Chem 130 **Name_____**
Exam 4, Ch 15, with parts of 10 and 14 **December 5, 2018**
100 Points

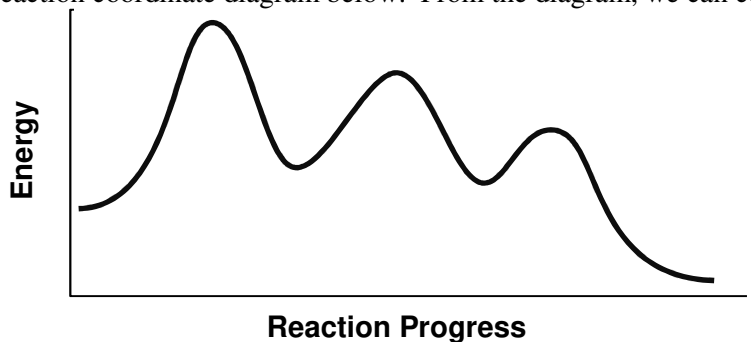
Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Part 0: Warmup. 3 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. Answer _____b_____
   d. the concentration of reactants is small compared to the equilibrium constant.

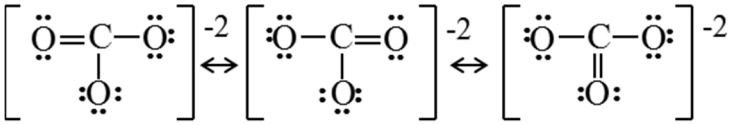
2. The pressure of a reaction vessel that contains an equilibrium mixture in the reaction $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is increased. When equilibrium is reestablished:
   a. the amount of Cl_2 will have increased.
   b. the amount of SO_2 will have decreased. Answer _____b_____
   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..

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. Answer _____c_____
   c. The first step of the mechanism is the rate-determining step.
   d. The reaction is nonspontaneous.

4. The structure of the carbonate can be described by these three resonance structures. This means that



   a. two CO bonds are single bonds and one is a double bond.
   b. three distinct forms of carbonate exist in equilibrium. Answer _____d_____
   c. the structure of carbonate cycles between the three forms.
   d. carbonate exists as a single form, which is the average or hybrid of these structures.

Part I Equilibrium. Answer <u>three (3)</u> of problems 5-8. Clearly mark the problems you do not want graded. 15 points each

5. In the gas phase, iodine reacts with cyclopentane to produce cyclopentadiene and hydrogen iodide. **<u>Explain</u>** how each of the following affects the amount of HI (g) present in the equilibrium mixture in the reaction below. No calculations are necessary.

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

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**. Actually, K increases as T increases for endothermic reactions.
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**.

6. A mixture consisting of 0.150 mol H_2, 0.150 mol I_2, and 3.00 mol HI is brought to equilibrium at 445°C in a 1.50 L flask. What are the equilibrium concentrations of each species?

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

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 use the K_c. We start buy determining initial concentrations:

$$0.150\text{ mol } H_2 \times \frac{1}{1.500\text{ L}} = 0.100\text{ M } H_2 \qquad 0.150\text{ mol } I_2 \times \frac{1}{1.500\text{ L}} = 0.100\text{ M } I_2$$

$$3.00\text{ mol HI} \times \frac{1}{1.500\text{ L}} = 2.00\text{ M HI}$$

Calculate Q to determine the direction of the reaction:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2.00)}{(0.100)(0.100)} = 400 > K_c \text{ so the reaction must go to the left}$$

Mapping out the chemistry:

	H_2	+	I_2	$\rightleftharpoons$	2 HI
i	0.100 M		0.100		2.00
c	+x		+x		-2x
e	0.100 + x		0.100 + x		2.00 - 2x

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

$$K_c = \frac{[2.00-2x]^2}{[0.100+x][0.100+x]} = \frac{[2.00-2x]^2}{[0.100+x]^2}$$

Now some algebra. Since both the numerator and denominator are squares, we can take the square root of both sides to get rid of them:

$$(K_c)^{1/2} = 7.085 = \frac{2.00 - 2x}{0.100 + x}$$

$$7.085(0.100 + x) = 2.00 - 2x, \quad 0.7085 + 7.085x = 2.00 - 2x, \quad 9.085x = 1.2915, \quad x = 0.1422$$

Note that you could also FOIL the numerator and denominator in the K_c expression and solve the quadratic that results. In that case you end up with 0.1422 as the chemically sensible root.

Therefore the equilibrium concentrations of the three species are:

$[H_2] = [I_2] = 0.100M + 0.1422M = 0.242$ M

$[HI] = 2.00 - 2x = 2.00M - 2(0.1422M) = 1.72$ M

7. Formamide, used in the manufacture of pharmaceuticals, dyes, and agricultural chemicals, decomposes at high temperatures by the equilibrium below, with $K_c = 4.84$ at 400K. If 0.186 mol of $HCONH_2$ dissociates at 400Kin a 2.16L vessel, what will be total number of moles of gas present at equilibrium? If the total pressure, $P_t = n_{total}RT/V$, what is the total pressure in the vessel at equilibrium?

$$HCONH_2\ (g) \rightleftharpoons CO\ (g) + NH_3\ (g)$$

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

$$0.186 \text{ mol } HCONH_2 \quad x \quad \frac{1}{2.16 \text{ L}} = 0.0861 \text{ M } HCONH_2$$

Now the ICE table:

