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
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Prof. Jose-Luis Jimenez

Outline of Lecture
A. Introduction
B. Solubility of gases in rain / fog / clouds
C. Oxidation of SO$_2$
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 H₂O
  - 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. HNO₃
  - Naming is independent of whether surface is dry or wet

- **Acid Deposition**
  - pH of rain decreases, mostly due to H₂SO₄
  - Dire effects if soil cannot neutralize acids
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 organic gases in the particles correlate with gas-phase CO, whereas sulfate is better correlated with SO$_2$. 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-in-loco liquid sampler operated by the Georgia Institute of Technology.
Major Acids

- Sulfuric acid, $\text{H}_2\text{SO}_4$
- Nitric acid, $\text{HNO}_3$
- Nitrous acid, $\text{HONO} = \text{HNO}_2$
  - Less well known, hard to measure
  - Indoor air
- Organic acids

Henry’s Law

- Pure $\text{H}_2\text{O}$ concentration in M (moles l$^{-1}$)?
- $\text{O}_3$ aqueous concentration at 50 ppb in gas?
- $\text{H}_2\text{O}_2$ a.c. at 1 ppb?
- $\text{CO}_2$?
- Fractions for 1 g m$^{-3}$ liquid $\text{H}_2\text{O}$?

<table>
<thead>
<tr>
<th>Gas</th>
<th>$H$ (mol·L$^{-1}$·atm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>Loomis, 1928</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>$1.9 \times 10^{-2}$</td>
<td>Loomis, 1928</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O}$</td>
<td>$4.9 \times 10^{-5}$</td>
<td>Loomis, 1928</td>
</tr>
<tr>
<td>$\text{NO}_2$</td>
<td>$1.2 \times 10^{-3}$</td>
<td>Loomis, 1928, Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_5$</td>
<td>$1.4$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_4$</td>
<td>$0.6$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$(0.02 \pm 0.10) \times 10^{-7}$</td>
<td>Stuehrer et al., 1983, Buser and Peronnet, 1939</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_3$</td>
<td>$2.5 \times 10^{-4}$</td>
<td>Loomis, 1928</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>$3.4 \times 10^{-4}$</td>
<td>Loomis, 1928</td>
</tr>
<tr>
<td>$\text{NO}_2$</td>
<td>$1.2$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{NO}_3$</td>
<td>$49$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>$62$</td>
<td>Van Raan et al., 1949</td>
</tr>
<tr>
<td>$\text{HNO}_3$</td>
<td>$7.1 \times 10^{-7}$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$(1.03 \pm 0.02) \times 10^{-3}$</td>
<td>Schwane and Wolfe, 1963</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>$30$</td>
<td>Gelzinis et al., 1993, Hanau et al., 1992</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$30$</td>
<td>Gelzinis et al., 1993, Hanau et al., 1992</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$5$</td>
<td>Gelzinis et al., 1993, Hanau et al., 1992</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$0.02$</td>
<td>Gelzinis et al., 1993, Hanau et al., 1992</td>
</tr>
</tbody>
</table>

* Adapted from Schwartz, 1984; see also Web site in Appendix IV.
* Physical volatility, moles with liquid water.
* Physical volatility, moles of acid from equilibrium.
* For Clorox and household cleaners, see Schauer and Chiggio (1986) for temperature dependence.
CO₂ Uptake and Buffering

- CO₂(g) + H₂O(l) ↔ CO₂·H₂O(aq)
  - H₁ = 3.4 x 10⁻² M atm⁻¹
- CO₂·H₂O(aq) ↔ HCO₃⁻ + H⁺
  - K₂ = 4.3 x 10⁻⁷ M
- HCO₃⁻ ↔ CO₃²⁻ + H⁺
  - K₂ = 4.7 x 10⁻¹¹ 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

- pH = -log [H⁺] (Brønsted-Lowry)
- H₂O ↔ H⁺ + OH⁻
- In pure neutral water: [H⁺] = [OH⁻] = 10⁻⁷ per liter.
  - Note: H⁺ really present as H₃O⁺
- pH < 7, the solution is acidic
- pH = 7, the solution is neutral
- 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 SO$_2$

- Gas-phase w/ OH
- Liquid phase
  - Many mechanisms, most of this chapter
  - Most important are H$_2$O$_2$ and O$_3$
- Typically $>50\%$ of SO$_2$ oxidation globally is thought to occur in clouds

Gas Phase SO$_2$ 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:
  - $k_4 \sim 9 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$
  - Lifetime of SO$_2$?
- Then:
  - $\text{HOSO}_2 + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{SO}_3$
  - $k_4 \sim 4.3 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$
  - Lifetime of HOSO$_2$?
Gas Phase SO₂ Oxidation II

- Note that HO₂ is produced, then:
  - \( \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \)
  - So no HOₓ is destroyed, and O₃ is produced
  - \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \)
    - Very important for aqueous-phase oxidation
- Fate of SO₃
  - \( \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \)
- Note that oxidants for SO₂ (OH, H₂O₂, O₃) are formed in NOₓ+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
- SO₂H₂O does not react directly
- Rather SO₂H₂O + H₂O

**FIGURE 8.4** Predicted energetics for various mechanisms for the SO₃–H₂O reaction transition states are marked with a \( \ddagger \) 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?

