plumes and reacts in gas phase via OH* or other radicals, to form H₂SO₄ which instantly acquires water and condenses. Gas phase reactions can contribute up to 1% hr⁻¹ SO₂ conversion rate. Much higher observed conversion rates (see Table 5) indicate the importance of heterogeneous reactions. For solubility, definition of phase equilibrium, Henry's constant and modified Henry's constant, see chapter 3N. Temperature dependence of some Henry's constants is in Table 7.

TABLE 5: Field measurements on the rates of SO₂ oxidation in plumes

Plume Type Location	SO ₂ Oxidation Rate (% hr ⁻¹)	Method	Reference
Power Plant			
Keystone (Pennsylvania)	0–10	32 _s /34 _s ratio, change with oxidation	Newman et al. (1975)
Labadie (Missouri)	0.41–4.9	Total change in particle volume	Cantrell and Whitby (1978)
Muscle Shoals (Alabama)	0–5	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977a)
Four Corners (New Mexico)	2–8	Cloud condensation nuclei (CCN) production (CCN to SO ₂ ratios)	Pueschel and Van Valin (1978)
Labadie (Missouri)	0–4	Particulate sulfur to total sulfur ratio	Gillani (1978) Gillani et al. (1978) Husar et al. (1978)
Cumberland (Tennessee)	0–7	Particulate sulfur to total sulfur ratio	Meagher et al. (1978) Forrest et al. (1981)
Great Canadian Oil Sands (Alberta, Canada)	0–3	Particulate sulfur to total sulfur ratio	Lusis et al. (1978)
Keystone (Pennsylvania)	0–5	Particulate sulfur to total sulfur ratio	Dittenhoefer and dePena (1978)
Central (Washington)	0–6	Total change in particle volume	Hobbs et al. (1979)
Four Corners (New Mexico)	0.15–0.5	CCN production (CCN to SO ₂ ratios)	Mamane and Pueschel (1980)
Sherburne County (Minnesota)	0–5.7	Total change in particle volume	Hegg and Hobbs (1980)
Big Brown (Texas)	0.4–14.9	Total change in particle volume; particulate sulfur to total sulfur ratio	Hobbs et al. (1979) Hegg and Hobbs (1980)
Smelter			
INCO Nickel (Copper Cliff, Canada)	0–7	Particulate sulfur to total sulfur ratio	Lusis and Wiebe (1976) Forrest and Newman (1977b) Chan et al. (1980)
Mt. Isa Mines (Mt. Isa, Australia)	0.25 ^a	Particulate sulfur to total sulfur ratio	Roberts and Williams (1979)
Urban			
Los Angeles (California)	1.2–13	Particulate sulfur to total sulfur ratio	Roberts and Friedlander (1975)
St. Louis (Missouri)	7–12.5	Particulate sulfur to total sulfur ratio	Alkezweeny and Powell (1977)
St. Louis (Missouri)	3.6–4.2	Particulate sulfur to total sulfur ratio	Chang (1979)

^a Diurnal average rate

TABLE 6: Henry's Law coefficients of atmospheric gases dissolving in liquid water^a

Gas	$H, \text{ M atm}^{-1} (298 \text{ K})$
O ₂	1.3×10^{-3}
NO	1.9×10^{-3}
C ₂ H ₄	4.9×10^{-3}
O ₃ ^d	9.4×10^{-3}
NO ₂ ^b	1×10^{-2}
N ₂ O	2.5×10^{-2}
CO ₂ ^c	3.4×10^{-2}
SO ₂ ^c	1.24
HNO ₂ ^c	49
NH ₃ ^{b,c}	62
HCl	2.5×10^3
HCHO ^f	6.3×10^3
H ₂ O ₂	7.1×10^4 ^e
HNO ₃ ^c	2.1×10^5

^aAdapted from Schwartz (1983) and Martin (1984a).

^bPhysical solubility only. Dissolved NO₂ reacts with liquid water.

^cPhysical solubility only. These species participate in acid-base equilibria that are not reflected in the values of H given.

^dOzone is actually a reacting solute in water (Roth and Sullivan, 1981).

For our purposes here we will use only the Henry's law coefficient as presented here and as a function of temperature in Table 5.4. The Henry's law coefficient of Roth and Sullivan is presented as $H = 3.84$

$\times 10^7 [\text{OH}^-]^{0.035} \exp(-2428/T)$ [atm mole fraction⁻¹], defined by

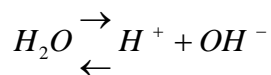
$$p_A = H_A x_A.$$

^eA more recent measurement of the H₂O₂ Henry's law constant is that of Yoshizumi et al. (1984) who report $H_{\text{H}_2\text{O}_2} = 1.42 \times 10^5 \text{ M atm}^{-1}$ at 293 K.

^fHCHO exists in solution primarily in the gem-diol form: $\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{C}(\text{OH})_2$. The Henry's law coefficient given in the table includes both dissolved HCHO and H₂C(OH)₂.

Water Ionization

The ionization or recombination reaction for water is for all practical purposes infinitely fast



so that equilibrium is always established

$$K_w' = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.82 \times 10^{-16} \text{ M at } 298 \text{ K}$$

Since molar concentration of water is constant, we get

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}^2 \text{ at } 298 \text{ K}$$

For pure water $[H^+] = [OH^-] = 1.0 \cdot 10^{-7}$ M. Recall that

$$pH = -\log [H^+]$$

so that $pH = 7$ for pure water at 298K.

TABLE 7: Thermodynamic data for calculating temperature dependence of aqueous equilibrium constants

Equilibrium	ΔH_{298} , kcal mole ⁻¹	K at 298 K, M
$H_2O \rightleftharpoons H^+ + OH^-$	13.345	1.008×10^{-14}
$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$	1.825	4.283×10^{-7}
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	3.55	4.687×10^{-11}
$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$	8.65	1.709×10^{-5}
$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$	-4.161	1.29×10^{-2}
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	-2.23	6.014×10^{-8}

^aMaahs (1982) has reviewed the data on SO_2/H_2O equilibria and has recommended the following values of $K_{h,s}$, K_{s1} , and K_{s2} :

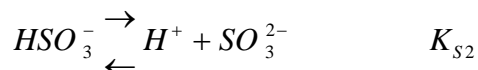
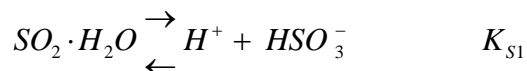
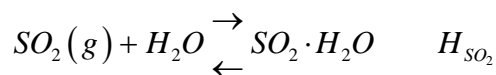
$$\log K_{h,s} = \frac{1376.1}{T} - 4.521$$

$$\log K_{s1} = \frac{853}{T} - 4.74$$

$$\log K_{s2} = \frac{621.9}{T} - 9.278$$

Sulfur Dioxide/Water Equilibrium

The scenario is similar as in the case of CO_2 absorption



The concentration of dissolved species are

$$[SO_2 \cdot H_2O] = H_{SO_2} p_{SO_2}$$

$$[HSO_3^-] = \frac{H_{SO_2} K_{S1} p_{SO_2}}{[H^+]}$$

$$[SO_3^{2-}] = \frac{H_{SO_2} K_{S1} K_{S2} p_{SO_2}}{[H^+]^2}$$

Satisfying the electroneutrality relation requires

$$[H^+]^3 - (K_w + H_{SO_2} K_{S1} p_{SO_2}) [H^+] - 2 H_{SO_2} K_{S1} K_{S2} p_{SO_2} = 0$$

The total dissolved sulfur in oxidation state + 4 is S(IV) and its concentration is given by

