

Lecture 20: Acid Deposition

Required Reading: FP Chapter 4 (only sections that I cover)

Suggested Reading: Jacob Chapter 13

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

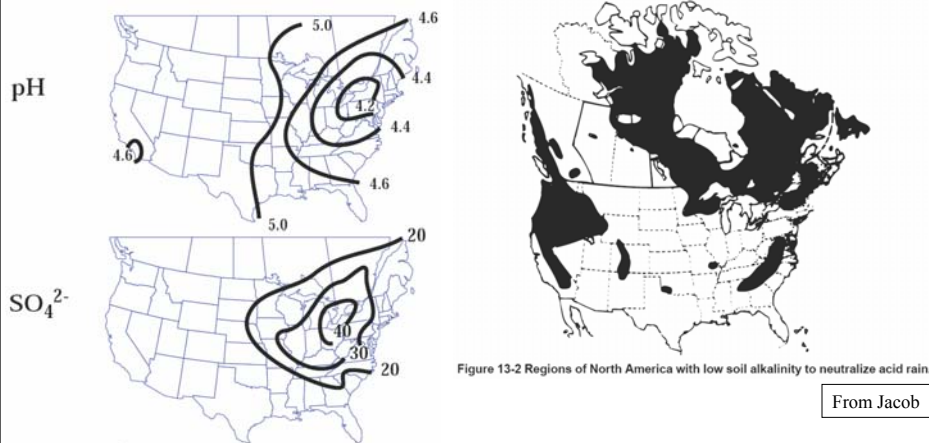
Outline of Lecture

- A. Introduction
- B. Solubility of gases in rain / fog / clouds
- C. Oxidation of SO₂

Acid Rain vs. Acid Deposition

- Acid Rain
 - Refers to hydrometeors, sizes ~ several mm
 - Also cloud or fog droplets ~ several μm
 - Very dilute solutions of acids in H_2O
 - Also known as “wet deposition”
- Acid Deposition
 - Includes wet deposition
 - Also “dry deposition”
 - Direct deposition of aerosols
 - Dry particles, or very concentrated solutions
 - Also deposition of the gas-phase acids, e.g. HNO_3
 - Naming is independent of whether surface is dry or wet

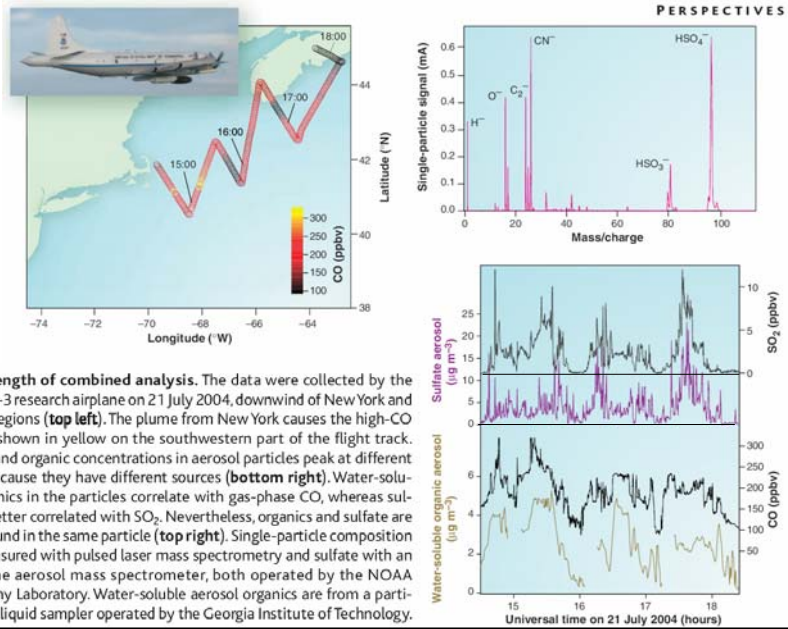
Acid Deposition



- pH of rain decreases, mostly due to H_2SO_4
- Dire effects if soil cannot neutralize acids

