**PROBLEMS**

13.1 What goes up must come down

1. The United States presently emit to the atmosphere $1.3 \times 10^9$ moles day$^{-1}$ of NO$_x$ and $1.0 \times 10^9$ moles day$^{-1}$ of SO$_2$. We assume that all of the emitted NO$_x$ and SO$_2$ are precipitated back over the United States as HNO$_3$ and H$_2$SO$_4$, respectively (this is not a bad approximation). The area of the United States is $1.0 \times 10^7$ km$^2$ and the mean precipitation rate is 2 mm day$^{-1}$. Assuming that HNO$_3$ and H$_2$SO$_4$ are the only impurities in the rain, show that the resulting mean pH of precipitation over the United States is 3.8.

2. What is the actual range of rainwater pH values over the United States? Explain your overestimate of rainwater acidity in question 1.

13.2 The true acidity of rain

The pH of rain reported by monitoring agencies is based on analysis of rain samples collected weekly in buckets. The weekly collection schedule is fine for HNO$_3$ and H$_2$SO$_4$, which do not degrade; however, formic acid (HCOOH) is rapidly consumed by bacteria in the buckets and therefore escapes analysis. The Henry’s law and acid dissociation equilibria for HCOOH are

\[
HCOOH(g) \rightleftharpoons HCOOH(aq) \quad K_H = 3.7 \times 10^3 \text{ M atm}^{-1}
\]

\[
HCOOH(aq) \rightleftharpoons HCOO^- + H^+ \quad K_1 = 1.8 \times 10^{-4} \text{ M}
\]

If the monitoring agency reports a rainwater pH of 4.7, calculate the true pH of the rain. Assume 1 ppbv HCOOH in the atmosphere (a typical value for the eastern United States).

[To know more: Keene, W. C., and J. N. Galloway, The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding, Tellus, 40B, 322-334, 1988.]

13.3 Aqueous-phase oxidation of SO$_2$ by ozone

A pathway for production of H$_2$SO$_4$ in clouds is by dissolution of SO$_2$ in cloud droplets followed by reaction of SO$_3^{2-}$ with O$_3(aq)$:

\[
SO_3^{2-} + O_3(aq) \rightarrow SO_4^{2-} + O_2(aq) \quad (1)
\]

with rate constant $k_1 = 1.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. Relevant equilibria are

\[
SO_2(g) \rightleftharpoons SO_2 \cdot H_2O \quad (2)
\]
with equilibrium constants $K_2 = 1.2 \text{ M atm}^{-1}$, $K_3 = 1.3 \times 10^{-2} \text{ M}$, $K_4 = 6.3 \times 10^{-8} \text{ M}$, $K_5 = 1.1 \times 10^{-2} \text{ M atm}^{-1}$.

1. Explain how reaction (1) increases the acidity of the droplet even though $H^+$ does not appear as an explicit product of the reaction.

2. For an atmosphere containing 1 ppbv $SO_2$ and 50 ppbv $O_3$, calculate the rate of sulfate production by reaction (1) as a function of $[H^+]$. Can this reaction be a significant contributor to acid rain?


### 13.4 The acid fog problem

The southern San Joaquin Valley of California experiences extended stagnation episodes in winter due to strong and persistent subsidence inversions. These stagnation episodes are often accompanied by thick valley fogs. We use here a box model to describe the valley air during such a foggy stagnation episode. The top of the box is defined by the base of the inversion, 400 m above the valley floor. We assume no ventilation out of the box. The temperature in the box is 273 K.

1. The major sources of air pollution in the valley are steam generators for oil recovery, emitting $SO_2$ with a mean flux $E = 4 \times 10^2 \text{ moles km}^{-2} \text{ day}^{-1}$. This $SO_2$ is removed from the valley air by deposition to the surface (first-order rate constant $k_d = 0.5 \text{ day}^{-1}$) and by oxidation to $H_2SO_4$ (first-order rate constant $k_o = 1 \text{ day}^{-1}$). Calculate the steady state $SO_2$ concentration in the valley in units of ppbv. Compare to the EPA air quality standards of 140 ppbv for 1-day exposure and 30 ppbv for 1-year exposure.