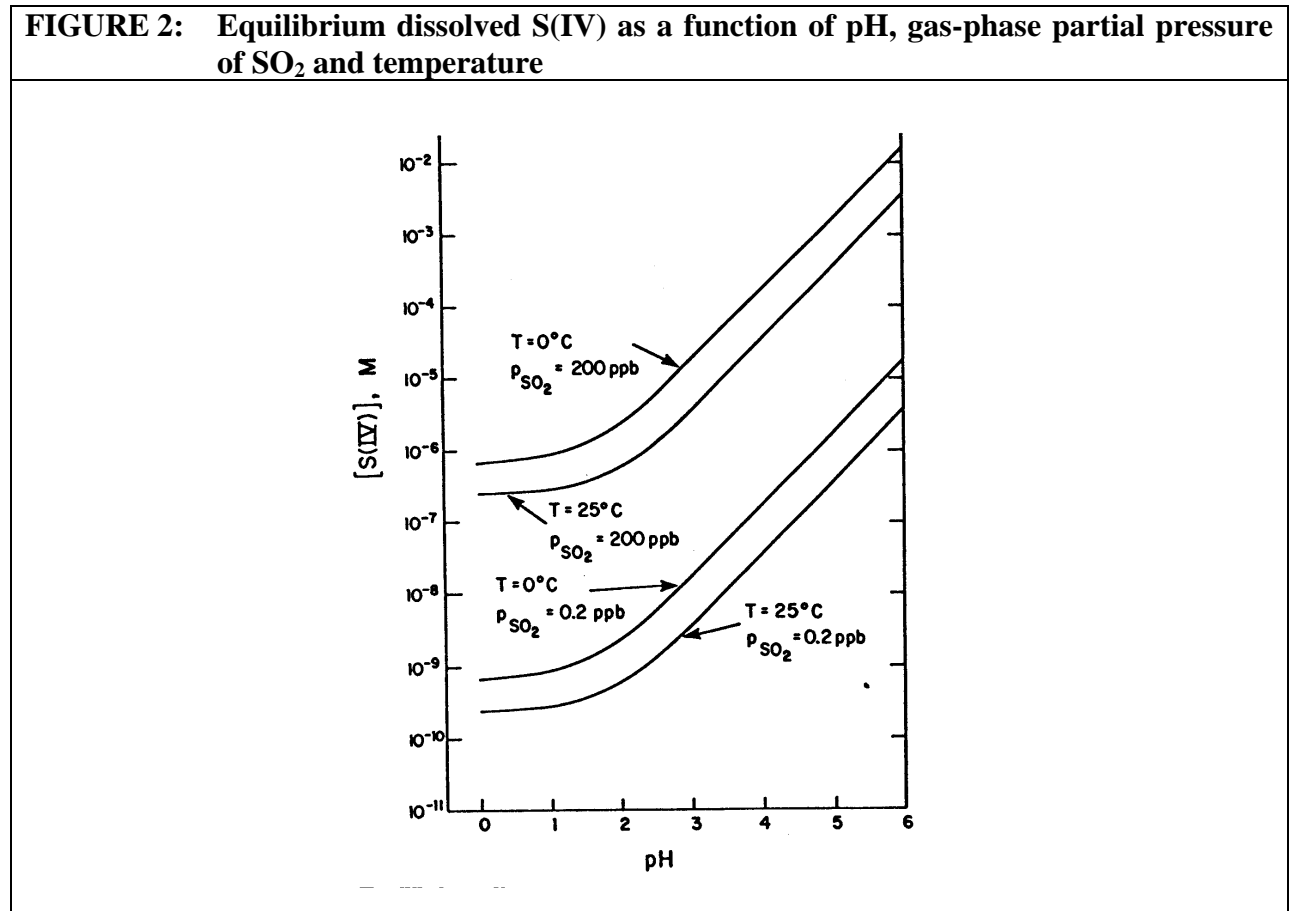
$$[S(IV)] = H_{SO_2} p_{SO_2} \left[1 + \frac{K_{S1}}{[H^+]} + \frac{K_{S1} K_{S2}}{[H^+]^2} \right] = H_{S(IV)}^* p_{SO_2}$$

where $H_{S(IV)}^*$ is the modified Henry's constant which we can express as

$$H_{S(IV)}^* = H_{SO_2} \left[1 + 10^{pH} K_{S1} + 10^{2pH} K_{S1} K_{S2} \right]$$

Clearly the modified constant H^* is dependent on pH. The larger the pH, i.e the more alkaline the solution, the larger the equilibrium content of S(IV). This is illustrated in Figure 2 for

$p_{SO_2} = 0.2$ ppb and 200 ppb.



Let us express now mole fractions of various dissolved sulfur species as function of pH (really these are mole ratios, *i.e.* moles of a particular sulfur species divided by total moles of $S(IV)$ or mole fractions on water free basis since water is the dominant component.

$$\alpha_0 = X_{SO_2 \cdot H_2O} = \frac{[SO_2 \cdot H_2O]}{[S(IV)]} = [1 + K_{S1} 10^{pH} + K_{S1} K_{S2} 10^{2pH}]^{-1}$$

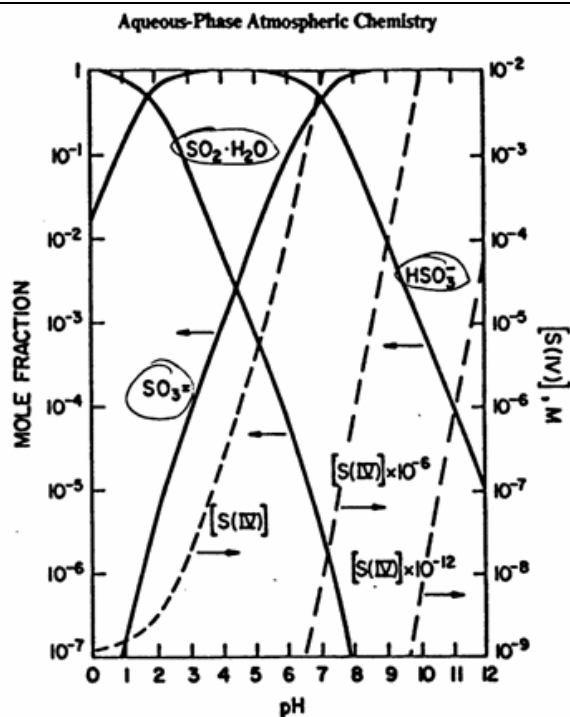
$$\alpha_1 = X_{HSO_3^-} = \frac{[HSO_3^-]}{[S(IV)]} = [1 + K_{S1}^{-1} 10^{-pH} + K_{S2} 10^{pH}]^{-1}$$

$$\alpha_3 = X_{SO_3^{2-}} = \frac{[SO_3^{2-}]}{[S(IV)]} = [1 + K_{S2}^{-1} 10^{-2pH} + (K_{S1} K_{S2})^{-1} 10^{-2pH}]^{-1}$$

Common notation for these are $\alpha_0, \alpha_1, \alpha_2$ in aquatic chemistry.

Figure 3 illustrates the three mole fractions for $p_{SO_2} = 10^{-9}$ atm (1 ppb). Since these species have different reactivities pH will affect reaction rates. At low pH $SO_2 \cdot H_2O$ dominates, at high pH all $S(IV)$ is in the form of SO_3^{2-} . Intermediate pH contains mainly HSO_3^- .

