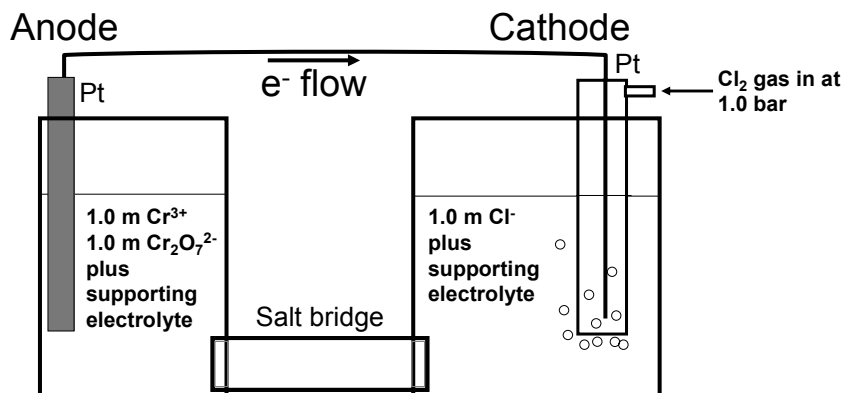


CHEM 121
Spring 2006
Quiz 10

Name: _____

1. Consider the unbalanced overall redox reaction $\text{Cr}^{3+}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{Cl}^-(\text{aq})$.

a. (6 Points) Sketch the galvanic cell based on this reaction. Assume standard conditions. Label the cathode and anode and indicate what each is made of. Indicate what is in each of the solutions.



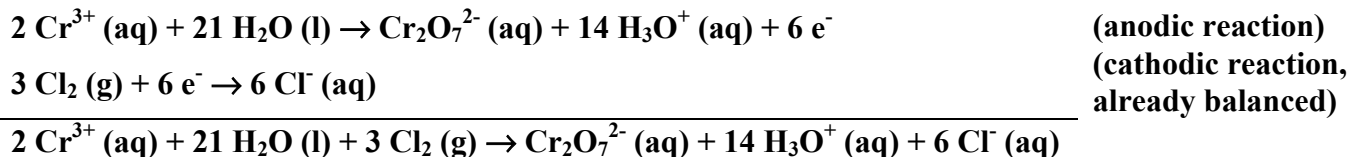
Cr^{3+} is oxidized to $\text{Cr}_2\text{O}_7^{2-}$ (note that the oxidation number of Cr in $\text{Cr}_2\text{O}_7^{2-}$ is +6), and so this is the reaction that takes place at the anode.

Cl_2 is reduced to Cl^- (the oxidation number of Cl changes from 0 in Cl_2 to -1 in Cl^-) and this must take place at the cathode.

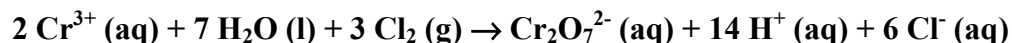
Neither electrode participates in the redox reaction directly. So, they can be any inert substance (e. g., Pt).

The supporting electrolytes in each half cell are not indicated. For the cathodic half cell it could be something like NaNO_3 (it can't be Cl^- because it is part of the redox reaction) and for the anodic cell it could be HNO_3 (we need acid in this half cell, see part b).

b. (4 Points) Using the attached table of standard reduction potentials, balance the reaction and determine E^0 for this cell.



If you wrote H_3O^+ as H^+ you would have found the balanced chemical equation to be



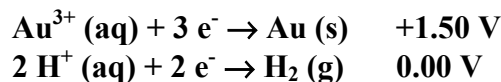
The cell potential is

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = +1.360 \text{ V} - +1.33 \text{ V} = +0.03 \text{ V}$$

The cell potential under standard conditions is +0.03 V.

2. (5 Points) Will gold dissolve in acid? Explain using standard reduction potentials.

The standard reduction potentials are

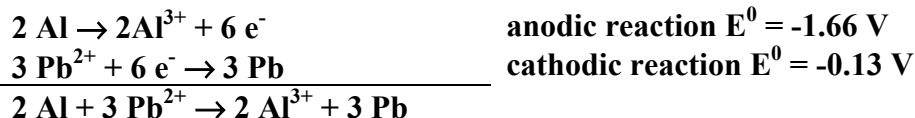


The direction of spontaneous change is for Au^{3+} to be reduced to Au metal (and hence H_2 to be oxidized). The reverse reaction corresponding to Au dissolving in acid to give Au^{3+} is not spontaneous. Therefore, gold will not dissolve in acid.

