

CHM 3400 – Problem Set 7

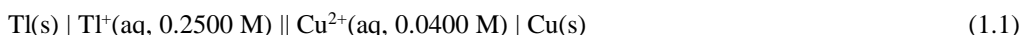
Due date: Monday, March 8<sup>th</sup> (by 11:59pm). Please turn in your homework by sending it to me at my FIU email address joensj@fiu.edu. Indicate in your email that you are sending me your Homework 7 solutions.

NOTE: Exam 2 is Friday, March 12<sup>th</sup>, in class. It will cover material from Chapter 4 (all), Chapter 5 (all), and Chapter 6 (6A to 6B, and so rate laws, method of initial rates, zero, first, and second order kinetics, collision theory, and the Arrhenius equation).

Do all of the following problems. Show your work. NOTE: Unless otherwise stated, assume  $T = 25.0\text{ }^{\circ}\text{C}$  for the value for temperature.

“But you’ll have to have them all pulled out after the savoy truffles.” – George Harrison

1) Consider a galvanic cell whose cell diagram is as given below:



Find the following:

- The half-cell oxidation reaction, the half-cell reduction reaction, and the net cell reaction for the galvanic cell.
- $E^{\circ}_{\text{cell}}$ , the cell potential for standard conditions.
- $E_{\text{cell}}$ , the cell potential for the conditions given in the cell diagram. Assume ideal behavior for the solute ions.
- $\Delta G^{\circ}_{\text{cell}}$  and  $\Delta G_{\text{cell}}$ , the free energy change for the net cell reaction for standard conditions and for the conditions given in the cell diagram. Again assume ideal behavior for the solute ions.

2) In a disproportionation reaction the same ion is both oxidized and reduced.

As an example of a disproportionation reaction, consider the conversion of copper I ions can into copper II ions and copper metal by the process



- Write the expression for  $K$ , the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.
- Give the expression for  $K$ , the equilibrium constant for the above reaction, assuming ideal behavior.
- Using the table of half-cell reduction reaction in the Chapter 5 handout (Table 2), find the numerical value for  $K$  for the above reaction.

3) Cadmium hydroxide ( $\text{Cd(OH)}_2(\text{s})$ ) is a slightly soluble ionic compound.

- Write the correctly balanced solubility reaction for  $\text{Cd(OH)}_2(\text{s})$  in water.
- Find a combination of a half-cell oxidation reaction and a half-cell reduction reaction that, when combined, add up to the reaction found in part a of this problem.
- Using the information in Table 2 of the Chapter 5 notes, find the value for  $E^{\circ}_{\text{cell}}$ , the standard cell potential for the galvanic cell whose net cell reaction is that found in part a of this problem.
- Based on your answers in parts a-c of this problem, find the numerical value for  $K_{\text{sp}}(\text{Cd(OH)}_2(\text{s}))$ .

4) A particular irreversible chemical reaction of the form



is studied under conditions where  $[B]_0 > [A]_0$ , that is, where A is the limiting reactant.

In a particular experiment the initial concentration of A is  $[A]_0 = 0.0418 \text{ mol/L}$ . After 200.0 s the concentration of A is  $[A]_{200} = 0.0294 \text{ mol/L}$ .

a) Assuming the above reaction obeys first order homogeneous kinetics

$$d[A]/dt = -k[A] \quad (4.2)$$

find the numerical value for k (including correct units) and the concentration of A expected to be present when  $t = 500. \text{ s}$ .

b) Assuming the above reaction obeys second order homogeneous kinetics

$$d[A]/dt = -k[A]^2 \quad (4.3)$$

find the numerical value for k (including correct units) and the concentration of A expected to be present when  $t = 500. \text{ s}$ .

5) In the lower atmosphere (troposphere) the initial reaction in the oxidation of gas phase organic molecules is usually reaction with hydroxyl radical (OH). These reactions have therefore been extensively studied in the laboratory.