FIGURE 3: Mole fractions and concentrations of the three dissolved S(IV) species, $SO_2 \cdot H_2O$, HSO_3^- , and SO_3^{2-} , as a function of pH at $T = 298$ K, and $p_{SO_2} = 10^{-9}$ atm (1ppb).



Abundance of Liquid Water in the Atmosphere

Liquid water content is expressed in (g water/m³ air) or (m³ water/m³ air). Let L be the second dimensionless measure. Then

clouds	$L = 10^{-7}$ to 10^{-6}
fog	$L = 10^{-8}$ to 5×10^{-7}
aerosols	$L = 10^{-11}$ to 10^{-10}

The distribution of a species A between gas and aqueous phases, in say a cloud, can be expressed as

$$\frac{\text{moles of A in solution per m}^3 \text{ of air}}{\text{moles of A in air per m}^3 \text{ of air}} = \frac{H_A P_A L}{\frac{P_A}{RT}} = H_A R T L$$

$$H_A R T L \ll 1$$

species A is mainly in the gas

$$H_A R T L \gg 1$$

species A mainly in the liquid

$$\text{For } L = 10^{-6}, (RTL)^{-1} \approx 4 \times 10^4 \text{ M atm}^{-1}$$

Hence for

$$H_A \ll 4 \times 10^4 \text{ M atm}^{-1}$$

species A in the gas

$$H_A \gg 4 \times 10^4 \text{ M atm}^{-1}$$

species A in the liquid

Table 6 indicates that, with exception of $HC\ell$, $HCHO$ and especially H_2O_2 and HNO_3 , other species will remain mainly confined to the gas phase.

For SO_2 at pH = 4, $H_{S(IV)}^* \approx 10^2$ and at $L = 10^{-6}$ $H_{S(IV)}^* \leq (RTL)^{-1}$ and most of (almost all of) the $S(IV)$ is in the gas phase. In contrast for HNO_3 the modified Henry's constant is $H^* = 10^{10}$ and all of nitric acid is in solution.

Maximum Solubility

For example, the equilibrium dissolved concentration of A is given by

$$[A_e] = H_A P_A$$

but the total amount of species present is

$$\begin{aligned} N_{totA} &= C_{A_g} V_g + C_{A_L} V_L \\ &= V_g \left[C_{A_g} + C_{A_L} \frac{V_L}{V_g} \right] = V_g \left[\frac{P_A}{RT} + C_{A_L} L \right] \end{aligned}$$

$$\frac{N_{totA}}{V_g} = C_{A_{go}} = \frac{P_{A_{go}}}{RT} = \frac{P_A}{RT} + C_{A_L} L$$

Since the following relationships hold

$$C_{A_L} = H_A P_A$$

$$\frac{P_{A_{g_0}}}{RT} = P_A \left[\frac{1}{RT} + H_A L \right] = \frac{P_A}{RT} [1 + H_A R T L]$$

$$P_A = \frac{P_{A_0}}{1 + H_A R T L}$$

$$C_{A_L} = \frac{H_A P_{A_0}}{1 + H_A R T L}$$

Then, when

$$H_A R T L \gg 1$$

the maximum concentration of dissolved A is:

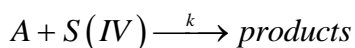
$$C_{A_{\max}} = \frac{P_{A_0}}{R T L}$$

Clearly, then, for a very highly soluble gas we must take precautions in calculating the equilibrium composition not to violate the mass balance, (i.e. "not to dissolve more gas than there is available"). The maximum concentration in the liquid reachable by the highly soluble gas is as shown above and repeated here with different notation

$$[A]_{\max} = \frac{P_A}{R T L}$$

and this cannot be exceeded. Say $P_A = 10^{-9}$ atm (1 ppb) and $L = 10^{-6}$, $[A]_{\max} = 4 \times 10^{-5} M$. Regardless of the value of H , say $H = 10^{10}$ and $[A]_{\text{eq}} = 10 M$, clearly $[A]_{\max}$ cannot be exceeded. $[A]_{\max}$ can only be exceeded if the droplets are brought into contact with much larger volume of air not just the volume containing L amount of water.

Let us now develop a methodology for comparison of gas and liquid phase reactions. Consider the aqueous reaction



with the rate

$$R(M s^{-1}) = k [A(aq)][S(IV)]$$

The same rate can be written in terms of equilibrium partial pressures

$$R = k H_A H_{S(IV)}^* P_A P_{SO_2}$$

Note that R is the rate of depletion of A (or $S(IV)$) per unit volume of water and per unit time. To convert to the basis of unit volume of air we must multiply by L

$$R_a = L R$$

Further conversion of units is often practiced. For example

$$\frac{R_a \cdot RT}{P_a} \times 10^9 \times 3600$$

yields the rate in (ppb h^{-1}) based on volume of air.

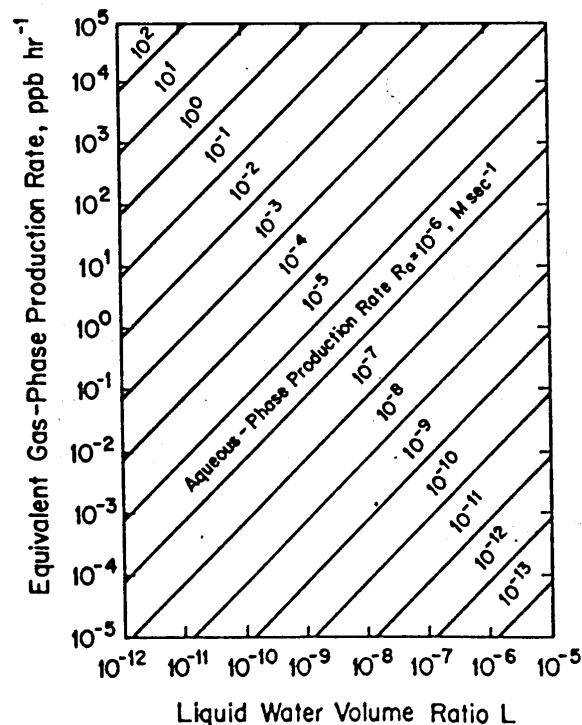
$$\tilde{R}_a = \frac{LR}{[A]_g} = \frac{LRT R}{P_A} (s^{-1})$$

is the fractional rate of conversion. Characteristic reaction time is

$$\tau_R = \frac{1}{\tilde{R}_a}$$

A nomogram for rate conversion is presented in Figure 3.

FIGURE 3: Nomogram relating aqueous reaction rates, in $M \text{ sec}^{-1}$, to equivalent gas phase reaction rates, in ppb hr^{-1} , at $T = 298 \text{ K}$, $p = 1 \text{ atm}$, and given liquid water content L . The diagonal lines are constant aqueous reaction rates (National Center for Atmospheric Research, 1982).



Reaction Kinetics of Sulfur in Aqueous Phase

Dissolved SO_2 generates three aqueous $S(IV)$ species: $SO_2 \cdot H_2O$, HSO_3^- and SO_3^{2-} . Various oxidants converts $S(IV)$ to $S(VI)$. The main oxidants are dissolved oxygen, ozone and hydrogen peroxide. Due to their large Henry's constants the last two are particularly abundant. The oxidation reactions can be catalyzed by dissolved metal ions.

