Chem 130 **Name_______________________________**
Exam 3, Ch 14 and 15 **December 7, 2016**
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.

Part 0: Warmup. 4 points each

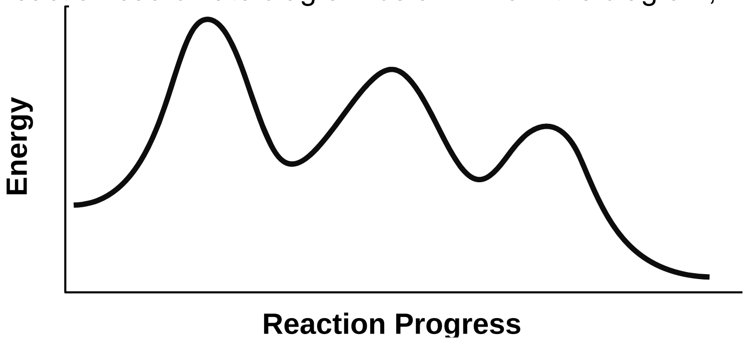
1. The steady-state approximation is most useful when
   a. the equilibrium constant for a reaction is small.
   b. there is no clear slow step in a proposed reaction mechanism.
   c. a reaction occurs through a single-step mechanism.
   d. the concentration of reactants is small compared to the equilibrium constant.

Answer _____b______

2. The pressure of a reaction vessel that contains 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.
   d. the amounts of all SO_2, Cl_2, and SO_2Cl_2 will have decreased..

Answer _____b______

3. Consider the reaction coordinate diagram below. From the diagram, we can conclude:



   a. The reaction is endothermic.
   b. The reaction occurs by a two-step mechanism.
   c. The first step of the mechanism is the rate-determining step.
   d. The reaction is nonspontaneous.

Answer _____c______

4. For the reaction $CO(g) + 2H_2\ (g) \rightleftarrows CH_3OH(g)$ $K_c = 14.5$. If 5.00 mol CO, 2.00 mol H_2 and 3.00 mol of CH_3OH are brought together and allowed to react, which of the following describes the composition of the system at equilibrium?
   a. Some CO and H_2 will have been consumed to make more CH_3OH.
   b. Some CH_3OH will have been consumed to make more CO and H_2
   c. The amounts of CO, H_2, and CH_3OH will be unchanged from their initial values.
   d. There is not enough information to determine the equilibrium composition.

Answer _____a______

Part I Kinetics. Answer three (3) of problems 5-8. Clearly mark the problems you do not want graded. 14 points each.

5. Consider the data below. The data corresponds to the reaction below and shows dependence of concentration of A on time in experiments run at three temperatures. Assuming you know the reaction to be first order in A, describe how you could determine the activation energy for the reaction. No calculations are necessary. Feel free to include appropriate diagrams.

$$2A \rightarrow B + C$$

	T = 298 K	T = 348 K	T = 398 K
Time (sec)	[A] (M)	[A] (M)	[A] (M)
0	0.1000	0.1000	0.1000
1	0.0999	0.0991	0.0940
2	0.0999	0.0983	0.0883
8	0.0995	0.0932	0.0609
32	0.0980	0.0755	0.0137

We need to determine how the rate constant changes with time. In order to do so, we need the value for the rate constant at each temperature. To get this value, plot ln[A] versus time for each temperature. Since the reaction is first order, each plot should be linear and the slope of each line is –k for that temperature. Once we have determined k's we can take advantage of the relationship:

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \, .$$

If we plot ln k versus 1/T we should get a straight line with a slope of –(E_a/R). Since R is constant, we can calculate E_a.

NOTE: You could also use the relationship:

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

You still need the rate constants for two temperatures before you can solve this for E_a.

6. Experiment has shown that the rate law for the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ is Rate = $k[NO][Cl_2]$. One proposed mechanism for this process is shown below, with the second step being rate-determining. Is this a reasonable mechanism for the reaction? Justify your decision.

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NOCl_2 \text{ (fast)}$$

$$NOCl_2 + NO \overset{k_2}{\rightarrow} 2NOCl \text{ (slow)}$$

Your first step would be to check that the stoichiometry for the sum of the elementary steps matches that for the overall reaction. In this case, it does.