2. Sulfuric acid produced from $SO_2$ oxidation in the valley air is incorporated immediately into the fog droplets. These fog droplets are then removed from the valley air by deposition with a first-order rate constant $k'_d = 2 \text{ day}^{-1}$. The liquid water content of the fog is $1 \times 10^{-4} \text{ l water per m}^3 \text{ of air}$. Calculate the steady state fogwater pH if $H_2SO_4$ is the only substance dissolved in the fog droplets.

3. In fact, the valley also contains large sources of ammonia from livestock and fertilized agriculture. The $NH_3$ emission flux is estimated to be $5.6 \times 10^2 \text{ moles km}^{-2} \text{ day}^{-1}$. Is it enough to totally neutralize the $H_2SO_4$ produced from $SO_2$ emissions?

[To know more: Jacob, D.J., et al., Chemistry of a polluted cloudy boundary layer, *J. Geophys. Res.*, 94, 12,975-13,002, 1989.]
13.5 Acid rain: the preindustrial atmosphere

This problem examines the acidity of rain in the preindustrial atmosphere. Make use of the following equilibria:

\[ \text{CO}_2(g) \Leftrightarrow \text{CO}_2 \cdot \text{H}_2\text{O} \]  
(1)  

\[ \text{CO}_2 \cdot \text{H}_2\text{O} \Leftrightarrow \text{HCO}_3^- + \text{H}^+ \]  
(2)  

\[ \text{HCOOH}(g) \Leftrightarrow \text{HCOOH}(aq) \]  
(3)  

\[ \text{HCOOH}(aq) \Leftrightarrow \text{HCOO}^- + \text{H}^+ \]  
(4)  

\[ \text{CH}_3\text{COOH}(g) \Leftrightarrow \text{CH}_3\text{COOH}(aq) \]  
(5)  

\[ \text{CH}_3\text{COOH}(aq) \Leftrightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \]  
(6)

with equilibrium constants \( K_1 = 3.0 \times 10^{-2} \) M atm\(^{-1} \), \( K_2 = 4.2 \times 10^{-7} \) M, \( K_3 = 3.7 \times 10^{3} \) M atm\(^{-1} \), \( K_4 = 1.8 \times 10^{-4} \) M, \( K_5 = 8.8 \times 10^{3} \) M atm\(^{-1} \), \( K_6 = 1.7 \times 10^{-5} \) M.

1. The preindustrial atmosphere contained 280 ppmv CO\(_2\). Calculate the pH of the rain at equilibrium with this concentration of CO\(_2\).

2. The preindustrial atmosphere also contained organic acids emitted from vegetation, in particular formic acid (HCOOH) and acetic acid (CH\(_3\)COOH). Calculate the pH of the rain at equilibrium with 0.1 ppbv HCOOH(g), 0.1 ppbv CH\(_3\)COOH(g), and 280 ppmv CO\(_2\)(g). Which of CO\(_2\), HCOOH, or CH\(_3\)COOH is the most important source of rain acidity?

3. The preindustrial atmosphere also contained sulfur compounds emitted by marine plankton and volcanoes, and NO\(_x\) emitted by soils and lightning. These sources amounted globally to 1x10\(^{12}\) moles S yr\(^{-1}\) and 1x10\(^{12}\) moles N yr\(^{-1}\), respectively. Assume that all the emitted sulfur and NO\(_x\) are oxidized in the atmosphere to H\(_2\)SO\(_4\) and HNO\(_3\), respectively, which are then scavenged by rain.

3.1. Calculate the mean concentrations (M) of SO\(_4^{2-}\) and NO\(_3^-\) in the rain, assuming a global mean precipitation rate over the Earth of 2 mm day\(^{-1}\).

3.2. Calculate the resulting rainwater pH (again assuming equilibrium with 0.1 ppbv HCOOH(g), 0.1 ppbv CH\(_3\)COOH(g), and 280 ppmv CO\(_2\)(g)). Of all the acids in the preindustrial atmosphere, which one was the most important source of rainwater acidity?