1. Uncatalyzed oxidation of $S(IV)$ by dissolved oxygen has been proven to be negligibly slow mainly due to low reactivity of dissolved oxygen and small concentration of dissolved oxygen $H_{O_2} = 1.3 \times 10^{-3} M atm^{-1}$ which yields $[O_2 \cdot H_2O] \approx 3 \times 10^{-4} M$.

2. Oxidation of $S(IV)$ by dissolved ozone proceeds by nucleophilic attack on ozone by $SO_2 \cdot H_2O$, $HOSO_2^-$ and SO_3^{2-} with an increasing reactivity. The rate of reaction of $S(IV)$ can be written as

$$-R_{S(IV)} = (k_0 X_{SO_2 \cdot H_2O} + k_1 X_{HSO_3^-} + k_2 X_{SO_3^{2-}}) [S(IV)] [O_3]$$

At room temperature

$$k_0 = 2.4 \times 10^4 M^{-1} s^{-1},$$

$$k_1 = 3.7 \times 10^5 M^{-1} s^{-1}, \text{ and}$$

$$k_2 = 1.5 \times 10^9 M^{-1} s^{-1}$$

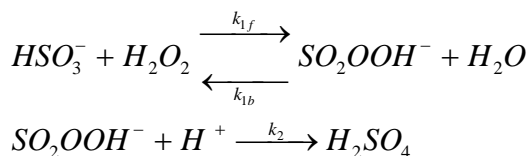
where X_j is the mole fraction of j .

$$[O_3] = H_{O_3} P_{O_3} \text{ where } H_{O_3} = 9.4 \times 10^{-3} M atm^{-1}.$$

At normal tropospheric ozone concentrations of 30-60 ppb, $[O_3]_{eq} \approx 2.84 \times 10^{-10}$ to $5.6 \times 10^{-10} M$. Since the rate depends on $[S(IV)]$, which decreases rapidly at low pH, the rate of reaction slows down at low pH.

3. Oxidation of $S(IV)$ by H_2O_2

The prevailing hypothesis is that this oxidation involves mainly the bisulfide ion in formation of peroxy-monosulfurous acid as reactive intermediate by the following mechanism



Use of PSSA and defining $k'_{1b} = k_{1b} [H_2O]$ yields the following rate of sulfuric acid formation

$$R_{H_2SO_4} = \frac{k_{1f} k_2 [H^+] [HSO_3^-] [H_2O_2]}{k'_{1b} + k_2 [H^+]}$$

which can be expressed as the rate of $S(IV)$ loss

$$-R_{S(IV)} = \frac{k[H^+][H_2O_2][S(IV)]X_{HSO_3}}{1 + K[H^+]}$$

where $k = \frac{k_{1f}k_2}{k_{1b}} = 7.47 \times 10^7 \text{ M}^{-2}\text{s}^{-1}$ and $K = \frac{k_2}{k_{1b}} = 13 \text{ M}^{-1}$ at 298K. For $\text{pH} < 1$ rate decreases with pH but above it is independent of pH .

4. Oxidation of $S(IV)$ catalyzed by iron

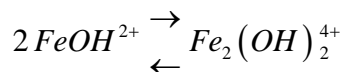
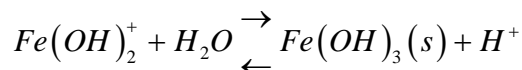
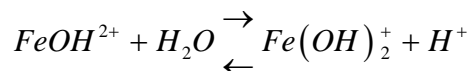
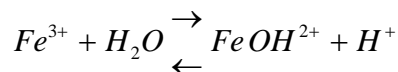
Several modes of interaction with iron and its compounds are possible.

- physical adsorption occurs on iron oxide
- chemisorption occurs with subsequent catalytic reaction on the particle surface
- aerosol particles containing iron oxide serve as catalysts
- dissolved iron catalyzes the reaction.

Detailed kinetic expression is only available for bulk aqueous phase Fe (III) catalyzed reaction with dissolved oxygen. The reaction rate depends on $[S(IV)]$, $[\text{Fe(III)}]$, pH , ionic strength and temperature.

It is very sensitive to the presence of certain anions (e.g. SO_4^{2-}) and cations (e.g. Mn^{2+}).

The equilibria involved are:



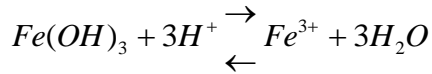
Total soluble iron is:

$$[\text{Fe}]_{\text{sol}} = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}_2(\text{OH})_2^{4+}]$$

Total iron present is:

$$[\text{Fe}]_{\text{tot}} = [\text{Fe}]_{\text{sol}} + [\text{Fe}(\text{OH})_3(s)]$$

The relative amounts of soluble iron species are a strong function of pH . The overall equilibrium between solid $\text{Fe}(\text{OH})_3$ and Fe^{3+} is



with (at 298°K)

$$K = 10^3 = \frac{[Fe^{3+}]}{[H^+]^3}$$

At pH = 4.5 this yields $[Fe^{3+}] \approx 3 \times 10^{-11} M$.

The following rate is observed

$$-R_{S(IV)} = k [Fe(III)][S(IV)] X_{SO_3^{2-}}$$

with $k = 1.2 \times 10^6 M^{-1} s^{-1}$ at 293K.

At pH \leq 4.5 solubility of iron decreases significantly and the rate changes to (at pH = 5)

$$-R_{S(IV)} = 5 \times 10^5 [Fe^{3+}][S(IV)] .$$

When *Fe (II)* is added to the mixture there is an induction period needed for *Fe (II)* oxidation before reaction proceeds.

Available rate expressions for

- oxidation promoted by Manganese
- oxidation catalyzed by Manganese and Iron
- oxidation by dissolved NO₂
- oxidation by dissolved HNO₂
- oxidation by carbon

are summarized in the enclosed Table 8. Needed data for nitrogen oxides is in Table 9.

Comparison of various rates at an assumed set of conditions is illustrated in Figure 4. At all pH < 5, *H₂O₂* oxidation rate is the fastest and relatively independent of pH. Catalyzed rates become significant at pH > 5.

The effect of temperature is as follows. Increased *T* lowers solubility but increases the rate constant. Except for *Mn* and *Fe* the solubility effect dominates, i.e the rate increases with decreasing temperature.

TABLE 8: Rate expressions for sulfate formation in aqueous solution

Oxidant	Rate Expression, $-\frac{d[S(IV)]}{dt}$	
O ₃	$(k_0[SO_2 \cdot H_2O] + k_1[H_2SO_3] + k_2[SO_3^{2-}])[O_3(aq)]$ $k_0 = 2.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K $k_1 = 3.7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ $k_2 = 1.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$	Hoffmann and Calvert (1985)
H ₂ O ₂	$\frac{k[H^+][H_2O_2(aq)]}{1 + K[H^+]}$ $k = 7.45 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K $k = 13 \text{ M}^{-1}$	Hoffmann and Calvert (1985)
Fe(III)	$k[Fe(III)][SO_3^{2-}]$ $k = 1.2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 293 K, pH ≤ 5	Hoffmann and Calvert (1985)
Mn(II)	$k_2[Mn(II)][HSO_3^-]$ $k_2 = 3.4 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K $[S(IV)] \leq 10^{-4} \text{ M}$ $[Mn(II)] \leq 10^{-5} \text{ M}$ $k_1[Mn^{2+}][H^+]^{-1}\beta_1$ $k_1 = 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ $\beta_1 = \frac{[Mn_2OH^{3+}][H^+]}{[Mn^{2+}]}$ $\beta_1 = 10^{-9.9}$ at 298 K	Hoffmann and Calvert (1985)
N(III) ^a	$k[H^+]^{1/2}H_{HNO_2}H_{S(IV)}^*P_{HNO_2}P_{SO_2}\left(1 + \frac{K_{n4}}{[H^+]}\right)$ $k = 142 \text{ M}^{-3/2} \text{ sec}^{-1}$ at 298 K	Lee and Schwartz (1982)
NO ₂	$kH_{NO_2}H_{S(IV)}^*P_{NO_2}P_{SO_2}$ $k = 2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K	Lee and Schwartz (1982)