Consider the following reaction of an ethane with OH radical



The rate constant for the above reaction is  $k = 1.30 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}$  at  $T = 250. \text{ K}$  and  $k = 2.55 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}$  at  $T = 300. \text{ K}$ . Assuming the Arrhenius equation applies, find the following:

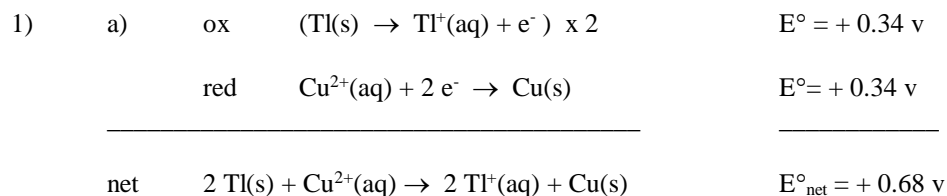
a)  $E_a$ , the activation energy for reaction 5.1 Give your answer in units of kJ/mol.

b) A, the pre-exponential factor for reaction 5.1 Give your answer in units of  $\text{cm}^3/\text{molecule}\cdot\text{s}$ .

c) The value expected for the rate constant for reaction 5.1 at  $T = 285. \text{ K}$ . Give your answer in units of  $\text{cm}^3/\text{molecule}\cdot\text{s}$ .

d) While atmospheric and gas phase chemists often use  $\text{molecule}/\text{cm}^3$  as a concentration unit, other chemists are more comfortable using mol/L for concentration. Find the value for k for reaction 5.1, at  $T = 300. \text{ K}$ , in units of  $\text{L}/\text{mol}\cdot\text{s}$ .

### Solutions



b)  $E^\circ_{\text{cell}} = +0.68 \text{ v}$  (See above. Note that  $E^\circ_{\text{net}}$  and  $E^\circ_{\text{cell}}$  mean the same thing.)

c)  $v = 2$        $Q = \frac{[\text{Tl}^+]^2}{[\text{Cu}^{2+}]} = \frac{(0.2500)^2}{(0.0400)} = 1.56$

From Nernst  $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{vF} \ln(Q) = 0.68 \text{ v} - \frac{(8.3145 \text{ J/mol}\cdot\text{K})(298.2 \text{ K}) \ln(1.56)}{(2)(96485 \text{ C/mol})}$

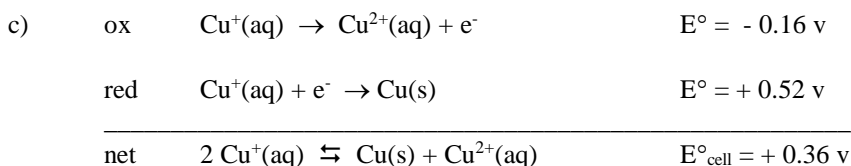
$$= 0.68 \text{ v} - 0.006 \text{ v} = 0.67 \text{ v}$$

d)  $\Delta G^\circ_{\text{cell}} = -vFE^\circ_{\text{cell}} = -(2)(96485 \text{ C/mol})(+0.68 \text{ v}) = -131.6 \text{ kJ/mol}$

$\Delta G_{\text{cell}} = -vFE_{\text{cell}} = -(2)(96485 \text{ C/mol})(+0.67 \text{ v}) = -129.3 \text{ kJ/mol}$

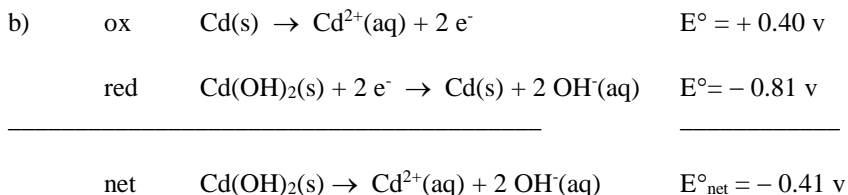
2) a) In terms of activities,  $K = \frac{(a_{\text{Cu}})(a_{\text{Cu}^{2+}})}{(a_{\text{Cu}^+})^2}$

b) If we assume ideal behavior, and substitute for the activities, we get  $K = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$



$\ln K = \frac{vFE^\circ_{\text{cell}}}{RT} = \frac{(1)(96485 \text{ C/mol})(+0.36 \text{ V})}{(8.3145 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})} = +14.02$  so  $K = e^{14.02} = 1.2 \times 10^6$

