CHEM 323
Fall 2008
Take-Home Portion of Exam 3

Name: _____

Instructions
Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it. Helpful hint: do your work on a separate sheet of paper and then copy your final answer to this booklet.

Show all work for full credit! For the word problems write your final answer in complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). Make all final graphs in Excel and please attach a copy of your completed worksheets at the end of this exam.

Before beginning this exam, download the file TakeHome3.xls from the class web page (under *Announcements*). Note that the data may not be presented to you in the form that you will ultimately need!

There are **11** pages, **0** blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received
1	31	
2	13	
3	20	
4	18	
5	13	
Free	5	5
Total	100	
	Bonus	
	Grand Total	

1a. (21 Points) The data in the problem 1 worksheet of TakeHome3.xls were obtained at 318.0 K for the reaction 2 N_2O_5 (g) → 4 NO_2 (g) + O_2 (g). Using the integrated rate laws determine the rate law and the rate constant (with its units and uncertainty) for this reaction. You will need to prepare three graphs (each with the best linear fit to the data when graphed according to the particular integrated rate law) and tape them in the allotted spaces.

Rate law = _____

Rate constant = _____

Figure 1. Graph of the N_2O_5 kinetics data to a zeroth-order integrated rate law.

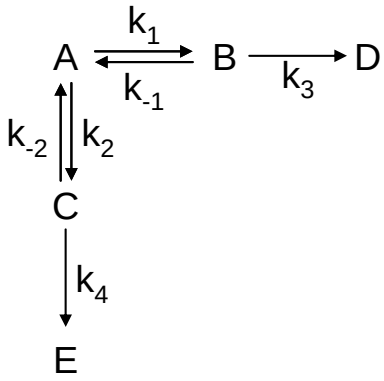
Figure 2. Graph of the N_2O_5 kinetics data to a first-order integrated rate law.

Figure 3. Graph of the N_2O_5 kinetics data to a second-order integrated rate law.

b. (10 Points) One problem with using the integrated rate laws is that it is easy to get tricked into thinking one's data conforms to one integrated rate law when it really conforms to another. To see this, test whether a second-order rate law could be made to fit the given data. Over how many half-lives do you have to obtain data so that you can be confident that a second-order rate law is, or is not, appropriate? Prepare a properly-labeled graph clearly showing your results (hint: it will look a lot like Fig. 3, but with more lines on it and a different scale) and tape it in the space below. Supply your own figure caption.

Figure 4.

2. Consider the following mechanism where compound A reacts by two different pathways to give two different products, D and E. Let K_1 be the equilibrium constant for the equilibrium between A and B and K_2 be the equilibrium constant for the equilibrium between A and C.



a. (5 Points) Derive an expression for the ratio $\frac{[D]}{[E]}$ at any time in terms of the rate constants and the equilibrium constants. Assume that both equilibria are rapidly established.

b. (4 Points) What determines whether product D or product E forms in the greater amount? Be specific (i. e., include rate constants and equilibrium constants in your discussion).

c. (4 Points) Now let's say that all of the steps are reversible. What determines which product forms in the greater amount?

3. Data for the cell Pt, H_2(g) (1 bar)| LiOH (0.0100 m), LiCl (m) | AgCl (s) | Ag (s) as a function of the molality of LiCl, m, at 298.15 K is given in the problem 3 worksheet of TakeHome3.xls. You are given that E^0 for the Ag/AgCl redox couple is +0.2224 V versus SHE.

a. (3 Points) Write the overall balanced chemical reaction that takes place in this cell.

b. (3 Points) Write the Nernst equation for this cell in terms of the activities of H^+ and Cl^-.

c. (5 Points) Rewrite the Nernst equation for this cell as a linear equation in terms of K_w (water's autoionization equilibrium constant), the molalities of Cl^- and OH^- and $\gamma_\pm$.

d. (9 Points) Graph the data according to your equation and tape it in the space below (you will need to write a figure caption). From your graph determine K_w (remember that this is defined at an ionic strength of 0) at 95% confidence (i. e., include the uncertainty).

Figure 4.

$K_w =$ _____

4. The reduction of $Cr_2O_7^{2-}$ in acidic aqueous media by H_2 (g) is catalyzed by Cu^{2+} (aq).

a. (8 Points) Write the overall balanced redox reaction that takes place between $Cr_2O_7^{2-}$ (aq) and H_2 (g) and determine E^0 for this reaction using the table of standard reduction potentials found in the back of the book. Write this reaction in using the cell notation discussed in class. Show all work for full credit.

b. (10 Points) It is observed that this reaction's rate law is $\text{rate} = k_{obs}[Cu^{2+}][H_2]$ at low $[H^+]$, where k_{obs} is the observed rate constant. However at high $[H^+]$, the rate law is found to have an inverse dependence on $[H^+]$ (i. e., the rate went down as the $[H^+]$ went up). Suggest a mechanism, and derive its rate law, that is consistent with both the observed rate law at low $[H^+]$ and the inhibition of the reaction by H^+ at high $[H^+]$.

5a. (8 Points) A 0.100 M solution of sodium palmitate ($C_{15}H_{31}COONa$) is separated from a 0.200 M NaCl solution by a membrane barrier that is permeable to Na^+ and Cl^-, but not to palmitate ions. Calculate the concentrations of the ions on both sides of the barrier once equilibrium is established.

b. (5 Points) What is the potential difference across the membrane due to the equilibrium that was established in part *a*?