3. (10 Points) Consider the cell $\text{Al} | \text{Al}^{3+} (1.00 \text{ M}) || \text{Pb}^{2+} (1.00 \text{ M}) | \text{Pb}$. Calculate the cell potential after the reaction has run long enough at $25.0 \text{ }^\circ\text{C}$ for the $[\text{Al}^{3+}]$ to change by 0.60 M . You are given that the half reaction $\text{Pb}^{2+} + 2 \text{e}^- \rightarrow \text{Pb} (\text{s})$ has $E^0 = -0.13 \text{ V}$, the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln Q \quad \text{where } R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1} \text{ and } F = 96485 \text{ C}\cdot\text{mole}^{-1}.$$

The half reactions are as follows. Note these are already balanced for number of electrons lost and gained.



The cell potential is

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = -0.13 \text{ V} - -1.66 \text{ V} = +1.53 \text{ V}$$

Write the Nernst equation that describes this process.

$$E = E^0 - \frac{RT}{nF} \ln Q = +1.53 \text{ V} - \frac{RT}{6F} \ln \left(\frac{[\text{Al}^{3+}]^2}{[\text{Pb}^{2+}]^3} \right)$$

Determine the concentration of Al^{3+} and Pb^{2+} .

Since we know that the $[\text{Al}^{3+}]$ has changed by 0.60 M, and that it went up (it is the product of the reaction), we know that the $[\text{Al}^{3+}]$ is now 1.60 M.

The change in the $[\text{Pb}^{2+}]$ is calculated as follows.

$$\left(\frac{0.60 \text{ mole Al}^{3+}}{1 \text{ L}} \right) \left(\frac{3 \text{ mole Pb}^{2+}}{2 \text{ mole Al}^{3+}} \right) = 0.90 \text{ M Pb}^{2+}$$

Since the initial $[\text{Pb}^{2+}]$ was 1.00 M, the $[\text{Pb}^{2+}]$ is now 0.10 M.

Substitute all known quantities into the Nernst equation and solve for E.

$$E = +1.53 \text{ V} - \frac{(8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})}{6(96485 \text{ C} \cdot \text{mole}^{-1})} \ln \left(\frac{(1.60)^2}{(0.10)^3} \right)$$

$$E = +1.53 \text{ V} - (4.282_1 \times 10^{-3} \text{ V}) \ln \left(\frac{2.56}{1.0 \times 10^{-3}} \right)$$

$$E = +1.53 \text{ V} - (4.282_1 \times 10^{-3} \text{ V}) \ln(2.5_6 \times 10^3)$$

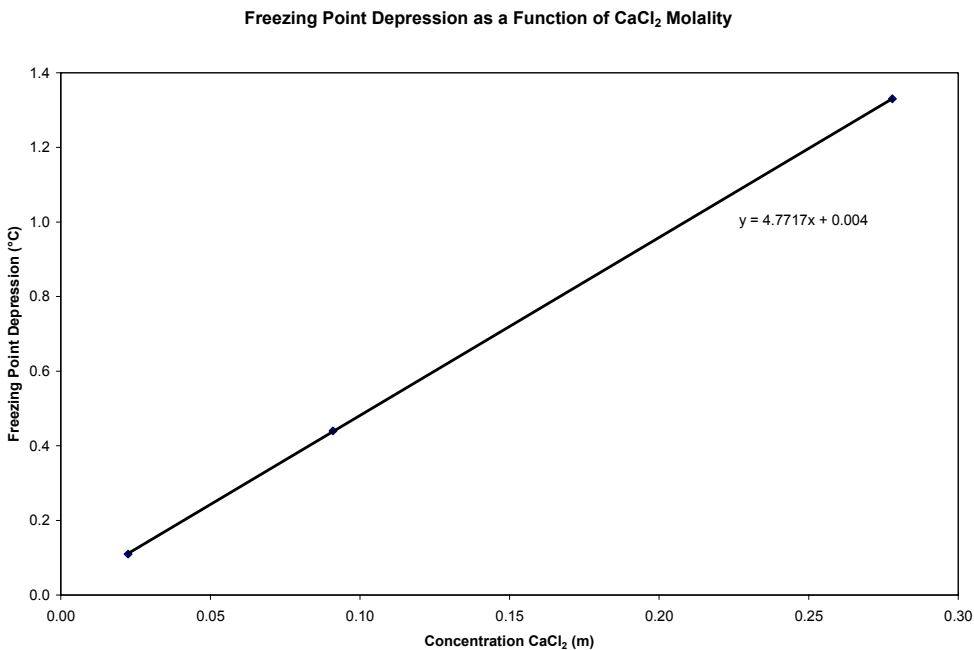
$$E = +1.53 \text{ V} - (4.282_1 \times 10^{-3} \text{ V})(7.84_7)$$

$$E = +1.53 \text{ V} - 0.0336 \text{ V} = +1.50 \text{ V}$$

The cell's potential will be +1.50 V.

