Chem 120   Name_____
Exam 4, Ch 14, 15 and a little 16   **December 4, 2008**
100 Points

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions. I have intentionally left a great deal of space for each problem. I do not expect each problem to take up all of the space provided!

Part 0: Warmup. 4 points each
1. The reaction A→products has been determined to be first order in A. The reaction is run with $[A]_0$ = 0.20 M and is found to have a half-life of 124 seconds. What is the rate constant for the reaction?

    a. 8.06×10^{-4} s^{-1}.
    b. $8.06 \times 10^{-4} M^{-1}s^{-1}$
    c. 5.59×10^{-3} s^{-1} Answer _____**C**_____
    d. 5.59×10^{-3} $M^{-1}s^{-1}$

2. For the reaction A + B → 2C, which proceeds by a single-step bimolecular elementary process,

    a. $t_{1/2}$ = 0.693/k.
    b. the rate of appearance of C = - rate of disappearance of A.
    c. rate of the reaction = k[A][B].   Answer _____**C**_____
    d. $\ln[A]_t$ = -kt + $\ln[A]_0$

3. The volume of the reaction vessel containing an equilibrium mixture in the reaction SO_2Cl_2 (g) $\rightleftarrows$ SO_2 (g) + Cl_2(g) is increased. When equilibrium is reestablished,

    a. the amount of Cl_2 will have increased.
    b. the amount of SO_2 will have decreased.
    c. the amounts of SO_2 and Cl_2 will have remained the same.   Answer _____**A**_____
    d. the amount of SO_2Cl_2 will have increased.

4. For the reaction CO (g) + H_2O (g) $\rightleftarrows$ H_2 (g) + CO_2(g) at 1000K, K_c = 0.66 and ΔH^0 = -42 kJ. After an initial equilibrium is established in a 1.00 L container, the equilibrium amount of H_2 can be increased by,

    a. adding a catalyst.
    b. increasing the temperature.
    c. transferring the mixture to a 10.0 L container.   Answer _____**D**_____
    d. some way other than (a), (b), or (c).

5. Which of the acids below would have the *weakest conjugate base*?

    a. CH_3COOH (acetic acid, K_a = 1.8 x 10^{-5})
    b. HCl (hydrochloric acid, K_a = 1000).
    c. HOCl (hypochlorous acid, K_a = 3.0 x 10^{-8}).
    d. HCO_2H (formic acid, K_a = 1.8 x 10^{-4})   Answer _____**B**_____

Bonus (5 points). I wrote a concentration on the board at the start of class one day and said it would be an answer on the exam. Write that concentration here with the correct units.
                    2.42×10^{-3}M

Part I: Complete all of problems 6-8.

6. Complete the following reaction and identify the conjugate acid-base pairs. For each pair, identify the acid and the conjugate base. (8 points)

$$HCl \ (aq) + NH_3 \ (aq) \rightleftarrows NH_4^+ \ (aq) + Cl^- \ (aq)$$
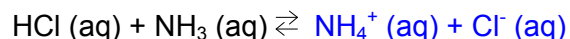
HCl is an acid and Cl^- is its conjugate base
NH_3 is behaving as a base and NH_4^+ is its conjugate acid

7. Briefly describe what we mean when we say that a system is *at equilibrium*. Why do we use a double-headed arrow (like $\rightleftarrows$) when we write these reactions? (12 points)

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. (Note that this does **not** mean that the concentrations are equal or that the rate constants are equal!). Both the forward and reverse reactions are still proceeding at equilibrium, only reactants and products are both being consumed at equal rates. As a result, there is no net change in concentrations of reactants or products. At equilibrium, the K expression is satisfied. We use the double-headed arrow to indicate that the reaction is proceeding in both directions

8. How does a catalyst impact the rate of a reaction and the extent to which the reaction goes to completion? (8 points)

A catalyst provides an alternate mechanism for the reaction. The catalytic mechanism has a smaller activation energy for the reaction, allowing the rate of the reaction to increase. The catalyst has no impact, however, on the extent of the reaction. The extent to which the reaction goes to completion is controlled by the thermodynamics of the reaction (free energy) and not by the kinetics of the reaction.

Part II Kinetics. Answer two (2) of problems 9-11. Clearly mark the problems you do not want graded. 14 points each.