^a[N(III)] = [HNO₂(aq)] + [NO₂]. Based on

$$HNO_2(g) \rightleftharpoons HNO_2(aq) \quad H_{HNO_2}$$

$$HNO_2(aq) \rightleftharpoons H^+ + NO_2^- \quad K_{n4}$$

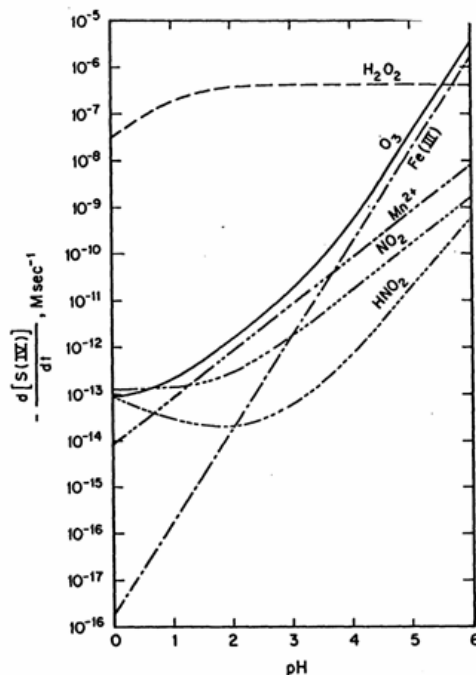
we obtain

$$[N(III)] = H_{NO_2}P_{HNO_2}[1 + K_{n4}/[H^+]]$$
TABLE 9: Equilibrium constants for aqueous-phase nitrogen oxide reactions^a

Reaction	Equilibrium Constant at 298 K
NO(g) ⇌ NO(aq)	$H_{NO} = 1.93 \times 10^{-3} \text{ M atm}^{-1}$
NO ₂ (g) ⇌ NO ₂ (aq)	$H_{NO_2} = 1.0 \times 10^{-2} \text{ M atm}^{-1}$
2NO ₂ (aq) ⇌ N ₂ O ₄ (aq)	$K_{n1} = 7 \times 10^4 \text{ M}^{-1}$
NO(aq) + NO ₂ (aq) ⇌ N ₂ O ₃ (aq)	$K_{n2} = 3 \times 10^4 \text{ M}^{-1}$
HNO ₃ (aq) ⇌ H ⁺ + NO ₃ ⁻	$K_{n3} = 15.4 \text{ M}$
HNO ₂ (aq) ⇌ H ⁺ + NO ₂ ⁻	$K_{n4} = 5.1 \times 10^{-4} \text{ M}$
2NO ₂ (g) + H ₂ O ⇌ 2H ⁺ + NO ₂ ⁻ + NO ₃ ⁻	$K_1 = 2.44 \times 10^2 \text{ M}^4 \text{ atm}^{-2}$
NO(g) + NO ₂ (g) + H ₂ O ⇌ 2H ⁺ + 2NO ₂ ⁻	$K_2 = 3.28 \times 10^{-5} \text{ M}^4 \text{ atm}^{-2}$

^aSchwartz and White (1981, 1983).

FIGURE 4: Comparison of aqueous-phase SO₂ oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are: [SO₂(g)]=5ppb; [HNO₂(g) = 2ppb; [H₂O₂(g)] = 1 ppb; [NO₂(g)] = 1 ppb; [O₃(g)] = 50 ppb; [Fe³⁺(aq)] = 3x10⁻⁷ M; [Mn²⁺(aq)] = 3x10⁻⁸ M.



Dynamic Behavior

If instead of the instantaneous values of the rates of conversion at a given set of conditions we are interested in the variation of species concentration in time, *i.e.* the dynamics of the system, we must set up appropriate species balances based on our control volume and basic conservation equation.

The control volume is the largest arbitrarily selected volume of the system within which, at a given instant of time, there are no spatial gradients in composition. Now, to this control volume we apply for the mass of each species of interest our fundamental conservation law

$$\begin{array}{ccccccc} (\text{Rate of Input}) & - & (\text{Rate of Output}) & + & (\text{Rate of Generation}) & = & (\text{Rate of Accumulation}) \\ (1) & - & (2) & + & (3) & = & (4) \end{array}$$

If our system (control volume) is closed, *i.e.* no material streams cross its boundaries by convection or diffusion, then terms (1) and (2) are identically zero. Rate of generation (which is negative if species is depleted) is equal to the rate of accumulation, which is the time rate of change of the observed quantity.

If the system is open then all terms are present, unless the system is at steady state in which case term (4) is identically zero.

If more than one phase exists in the system then the above balance has to be applied to each phase and the input-output terms contain the interphase transfer term (what is input to one phase had to come from the other

and hence is the output for the balance on the other phase). Moreover, knowledge of phase holdup, i.e volume functions occupied by each phase, are needed (e.g. knowledge of L in our air droplets system).

Consider now a closed system (air + droplets) containing $P_{H_2O_2} = \text{const}$ (no reaction). If $P_{H_2O_2}$ is the partial pressure of H_2O_2 , and $[H_2O_2(aq)]$ is the concentration of the dissolved peroxide, then at equilibrium (which is very rapidly established) we have

$$n_{H_2O_2_{tot}} = n_{H_2O_2(g)} + n_{H_2O_2(aq)}$$

$$[H_2O_2]_{tot} V = \frac{P_{H_2O_2}}{RT} V_{air} + [H_2O_2(aq)] V_L$$

But

$$\frac{V_L}{V} = L \text{ and } \frac{V_{air}}{V} = 1 - L \approx 1$$

$$[H_2O_2]_{tot} = \frac{P_{H_2O_2}}{RT} + [H_2O_2(aq)] L$$

where

$$[H_2O_2(aq)] = H_{H_2O_2} P_{H_2O_2}$$

The concentration of the dissolved species is

$$[H_2O_2(aq)] = \frac{[H_2O_2]_{tot}}{\frac{1}{H_{H_2O_2} RT} + L} = \frac{H_{H_2O_2} RT [H_2O_2]_{tot}}{1 + H_{H_2O_2} RT L}$$

and the remaining equilibrium vapor pressure is:

$$P_{H_2O_2} = \frac{RT [H_2O_2]_{tot}}{1 + H_{H_2O_2} RT L}$$

The fraction of total peroxide that resides in the liquid phase is:

$$\frac{[H_2O_2(aq)] L}{[H_2O_2]_{tot}} = \frac{H_{H_2O_2} L RT}{1 + H_{H_2O_2} L RT}$$

with $H_{H_2O_2} = 7.1 \times 10^4 \text{ M atm}^{-1}$ at 298K.