	$HCONH_2$	+	CO	$\rightleftharpoons$	NH_2
i	0.0861 M		0		0
c	-x		+x		+x
e	0.0861 - x		x		x

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

$$K_c = \frac{x^2}{[0.0861 - x]}$$

A little algebra produces the quadratic: $x^2 + 4.84x - 0.4168 = 0$, which has roots of x = 0.0846 and x = -4.925. A negative root does not make sense since we defined x at a concentration, so the sensible root is x = 0.0846M and $[CO] = [NH_3] = 0.0846$ M and $[HCONH_2] = 0.00148$ M, and the moles of each species are: mol CO = mol NH_3 = 0.0846 M x 2.16 L = 0.183 mol and mol $HCONH_3$ = 0.00148 M x 2.16 L = 0.00319 mol. So, the total moles of gas are:

0.183 mol CO + 0.183 mol NH_3 + 0.00319 mol $HCONH_3$ = **0.369 mol**

The total pressure is (0.369 mol)(0.08206 L atm mol^{-1} K^{-1})(400 K)/2.16 L = **5.61 L**

8. Given the equilibrium constant, K_c, values for the reactions below, determine the value of K_p at 100.0° C for the reaction $2\ N_2O\ (g) + 3\ O_2\ (g) \rightleftharpoons 2\ N_2O_4\ (g)$.

$N_2\ (g) + ½\ O_2\ (g) \rightleftharpoons N_2O\ (g)$ $\quad K_c = 2.7 \times 10^{-18}$

$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$ $\quad K_c = 4.6 \times 10^{-3}$

$½\ N_2\ (g) + O_2\ (g) \rightleftharpoons NO_2\ (g)$ $\quad K_c = 4.1 \times 10^{-9}$

$$2\ N_2O(g) \rightleftharpoons 2\ N_2(g) + O_2(g) \qquad K_c = \frac{1}{(2.7\times10^{-18})^2}$$

$$4\ NO_2(g) \rightleftharpoons 2\ N_2O_4(g) \qquad K_c = \frac{1}{(4.6\times10^{-3})^2}$$

$$2\,N_2(g) + 4\,O_2(g) \rightleftharpoons 4NO_2(g) \qquad K_c = (4.1\times10^{-9})^4$$

$$\text{net}: 2\ N_2O(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2O_4(g) \quad K_{c(Net)} = \frac{(4.1\times10^{-9})^4}{(2.7\times10^{-18})^2(4.6\times10^{-3})^2} = 1.8\times10^6$$

$K_p = K_c(RT)^{\Delta n} = 1.8 \times 10^6 (8.314 J\ mol^{-1} K \times 373\ K)^{-3}$ = **63**

Part II. <u>Kinetics and Bonding</u>. Answer <u>three (3)</u> of problems 9-12. Clearly mark the problem you do not want graded. 15 points each.

9. 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.

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

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

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

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

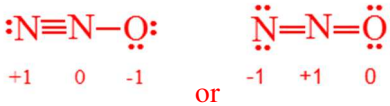
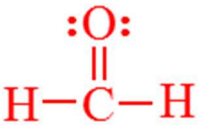
$$\text{Rate} = k[NO]^2[Cl_2]$$

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

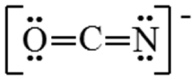
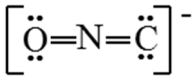
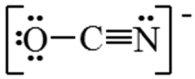
10. In our kinetics experiment we used the *isolation method* (sometimes called *pseudo-order* kinetics) to determine the rate law for the reaction of crystal violet with hydroxide ion. Describe how the isolation method allows the determination of the reaction orders for multiple reactants, as well as the overall rate constant for a reaction. You may wish to use the CV reaction as an example. *Hint: how did we "isolate" the impact of CV on the kinetics from that of OH^-?*

Consider the reaction $A + B \rightarrow C$, 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.

11. Complete the table **for three (3)** of the species below. If more than one structure is possible, indicate the structure you expect to be most representative of the actual structure of the species.

Species	Lewis Structure	Species	Lewis Structure
OCl_2		**N_2O**	 or The structure on the left is preferred because it has the negative formal charge on oxygen. We expect nitrogen in the middle because it is less electronegative than oxygen.
HCN		**CH_2O**	

12. The Lewis structure for the cyanate ion (a polyatomic anion comprised of one atom each of C, N, and O) could be drawn in several ways, three of which are shown below. Each of these structures utilize all of the valence electrons and all atoms have filled octets. Which one of these structures is most likely to be representative of the real structure of cyanate? Justify your answer.

 OR  OR 

Structure II is not preferred because we expect the carbon atom to be the central atom, since it is the least electronegative of the three. That leaves structures I and III to differentiate. To begin, we need to calculate the formal charges on each atom in each structure.

Structure	Formal Charge on O	Formal Charge on C	Formal Charge on N
I	0	0	-1
III	-1	0	0

Both structures only have one atom with a nonzero formal charge, so we need to determine if the negative formal charge is better located in one of the structures. We expect the structures where negative formal charges are on the most electronegative atom to be preferred. Since oxygen is more electronegative than nitrogen, we expect the structure with the negative formal charge on oxygen to be preferred, this corresponds to structure **III**.

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}
$pV = nRT$	$\Delta G = -RT\ln K = \Delta H - T\Delta S$	$K_p = K_c(RT)^{\Delta n}$
$k = Ae^{-E_{a/RT}}$	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$	$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

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)