9. The initial rate data below is for the reduction of mercury with oxalate ion. Using this information, determine the rate law for the reaction as well as the rate constant (with appropriate units).

$$2\ HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$$
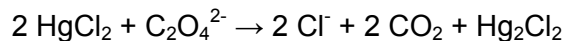
Experiment	$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	Initial Rate, M min^{-1}
1	0.105	0.300	7.18×10^{-5}
2	0.052	0.300	3.56×10^{-5}
3	0.208	0.600	5.69×10^{-4}

Comparing experiments 1 and 2: $[C_2O_4^{2-}]$ is constant, while $[HgCl_2]$ doubles. As a result the rate of the reaction doubles.

$$\frac{Rate_1}{Rate_2} = \frac{k[HgCl_2]^x[C_2O_4^{2-}]^y}{k[HgCl_2]^x[C_2O_4^{2-}]^y} = \frac{7.18\times10^{-5}}{3.56\times10^{-5}} = 2 = \frac{k[0.105]^x[0.300]^y}{k[0.052]^x[0.300]^y} = 2^x \quad x = 1$$

Now examining the other pair of data sets will allow us to find the order for $C_2O_4^{2-}$.

$$\frac{Rate_3}{Rate_2} = \frac{k[HgCl_2]^1[C_2O_4^{2-}]^y}{k[HgCl_2]^1[C_2O_4^{2-}]^y} = \frac{5.69\times10^{-4}}{3.56\times10^{-5}} = 16 = \frac{k[0.208]^1[0.600]^y}{k[0.052]^1[0.300]^y}$$

$$4 = \frac{[0.600]^y}{[0.300]^y} \quad y = 2$$

$$\textbf{Rate} = \textbf{k[HgCl}_2\textbf{]}^1\textbf{[C}_2\textbf{O}_4{}^{2-}\textbf{]}^2$$

Use any single data set to calculate k.

$$k = \frac{Rate}{[HgCl_2]^1[C_2O_4^{2-}]^2} = \frac{7.18\times10^{-5}\ \text{mol/L}\cdot min}{(0.105\ \text{mol/L})(0.300\ mol/L)^2} = \textbf{7.6}\times\textbf{10}^{-3}\ \textbf{L}^2\textbf{mol}^{-1}\textbf{min}^{-1}$$

So,

$$\textbf{Rate} = \textbf{7.6}\times\textbf{10}^{-3}\ \textbf{M}^{-2}\textbf{min}^{-1}\ \textbf{[HgCl}_2\textbf{][C}_2\textbf{O}_4{}^{2-}\textbf{]}^2$$

10. You are investigating the reaction of a newly discovered cancer drug named LAMPROCKS (abbreviated L). You have been charged with determining the rate law for the decomposition of LAMPROCKS into its two components, LAMP and ROCKS. The rate only depends on L and no other reactants. You have collected the following data and made the plots below. Based on this data, what is the <u>rate law</u> for this reaction and what is the value of the <u>rate constant</u> with the appropriate units? *Justify your choice for the rate law and show your work for the k determination.*

Time, sec	[L], M
0.00	0.200
1.00	0.173
2.00	0.152
3.00	0.136
4.00	0.123
5.00	0.112
6.00	0.103
7.00	0.0950
8.00	0.0884
9.00	0.0826
10.00	0.0776
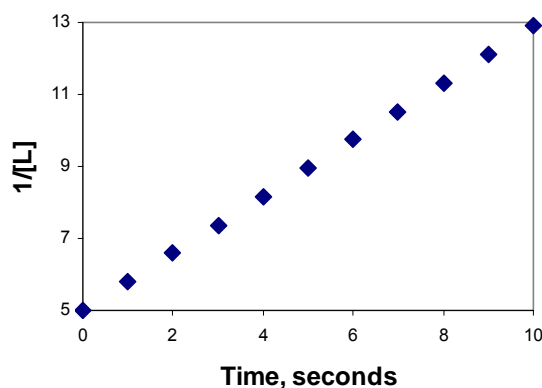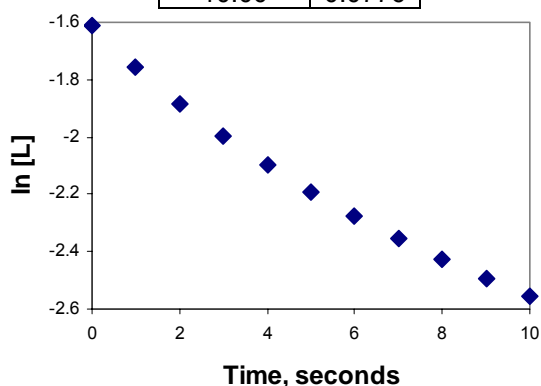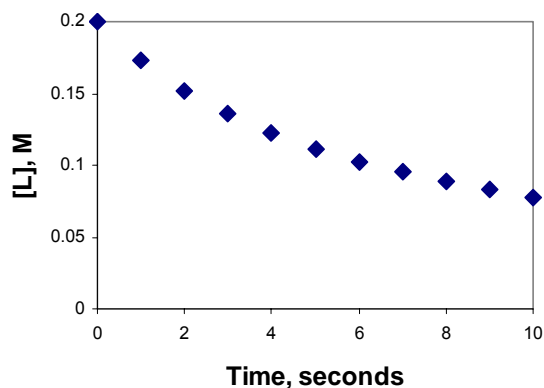
Since the plot of 1/[L] versus time is linear, the reaction must be second order in L, since this relationship corresponds to a second order rate law in the form:

