

Lecture 22. Acid rain.

Part1. Acid rain formation.

Objectives:

1. Discovery of acid rain.
2. Acids in water.
3. Sources of environmental acids.

Readings: Turco: p. 259-278; Brimblecombe: p. 173-177

1. Discovery of acid rain.

- 1872, England: Robert A. Smith published a book titled “Air and rain: the beginning of a chemical climatology.” Term “**acid rain**” was introduced to the world. He found that the concentrations of sulfate (SO_4^{2-}) were greater in rain collected near cities, and particularly coal-burning facilities.
- 1950, Europe: Acid rain was recognized as a regional problem. For instance, Swedish precipitation network revealed that the phenomenon of acid rain was regional in scale and that acid deposited in Sweden was coming largely from European sources.
- 1970, USA and Canada: recognized acid rain problem. In 1980, the U.S. Acid Precipitation Act was passed, and the National Acid Precipitation Assessment Program (NAPAP), an intensive 10-year study of the problem, was initiated.

Natural rainwater is slightly acidic because:

1. at atmospheric concentrations (380 ppmv), CO₂ gas dissolves in water, forming carbonic acid, H₂CO₃, with pH about 5.6;
2. natural sources of sulfur and nitrogen oxides also contribute to the background acidity. For instance, SO₂ from volcanic eruptions and NO generated by lightning are converted into acids that can lower pH of precipitation.

Thus, **pH of natural rainwater is in the range from about 5 to 5.6.**

Acid rain with pH of 5.0 or lower is identified as acid rain caused by industrial activity.

- Acid rain typically has pH between roughly 3 and 5. In extreme cases, rain with pH < 3 is measured.

Acid rain causes adverse effects upon

- ◆ Vegetation (affecting productivity);
- ◆ Soils (accelerating leaching of cations and reducing soil fertility);
- ◆ Aquatic systems (adversely affecting fisheries);
- ◆ Building and materials (causing erosion and damage).

NOTE: effects of acid rain are discussed in Lecture 23.

- Acid rain today is produced mainly from emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) generated by human activities, which are oxidized in the atmosphere to form sulfuric and nitric acids, respectively. However, various species can be found in rainwater.

Chemical analysis of both rainwater and of the water-soluble component of atmospheric aerosol particles normally reveals the presence of the following ionic components:

- I. Na^+ , Mg^{2+} , and Cl^- , predominantly from sea spray;
- II. K^+ and Ca^{2+} , predominantly soil-derived;
- III. H^+ from strong acids;
- IV. NH_4^+ from ammonia neutralization of strong acids;
- V. SO_4^{2-} , and NO_3^- from oxidation of SO_2 and NO_2 , respectively.

NOTE: Actual composition of rainwater is highly variable from place to place.

2. Acids in water.

Acids are the proton (H^+) donors, and **bases** (alkalis) are the proton acceptors.

NOTE: recall pH of the solutions discussed in Lecture 13.

The pH of an aqueous solution with the concentration of hydrogen ions H^+ expressed in moles per liter (abbreviated M) is

$$\text{pH} = -\log([\text{H}^+])$$

Problem.

A hydronium ion concentration of 0.00000001 M is common for fresh eggs. What is pH of a fresh egg?

Solution.

$$[\text{H}^+] = 0.00000001 \text{ M} = 10^{-8} \text{ M}$$

$$\text{pH} = -\log([\text{H}^+]) = -\log(10^{-8}) = 8$$

- If pH is known, the concentration of H^+ can be found as

$$[H^+] = 10^{-pH}$$

Problem.

A typical pH of a soft drink is 3.0. What is the concentration of H_3O^+ for a soft drink?

Solution.

NOTE: H_3O^+ is the different notation for H^+ .

Because $pH=3$, we have $[H_3O^+] = [H^+] = 10^{-3} M$

NOTE: recall reversible reactions and equilibrium, and constant rate discussed in Lecture 7.

For a hypothetical reaction $aA + bB \leftrightarrow cC + dD$,

the type of equilibrium that exist between opposing reactions is called chemical equilibrium. In chemical equilibrium the forward and reverse reactions take place with the same rate: $Rate_f = Rate_r$

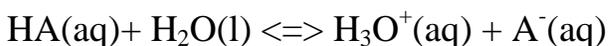
Equilibrium constant at a given temperature is equal to the ratio of the equilibrium concentrations of the product to the equilibrium concentrations of the reactants, each raised to their respective coefficients in the balanced chemical equation:

$$K = [C]^c [D]^d / [A]^a [B]^b = k_f / k_r$$

where k_f and k_r are the rate constants for forward and reverse reactions, respectively.

