CHAPTER 13. ACID RAIN

Acid rain was discovered in the 19th century by Robert Angus Smith, a pharmacist from Manchester (England), who measured high levels of acidity in rain falling over industrial regions of England and contrasted them to the much lower levels he observed in less polluted areas near the coast. Little attention was paid to his work until the 1950s, when biologists noticed an alarming decline of fish populations in the lakes of southern Norway and traced the problem to acid rain. Similar findings were made in the 1960s in North America (the Adirondacks, Ontario, Quebec).   These findings spurred intense research to understand the origin of the acid rain phenomenon.
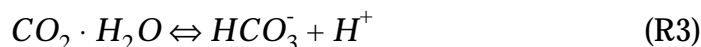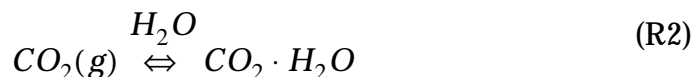
13.1 CHEMICAL COMPOSITION OF PRECIPITATION

13.1.1 Natural precipitation

Pure water has a pH of 7 determined by dissociation of H_2O molecules:

$$H_2O \Leftrightarrow H^+ + OH^- \tag{R1}$$

Rainwater falling in the atmosphere always contains impurities, even in the absence of human influence. It equilibrates with atmospheric CO_2, a weak acid, following the reactions presented in chapter 6:

$$CO_2(g) \overset{H_2O}{\Leftrightarrow} CO_2 \cdot H_2O \tag{R2}$$

$$CO_2 \cdot H_2O \Leftrightarrow HCO_3^- + H^+ \tag{R3}$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \tag{R4}$$

The corresponding equilibrium constants in dilute solution at 298 K are K_H = $[CO_2 \cdot H_2O]/P_{CO2}$ = 3×10^{-2} M atm^{-1}, K_1 = $[HCO_3^-][H^+]/[CO_2 \cdot H_2O]$ = 4.3×10^{-7} M (pK_1 = 6.4), and K_2 = $[CO_3^{2-}][H^+]/[HCO_3^-]$ = $4.7 \times 10^{-11} M$ (pK_2 = 10.3). From these constants and a preindustrial CO_2 concentration of 280 ppmv one calculates a rainwater pH of

5.7. Other natural acids present in the atmosphere include organic acids emitted by the biosphere, HNO_3 produced by atmospheric oxidation of NO_x originating from lightning, soils, and fires (section 11.4), and H_2SO_4 produced by atmospheric oxidation of reduced sulfur gases emitted by volcanoes and by the biosphere. A comparative analysis of these different natural sources of acidity is conducted in problem 13. 5. The natural acidity of rain is partly balanced by natural bases present in the atmosphere, including NH_3 emitted by the biosphere and $CaCO_3$ from suspended soil dust.

When all of these influences are taken into account, the pH of natural rain is found to be in the range from 5 to 7. The term *acid rain* is customarily applied to precipitation with a pH below 5. Such low pH values are generally possible only in the presence of large amounts of anthropogenic pollution.

13.1.2 Precipitation over North America

Figure 13-1 shows the mean pH values of precipitation measured over North America. pH values less than 5 are observed over the eastern half. We can determine the form of this acidity by examining the ionic composition of the precipitation; data for two typical sites are shown in Table 13-1. For any precipitation sample, the sum of concentrations of anions measured in units of charge equivalents per liter must equal the sum of concentrations of cations, since the ions originated from the dissociation of neutral molecules. This charge balance is roughly satisfied for the data in Table 13-1; an exact balance would not be expected because the concentrations in the Table are given as medians over many samples.

