Chem 130
Exam 4, Ch 15, with parts of 10 and 14
100 Points

Name______________________________
December 5, 2018

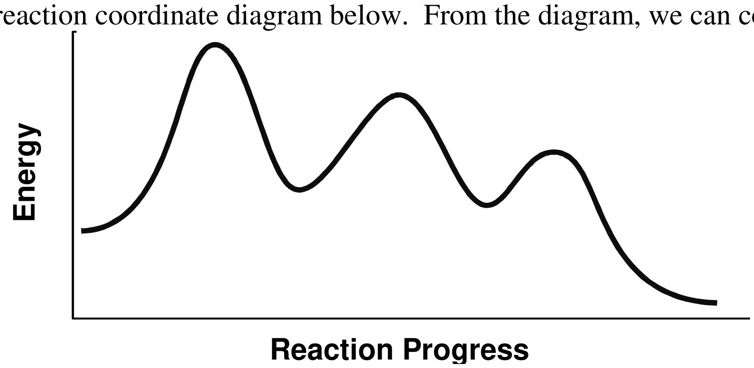
Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

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 ____________
   d. the concentration of reactants is small compared to the equilibrium constant.

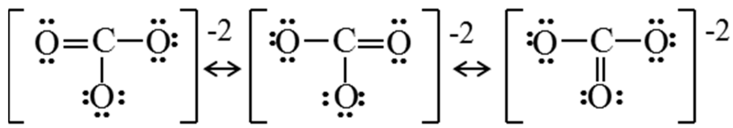
2. The pressure of a reaction vessel that contains an equilibrium mixture in the reaction $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is increased. When equilibrium is reestablished:
   a. the amount of Cl_2 will have increased.
   b. the amount of SO_2 will have decreased. Answer ____________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

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

   a. raising the temperature of the mixture while keeping the volume constant.

   b. doubling the volume of the container holding the mixture, while keeping the temperature constant.

   c. introducing more $C_5H_6(g)$.

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?

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

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 400K in a 2.16 L 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 equilibrium pressure in the vessel?

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

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

$N_2\ (g) + \frac{1}{2}\ O_2\ (g) \rightleftharpoons N_2O\ (g)$	$K_c = 2.7 \times 10^{-18}$
$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$	$K_c = 4.6 \times 10^{-3}$
$\frac{1}{2}\ N_2\ (g) + O_2\ (g) \rightleftharpoons NO_2\ (g)$	$K_c = 4.1 \times 10^{-9}$

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.

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

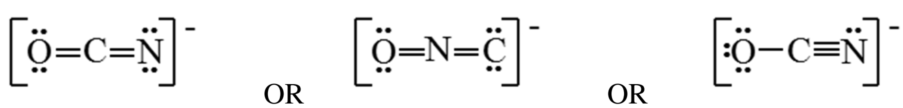
$$NOCl_2 + NO \xrightarrow{k_2} 2NOCl \text{ (slow)}$$

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^-?*

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**	
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.



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Possibly Useful Information

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

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 8B	9 8B	10 8B	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)