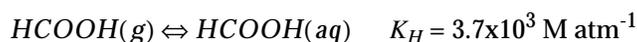## *PROBLEMS*

13. 1 What goes up must come down

1. The United States presently emit to the atmosphere 1.3×10^9 moles day^{-1} of NO_x and 1.0×10^9 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_2SO_4, respectively (this is not a bad approximation). The area of the United States is 1.0×10^7 km^2 and the mean precipitation rate is 2 mm day^{-1}. Assuming that HNO_3 and H_2SO_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_2SO_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

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

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

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_2SO_4 in clouds is by dissolution of SO_2 in cloud droplets followed by reaction of SO_3^{2-} with O_3(aq):

$$SO_3^{2-} + O_3(aq) \rightarrow SO_4^{2-} + O_2(aq) \tag{1}$$
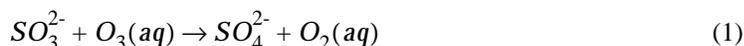
with rate constant $k_1 = 1.0 \times 10^9$ M^{-1} s^{-1}. Relevant equilibria are

$$SO_2(g) \Leftrightarrow SO_2 \cdot H_2O \tag{2}$$

$$SO_2 \cdot H_2O \Leftrightarrow HSO_3^- + H^+ \tag{3}$$

$$HSO_3^- \Leftrightarrow SO_3^{2-} + H^+ \tag{4}$$

$$O_3(g) \Leftrightarrow O_3(aq) \tag{5}$$

with equilibrium constants $K_2 = 1.2$ M atm^{-1}, $K_3 = 1.3 \times 10^{-2}$ M, $K_4 = 6.3 \times 10^{-8}$ M, $K_5 = 1.1 \times 10^{-2}$ 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?

[To know more: Hoffmann, M.R., On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone, *Atmos. Environ., 20,* 1145-1154, 1986.]

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 epsiodes 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 $E = 4 \times 10^2$ moles km^{-2} day^{-1}. This SO$_2$ is removed from the valley air by deposition to the surface (first-order rate constant $k_d = 0.5$ day^{-1}) and by oxidation to H$_2$SO$_4$ (first-order rate constant $k_o = 1$ 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.
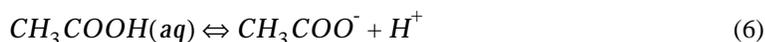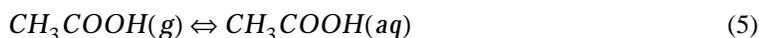
2. Sulfuric acid produced from SO$_2$ oxidation in the valley air is incorporated immediately into the fog droplets. These fog droplets are then removed from the valley air by deposition with a first-order rate constant $k'_d = 2$ day^{-1}. The liquid water content of the fog is 1×10^{-4} l water per m^3 of air. Calculate the steady state fogwater pH if H$_2$SO$_4$ 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 5.6×10^2 moles km^{-2} day^{-1}. Is it enough to totally neutralize the H$_2$SO$_4$ 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:

$$CO_2(g) \Leftrightarrow CO_2 \cdot H_2O \qquad (1)$$

$$CO_2 \cdot H_2O \Leftrightarrow HCO_3^- + H^+ \qquad (2)$$

$$HCOOH(g) \Leftrightarrow HCOOH(aq) \qquad (3)$$

$$HCOOH(aq) \Leftrightarrow HCOO^- + H^+ \qquad (4)$$

$$CH_3COOH(g) \Leftrightarrow CH_3COOH(aq) \qquad (5)$$

$$CH_3COOH(aq) \Leftrightarrow CH_3COO^- + H^+ \qquad (6)$$

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_3COOH). Calculate the pH of the rain at equilibrium with 0.1 ppbv HCOOH(g), 0.1 ppbv CH_3COOH(g), and 280 ppmv CO_2(g). Which of CO_2, HCOOH, or CH_3COOH is the most important source of rain acidity?

3. The preindustrial atmosphere also contained sulfur compunds emitted by marine plankton and volcanoes, and NO_x emitted by soils and lightning. These sources amounted globally to 1×10^{12} moles S yr^{-1} and 1×10^{12} moles N yr^{-1}, respectively.   Assume that all the emitted sulfur and NO_x are oxidized in the atmosphere to H_2SO_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_3COOH(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?

[To know more: Galloway, J.N., et al., The composition of precipitation in remote areas of the world, *J. Geophys, Res, 87*, 8771,1982.]