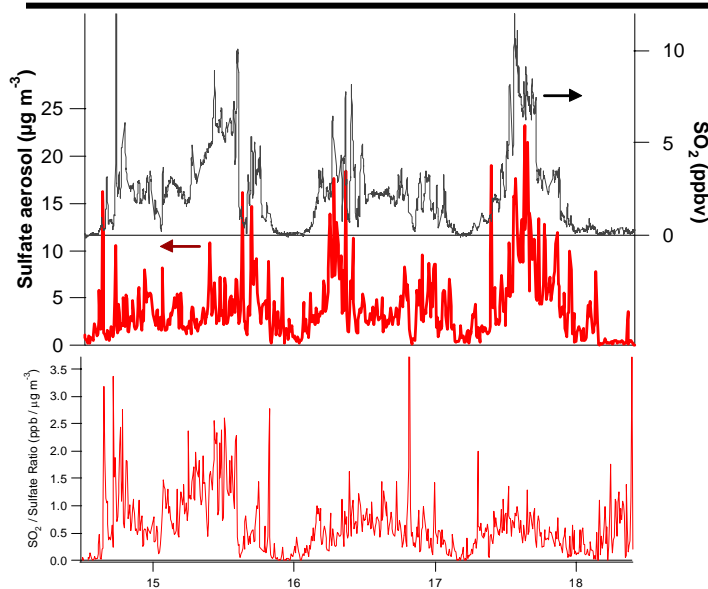
Conversion of SO₂ to Sulfate

Atmospheric Science: Something in the Air, Daniel M. Murphy, Science 307(5717): 1888-1890, March 2005.



The strength of combined analysis. The data were collected by the NOAA P-3 research airplane on 21 July 2004, downwind of New York and nearby regions (**top left**). The plume from New York causes the high-CO regions shown in yellow on the southwestern part of the flight track. Sulfate and organic concentrations in aerosol particles peak at different times because they have different sources (**bottom right**). Water-soluble organics in the particles correlate with gas-phase CO, whereas sulfate is better correlated with SO₂. Nevertheless, organics and sulfate are often found in the same particle (**top right**). Single-particle composition was measured with pulsed laser mass spectrometry and sulfate with an Aerodyne aerosol mass spectrometer, both operated by the NOAA Aeronomy Laboratory. Water-soluble aerosol organics are from a particle-into-liquid sampler operated by the Georgia Institute of Technology.

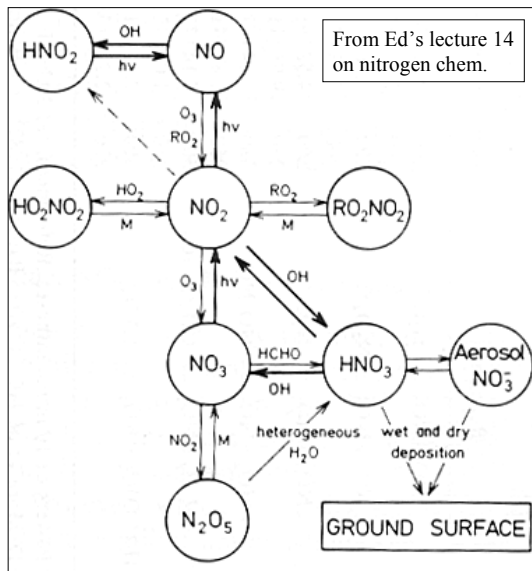
Evolution of SO₂ to Sulfate Ratio



Data courtesy of D. Murphy, NOAA AL

Major Acids

- Sulfuric acid, H_2SO_4
- Nitric acid, HNO_3
- Nitrous acid, $\text{HONO} = \text{HNO}_2$
 - Less well known, hard to measure
 - Indoor air
- Organic acids



Henry's Law

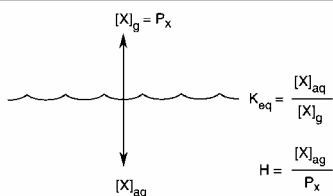


FIGURE 8.1 Henry's law applied to atmospheric system

- Pure H_2O concentration in M (moles l^{-1})?
- O_3 aqueous concentration at 50 ppb in gas?
- H_2O_2 a.c. at 1 ppb?
- CO_2 ?
- Fractions for 1 g m^{-3} liquid H_2O ?