Aqueous Phase Equilibria of SO₂

- SO₂(g) + H₂O(l) ↔ SO₂Η₂O(aq)
  - H₁ = 1.242 M atm⁻¹
- SO₂Η₂O(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

![Graph showing 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 $4[S(IV)]$ for two cases: (a) rate constant $k$ decreases with pH; (b) $k$ increases with pH.

Steps to Aqueous Phase Oxidation

- 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

![Diagram showing 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. SO₃(g) = SO₂ at the water-air interface.
Potential Oxidants of SO₂ in Aqueous Phase

- Free radicals: OH and HO₂
- O₂
- O₃
- H₂O₂
- NOₓ: 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(II)] = 1 × 10⁻⁹ M, [Fe(IV)] = 1 × 10⁻⁷ M, and I = 0.05. 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)
    - \(-d[S(IV)]/dt = k[Fe(III)][S(IV)])[H^+]\)
  - 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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2Fe(OH)_2^+ \rightarrow Fe_2(OH)_2^{2+})</td>
<td>(K)</td>
</tr>
<tr>
<td>(Fe_3(OH)_2^{2+} + OH^- \rightarrow OH_2 + Fe(OH)_2 + Fe(OH)_2^{2+})</td>
<td>(k_1)</td>
</tr>
<tr>
<td>(Fe(OH)_2 \rightarrow Fe^{2+} + 2OH^-)</td>
<td>(fast)</td>
</tr>
<tr>
<td>(OH^- + SO_2 \rightarrow SO_3^- + H_2O)</td>
<td>(k_2)</td>
</tr>
<tr>
<td>(SO_3^- + O_2 \rightarrow SO_5^-)</td>
<td>(k_3)</td>
</tr>
<tr>
<td>(SO_3^- + SO_4^{2-} \rightarrow SO_4^{2-} + SO_3^-)</td>
<td>(k_4)</td>
</tr>
<tr>
<td>(SO_2 + SO_3^{2-} \rightarrow SO_2^+ + SO_3)</td>
<td>(k_5)</td>
</tr>
<tr>
<td>(SO_2 + SO_4^{2-} \rightarrow SO_2^+ + SO_3)</td>
<td>(k_6)</td>
</tr>
<tr>
<td>(SO_4^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-})</td>
<td>(k_7)</td>
</tr>
<tr>
<td>(SO_5^- + organic \rightarrow SO_2^{2-} + products)</td>
<td>(k_8)</td>
</tr>
<tr>
<td>(SO_2^{2-} \rightarrow products)</td>
<td>(k_9)</td>
</tr>
</tbody>
</table>

SO₂ Oxidation by O₃

- \(SO_2\cdot H_2O\), \(HSO_3^-\), and \(SO_3^{2-}\) react independently

**TABLE 8.8:** Rate Constants for Reactions of \(SO_2\cdot H_2O\), \(HSO_3^-\), and \(SO_3^{2-}\) with O₃ in Aqueous Solution at Room Temperature

<table>
<thead>
<tr>
<th>Reacting species</th>
<th>(k) (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SO_2\cdot H_2O)</td>
<td>((2.4 \pm 1.1) \times 10^4)</td>
</tr>
<tr>
<td>(HSO_3^-)</td>
<td>((3.7 \pm 0.7) \times 10^3)</td>
</tr>
<tr>
<td>(SO_3^{2-})</td>
<td>((1.5 \pm 0.6) \times 10^9)</td>
</tr>
</tbody>
</table>

\(d\) From Hoffmann (1986).
SO₂ Oxidation by O₃, Part II

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

![Graph showing 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).]

**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 $H = 1 \times 10^5$ M atm⁻¹
  - Significant concentrations, ~1 ppb
  - $10^6$ times larger than O₃ in solution!
- Most important oxidation pathway of SO₂ in troposphere
- HOCH₂OOH may be important in some cases

![Graph showing $k_o$ in expression $\frac{d[S(VI)]}{dt} = k_o[H_2O_2][S(IV)]$; effect of buffer removed and results converted to 25°C (adapted from Martin and Damschen, 1981).]

**FIGURE 8.16** $k_o$ in expression $\frac{d[S(VI)]}{dt} = k_o[H_2O_2][S(IV)]$; effect of buffer removed and results converted to 25°C (adapted from Martin and Damschen, 1981).
Relative Importance of Pathways

- $\text{H}_2\text{O}_2$ important at all pH
- $\text{O}_3$ and Fe catalysis play a role at higher pH

**FIGURE 8.21** Estimated rates of oxidation of $\text{S(IV)}$ 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 $\text{SO}_2$ as a function of pH (adapted from Martin, 1984; Martin *et al.*, 1991).

Aqueous vs. Gas-Phase

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