Problems Set #4

1. For the following galvanic cells, calculate the cell voltage at 25°C, identify the anode, write a balanced equation for the overall cell reaction, and indicate the direction of the spontaneous reaction.

   a) \( \text{Pt} | \text{VO}_2^+ (1.0 \times 10^{-2} \text{M}), \text{VO}^{2+}(1.0 \times 10^{-3} \text{M}), \text{H}^+ (1.0 \times 10^{-4} \text{M}) || \text{Fe}^{3+}(0.10 \text{M}), \text{Fe}^{2+}(1.0 \times 10^{-3} \text{M}) | \text{Pt} \)

   \[
   (\text{VO}_2^+ + 2\text{H}^+ + e^- = \text{VO}^{2+} + \text{H}_2\text{O} \quad E^0 = +1.00 \text{ V.})
   \]

   \[
   \text{Fe}^{3+} + e^- = \text{Fe}^{2+} \quad E^0 = +0.77 \text{ V.}
   \]

   b) \( \text{Sb} | \text{SbO}^+ (5.0 \times 10^{-2} \text{M}), \text{H}^+ (1.0 \times 10^{-2} \text{M}) || \text{Pb}^{2+}(1.0 \times 10^{-4} \text{M}) | \text{Pb} \)

   \[
   (\text{SbO}^+ + 2\text{H}^+ + 3e^- = \text{Sb(s)} + \text{H}_2\text{O} \quad E^0 = +0.212 \text{ V.})
   \]

   \[
   \text{Pb}^{2+} + 2e^- = \text{Pb(s)} \quad E^0 = -0.126 \text{ V.}
   \]

2. Calculate the solubility product for AgCl from the following data:

   \[
   \text{Ag}^+ + e^- = \text{Ag(s)} \quad E^0 = +0.799 \text{ V.}
   \]

   \[
   \text{AgCl(s)} + e^- = \text{Ag(s)} + \text{Cl}^- \quad E^0 = +0.222 \text{ V.}
   \]

   Hint: Construct the galvanic cell: \( \text{Ag} | \text{Ag}^+ || \text{Cl}^- | \text{AgCl} | \text{Ag} \) and relate its \( E(\text{cell}) \) to the equilibrium constant for the cell reaction.

3. Given the following half-reaction:

   \[
   \text{Sn}^{2+} + 2e^- = \text{Sn(s)} \quad E^0 = -1.36 \text{ V;} \quad \text{Pb}^{2+} + 2e^- = \text{Pb(s)} \quad E^0 = -0.126 \text{ V},
   \]

   calculate the equilibrium constant for the reaction:

   \[
   \text{Sn(s)} + \text{Pb}^{2+} = \text{Sn}^{2+} + \text{Pb(s)}
   \]
4. The voltage of the cell $\text{Zn(s)|Zn}^{2+}(\text{xM})||\text{Cu}^{2+}(0.1\text{M})|\text{Cu(s)}$ was measured to be 1.150 V. Calculate the $\text{Zn}^{2+}$ concentration.

5. The following cell was used to determine the formation constant of the complex $\text{Cd(CN)}_4^{2-}$. (The formation constant is the equilibrium constant for the reaction $\text{Cd}^{2+} + 4\text{CN}^- = \text{Cd(CN)}_4^{2-}$.)

$$\text{Cd|Cd(CN)}_4^{2-}(8.0 \times 10^{-2}\text{M}), \text{CN}^-(0.10\text{M})||\text{H}^+(1.0\text{M})|\text{H}_2(1\text{ atm}), \text{Pt}$$

If the measured cell potential was +0.873 V, what is the formation constant?

6. a) Calculate the standard electrode potential for the half-reaction

$$\text{CuBr(s) + e}^- = \text{Cu(s) + Br}^-$$

b) Write a schematic representation of a cell with a Cu indicator electrode and an SCE that could be used to determine the $\text{Br}^-$ concentration in an unknown solution.

c) Derive an equation relating the measured potential of the cell in b) to $\text{Br}^-$ concentration.