Then, determine the rate law for this mechanism, starting with the rate law for the slow step.

$$\text{Rate} = k_2[NOCl_2][NO]$$

Since $NOCl_2$ is an intermediate, we need to find an expression for it in terms of reactants. Because step 1 is an equilibrium, the rate of the forward and reverse reactions are equal

$$k_1[NO][Cl_2] = k_{-1}[NOCl_2]$$

Solving for $[NOCl]_2$:

$$(k_1[NO][Cl_2])k_{-1} = [NOCl_2]$$

Inserting this into the original rate law gives us

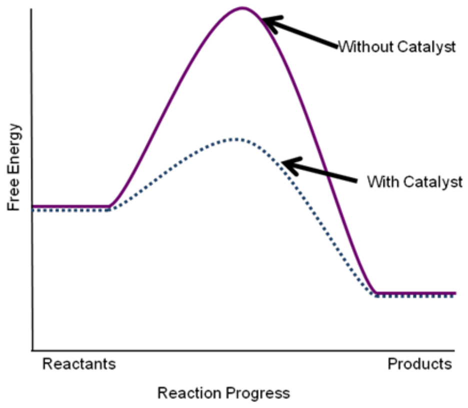
$$\text{Rate} = k_2\ (k_1[NO][Cl_2])k_{-1}\ [NO]$$

$$\text{Rate} = k[NO]^2[Cl_2]$$

This does not match the experimental rate law, indicating that the mechanism is not reasonable, assuming the experimentally-determined rate law is valid.

7. The decomposition of hydrogen peroxide (H_2O_2) to liquid water and oxygen gas is a spontaneous process, but occurs slowly, allowing for a reasonable shelf-life for peroxide solutions. In the presence of a catalyst (like the iron in your blood), the decomposition is much more rapid. Draw and correctly label reaction coordinate diagrams that represent each of the two situations and describe how each diagram reflects the thermodynamics and kinetics of the situation.

Your diagrams should bear some resemblance to the picture at the right and meet the following requirements: 1) the axes must be labeled, 2) the free energy for the reactants must be higher than the free energy of the products so that ΔG is negative (spontaneous), 3) the size of the activation barrier (hill) must be present, and relatively large to indicate a slow reaction. Your discussion should point out these items. The only difference between the catalyzed and non-catalyzed diagram should be that the size of the activation barrier is less in the catalyzed process because the catalyst provides an alternate, lower activation energy, mechanism for the reaction. (There may be a different number of steps in the catalyzed mechanism, but the activation barrier for the slow step must be smaller than in the uncatalyzed diagram.



8. In our kinetics experiment we used the *isolation method* (sometimes called *pseudo-order* kinetics) to determine the rate law for the reaction of crystal violet with hydroxide ion. Describe how the isolation method allows the determination of the reaction orders for multiple reactants, as well as the overall rate constant for a reaction. You may wish to use the CV reaction as an example.

Consider the reaction A + B → C, we isolate the influence of one reactant (for example A), by making the concentrations of all other reactants (B in this case) large relative to the concentration of that single reactant. In doing so, the rate of the reaction depends solely on A: rate = $k_{obs}[A]^n$, where $k_{obs} = k[B]^m$. If we collect data on the extent of the reaction as a function of time, we can find the order in A and k_{obs}. If the experiment is repeated for a variety of concentrations of B, we can use the dependence of k_{obs} on [B] to determine the order in B and the overall rate constant.

Part II Equilibrium. Answer three (3) of problems 9-12. Clearly mark the problems you do not want graded. 14 points each

9. What do we mean when we say a system has *come to equilibrium*? Describe the equilibrium condition and why we don't use a single headed arrow when we write equilibria. What does a small equilibrium constant mean in terms of thermodynamics?

   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.

   As small equilibrium constant indicates a reaction that is not product favored. The tendency of the reaction is to favor the reactant side. As K decreases, the reaction becomes less spontaneous.

