CEE 543 Aut 2012 HW#3

1. The Boeing Co. has developed a process for removing copper from wastewaters generated during electroplating and printed-circuit board manufacturing. The central feature of the process is addition of scrap aluminum metal to an acidic solution containing dissolved copper ions. If the solution contains enough fluoride or chloride ions, a reaction proceeds in which the aluminum dissolves and the copper precipitates as metallic Cu(*s*), which can then be removed from the suspension by settling and/or filtration. The relevant reaction can be written as follows:

$$3Cu^{2+} + 2Al^{o}(s) \rightleftharpoons 3Cu(s) + 2Al^{3+}$$

Standard Gibbs energies of formation of the ionic species in the above reaction are $\overline{G}^{o}_{f,Cu^{2+}}$ = 65.5 kJ/mol and $\overline{G}^{o}_{f,Al^{3+}}$ = –489.4 kJ/mol. If a wastewater initially containing 300 mg/L Cu^{2+} and no dissolved aluminum is dosed with 100 mg/L of Al scraps, and the above reaction proceeds until equilibrium is reached, what will the final concentrations of Cu^{2+}, Al^{3+}, $Cu^{o}(s)$, and $Al^{o}(s)$ be?

2. Citric acid, HOOC—CH_2—C(OH)(COOH)—CH_2—COOH, which we can abbreviate as H_3Cit, is a triprotic carboxylic acid with acidity constants pK_{a1} = 3.13, pK_{a2} = 4.76, and pK_{a3} = 6.40.

a. Consider a solution made by adding lemon juice to water until the pH of the solution is 2.20. Assuming all the acidity is from dissociation of citric acid, find the total concentration of citrate species, i.e., *TOT*Cit, and the concentration of $HCit^{2-}$.

b. The solution in part (*a*) is diluted l:10 and partly neutralized by addition of sodium bicarbonate ($NaHCO_3$). Designating the total concentration of carbonate species added as $TOTCO_3$, write out all the equations necessary to compute the new pH. You need not solve the equations.

c. If the final pH of the solution in part *b* is 6.0, what is the ratio of $\{HCO_3^-\}$ to $\{H_2CO_3\}$ in the solution? What is the ratio of $\{CO_3^{2-}\}$ to $\{H_2CO_3\}$? Would these ratios change if the pH were still 6.0, but *TOT*Cit were doubled?

3. Cyanide ion, CN^-, is important in metal plating industries because it can keep metals dissolved under conditions where they would otherwise form solids (precipitate) and settle out of solution. The details of how this occurs are presented in Chapter 9. It is important to maintain pH > 10.5 in these solutions to avoid forming toxic hydrogen cyanide gas. If a solution is prepared by dissolving 10^{-2} *M* NaCN in water, will the pH be in the region where the solution is safe? What is the HCN concentration in the solution?

4. Consider an acid H_2A, with pK_{a1} = 5.5 and pK_{a2} = 9.5, in a solution of 10^{-2} *M TOT*A.

a. At what pH or in what pH range (if any) will the following conditions be met?

i. The activity of A^{2-} increases by approximately a factor of 100 for every increase of one pH unit.

ii. The activity of HA^- decreases by approximately a factor of 10 for every increase of one pH unit.

iii. The activity of H_2A increases by approximately a factor of 10 for every increase of one pH unit.

iv. The ratio $\{H_2A\}/\{A^{2-}\}$ decreases by approximately a factor of 100 for every increase of one pH unit.

v. The value of p$\{HA^-\}$ is approximately 2.3.

vi. The value of p$\{H_2A\}$ is approximately 4.0.

b. What is the pH of a solution of 0.005 *M* H_2A + 0.005 *M* NaHA?

c. What is the pH of a solution of 0.005 *M* H_2A + 0.005 *M* Na_2A?

d. Will a solution of 0.01 *M* NaHA be acidic, neutral, or alkaline?

e. Write the equilibrium equation and the form and the value of K_b for the base HA^-.