NOTE: recall acid strength, strong and weak acids discussed in Lecture 13.

Acid strength is defined by the equilibrium position of its dissociation reaction:



the equilibrium expression is

$$K_a = [\text{H}_3\text{O}^+] [\text{A}^-] / [\text{HA}] = [\text{H}^+] [\text{A}^-] / [\text{HA}]$$

Strong acid is one for which this equilibrium lies far to the right: means that almost all of the original HA is dissociated at equilibrium. Conversely, a **weak acid** is one for which equilibrium lies far for the left.

Problem.

Calculate the pH of the following solutions:

- (i) 0.1 M HCl
- (ii) 0.1 M CH_3COOH (acetic acid) with $K_a = 1.78 \times 10^{-5}$

Solution.

- (i) 0.1 M HCl

HCl is a strong acid and so completely dissociates



Thus, $[\text{H}^+] = [\text{HCl}] = 0.1 \text{ M}$

$$\text{pH} = -\log([\text{H}^+]) = -\log(0.1) = -\log(10^{-1}) = \mathbf{1}$$

- (ii) CH_3COOH is a weak acid, and so not all of the acid will be dissociated.



$$K_a = [\text{CH}_3\text{COO}^-] [\text{H}^+] / [\text{CH}_3\text{COOH}]$$

Assuming that X moles of the acid dissociate, we have

$$[\text{CH}_3\text{COOH}] = 0.1 - X$$

$$[\text{CH}_3\text{COO}^-] = X$$

$$[\text{H}^+] = X$$

$$\text{thus } 1.78 \cdot 10^{-5} = X \cdot X / (0.1 - X)$$

$$X^2 + 1.78 \cdot 10^{-5} X - 1.78 \cdot 10^{-6} = 0$$

This quadratic equation is solved using

$$X = -b + (b^2 - 4ac)^{1/2} / 2a$$

$$\text{where } a = 1; b = 1.78 \cdot 10^{-5}; c = -1.78 \cdot 10^{-6}$$

$$\text{so } X = 1.34 \cdot 10^{-3}$$

Therefore $[\text{H}^+] = X$ and

$$\text{pH} = -\log([\text{H}^+]) = -\log(1.34 \cdot 10^{-3}) = \mathbf{2.873}$$

3. Sources of environmental acids.

Inorganic acids that contribute to the acidity of rain:

H₂SO₄: sulfuric acid is generated from anthropogenic SO₂ emissions and natural sulfur emissions. The latter includes, hydrogen sulfide (H₂S) and dimethyl sulfide (DMS), which are oxidized to sulfur dioxide.

HNO₃: nitric acid is derived from both anthropogenic and natural NO_x emissions.

HCl: hydrochloric acid has significant natural (volcanoes) and anthropogenic sources. Always secondary in importance to sulfuric and nitric acid in precipitation.

H₂CO₃: carbonic acid is negligible in acid rain. Source is CO₂, mostly natural, but has increased due to fossil fuel burning

H₂SO₃: sulfurous acid makes a negligible contribution to acidic precipitation.

Organic acids that contribute to the acidity of rain:

HCOOH: formic acid, the most common organic acid found in precipitation, is a by-product of the oxidation of more complex hydrocarbons.

CH₃COOH: acetic acid is generated as a by-product of organic photochemical decomposition in air.

C₃H₇COOH: butyric acid is not very common in precipitation.

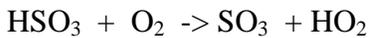
C₅H₁₁COOH: caproic acid is not found in very large amounts in precipitation.

- Both natural and anthropogenic emissions contribute to acidity.
- Both inorganic and organic species are significant.
- However, primary sources of acid rain and fog, and environmental acidity in general, are emissions of sulfur and nitrogen oxides by human activities.

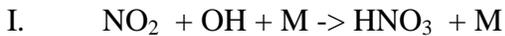
In the atmosphere, nitric and sulfuric acids can be formed in two ways:

1) Gas-phase conversion of SO₂ to sulfuric acid gas (H₂SO₄), and NO_x to nitric acid gas (HNO₃).