Consider the data for the New York site in Table 13-1. The median pH at that site is 4.34, typical of acid rain in the northeastern United States. The H^+ ion is the dominant cation and is largely balanced by SO_4^{2-} and NO_3^-, which are the dominant anions. We conclude that H_2SO_4 and HNO_3 are the dominant contributors to the precipitation acidity. Both are strong acids which dissociate quantitatively in water to release H^+:
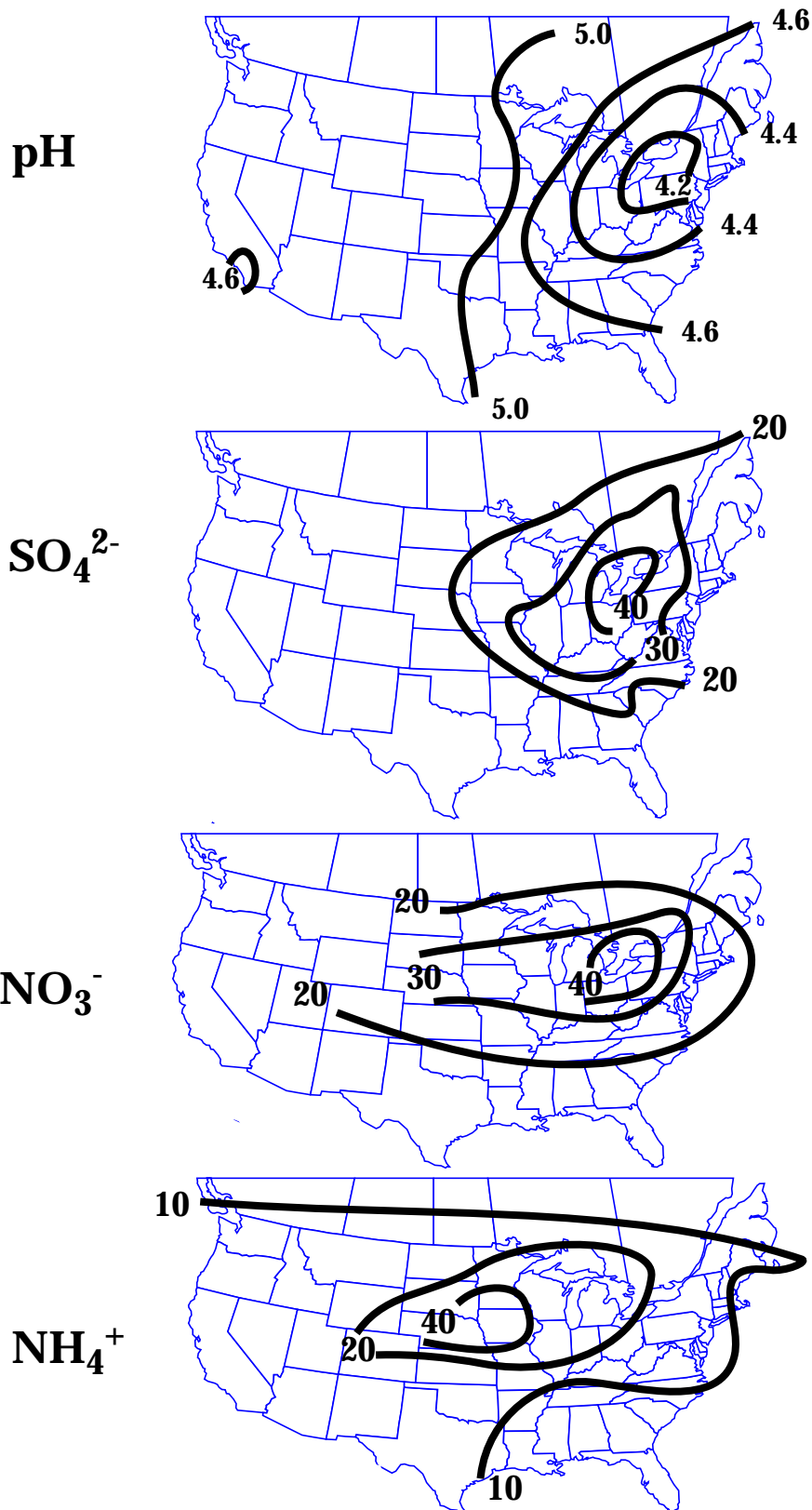
$$HNO_3(aq) \rightarrow NO_3^- + H^+ \tag{R5}$$

$$H_2SO_4(aq) \rightarrow SO_4^{2-} + 2H^+ \tag{R6}$$
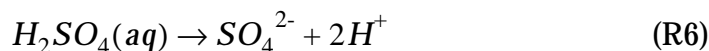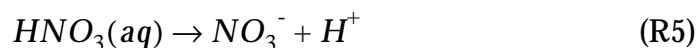
Figure 13-1 Mean pH and concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ (μeq l^{-1}) in precipitation over North America during the 1970s.

Table 13-1 Median concentrations of ions (μeq l^{-1}) in precipitation at two typical sites in the United States.

| Ion	rural New York State	southwest Minnesota
SO_4^{2-}	45	46
NO_3^-	25	24
Cl^-	4	4
HCO_3^-	0.1	10
SUM ANIONS	**74**	**84**
H^+ *(pH)*	46 *(4.34)*	0.5 *(6.31)*
NH_4^+	8.3	38
Ca^{2+}	7	29
Mg^{2+}	1.9	6
K^+	0.4	2.0
Na^+	5	14
SUM CATIONS	**68**	**89**

As shown in Figure 13-1, SO_4^{2-} and NO_3^- concentrations throughout the United States are more than enough to balance the local H^+ concentrations.   More generally, analyses of rain composition in all industrial regions of the world demonstrate that H_2SO_4 and HNO_3 are the main components of acid rain.