Similarly for ozone

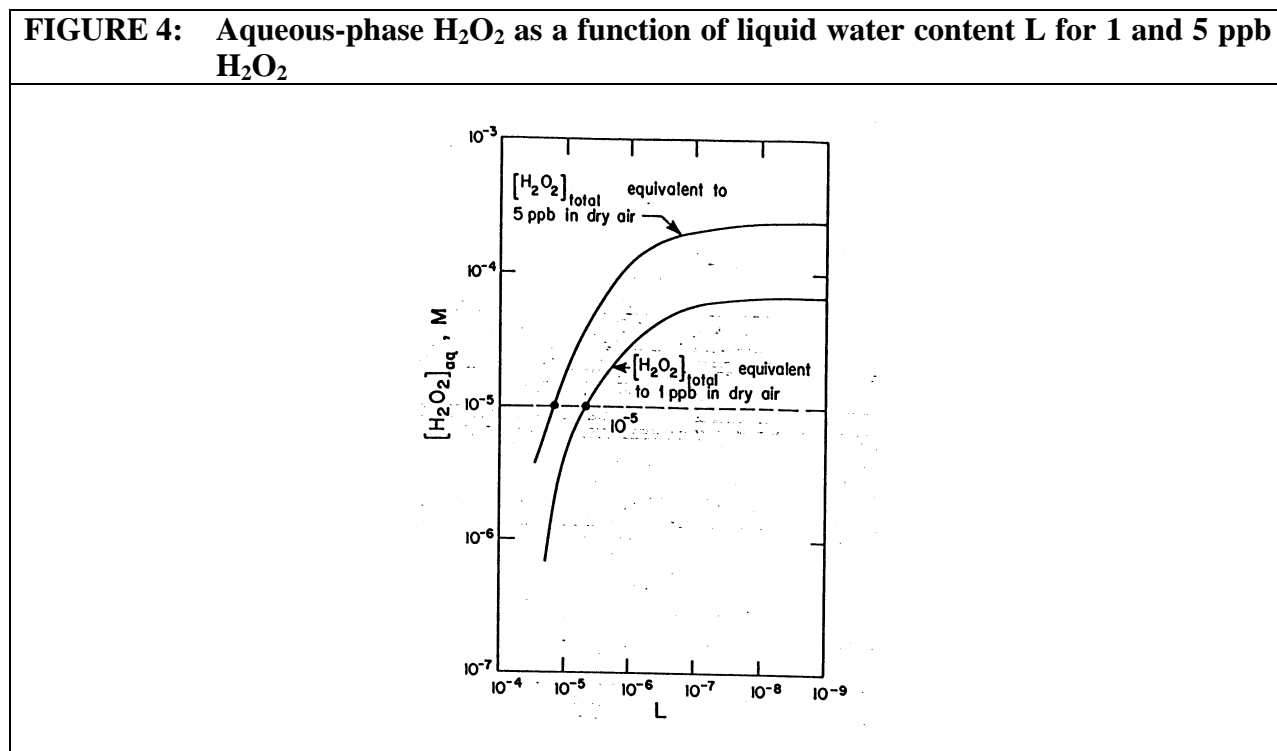
$$\frac{[O_3(aq)] L}{[O_3]_{tot}} = \frac{H_{O_3} L RT}{1 + H_{O_3} L RT}$$

with $H_{O_3} = 9.4 \times 10^{-3} \text{ M atm}^{-1}$.

This results in the following comparison:

L	10^{-5}	10^{-6}	10^{-7}
aqueous fraction H_2O_2	0.95	0.63	0.15
aqueous fraction O_3	2.3×10^{-6}	2.3×10^{-7}	2.3×10^{-8}

Figure 4 indicates that aqueous peroxide concentration rapidly approaches equilibrium value for $L \ll 10^{-7}$.



The same approach can be used for dissociating species such as HNO_3

$$[HNO_3]_{tot} = \frac{P_{HNO_3}}{RT} + ([HNO_3(aq)] + [NO_3^-])L$$

$$[HNO_3(aq)] = H_{HNO_3} P_{HNO_3}$$

$$[NO_3^-] = \frac{K_{n1} [HNO_3(aq)]}{[H^+]} = \frac{H_{HNO_3} K_{n1} P_{HNO_3}}{[H^+]}$$

$$[NO_3^-] = H_{HNO_3} K_{n1} P_{HNO_3} / [H^+]$$

Total concentration of aqueous species

$$[HNO_3(aq)] + [NO_3^-] = H_{HNO_3} (1 + K_{n1} 10^{pH}) P_{HNO_3} = H_{HNO_3}^* P_{HNO_3}$$

Hence

$$[HNO_3(aq)] + [NO_3^-] = \frac{H_{HNO_3}^* RT}{1 + H_{HNO_3}^* RT L} [HNO_3]_{tot}$$

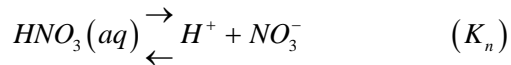
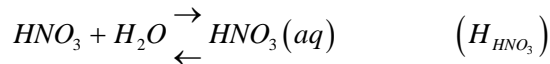
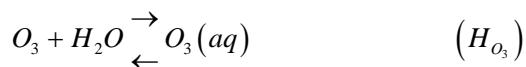
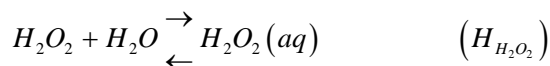
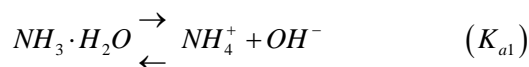
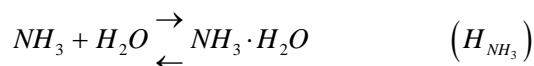
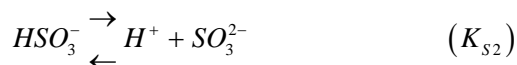
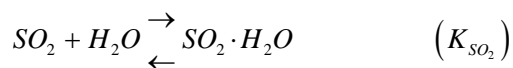
and the total fraction of dissolved species is

$$\frac{([\text{HNO}_3(\text{aq})] + [\text{NO}_3^-])L}{[\text{HNO}_3]_{\text{tot}}} = \frac{H_{\text{HNO}_3}^* RT L}{1 + H_{\text{HNO}_3}^* RT L}$$

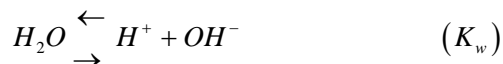
Dynamics of Reactions in a Droplet

Consider now a droplet immersed at $t=0$ in air containing SO_2 , NH_3 , H_2O_2 , O_3 and HNO_3 .

We write the mechanism, i.e. the set of plausible physical and chemical steps involved:



and finally

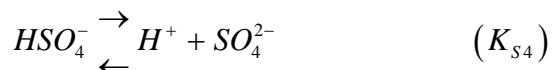
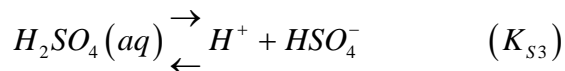


All the above absorption and dissociation steps are fast and can be assumed in equilibrium. The appropriate equilibrium constants are given in parenthesis. Now the rate limiting step is the oxidation of $S(\text{IV})$ to $S(\text{VI})$. If we assume that no metal ions are present then

$$\begin{aligned} -R_{S(\text{IV})} &= (k_{0o} [\text{SO}_2 \cdot \text{H}_2\text{O}] + k_{1o} [\text{HSO}_3^-] + k_{2o} [\text{SO}_3^{2-}]) [\text{O}_3] \\ &+ \frac{k_p [\text{H}^+] [\text{H}_2\text{O}_2] [\text{S}(\text{IV})] X_{\text{HSO}_3^-}}{1 + K_p [\text{H}^+]} \\ &+ 2 \times 10^6 [\text{S}(\text{IV})] [\text{NO}_2] \end{aligned}$$

where above all concentrations indicated by [] are for the aqueous species, subscript *o* refers to ozone and *p* to peroxide.