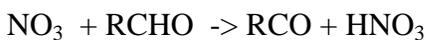
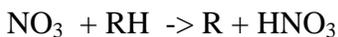
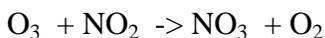
The gas phase conversion of SO₂ requires three steps:



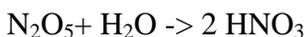
The gas phase conversion of NO_x to HNO₃ can proceed by several different pathways:



II. Formation of HNO₃ in NO_y/alkanes (RH)/ aldehydes (RCHO) system:

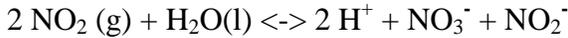


III. Dinitrogen pentoxide, N₂O₅, is hydrolyzed to form nitric acid in gas phase



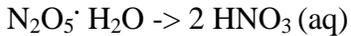
2) Direct dissolution of SO₂ and NO_x into water drop and subsequent aqueous-phase oxidation.

Aqueous phase reactions forming HNO₃:



or

aqueous phase hydrolysis of N₂O₅:



- Most important chemical transformation in cloud water which contributes to acid rain:



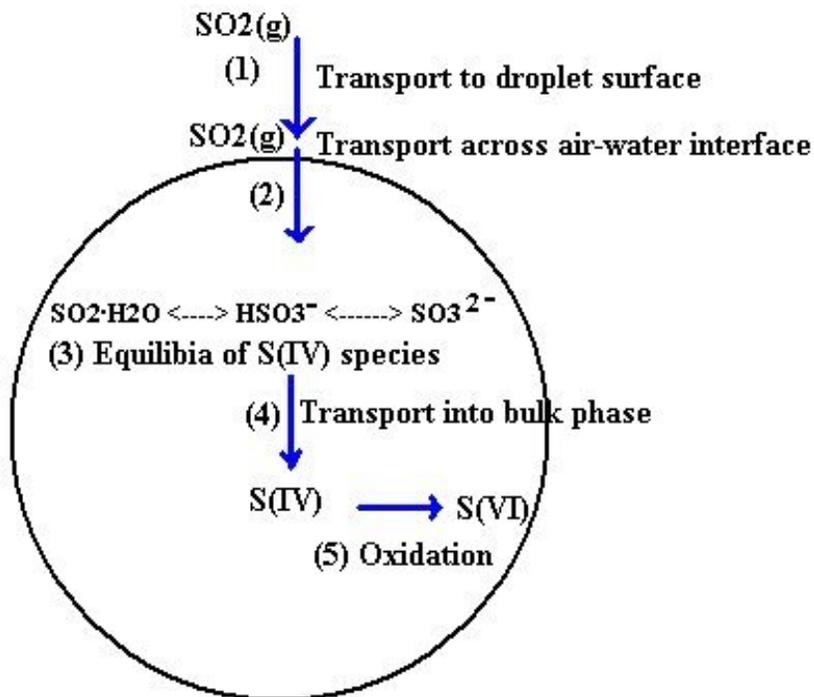
S(IV) aqueous species : sulfur dioxide SO₂(aq) and its dissociation products: bisulfite ion HSO₃⁻(aq) and sulfite ion SO₃²⁻(aq).

S(VI) aqueous species : sulfuric acid H₂SO₄(aq) and its dissociation products: bisulfate HSO₄⁻(aq) and sulfate SO₄²⁻(aq).

Before S(IV) will be oxidized in aqueous solution the following consequence of steps should take place:

1. Transport of the gas to the surface of the droplet.
2. Transfer of the gas across the air-liquid interface.
3. Formation of aqueous phase equilibrium of the dissolved species (as above reaction (1)-(3) for SO₂).
4. Transport of the dissolved species from the surface to the bulk aqueous phase of the droplet.
5. Reaction in the droplet.

Figure 22.1 Schematic steps involved in the transfer of SO₂ from the gas to the aqueous phase.