TABLE 8.1 Henry's Law Coefficients (H) for Some Atmospheric Gases Dissolving in Liquid Water at $20-25^\circ\text{C}^a$

| Gas | H ($\text{mol L}^{-1} \text{atm}^{-1}$) | Reference |
|---------------------------------------|---|---|
| O_2 | 1.3×10^{-3} | Loomis, 1928 |
| NO | 1.9×10^{-5} | Loomis, 1928 |
| C_2H_4 | 4.9×10^{-3} | Loomis, 1928 |
| NO_2^b | 1×10^{-2} | Schwartz and White, 1983 |
| N_2O_2 | 1.4 | Schwartz and White, 1981 |
| N_2O_3 | 0.6 | Schwartz and White, 1981 |
| O_3 | $(0.82-1.3) \times 10^{-2}$ | Shorter <i>et al.</i> , 1995; Briner and Perrotet, 1939 |
| N_2O | 2.5×10^{-2} | Loomis, 1928 |
| CO_2^c | 3.4×10^{-2} | Loomis, 1928 |
| SO_2^c | 1.2 | Sillén and Martell, 1964; Maahs, 1982; Shorter <i>et al.</i> , 1995 |
| HONO^d | 49 | Schwartz and White, 1981 |
| NH_3^d | 62 | Van Krevelen <i>et al.</i> , 1949 |
| HNO_3^d | 2.1×10^5 | Schwartz and White, 1981 |
| HO_2 | $(1-3) \times 10^3$ | Schwartz, 1984b |
| OH | 30 | Golden <i>et al.</i> , 1990; Hanson <i>et al.</i> , 1992 |
| PAN | 5 | Holdren <i>et al.</i> , 1984 |
| CH_3SCH_3 | 0.48-0.56 | Shorter <i>et al.</i> , 1995; De Bruyn <i>et al.</i> , 1995; Dacey <i>et al.</i> , 1984 |
| NO_3 | 0.6-1.8 | Rudich <i>et al.</i> , 1996; Thomas <i>et al.</i> , 1998 |
| CH_3SH | 0.20 | De Bruyn <i>et al.</i> , 1995 |
| H_2O_2 | 8.3×10^4 | O'Sullivan <i>et al.</i> , 1996 |
| | 1.1×10^5 | Zhou and Lee, 1992; Staffelbach and Kok, 1993 |
| CH_3OOH | 3.1×10^2 | O'Sullivan <i>et al.</i> , 1996 |
| HOCH_2OOH | 1.7×10^6 | O'Sullivan <i>et al.</i> , 1996 |
| | 1.7×10^6 | Staffelbach and Kok, 1993 |
| | 5×10^5 | Zhou and Lee, 1992 |
| $\text{HOCH}_2\text{OOCH}_2\text{OH}$ | 6×10^5 | Zhou and Lee, 1992 |
| $\text{CH}_3\text{C(O)OOH}$ | 8.4×10^2 | O'Sullivan <i>et al.</i> , 1996 |
| $\text{C}_2\text{H}_5\text{OOH}$ | 3.4×10^2 | O'Sullivan <i>et al.</i> , 1996 |
| H_2S | 0.087 | Shorter <i>et al.</i> , 1995; De Bruyn <i>et al.</i> , 1995 |
| COS | 0.022 | Shorter <i>et al.</i> , 1995; De Bruyn <i>et al.</i> , 1995 |
| CS_2 | 0.055 | De Bruyn <i>et al.</i> , 1995 |

^a Adapted from Schwartz, 1984a; see also Web site in Appendix IV.

^b Physical solubility; reacts with liquid water.

^c Physical solubility; exclusive of acid-base equilibria.

^d See Clegg and Brimblecombe (1988) and Brimblecombe and Clegg (1988) for temperature dependence.

CO₂ Uptake and Buffering

- $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CO}_2 \cdot \text{H}_2\text{O}(\text{aq})$
 - $H_1 = 3.4 \times 10^{-2} \text{ M atm}^{-1}$
- $\text{CO}_2 \cdot \text{H}_2\text{O}(\text{aq}) \leftrightarrow \text{HCO}_3^- + \text{H}^+$
 - $K_2 = 4.3 \times 10^{-7} \text{ M}$
- $\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$
 - $K_2 = 4.7 \times 10^{-11} \text{ M}$
- Can show that pH ~ 5.6 in equilibrium with CO₂
 - What is pH?
- pH of rain: common ~4.5
- In some cases pH~1.7-2.5

Reminder: definition of pH

- $\text{pH} = -\log [\text{H}^+]$ (Brønsted-Lowry)
- $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$
- In pure neutral water: $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ per liter.
 - Note: H^+ really present as H_3O^+
- $\text{pH} < 7$, the solution is acidic
- $\text{pH} = 7$, the solution is neutral
- $\text{pH} > 7$, the solution is basic (alkaline)
- Example: H^+ concentration of a solution with a pH of 1.0 is 100 times greater than a solution with a pH of 3.0.