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

The slope of this relationship gives us the value for k. We can determine the slope from any two points of the line. For example for the points at 0 and 1 seconds:
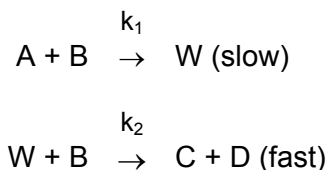
At t=0, 1/[L] = 1/0.200M = 5.000M^{-1} and at t = 1 sec, 1/[L] = 1/0.173M = 5.780M^{-1}

$$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{(5.780 - 5.000)M^{-1}}{(1.00 - 0.00)\,\text{sec}} = 0.780 M^{-1}\,\text{sec}^{-1} = k$$

So our rate law is: rate = 0.780 $M^{-1}s^{-1}[L]^2$

11. For the reaction $A + 2B \rightarrow C + D$, the rate law is: rate = $k[A][B]$.

    a. Show that the following mechanism is consistent with the stoichiometry of the overall reaction and with the rate law.

$$A + B \xrightarrow{k_1} W \text{ (slow)}$$

$$W + B \xrightarrow{k_2} C + D \text{ (fast)}$$

To confirm the stoichiometry, we add the two reactions together to get: $A + B + W + B \rightarrow W + C + D$. This simplifies to $A + 2B \rightarrow C + D$, corresponding to the known reaction stoichiometry.

The rate law is governed by the rate-determining step. Since this is the first step, we can write the rate law based on this elementary step alone. In this case, **rate = k[A][B]**, which corresponds to the experimental rate law.

    b. Show that the following mechanism is consistent with the stoichiometry of the overall reaction, but <u>not</u> with the rate law.

$$2B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_2 \text{ (fast)}$$

$$A + B_2 \xrightarrow{k_2} C + D \text{ (slow)}$$
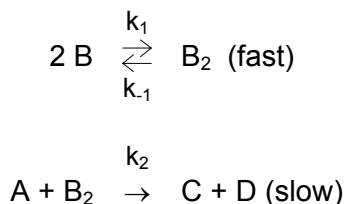
Again, to confirm the stoichiometry, we add the two reactions together to get: $2B + A + B_2 \rightarrow B_2 + C + D$. This simplifies to $A + 2B \rightarrow C + D$, corresponding to the known reaction stoichiometry.

We begin with the second step (slow step) in writing the rate law. In this case rate = $k[A][B_2]$. Since B_2 is an intermediate, we must find an expression for it in terms of reactants and products. From the first step, $(k_1/k_{-1}) = [B_2]/[B]^2$. Rearranging gets us to $[B_2] = [B]^2(k_1/k_{-1})$. Substituting this into the rate law gives rate = $k[A][B]^2(k_1/k_{-1})$. Combining constants give a final form of **rate = k[A][B]^2**, which is not the experimental rate law.

5

Part III Equilibrium. Answer two (2) of problems 12-14. Clearly mark the problems you do not want graded. 14 points each.

12. For the equilibrium below, $K_c = 2.0 \times 10^{-6}$. What is the equilibrium concentration of oxygen (in moles/L) if 0.20 mol CO_2 and 0.10 mol CO were initially placed into a 0.50 L vessel and the system is allowed to come to equilibrium?

$$2CO_2 \text{ (g)} \rightleftarrows 2CO \text{ (g)} + O_2 \text{ (g)}$$

Since we have a K_c, it is useful to get all materials in terms of concentration to start with:
$$[CO_2] = 0.20 \text{ mol}/0.50 \text{ L} = 0.40 \text{ M } CO_2$$
$$[CO] = 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M CO}$$

Now we can begin to work through the equilibrium. Since we have zero O_2 intitially, we know we cannot be at equilibrium so we must use an ICE table or some other approach to find equilibrium concentrations.