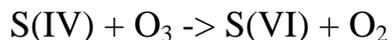


Important to remember:

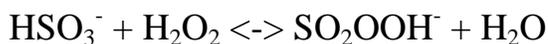
- Dissolution of SO₂ in water results in the formation of three chemical species: hydrated SO₂ (SO₂ · H₂O), the bisulfite ion (HSO₃⁻), and the sulfite ion (SO₃²⁻), referred to as S(IV) since sulfur in these species is in oxidation state 4.
- At pH of atmospheric interest (pH = 2 to 7) most of the S(IV) is in the form of HSO₃⁻; at low pH (pH < 2) , all S(IV) occurs as SO₂ · H₂O; at high pH (pH > 7) S(IV) is in the form of SO₃²⁻.
- Dissociation of dissolved SO₂ enhances its aqueous solubility so that the total amount of dissolved S(IV) always exceeds that predicted by Henry's law for SO₂ alone and quite pH dependent.

Most important pathways for S(IV) transformation to S(VI) in aqueous phase:

- 1) oxidation of S(IV) by dissolved ozone:



- 2) oxidation of S(IV) by hydrogen peroxide H_2O_2 , which is one of the most effective oxidants of S(IV) in clouds and fogs:



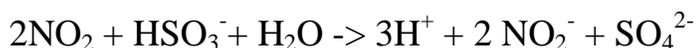
(SO_2OOH^- is peroxymonosulfurous acid)

- 3) oxidation of S(IV) by oxygen, O_2 , catalyzed by iron or manganese:



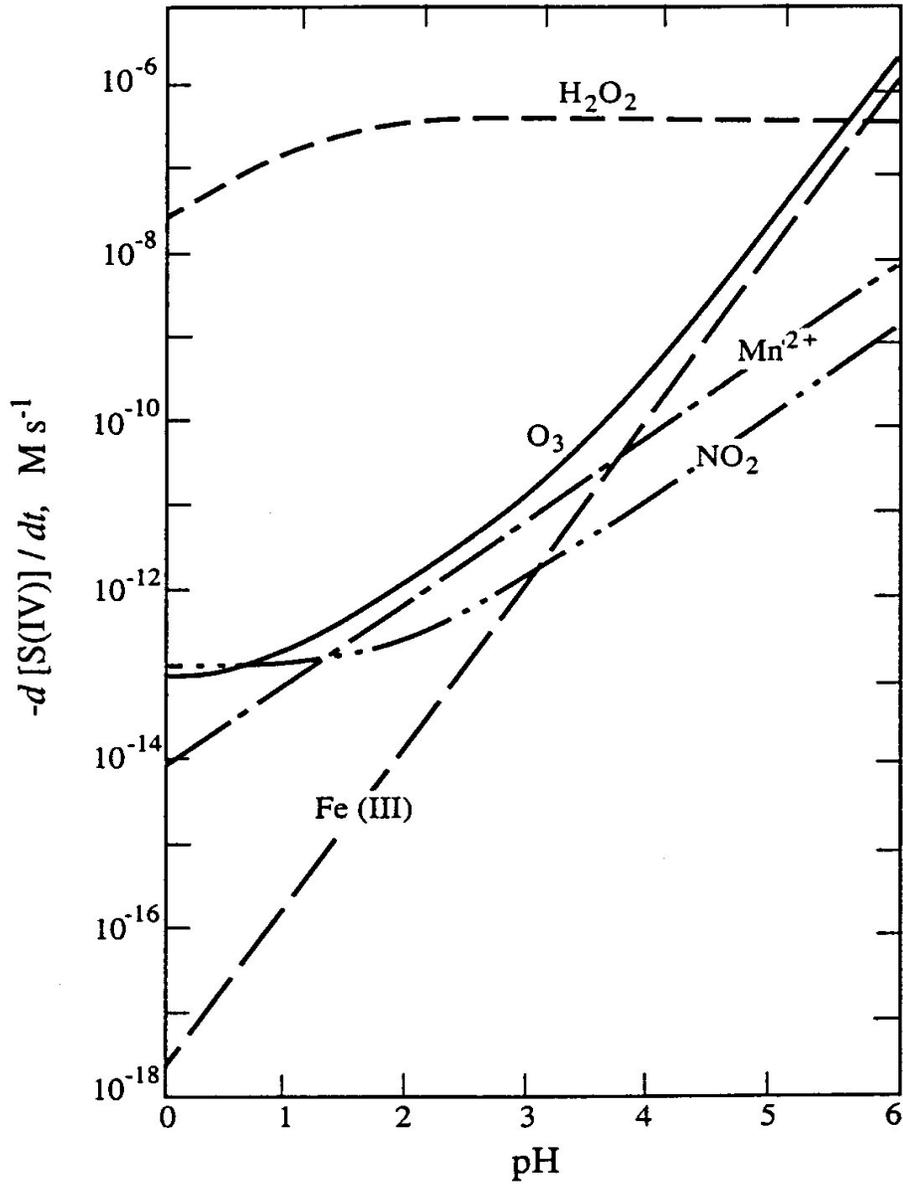
- 4) oxidation of S(IV) by free radicals such OH and HO_2 (typically goes through the reaction chain);

- 5) oxidation of S(IV) by oxides of nitrogen.