10. Suppose the reaction system below has already reached equilibrium. Predict the effect of the following changes on the system. Justify your predictions with a brief statement.

$$UO_2(s) + 4HF(g) \rightleftarrows UF_4(g) + 2H_2O(g)$$

   a. More UO_2 is added to the system.
      Since UO_2 is a solid, it does not show up in the equilibrium constant expression, so its addition will have no impact on the position of the equilibrium.

   b. The reaction is performed in a glass reaction vessel and the HF reacts with the glass.
      HF, a reactant is being consumed; therefore the equilibrium will shift to the left to generate additional reactant.

   c. Water vapor is removed.
      H_2O, a product is being consumed; therefore the equilibrium will shift to the right to generate additional product.

   d. The volume is increased.
      An increase in volume would lead to a decrease in pressure, which will cause the equilibrium to shift in the direction of the most molecules of gas, in this case, to the left.

11. A mixture consisting of 0.150 mol H_2 and 0.150 mol I_2 is brought to equilibrium at 445°C in a 1.50 L flask. What are the equilibrium concentrations of each species?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 50.2 \text{ at } 445^{o}C$$

So, the equilibrium constant expression (K_c) is:

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

We need equilibrium concentrations of each species to find the K_c. We start buy determining initial concentrations:

$$0.150 \text{ mol } H_2 \times \frac{1}{1.500 \text{ L}} = 0.100 \text{ M } H_2$$

$$0.150 \text{ mol } I_2 \times \frac{1}{1.500 \text{ L}} = 0.100 \text{ M } I_2$$

Mapping out the chemistry:

	H_2	+	I_2	$\rightleftarrows$	2 HI
i	0.100 M		0.100		0
c	$-x$		$-x$		$+2x$
e	$0.100 - x$		$0.100 - x$		$2x$

Inserting these into the equilibrium constant expression (K_c) gives:

$$K_c = \frac{[2x]^2}{[0.100 - x][0.100 - x]}$$

Now some algebra:

$$K_c = \frac{4x^2}{0.0100 - 0.200x + x^2}$$

$$0.0100K_c - 0.200K_cx + K_cx^2 = 4x^2$$

$$0.502 - 10.04x + 50.2x^2 = 4x^2$$

$$0 = 46.2x^2 - 10.04x + 0.502$$

From the quadratic, x = 0.139M, 0.078M. Of these, only 0.078 makes chemical sense because if x = 0.139 M, then the equilibrium concentration of H_2 and I_2 would both be negative (0.100 - 0.139 = -0.039), which does not make chemical sense. Therefore the equilibrium concentrations of the three species are:

$[H_2] = [I_2] = 0.100M - 0.078M = 0.022$ M

$[HI] = 2x = 2(0.078M) = 0.156$ M

12. For the reaction below, an equilibrium mixture contains 0.550 mol of each of the products (carbon dioxide and hydrogen gas) and 0.200 mol of each of the reactants (carbon monoxide and water vapor) in a 1.00-L container. How many moles of carbon dioxide would have to be added at constant temperature and volume to increase the amount of carbon monoxide to 0.300 mol once equilibrium has been reestablished?

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Since the container has a volume of 1.00 L, the concentrations of reactants are 0.200 M and the concentrations of products are 0.550 M. Since these are initially equilibrium concentrations, we can calculate the equilibrium constant:

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{[0.550M][0.550M]}{[0.200M][0.200M]} = 7.56$$

Mapping out the chemistry after the addition of some unknown amount of CO_2, that we will call “z”. In order for the CO concentration to be 0.300 M at the new equilibrium point, it must have increased by 0.100 M, meaning the other concentrations must also have increased proportionally based on the stoichiometry

	H_2O	+	CO	⇄	H_2	+	CO_2
i	0.200 M		0.200M		0.550M		0.550M + z
c	+0.100M		+0.100M		-(0.100M)		-(0.100M)
e	0.300M		0.300M		0.450M		(0.550M + z) – 0.100M= 0.450M + z

Returning to the equilibrium constant expression:

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{[0.450M][0.450M + z]}{[0.300M][0.300M]} = 7.56$$