Oxidation of SO₂

- Gas-phase w/ OH
- Liquid phase
 - Many mechanisms, most of this chapter
 - Most important are H₂O₂ and O₃
- Typically >50% of SO₂ oxidation globally is thought to occur in clouds

Gas Phase SO₂ Oxidation

- Most important is OH reaction:
$$\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2$$
- Termolecular, in the falloff region at 1 atm
- Effective rate at room T & 1 atm:
 - $k_4 \sim 9 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
 - Lifetime of SO₂?
- Then:
 - $\text{HOSO}_2 + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{SO}_3$
 - $k_4 \sim 4.3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
 - Lifetime of HOSO₂?

Gas Phase SO₂ Oxidation II

- Note that HO₂ is produced, then:
 - HO₂ + NO → OH + NO₂
 - So no HO_x is destroyed, and O₃ is produced
 - HO₂ + HO₂ → H₂O₂ + O₂
 - Very important for aqueous-phase oxidation
- Fate of SO₃
 - SO₃ + H₂O → H₂SO₄
- Note that oxidants for SO₂ (OH, H₂O₂, O₃) are formed in NO_x+VOC+UV system
 - Need to model the whole chemistry, e.g. “RADM”, Regional Acid Deposition Model

SO₃ + H₂O

- Observed to be 2nd order on H₂O
- SO₂·H₂O does not react directly
- Rather SO₂·H₂O + H₂O

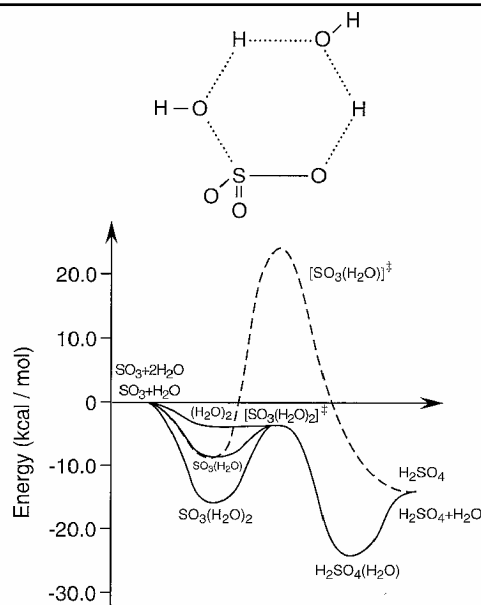


FIGURE 8.4 Predicted energetics for various mechanisms for the SO₃-H₂O reaction transition states are marked with a ‡ symbol (adapted from Morokuma and Muguruma, 1994).

Aqueous Oxidation of SO₂

- Aqueous phases in atmosphere:
 - Wet aerosols: ~0.3 μm, 50% H₂O, 1 x 10⁻⁵ g m⁻³, 1 week
 - Fogs: 0.5-10 μm, 0.1 g m⁻³, hrs
 - Clouds: 5-50 μm, 1 g m⁻³, hrs
 - Raindrops (“hydrometeors”): 200-3000 μm, minutes
- Rate increases with amount of H₂O(l)
- Why?

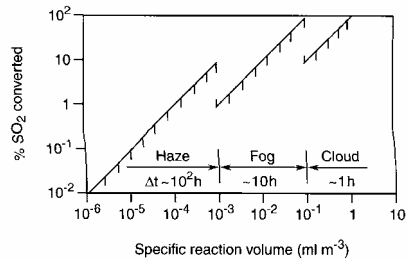


FIGURE 8.12 Percentage of SO₂ converted to sulfate after a time interval Δt in small “haze” particles, fogs, and clouds as a function of the aqueous reaction volume; note that the time intervals for each one are different, reflecting how long they typically last in the atmosphere (adapted from Lamb *et al.*, 1987).