Thus main oxidants for S(IV) in aqueous solution are O_3 , H_2O_2 , O_2 (catalyzed by Mn(II) and Fe(III)), free radicals such as OH and HO_2 , and oxides of nitrogen. However, relative importance of these oxidants depends on the pH of the solution.

Figure 22.2 Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are: $[\text{SO}_2(\text{g})] = 5\text{ppb}$; $[\text{NO}_2(\text{g})] = 1\text{ppb}$; $[\text{H}_2\text{O}_2(\text{g})] = 1\text{ppb}$; $[\text{Fe}(\text{III})] = 0.3\ \mu\text{M}$; $[\text{Mn}(\text{II})] = 0.03\ \mu\text{M}$ (from Seinfeld and Pandis, 1997).



- ◆ Sulfuric and nitric acids, formed in the atmosphere, have some similarities and differences.

Similarities:

- Both acids can react with bases present in the atmosphere to form salts. For instance, $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$
- Their chemistries are intertwined via the OH radical and other oxidants in converting NO_x and SO_2 into the acids.

Differences:

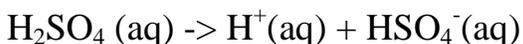
- Nitric acid is more volatile and thus can exist in significant concentrations in the gas phase, while sulfuric acid has a very low vapor pressure under ambient conditions and hence exists in the form of particles.
- Nitric acid can relatively easily revolatilize even after forming the ammonium salt; no analogous chemical and physical changes exist for sulfuric acid.
- Nitric acid is a strong monoprotic acid (an acid having one acidic proton). Sulfuric acid is a strong diprotic acid (an acid having two acidic protons). Virtually 100% of H_2SO_4 dissociated in water: $\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$ but the HSO_4^- ion is a weak acid: $\text{HSO}_4^-(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Problem.

Calculate the pH of a 1.0 M H_2SO_4 aqueous solution. Take dissociation constant for the second step of $K_{a2} = 1.2 \cdot 10^{-2}$

Solution.

H_2SO_4 is a strong acid in its first dissociation step:



thus after this step we have concentration of H^+ as least 1.0 M, since this amount of H_2SO_4 is dissociated. Now we must find how much H^+ will be added to the solutions from dissociation of $\text{HSO}_4^-(\text{aq})$, which is a weak acid.

$\text{HSO}_4^- (\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$, where

$$K_{a2} = [\text{H}^+] [\text{SO}_4^{2-}] / [\text{HSO}_4^-]$$

Initial concentrations (after first dissociation step) are

$$[\text{HSO}_4^-] = 1.0 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0$$

$$[\text{H}^+] = 1.0 \text{ M}$$

Assuming that X moles of the acid HSO_4^- dissociate, we have

$$[\text{HSO}_4^-] = 1.0 - X$$

$$[\text{SO}_4^{2-}] = X$$

$$[\text{H}^+] = 1.0 + X$$

Note that initial $[\text{H}^+]$ is not equal to zero, as is usually the case for a weak acid, because the first dissociation step has already produced some H^+ .

Substituting the equilibrium concentrations into the expression for K_{a2} , we have

$$K_{a2} = (1+X) X / 1-X$$

Let's assume that X is much smaller than 1, thus we have

$$K_{a2} = 1 X / 1 = X$$

or $X = 1.2 \cdot 10^{-2}$ (since $1.2 \cdot 10^{-2}$ is much smaller than 1, our approximation used above is valid). Note that we made this approximation to avoid solving the quadratic equation.

Therefore

$$[\text{H}^+] = 1.0 + X = 1.0 + 1.2 \cdot 10^{-2} = 1$$

Thus since the dissociation of HSO_4^- does not make a significant contribution to the concentration of H^+ ,

$$[\text{H}^+] = 1 \text{ M} \text{ and } \text{pH} = 0$$