4. (5 Points) Attach problem 17-76.

The freezing point depression expression that includes the van't Hoff factor, i , is $\Delta T_f = i \cdot m \cdot K_f$. This expression predicts that a graph of freezing point depression (ΔT_f) as a function of solute molality (m) should yield a straight line with a slope of $i \cdot K_f$ and an intercept of 0. Such a graph of the given data is shown below.



The slope of this line is $4.77_{17} \text{ } ^\circ\text{C} \cdot \text{kg} \cdot \text{mole}^{-1}$. With the known K_f for water of $1.86 \text{ } ^\circ\text{C} \cdot \text{kg} \cdot \text{mole}^{-1}$, we can solve for i giving a value of 2.57.

If CaCl_2 dissociated completely, we would expect the van't Hoff factor to be 3 (three particles for every formula unit). Since it is not, we conclude that some ion pairing has occurred.

5. (10 Points) Attach problem 17-98.

We will use the freezing point depression to find the molality of the solution. This molality will not be the same as we would calculate based on the amount of VCl_4 that we added because of the equilibrium. Since we know the total number of moles of solute present, how many moles of VCl_4 that we started with and the balanced chemical equation, we can determine moles of VCl_4 and V_2Cl_8 present at equilibrium.

Calculate moles of VCl_4 present initially.

$$6.6834 \text{ g } VCl_4 \left(\frac{1 \text{ mole}}{192.75_4 \text{ g}} \right) = 0.034673_2 \text{ mole } VCl_4$$

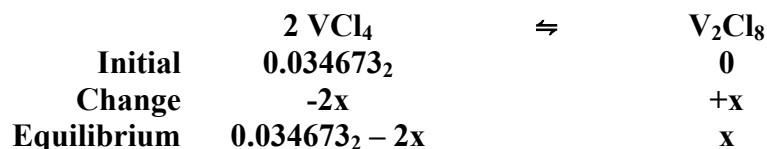
Determine moles of solute present.

$$\Delta T = m \cdot K_f$$

$$m = \frac{K_f}{\Delta T} = \frac{29.8 \text{ }^\circ\text{C} \cdot \text{kg} \cdot \text{mole}^{-1}}{5.97 \text{ }^\circ\text{C}} = 0.200_3 \text{ m}$$

$$0.1000 \text{ kg} \left(\frac{0.200_3 \text{ mole}}{1 \text{ kg}} \right) = 0.0200_3 \text{ mole}$$

Set up the equilibrium table to get an expression for the moles of reactant and product present at equilibrium.



So, the total moles of solute present at equilibrium is

$$0.0200_3 \text{ mole} = \text{mole } VCl_4 + \text{mole } V_2Cl_8 = 0.034673_2 - 2x + x = 0.034673_2 - x$$

$$x = 0.0146_4 \text{ mole}$$

We can't simply substitute moles of each solute into the expression for K ($K = \frac{[V_2Cl_8]}{[VCl_4]^2}$)

because of the square in the denominator. We will need to convert moles per total mass of the solution into a concentration, which we can then use to find K .

$$\text{The total mass of the solution is } 100.0 \text{ g} + 6.6834 \text{ g} = 106.6_8 \text{ g.}$$

From the solution's density, determine the volume.

$$106.6_8 \text{ g} \left(\frac{1 \text{ mL}}{1.696 \text{ g}} \right) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.06290 \text{ L}$$

Now calculate the concentrations.

$$\frac{0.0146_4 \text{ mole V}_2\text{Cl}_8}{0.06290 \text{ L}} = 0.232_7 \text{ M}$$

$$\frac{0.034673_2 - 2(0.0146_4) \text{ mole VCl}_4}{0.06290 \text{ L}} = \frac{0.0053_9 \text{ mole VCl}_4}{0.06290 \text{ L}} = 0.085_7 \text{ M}$$

And finally, find K .

$$K = \frac{[\text{V}_2\text{Cl}_8]}{[\text{VCl}_4]^2} = \frac{0.232_7}{(0.085_7)^2} = 32.$$

The equilibrium constant for this reaction is 32.