	$2CO_2$	$\rightleftarrows$	$2CO$	+	O_2
I	0.40 M		0.20 M		0
C	-2x		+2x		+x
E	0.40-2x		0.20+2x		x

The equilibrium constant expression becomes:

$$K_c = \frac{[CO]^2[O_2]}{[CO_2]^2} = \frac{(0.20+2x)^2 x}{(0.40-2x)^2}$$

Without some simplification, we will need to solve a third order polynomial. Can we simplify? Since K is small, we would not expect the reaction to proceed very far to the right. Also, the presence of CO intitially will further impede the reaction. So, we expect x to be small. Lets assume x<<0.20. If this is so, the K_c expression changes.

$$K_c = \frac{(0.20+\cancel{2x})^2 x}{(0.40-\cancel{2x})^2} = \frac{(0.20)^2 x}{(0.40)^2}$$

After rearranging we find that $x = K_c(0.40)^2/(0.20)^2 = 8.0 \times 10^{-6}$.

So, **$[O_2] = 8.0 \times 10^{-6}$ M.** Was our assumption OK? 0.20 – 0.0000080 = 0.1999920, which to the correct number of sig figs is indistinguishable from 0.20, so our assumption is fine.

We could have used a calculator or computer to solve the third order polynomial. Doing so on my calculator gave a value for x of 7.998×10^{-6}.

13. In the gas phase, iodine reacts with cyclopentane to produce cyclopentadiene and hydrogen iodide. Explain how each of the following affects the amount of HI (g) present in the equilibrium mixture in the reaction:

$$I_2 \text{ (g)} + C_5H_8 \text{ (g)} \rightleftarrows C_5H_6 \text{ (g)} + 2 \text{ HI (g)} \qquad \Delta H^o = +92.5 \text{ kJ}$$

a. raising the temperature of the mixture.

Since the reaction is endothermic, we can consider heat a reactant. Raising the temperature would cause the reaction to move to the right in order to get back to equilibrium. Therefore, the amount of HI should **increase**.

b. doubling the volume of the container holding the mixture.

Doubling the volume would decrease the pressure in the container, favoring the direction of the reaction that would involve fewer gas molecules or produce more gas. In this case, the reaction would move to the right as more gas molecules are produced in an effort to bring the pressure to equilibrium. Therefore, the amount of HI should **increase**.

c. introducing more C_5H_6(g).

Since C_5H_6 is a product, its addition will cause the reaction to shift to the left to produce more reactants and return to equilibrium. Therefore, the amount of HI should **decrease**.

14. For the reaction $2SO_2$ (g) + O_2 (g) $\rightleftarrows$ $2SO_3$ (g) occurring at a temperature 1000K, K_c =100. If 0.455 mol SO_2, 0.183 mol O_2, and 0.568 mol SO_3 are introduced simultaneously into a 1.90 L vessel at 1000K, is the system at equilibrium? If not, in which direction will a net change occur? *NOTE: you do not need to calculate the equilibrium concentrations, just clearly justify your answers.*

Since we have a K_c, we need to begin by calculation concentrations of the species:

$$[SO_2] = 0.455 \text{ mol}/1.90 \text{ L} = 0.239_5 \text{ M}$$
$$[O_2] = 0.183 \text{ mol}/1.90 \text{ L} = 0.0963_1 \text{ M}$$
$$[SO_3] = 0.568 \text{ mol}/1.90 \text{ L} = 0.298_9 \text{ M}$$

Now we are able to calculate the reaction quotient, Q:

$$Q \quad \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad = \quad \frac{(0.298_9 \text{ M})^2}{(0.239_5 \text{ M})^2(0.0963_1 \text{ M})} \quad = \quad 16.2$$

Since Q<K, the reaction not at equilibrium and is reactant heavy. In order to reach equilibrium (Q=K), the numerator must increase while the denominator decrease. Chemically, this corresponds to increasing the concentration of products while decreasing reactants. Therefore, we would say that the reaction would proceed to the right to reach equilibrium.

Possibly Useful Information

$\text{slope} = m = \dfrac{\Delta y}{\Delta x} = \dfrac{y_2 - y_1}{x_2 - x_1}$	$y = mx + b$	$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
$pH + pOH = 14$	$K_a K_b = K_w$	$K_p = K_c(RT)^{\Delta n}$
$k = Ae^{-E_a/RT}$	$\ln k = -\left(\dfrac{E_a}{R}\right)\left(\dfrac{1}{T}\right) + \ln A$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\text{rate} = k[A]^1$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$
$\text{rate} = k[A]^2$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 1/(k[A]_0)$
$\text{rate} = k[A]^0$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$t_{1/2} = 0.693/k$

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