Aqueous Phase Equilibria of SO₂

- SO₂(g) + H₂O(l) ↔ SO₂·H₂O(aq)
 - H₁ = 1.242 M atm⁻¹
- SO₂·H₂O(aq) ↔ HSO₃⁻ + H⁺
 - K₂ = 1.32 x 10⁻² M
- HSO₃⁻ ↔ SO₃²⁻ + H⁺
 - K₂ = 6.42 x 10⁻⁸ M
- Sum is referred to as **S(IV)**

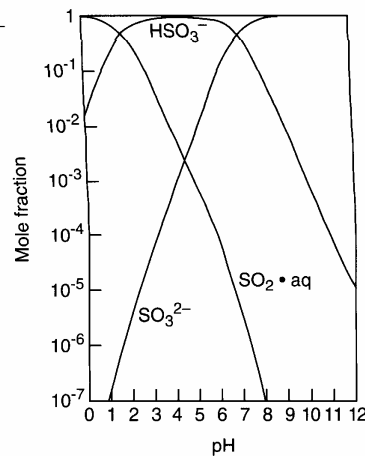


FIGURE 8.7 Mole fraction of sulfur species in solution at different acidities (adapted from Martin and Damschen, 1981).

Dependence on pH

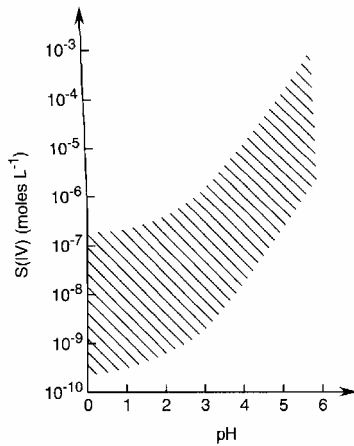


FIGURE 8.8 Range of expected aqueous S(IV) concentrations as a function of acidity for gas-phase SO₂ concentrations of 0.2–200 ppb (adapted from Martin, 1984).

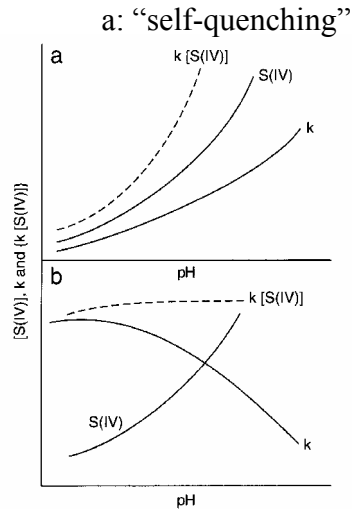


FIGURE 8.9 Schematic diagram of effect of pH on the rate constant k and on the concentration of dissolved S(IV) and its total rate of oxidation represented by $k[S(IV)]$ for two cases: (a) rate constant k decreases with pH; (b) k increases with pH.

Steps to Aqueous Phase Oxidation

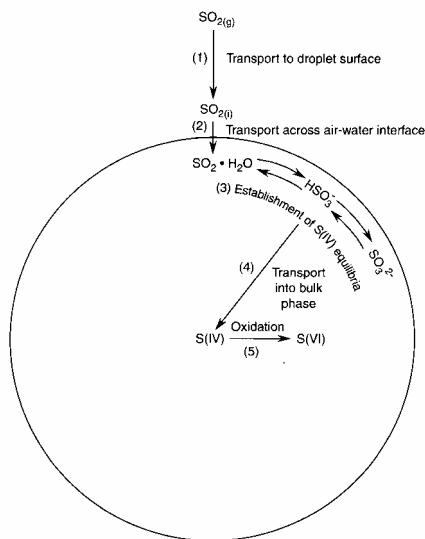


FIGURE 8.11 Schematic of steps involved in the transfer of SO₂ from the gas phase to the aqueous phase of an atmospheric water droplet and its oxidation in the liquid phase. SO_{2(aq)} = SO₂ at the water-gas interface.