3) a) The solubility reaction is  $\text{Cd(OH)}_2(\text{s}) \rightleftharpoons \text{Cd}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$



c)  $E^\circ_{\text{cell}} = -0.41 \text{ v}$  (see above)

d)  $\ln(K) = \frac{vFE^\circ_{\text{cell}}}{RT} = \frac{(2)(96485 \text{ C/mol})(-0.41 \text{ v})}{(8.3145 \text{ J/mol}\cdot\text{K})(298.2 \text{ K})} = -31.91$

$K = e^{-31.91} = 1.4 \times 10^{-14}$

4) a) For first order kinetics

$$\ln[A]_t = \ln[A]_0 - kt$$

So  $\ln([A]_t/[A]_0) = -kt$

$$k = \frac{\ln([A]_t/[A]_0)}{-t} = \frac{\ln([A]_0/[A]_t)}{t} = \frac{\ln(0.0418/0.0294)}{200. \text{ s}} = 1.76 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} \text{After 500. s} \quad [A]_t &= [A]_0 e^{-kt} \\ &= (0.0418 \text{ M}) \exp[ -(1.76 \times 10^{-3} \text{ s}^{-1}) (500. \text{ s}) ] = 0.0173 \text{ M} \end{aligned}$$

b) For second order kinetics

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

So  $k = \left\{ \frac{(1/[A]_t) - (1/[A]_0)}{t} \right\} = \left\{ \frac{(1/0.0294 \text{ M}) - (1/0.0418 \text{ M})}{200 \text{ s}} \right\} = 5.05 \times 10^{-2} \text{ L/mol}\cdot\text{s}$

$$\begin{aligned} \text{After 500. s} \quad [A]_t &= \frac{[A]_0}{1 + kt[A]_0} = \frac{(0.0418 \text{ M})}{[ 1 + (5.05 \times 10^{-2} \text{ L/mol}\cdot\text{s}) (500. \text{ s}) (0.0418 \text{ M}) ]} \\ &= 0.0203 \text{ M} \end{aligned}$$

Notice that at  $t = 500. \text{ s}$  the predicted concentration is lower for a first order reaction than for a second order reaction. That is because the half-life for a second order reaction increases as concentration decreases, slowing the rate of decrease of the reactant.

5) a) We have a value for  $k$  at two different temperatures, and so we can use the relationship

$$\ln(k_2/k_1) = - (E_a/R) \left\{ (1/T_2) - (1/T_1) \right\}$$

So  $E_a = - \frac{R \ln(k_2/k_1)}{\left\{ (1/T_2) - (1/T_1) \right\}} = - \frac{(8.3145 \text{ J/mol}\cdot\text{K}) \ln(2.55/1.30)}{\left\{ (1/300. \text{ K}) - (1/250. \text{ K}) \right\}} = 8403. \text{ J/mol} = 8.40 \text{ kJ/mol}$

b) To find  $A$  we can go to the Arrhenius equation

$$k = A e^{-E_a/RT} \quad A = k e^{+E_a/RT} \quad \text{If we use the value for } k \text{ at } T = 250 \text{ K, then}$$

$$\begin{aligned} A &= (1.30 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) \exp[ (8400. \text{ J/mol})/(8.3145 \text{ J/mol}\cdot\text{K}) (250. \text{ K}) ] \\ &= (1.30 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}) e^{4.04} = 7.4 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s} \end{aligned}$$

c) At  $T = 285. \text{ K}$

$$\begin{aligned} k &= (7.4 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}) \exp[ -(8400. \text{ J/mol})/(8.3145 \text{ J/mol}\cdot\text{K}) (285. \text{ K}) ] \\ &= (7.4 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}) e^{-3.545} = 2.14 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s} \end{aligned}$$

Note that this value is between the values found at  $T = 250. \text{ K}$  and  $T = 300. \text{ K}$ , as expected.

d) To express k in units of L/mol•s

$$k = \frac{2.55 \times 10^{-13} \text{ cm}^3}{\text{molecule} \cdot \text{s}} \cdot \frac{6.022 \times 10^{23} \text{ molecule}}{\text{mol}} \cdot \frac{1 \text{ L}}{1000. \text{ cm}^3} = \frac{1.54 \times 10^8 \text{ L}}{\text{mol} \cdot \text{s}}$$