Consider now the data for the southwest Minnesota site in Table 13-1. The concentrations of SO_4^{2-} and NO_3^- are comparable to those of the New York site, indicating similar inputs of H_2SO_4 and HNO_3. However, the H^+ concentration is two orders of magnitude less; the pH is close to neutral. There must be bases neutralizing the acidity. To identify these bases, we examine which cations in Table 13-1 replace the H^+ originally supplied by dissociation of HNO_3 and H_2SO_4. The principal cations are NH_4^+, Ca^{2+}, and Na^+,

indicating the presence in the atmosphere of ammonia (NH_3) and alkaline soil dust ($CaCO_3$, Na_2CO_3).   Ammonia dissolved in rainwater scavenges H^+:

$$NH_3(aq) + H^+ \Leftrightarrow NH_4^+ \qquad (R7)$$
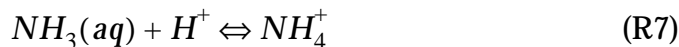
The equilibrium constant for *(R7)* is K = $[NH_4^+]/[NH_3(aq)][H^+]$ = 1.6×10^9 *M,* so that$[NH_4^+]/[NH_3(aq)]$ = 1 for pH = 9.2. At the pH values found in rain, NH_3 behaves as a strong base; it scavenges H^+ ions quantitatively and NH_4^+ appears as the cation replacing H^+. Neutralization of H^+ by dissolved soil dust proceeds similarly:

$$CaCO_3(s) \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (R8)$$

$$CO_3^{2-} + 2H^+ \Leftrightarrow CO_2(g) + H_2O \qquad (R9)$$
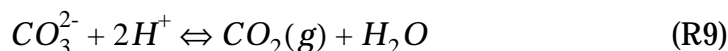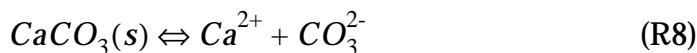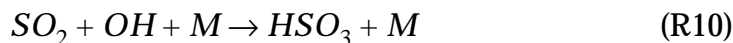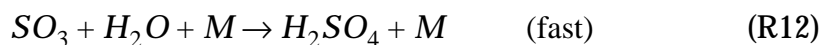
The relatively high pH of rain in the central United States (Figure 13-1) reflects the large amounts of NH_3 emitted from agricultural activities (fertilizer use, livestock), and the facile suspension of soil dust due to the semi-arid climate. Note from Figure 13-1 that NH_4^+concentrations are maximum over the central United States.
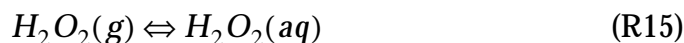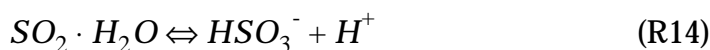
13.2 SOURCES OF ACIDS: SULFUR CHEMISTRY

It has been known since the 1960s that the high concentrations of HNO_3 and H_2SO_4 in acid rain are due to atmospheric oxidation of NO_x and SO_2 emitted by fossil fuel combustion. Understanding of the oxidation mechanisms is more recent. The mechanisms for oxidation of NO_x to HNO_3 were discussed in chapters 10 and 11, and in problem 11. 8. Both OH (day) and O_3 (night) are important oxidants and lead to a NO_x lifetime over the United States of less than a day. We focus here on the mechanisms for oxidation of SO_2 to H_2SO_4.

Sulfur dioxide (SO_2) is emitted from the combustion of sulfur-containing fuels (coal and oil) and from the smelting of sulfur-containing ores (mostly copper, lead, and zinc).   In the atmosphere, SO_2 is oxidized by OH to produce H_2SO_4:

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad (R10)$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \qquad \text{(fast)} \qquad \text{(R11)}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \qquad \text{(fast)} \qquad \text{(R12)}$$