- Transport to the surface: 10⁻¹⁰ to 10⁻⁴ s
- Transfer across surface: 10⁻⁴ to 10⁻¹ s (no bounce)
 - Many molecules bounce ~90% of the time or more
 - Mass accommodation coefficients, Table 8.5
- Establishing dissolved S(IV) equilibria: 10⁻³ s
- Transport in aqueous phase: 10⁻⁶ to 1 s

Potential Oxidants of SO₂ in Aqueous Phase

- Free radicals: OH and HO₂
- O₂
- O₃
- H₂O₂
- NO_y: NO, NO₂, HONO, HNO₃
- Some reactions are metal catalyzed
- Which ones are important? Look at:
 - Rate
 - Concentration of reactant
 - pH and T dependencies

Reaction with O₂

- Lots of controversy
 - Effect of impurities in experiments
 - Mechanism and kinetics are very complex
- S(IV) oxidation by O₂ in pure water is too slow
- Metals can catalyze reaction: Fe and Mn

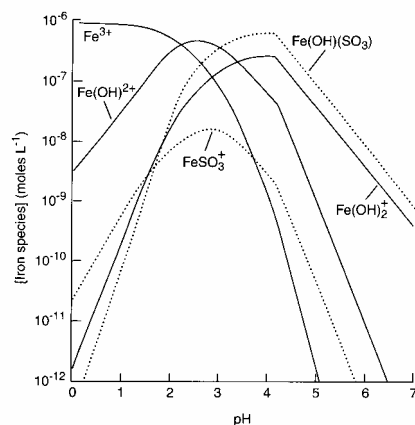
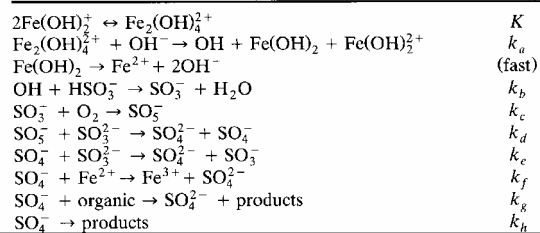


FIGURE 8.13 Calculated concentrations of iron species in aqueous solution for [Fe(III)] = 1×10^{-6} M, [S(IV)] = 1×10^{-5} M, and $I = 0.01$. The sulfur complexes are shown by the dotted lines (adapted from Martin, 1994).

Catalyzed Reaction with O₂

- Fe-catalyzed
 - Ionic mechanism at low pH (0-3.6)
 - $-d[\text{S(IV)}]/dt = k[\text{Fe(III)}][\text{S(IV)}]/[\text{H}^+]$
 - Free-radical mechanism at higher pH (4-7)
 - Very sensitive to organics, ionic strength...
 - Self-quenching. Why?

TABLE 8.7 Proposed Mechanism for the Catalyzed Oxidation of S(IV) in Aqueous Solutions of pH Range 4 – 7^a



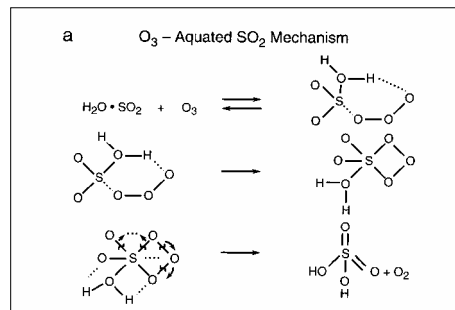
SO₂ Oxidation by O₃

- SO₂·H₂O, HSO₃⁻, and SO₃²⁻ react independently

TABLE 8.8 Rate Constants for Reactions of SO₂·H₂O_(aq), HSO₃⁻, and SO₃²⁻ with O₃ in Aqueous Solution at Room Temperature^a

| Reacting species | k (L mol ⁻¹ s ⁻¹) |
|---|--|
| SO ₂ ·H ₂ O _(aq) | $k_0 = (2.4 \pm 1.1) \times 10^4$ |
| HSO ₃ ⁻ | $k_1 = (3.7 \pm 0.7) \times 10^5$ |
| SO ₃ ²⁻ | $k_2 = (1.5 \pm 0.6) \times 10^9$ |

^a From Hoffmann (1986).



SO₂ Oxidation by O₃, Part II

- Again, self-quenching, but important at higher pH

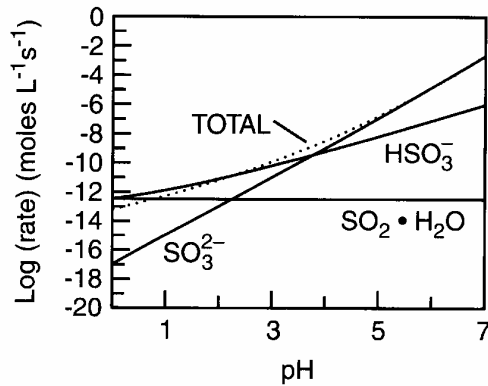


FIGURE 8.15 Rate of S(IV) oxidation by O₃ in the aqueous phase under conditions typical of a Los Angeles atmosphere, with SO₂ = 20 ppb and O₃ = 50 ppb (adapted from Hoffmann, 1986).

