CEE 550, Spring 2006, HW #3

1. (a) A volumetric flask is filled with 1.0 L of distilled water and is closed. Air occupies the 20 mL of headspace between the water surface and the plug. Determine the values of the following parameters for each of two scenarios – one in which oxygen and nitrogen reach redox equilibrium in the solution, and another (more realistic) one in which neither oxygen nor nitrogen undergoes redox reactions:

(i) the solution pH
(ii) the concentrations of dissolved O₂, N₂, and TOTCO₃
(iii) the partial pressures of the three gases in the headspace

(b) One liter of 10⁻² m NaOH is left stirring on a bench-top. Assuming that neither oxygen nor nitrogen undergoes redox reactions in the system, what is the solution composition once it reaches equilibrium with the atmosphere? What volume of gas (at STP) has dissolved? What proportions of this volume are accounted for by N₂, O₂, and CO₂? What volume of air is needed to provide the amount of CO₂ that dissolves?

2. Near the sediment/water interface of many lakes, low-pe water from deeper in the sediments can mix with more oxidized diffusing down from the bulk solution. Consider two such end-member solutions. The more reduced water contains 3 x 10⁻⁴ m TOTS(6), 5 x 10⁻⁴ m TOTS(−2), 2 x 10⁻⁴ m TOTN(−3), and 1.5 x 10⁻⁴ m TOTFe. The measured pe of the water is −1, and the pH is 7.4. The speciation of Fe in this water is controlled by the S(6)/S(−2) couple. The more oxidized water contains 1 mg/L dissolved O₂(aq), 1.3 x 10⁻³ m TOTS(6), 10⁻⁴ m TOTN(5), and negligible Fe, and is at pH 7.0. Although the measured pe is 8.0, the redox state of the water is controlled by the O(0)/O(−2) couple. Both solutions contain 2 x 10⁻³ TOTC(4).

(a) Determine the speciation of Fe in the reduced water.

(b) How well does the measured pe match the expectation based on S speciation?

(c) The redox reactions of N in the reduced water are thought to be able to convert the N among the +5, +3, and −3 oxidation states, but not the 0 oxidation state. Assuming that, like Fe, the N redox speciation is controlled by the S(6)/S(−2) couple, test the assumption that N(+3) and N(+5) species are negligible.

(d) Determine the composition of solutions that are generated when the two waters are mixed in ratios of such that the reduced solution accounts for 80%, 50%, 20%, 5%, and 2% of the mixture. Allow Fe(OH)₃(s) to precipitate if it is supersaturated. Discuss the trends in system composition as the mixing ratio gradually favors the oxidized solution.