The lifetime of SO_2 against reaction with OH is 1-2 weeks. A major research problem in the 1970s was to reconcile this relatively long lifetime with the observation that SO_4^{2-} concentrations in rain are maximum over SO_2 source regions (Figure 13-1). This observation implies that SO_2 must be oxidized to H_2SO_4 rapidly; otherwise, the emission plume would be transported far from the SO_2 source region by the time it was oxidized to H_2SO_4. Research in the early 1980s showed that most of the atmospheric oxidation of SO_2 actually takes place in cloud droplets and in the raindrops themselves, where SO_2 dissociates to HSO_3^- which is then rapidly oxidized in the liquid phase by H_2O_2 produced from self-reaction of HO_2 (chapter 11):

$$SO_2(g) \Leftrightarrow SO_2 \cdot H_2O \qquad \text{(R13)}$$

$$SO_2 \cdot H_2O \Leftrightarrow HSO_3^- + H^+ \qquad \text{(R14)}$$

$$H_2O_2(g) \Leftrightarrow H_2O_2(aq) \qquad \text{(R15)}$$

$$HSO_3^- + H_2O_2(aq) + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O \qquad \text{(R16)}$$

Reaction *(R16)* is acid-catalyzed (note the presence of H^+ on the left-hand side). The rate of aqueous-phase sulfate formation is

$$\frac{d}{dt}[SO_4^{2-}] = k_{12}[HSO_3^-][H_2O_2(aq)][H^+]$$
$$= k_{12}K_9K_{10}K_{11}P_{SO2}P_{H2O2} \qquad (13.1)$$

where the *K*'s are equilibrium constants. Acid catalysis is key to the importance of *(R16)* for generating acid rain; otherwise, the reaction would be suppressed at low pH because $[HSO_3^-]$ depends inversely on $[H^+]$ by equilibrium *(R14)* (see problem 13. 3). Substituting numerical values in *(13.1)* indicates that reaction *(R16)* is extremely fast and results in titration of either SO_2 or H_2O_2 in a cloud; measurements in clouds show indeed that SO_2 and H_2O_2 do not coexist. Reaction *(R16)* is now thought to provide the dominant atmospheric pathway for oxidation of SO_2 to H_2SO_4, although there are still unresolved issues regarding the mechanism for oxidation during the winter months when production of H_2O_2 is low.

13.3 EFFECTS OF ACID RAIN

Acid rain falling over most of the world has little environmental effect on the biosphere because it is rapidly neutralized after it falls. In particular, acid rain falling over the oceans is rapidly neutralized by the large supply of CO_3^{2-} ions (chapter 6). Acid rain falling over regions with alkaline soils or rocks is quickly neutralized by reactions such as *(R9)* taking place once the acid has deposited to the surface. Only in continental areas with little acid-neutralizing capacity is the biosphere sensitive to acid rain. Over North America these areas include New England, eastern Canada, and mountainous regions, which have granitic bedrock and thin soils (Figure 13-2).
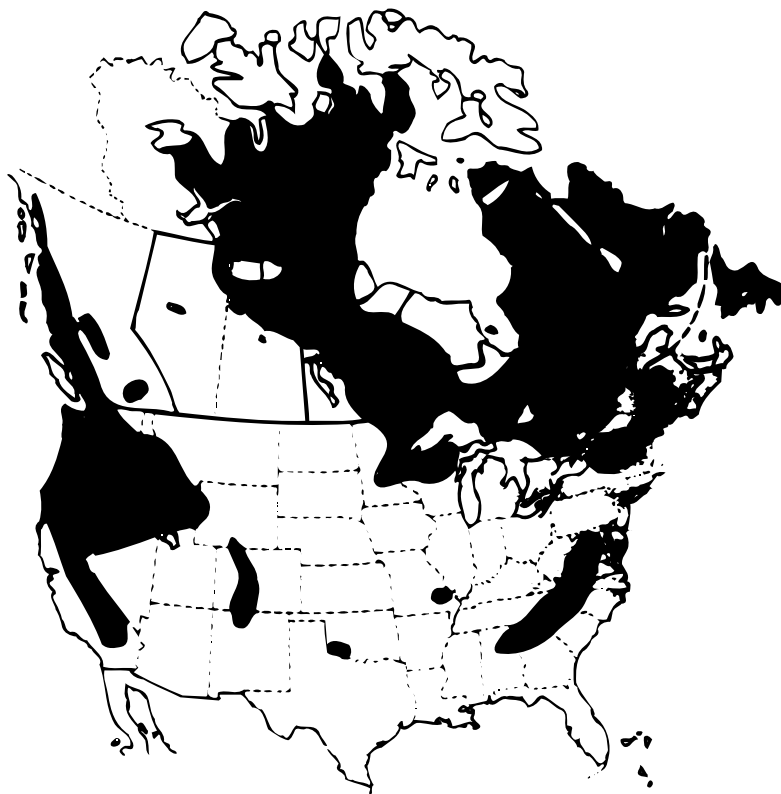

Figure 13-2 Regions of North America with low soil alkalinity to neutralize acid rain.