Finishing with some algebra:

$$[0.450M][0.450M + z] = 7.56[0.300M][0.300M] = 0.680_4$$

$$[0.450M + z] = 0.680_4/[0.450M] = 1.51_2$$

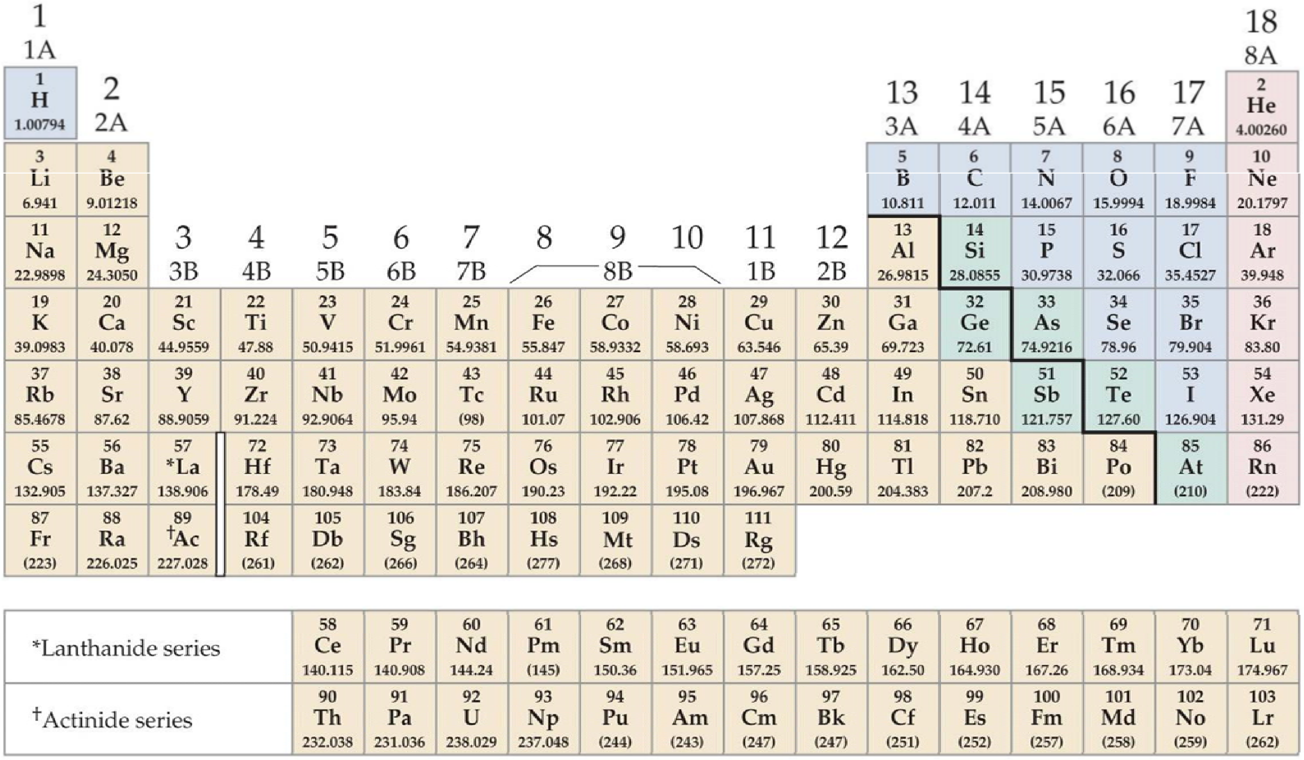
$$z = 1.512 – 0.450M = 1.06_2 \text{ M}$$

So, in a 1L vessel, 1.06 moles of CO_2must be added to reach the new equilibrium conditions.

Possibly Useful Information

$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$	R = 0.08206 L atm mol^{-1} K^{-1} R = 8.314 J mol^{-1} K^{-1}
$pV = nRT$	$\Delta G = -RT\ln K$	$K_p = K_c(RT)^{\Delta n}$
$k = Ae^{-E_a/RT}$	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$	$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
rate = $k[A]^1$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$
rate = $k[A]^2$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 1/(k[A]_0)$
rate = $k[A]^0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$t_{1/2} = 0.693/k$

To save some calculation time, you may round all atomic masses to two (2) decimal points.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)