Now, since *S* (VI) is formed, we consider its rapid dissociation also



In addition the electroneutrality principle holds:

$$\begin{aligned} [H^+] + [NH_4^+] &= [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] \\ &+ 2[SO_4^{2-}] + [HSO_4^-] + [NO_3^-] \end{aligned}$$

Clearly, if metal ions are present (especially *Mn*²⁺, *Fe*³⁺, etc.) additional rate forms need to be considered. One also needs to examine the possibility of ammonia and nitric oxides dynamics.

We now want to understand the dynamics of a closed system with droplets loading *L*. This would be the situation if droplets and air travel together and do not receive additional input of any species. We would make a balance on gas phase.

$$-\frac{d[SO_2]}{dt} = -R_{SO_2g}$$

but the rate of gas phase reaction is negligible and this equation can be neglected. The balance in the liquid phase yields

$$-\frac{d[S(IV)]}{dt} = -R_{S(IV)} = \frac{d[S(VI)]}{dt}$$

$$t=0 \quad [S(IV)] = [S(IV)]_o = \frac{H_{SO_2}^* RT [SO_2]_{tot_o}}{1 + H_{SO_2}^* RT L}$$

where

$$\begin{aligned} H_{SO_2}^* &= H_{SO_2} \left[1 + 10^{pH} K_{s_1} + 10^{2pH} K_{s_2} \right] \\ &= H_{SO_2} \left[1 + \frac{K_{s_1}}{[H^+]} + \frac{K_{s_1} K_{s_2}}{[H^+]^2} \right] \end{aligned}$$

We recognize that we can express all of the ionic concentrations in terms of the appropriate equilibrium constants, hydrogen ion concentrations and gas phase concentrations:

$$\begin{aligned}
\left[\text{HSO}_3^- \right] &= \frac{H_{\text{SO}_2} K_{s_1}}{\left[\text{H}^+ \right]} P_{\text{SO}_2} \\
\left[\text{SO}_3^{2-} \right] &= \frac{H_{\text{SO}_2} K_{s_1} K_{s_2}}{\left[\text{H}^+ \right]^2} P_{\text{SO}_2} \\
\left[\text{NH}_4^+ \right] &= \frac{H_{\text{NH}_3} K_{a1}}{K_w} P_{\text{NH}_3} \left[\text{H}^+ \right] \\
\left[\text{OH}^- \right] &= K_w / \left[\text{H}^+ \right] \\
\left[\text{NO}_3^- \right] &= \frac{H_{\text{HNO}_3} K_{n1} P_{\text{HNO}_3}}{\left[\text{H}^+ \right]} \\
\left[\text{HSO}_4^- \right] &= \frac{\left[\text{S(VI)} \right]}{\frac{\left[\text{H}^+ \right]}{K_{s_3}} + 1 + \frac{K_{s_4}}{\left[\text{H}^+ \right]}} \\
\left[\text{SO}_4^{2-} \right] &= \frac{\left[\text{S(VI)} \right]}{\frac{\left[\text{H}^+ \right]}{K_{s_3} K_{s_4}} + \frac{\left[\text{H}^+ \right]}{K_{s_4}} + 1}
\end{aligned}$$

In a closed system

$$\begin{aligned}
\left[\text{SO}_2 \right]_{\text{tot}} &= \left(\left[\text{HSO}_3^- \right] + \left[\text{SO}_3^{2-} \right] + \left[\text{SO}_2 \cdot \text{H}_2\text{O} \right] \right) L + \frac{P_{\text{SO}_2}}{RT} \\
\left[\text{SO}_2 \right]_{\text{tot}} &= \left[\text{S(IV)} \right] L + \frac{P_{\text{SO}_2}}{RT}
\end{aligned}$$

But

$$\left[\text{S(IV)} \right] = H_{\text{SO}_2}^* P_{\text{SO}_2} = \frac{H_{\text{SO}_2}^* RT}{1 + H_{\text{SO}_2}^* RT L} \left[\text{SO}_2 \right]_{\text{tot}}$$

and

$$P_{\text{SO}_2} = \frac{RT \left[\text{SO}_2 \right]_{\text{tot}}}{1 + H_{\text{SO}_2}^* RT L}$$

It follows then that

$$\begin{aligned}
\left[\text{S(IV)} \right]_o - \left[\text{S(IV)} \right] &= \left(\frac{H_{\text{SO}_2}^* RT}{1 + H_{\text{SO}_2}^* RT L} \right) \left[\text{SO}_2 \right]_{\text{tot}_o} \\
&\quad - \frac{H_{\text{SO}_2}^* RT}{1 + H_{\text{SO}_2}^* RT L} \left[\text{SO}_2 \right]_{\text{tot}}
\end{aligned}$$

In the rate form we need to substitute all concentrations now in terms of $[SO_2]_{tot}$ or other known quantities

$$[SO_2 \cdot H_2O] = H_{SO_2} P_{SO_2} = \frac{H_{SO_2} RT}{1 + H_{SO_2}^* RT L} [SO_2]_{tot}$$

$$[HSO_3^-] = \frac{H_{SO_2} K_{s1}}{[H^+]} \frac{RT}{1 + H_{SO_2}^* RT L} [SO_2]_{tot}$$

$$[SO_3^{2-}] = \frac{H_{SO_2} K_{s1} K_{s2}}{[H^+]^2} \frac{RT [SO_2]_{tot}}{1 + H_{SO_2}^* RT L}$$

$$[O_3] = \frac{H_{O_3} RT}{1 + H_{O_3} RT L} [O_3]_{tot}$$

$$[H_2O_2] = \frac{H_{H_2O_2} RT}{1 + H_{H_2O_2} RT L} [H_2O_2]_{tot}$$

$$[S(IV)] = \frac{H_{SO_2}^* RT}{1 + H_{SO_2}^* RT L} [SO_2]_{tot}$$

$$X_{HSO_3^-} = \frac{[HSO_3^-]}{[S(IV)]} = \frac{H_{SO_2} K_{s1}}{[H^+] H_{SO_2}^*}$$

$$[NO_2] = \frac{H_{NO_2} RT}{1 + H_{NO_2} RT L} [NO_2]_{tot}$$

In addition

$$H_{SO_2}^* = H_{S(IV)}^* = H_{SO_2} \left[1 + \frac{K_{s1}}{[H^+]} + \frac{K_{s1} K_{s2}}{[H^+]^2} \right]$$

Finally the needed $[H^+]$ is obtained from the electroneutrality equation.

$$\begin{aligned} [H^+] &+ \frac{H_{NH_3} K_{a1}}{K_w} \frac{RT}{(1 + H_{NH_3}^* RT L)} [NH_3]_{tot} [H^+] \\ &= \frac{K_w}{[H^+]} + \frac{H_{SO_2} K_{s1}}{[H^+]} \frac{RT}{(1 + H_{SO_2}^* RT L)} [SO_2]_{tot} \\ &\quad + 2 \frac{H_{SO_2} K_{s1} K_{s2}}{[H^+]^2} \frac{RT [SO_2]_{tot}}{1 + H_{SO_2}^* RT L} \\ &\quad + 2 \frac{[S(IV)]_o - [H_{SO_2}^* RT / (1 + H_{SO_2}^* RT L)] [SO_2]_{tot}}{\frac{[H^+]^2}{K_{s3} K_{s4}} + 1 + \frac{[H^+]}{K_{s4}}} \end{aligned}$$

$$+ \frac{[S(IV)]_o - \left[\frac{H_{SO_2}^* RT}{1 + H_{SO_2}^* RTL} \right] [SO_2]_{tot}}{\frac{[H^+]}{K_{s_3}} + 1 + \frac{K_{s_4}}{[H^+]}} + \frac{H_{NO_2} K_{n_1} RT [NO_2]_{tot}}{[H^+] (1 + H_{NO_2}^* RTL)}$$

Now we write the mass balance for other soluble species that participate in the $S(IV)$ oxidation reaction such as ozone, hydrogen peroxide, and nitrogen dioxide.

