Revised Homework Assignment 2
CE 59700 008, Fall 2009

1. Aqueous free chlorine is hypochlorous acid, HOCl, and hypochlorite ion, OCl^-, with the relative amounts depending on the pH of the solution.

   (a) Given that $pK_a = 7.5$ for HOCl at 25°C, what is the pH of a solution prepared by adding 10^{-3} mole of NaOCl to 1 liter of water?
   (b) What is the pH at which 50 percent of the total free chlorine is present as HOCl?
   (c) What is the pK_b for OCl^- and to what reaction does this constant apply? Neglect ionic strength effects; temperature = 25°C.

2. What is the pH of a 25°C solution containing 10^{-3} moles $NaHCO_3$ per liter if $\mu \approx 0$?

3. What is the pH of a 25°C solution containing 2×10^{-3} mole NH_3 per liter if $\mu \approx 0$?

4. Henry's constant, K_H, for the following equilibrium reaction is 0.1 M atm^{-1}:

$$K_H = \frac{[H_2S]_{aq}}{P_{H_2S}}$$

   Calculate

   (a) The partial pressure (in atm) of $H_2S_{(g)}$ overlying the water if the total soluble sulfide concentration, $C_{T,S} = [H_2S_{(ag)}] + [HS^-] + [S^{2-}]$, is 1 x 10^{-3} *M* and the solution pH is 8.5. Assume that the gas is in equilibrium with the water. ($K_{a,1} = 10^{-7}$ and $K_{a,2} = 10^{-14}$ for H_2S where $K_{a,1}$ is the equilibrium constant for $H_2S_{(ag)} = HS^- + H^+$ and $K_{a,2}$ is the equilibrium constant for $HS^- = S^2 + H^+$.)
   (b) RT converts gas phase partial pressure into gas phase mole/L units. For the species H_2S, calculate the dimensionless Henry's constant, H (mol/L water)/(mol/L gas) if $H = K_H RT$, where, R = 0.08206 atm / (K mol/L), and T = 298 K. If there is 1 Liter of gas above the solution, how many moles of H_2S are in the 1 L gas. (Note: acid dissociation does not occur in the gas phase.)

5. (a) Draw a logarithmic concentration diagram for a 10^{-2} *M* solution of hydrogen sulfide.
   (b) From the diagram, determine the pH for solutions which contain the following (1) 10^{-2} *M* H_2S, (2) 10^{-2} *M* Na_2S. Use $pK_{a1} = 7.0$ (for H_2S) and $pK_{a2} = 14$ (for HS^-).

   Do not do these problems for now. We will return to them.

6. Consider a water in equilibrium with $Ca_3(PO_4)_2(c)$. Assume there are no other solids and no complexes. Develop an equation that will allow you to solve for the pH of this water; that is, your equation will have only one unknown, $[H^+]$. Solve this equation for equilibrium pH by trial and error. *Answer:* pH = 9.59

7. An industrial wastewater is to be discharged to a receiving stream with a pH of 8.3 and a total alkalinity = 2 x 10^{-3} eq/liter. The wastewater contains 5 x 10^{-3} *M* H_2SO_4, and the pH of the stream should not be permitted to drop below 6.3.
   (a) What is the maximum dilution ratio (volume waste/volume stream water) that can be used for discharge of the wastewater?
   (b) What is the buffer intensity of the solution at pH 6.3?