In areas where the biosphere is sensitive to acid rain, there has been ample evidence of the negative effects of acid rain on freshwater ecosystems. Elevated acidity in a lake or river is directly harmful to fish because it corrodes the organic gill material and attacks the calcium carbonate skeleton. In addition, the acidity dissolves toxic

metals such as aluminum from the sediments. There is also ample evidence that acid rain is harmful to terrestrial vegetation, mostly because it leaches nutrients such as potassium and allows them to exit the ecosystem by runoff. Although NH_3 in the atmosphere neutralizes rain acidity by formation of NH_4^+, this acidity may be recovered in soil when NH_4^+ is assimilated into the biosphere as NH_3 or goes through the microbial nitrification process (section 6.3):

$$NH_4^+ + 2O_2 \quad \overset{microbes}{\rightarrow} \quad NO_3^- + 2H^+ + H_2O$$

(R17)
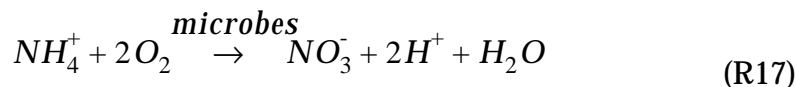
The benefit of neutralizing acid rain by NH_3 may therefore be illusory.

Beyond the input of acidity, deposition of NH_4^+ and NO_3^- *fertilizes* ecosystems by providing a source of directly assimilable nitrogen (section 6.3). This source has been blamed as an important contributor to the *eutrophication* (excess fertilization) of the Chesapeake Bay; a consequence of this eutrophication is the accumulation of algae at the surface of the bay, suppressing the supply of O_2 to the deep-water biosphere. Recent studies of terrestrial ecosystems in the United States show that increases in NH_4^+ and NO_3^- deposition do not stimulate growth of vegetation but lead instead to accumulation of organic nitrogen in soil. The long-term implications of this nitrogen storage in soil are unclear.

13.4 EMISSION TRENDS

Emissions of SO_2 and NO_x in the United States and other industrial countries have increased considerably over the past century due to fossil fuel combustion. Since 1970, however, emissions in the United States and Europe have leveled off due to pollution control efforts. Emissions of SO_2 in the United States have decreased by 25% since 1970, while NO_x emissions have remained flat. Technology for SO_2 emission control is expensive but readily available (scrubbers on combustion stacks, sulfur recovery during oil refining). The control of SO_2 emissions in the United States was initially motivated by the air quality standard for SO_2 (SO_2 is a toxic gas) rather than by concern over acid rain; the original Clean Air Act of 1970 did not include acid rain under its purview. The

revised Clean Air Act, which now targets acid rain, mandates a further decrease by a factor of 2 in SO_2 emissions from the United States over the next decade. Similar steps to further decrease SO_2 emissions in the future are being taken in European countries. By contrast, SO_2 emissions in eastern Asia are on a rapid rise fueled in large part by the industrialization of China and India relying on coal combustion as a source of energy. A serious acid rain problem may develop over eastern Asia in the decades ahead.

In the United States, the SO_2 control measures to be achieved under the revised Clean Air Act will provide significant environmental relief over the next decades but cannot be expected to solve the acid rain problem. First, current forecasts indicate little decrease in NO_x emissions over the next decade. Second, a reduction of acid levels by a factor of 2 is not enough to make rain innocuous to the biosphere (note that decreasing $[H^+]$ by a factor of 2 increases the pH by only 0.3 units). Third, acid rain is in part a cumulative problem; as the acid-neutralizing capacity of soils gets depleted the ecosystems become increasingly sensitive to additional acid inputs.

Recently, there has been considerable interest in the possibility that reductions of SO_2 emissions to combat the acid rain problem might have negative side effects on climate. As discussed in section 8.2.3, there is evidence that anthropogenic sulfate aerosol at northern midlatitudes has caused regional cooling, perhaps compensating in a complicated way for the effect of greenhouse warming. Could reductions in SO_2 emissions expose us to the full force of global warming? This is an interesting research question which should not, however, discourage us from going ahead with SO_2 emission reductions. We do not understand climate well enough to play with radiative forcing effects of opposite sign and hope that they cancel each other.