Appropriate differential equations have to be set for all of those

$$\frac{d[O_3]}{dt} = - \left(k_{0o} [SO_2 \cdot H_2O] + k_{10} [HSO_3^-] + k_{20} [SO_3^{2-}] \right) [O_3]$$

and

$$\frac{d[O_3]_{tot}}{dt} = \frac{1}{RT} \frac{dP_{O_3}}{dt} + \frac{d[O_3]}{dt} L$$

with

$$\frac{1}{RT} \frac{dP_{O_3}}{dt} = - R_{O_{3g}}$$

where $-R_{O_{3g}}$ is the ozone decomposition rate in the gas phase (due to OH^* or NO_2 reactions).

Similarly

$$\frac{d[H_2O_2]}{dt} = - \frac{K_p [H^+] [H_2O_2] [S(IV)] X_{HSO_3^-}}{1 + K_p [H^+]}$$

and

$$\frac{d[H_2O_2]_{tot}}{dt} = \frac{1}{RT} \frac{dP_{H_2O_2}}{dt} + L \frac{d[H_2O_2]}{dt}$$

with

$$\frac{1}{RT} \frac{dP_{H_2O_2}}{dt} = R_{H_2O_{2g}}$$

where $-R_{H_2O_{2g}}$ is the peroxide decomposition rate in the gas phase.

Finally for $[NO_2]$

$$\frac{d[NO_2]_{tot}}{dt} = \frac{1}{RT} \frac{dP_{NO_2}}{dt} + L \frac{d[NO_2(aq)]}{dt}$$

where

$$\frac{d[NO_2]}{dt} = -4 \times 10^6 [S(IV)][NO_2]$$

with

$$\frac{1}{RT} \frac{dP_{NO_2}}{dt} = -R_{NO_2g}$$

where - R_{NO_2g} is the rate of disappearance of NO_2 via gas phase reactions.

We can integrate now the differential equations for $[S(VI)]$, $[O_3]_{tot}$, $[H_2O_2]_{tot}$ and $[NO_2]_{tot}$ assuming instantaneous equilibration between the gas and liquid phase. The initial conditions are:

At $t=0$

$$\begin{aligned} [S(VI)] &= 0 \\ [O_3]_{tot} &= (H_{O_3} RTL + 1)(P_{O_3})_0 / RT \\ [H_2O_2]_{tot} &= (H_{H_2O_2} RTL + 1)P_{H_2O_2O_0} / RT \\ [NO_2]_{tot} &= (H_{NO_2} RTL + 1)P_{NO_2o} / RT \end{aligned}$$

The electroneutrality balance equation must also be solved at $t=0$ to evaluate the initial values of the concentrations of all ionized species and to obtain the initial value of all rates.

After each integration step, considering that this is a closed system, the total concentration of $[S(IV)]$ can be updated using the requirement that total sulfur concentration must be constant.

$$[S(VI)]L + [S(IV)] \frac{H_{S(IV)}^* LRT}{1 + H_{S(IV)}^* LRT} = \frac{P_{SO_2o}}{RT}$$

Since $S(VI)$ is obtained at next time step by integration, $S(IV)$ can be obtained from the balance equation shown. The electroneutrality balance is rerun due to presence of $S(VI)$ species and the new partial pressure of SO_2 can be evaluated

$$[S(IV)] = H_{S(IV)}^* P_{SO_2}$$

together with all other $S(IV)$ species.

We need to integrate all of these differential equations simultaneously and at each integration step calculate $[H^+]$ from the electroneutrality balance. In using the balance one should not forget that H^* are also functions of $[H^+]$.

Consider now the system with the following initial conditions at $t = 0$

$$[SO_2]_{tot} = 5 \text{ ppb} \quad pH = 6.17$$

$$[NO_2]_{tot} = 1 \text{ ppb}$$

$$[NH_3]_{tot} = 5 \text{ ppb} \quad L = 10^{-6}$$

$$[O_3]_{tot} = 5 \text{ ppb}$$

$$[H_2O_2]_{tot} = 1 \text{ ppb}$$

and compute $[S(IV)]$ in μM as a function of time (in minutes) in a closed system assuming absence of gas phase reactions.

Now consider an open system, i.e a system in which droplets are constantly exposed to the air of the same partial pressures as corresponds to the above initial total concentrations. This means that partial pressures are fixed at

$$P_{SO_2} = 3.03 \text{ ppb}$$

$$P_{NH_3} = 1.87 \text{ ppb}$$

$$P_{HNO_3} = 8.54 \times 10^{-9} \text{ ppb}$$

$$P_{O_3} = 5 \text{ ppb}$$

$$P_{H_2O_2} = 0.365 \text{ ppb}$$

Now the differential equation to be solved is

$$\frac{d[S(IV)]}{dt} = -R_{S(IV)}$$

where all concentrations are eliminated in terms of $[H^+]$ and partial pressures $P_{SO_2}, P_{NH_3}, P_{HNO_3}, P_{O_3}, P_{H_2O_2}$. The $[H^+]$ concentration is still obtained from the electroneutrality balance.

Comparison of closed and open system is shown in Figures 12 and 13. Less sulfate is produced in the closed system due to depletion of H_2O_2 and O_3 . pH increases less in the open system due to increased neutralization of more sulfate formed with NH_3 . The low pH in the closed system keeps SO_2 out i.e reduces dissolution and depresses sulfate formation via O_3 . Total HNO_3 decreases in the open system due to decrease in pH.

FIGURE 5: Aqueous sulfate concentration as a function of time for both open and closed systems. The conditions for the simulation are: $[S(IV)]_{total} = 5$ ppb; $[NH_3]_{total} = 5$ ppb; $[HNO_3]_{total} = 1$ ppb; $[O_3]_{total} = 5$ ppb; $[H_2O_2]_{total} = 1$ ppb; $L = 10^{-6}$; $pH_0 = 6.17$

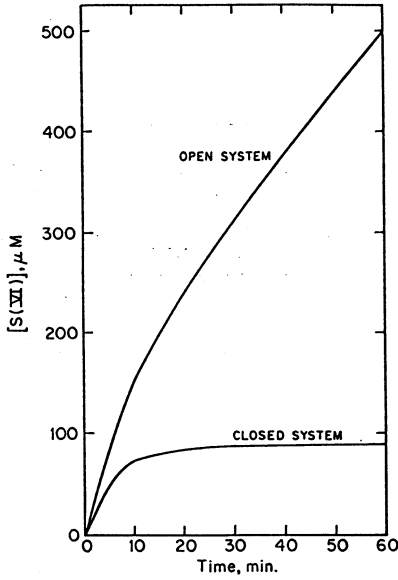


FIGURE 6: pH as a function of time for both open and closed systems as Figure 12.