Oxidation by H₂O₂

- H₂O₂ in aqueous phase:
 - Very large H = 1 × 10⁵ M atm⁻¹
 - Significant concentrations, ~ 1 ppb
 - 10⁶ times larger than O₃ in solution!
- Most important oxidation pathway of SO₂ in troposphere
- HOCH₂OOH may be important in some cases

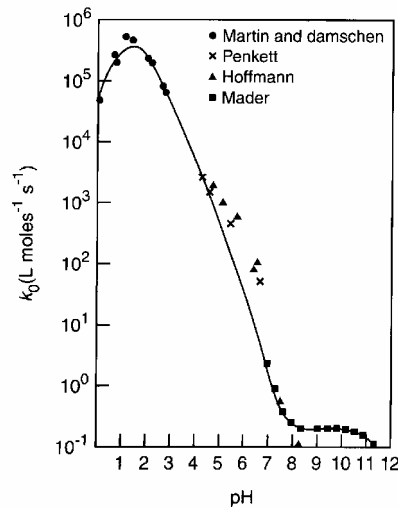


FIGURE 8.16 k_0 in expression $d[S(VI)]/dt = k_0[H_2O_2]S(IV)$; effect of buffer removed and results converted to 25°C (adapted from Martin and Damschen, 1981).

Relative Importance of Pathways

- H_2O_2 important at all pH
- O_3 and Fe catalysis play a role at higher pH

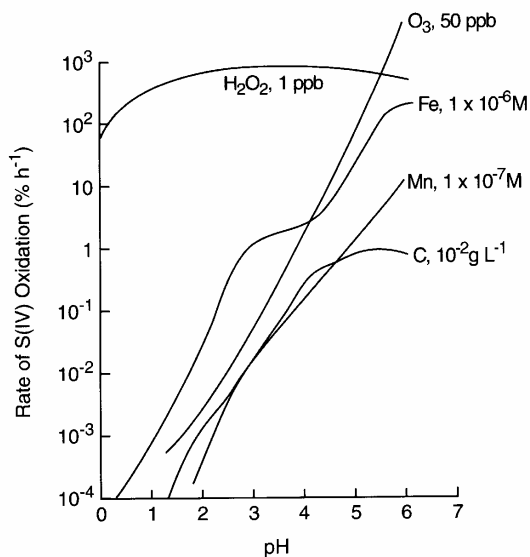


FIGURE 8.21 Estimated rates of oxidation of S(IV) in a hypothetical cloud with liquid water content of 1 mL m^{-3} (i.e., LWC of 1 g m^{-3}) based on 5 ppb gaseous SO_2 as a function of pH (adapted from Martin, 1984; Martin *et al.*, 1991).

Aqueous vs. Gas-Phase

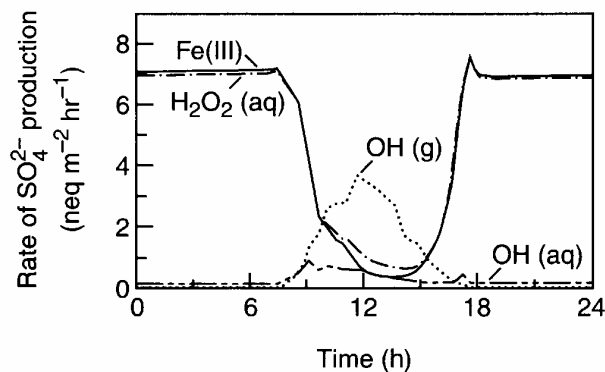


FIGURE 8.22 Calculated contributions to S(IV) oxidation in a cloud of the iron-catalyzed oxidation by $\text{O}_2/\text{Fe(III)}$, by H_2O_2 and OH in solution, and by OH in the gas phase, OH(g) , expressed in terms of rate of production of column S(IV) (adapted from Jacob *et al.*, 1989).