

AT 621 F 12
Homework #7
Due Friday, 16 November

Problem 1.

Problem 7.1 from Seinfeld and Pandis (pH of rainwater due to CO₂).

Problem 2.

Problem 13.1 from Jacob (pH of acid rain), as follows:

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 SO₂. We assume that all of the emitted NO_x and SO₂ are precipitated back over the United States as HNO₃ and H₂SO₄, respectively (this is not a bad approximation). The area of the United States is 1.0×10^7 km² and the mean precipitation rate is 2 mm day⁻¹. Assuming that HNO₃ and H₂SO₄ 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 overestimation of rainwater acidity in part 1.

Problem 3.

Consider a situation where sulfur dioxide is being oxidized to sulfuric acid in a foggy boundary layer. Assume that hydroxyl radical is the only important oxidant in the gas phase and ozone is the only important oxidant inside the cloud drops. The fog has a liquid water content of 0.1 g m⁻³ and its pH is buffered at 6.0. The boundary layer is capped by an inversion 200 m above the surface. Fog extends from the surface up to the top of the boundary layer. You may assume the pressure and temperature throughout the boundary layer are approximately 1 atm and 298 K, respectively. The mixing ratio of sulfur dioxide in the gas phase remains at a constant, steady-state value of 1 ppbv. The gas phase ozone mixing ratio is constant at 10 ppbv. The gas phase hydroxyl concentration is 10⁶ molecules cm⁻³.

(a) Calculate the rate of sulfate production in the fog drops (**M s⁻¹**).

(b) What rate of emission of sulfur dioxide into the boundary layer is required to balance the total rate of sulfur oxidation (in the gas and aqueous phases) and keep the gas phase sulfur dioxide mixing ratio constant at 1 ppbv?

Problem 4.

Get an expression for the effective Henry's law constant for NH₃ as a function of pH. Make a plot similar to figure 7.6 showing the effective Henry's law constant as a function of pH and make an additional plot similar to figure 7.8 showing the fraction of total dissolved NH₃ as a function of pH. (figures from Seinfeld and Pandis)