Chem 130
Exam 4
100 Points

Name______________________________
December 6, 2017

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 I: Complete all of problems 1-3. 4 points each.

1. 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. decreasing the temperature.
   c. transferring the mixture to a 10.0 L container.
   d. Decreasing the pressure

   Answer _____b______

2. Expansion of a valence shell to accommodate more than eight electrons is possible with:
   a. carbon.
   b. nitrogen.
   c. phosphorous.
   d. oxygen.

   Answer _____c______

3. 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_2O 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_2O will have been consumed to make more CH_3OH.
   b. Some CH_3OH will have been consumed to make more CO and H_2O
   c. The amounts of CO, H_2O, and CH_3OH will be unchanged from their initial values.
   d. There is not enough information to determine the equilibrium composition.

   Answer _____a______

Part II. <u>Equilibrium</u>. Answer <u>four (4)</u> of problems 4-8. Clearly mark the problems you do not want graded. 15 points each.

4. 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.

5. 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.

6. You have been tasked with determining the equilibrium constant for the reaction of H_2 and S_2 gases to produce hydrogen sulfide. A mixture of 1.00 g H_2 and 1.00 g H_2S in a 0.500 L flask comes to equilibrium at 1670 K. At equilibrium, there is 8.00 x 10^{-6} mol of S_2 present. What are the values for K_c and K_p at this temperature?

Start with a balanced chemical reaction:

$$2H_2 + S_2 \rightleftarrows 2H_2S$$

So, the equilibrium constant expression (K_c) is:

$$K_c = \frac{[H_2S]^2}{[H_2]^2[S_2]}$$

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

$$1.00 \text{ g } H_2 \times \frac{1 \text{ mol}}{2.01588 \text{ g}} \times \frac{1}{0.500 \text{ L}} = 0.992_1 \text{ M } H_2$$

$$1.00 \text{ g } H_2S \times \frac{1 \text{ mol}}{34.01819 \text{ g}} \times \frac{1}{0.500 \text{ L}} = 0.0586_9 \text{ M } H_2S$$

The equilibrium concentration of S_2 = (8.00x10^{-6} mol)/0.5 L = 1.60 x 10^{-5} M S_2

Mapping out the chemistry:

	$2H_2$	+	S_2	$\rightleftarrows$	$2\ H_2S$
i	0.992_1 M		0		0.0586_9 M
c	+2x		+x		-2x
e	$0.992_1 + 2(1.60 \times 10^{-5})$ = 0.992_2 M		1.60 x 10^{-5} M		$0.0586_9 - 2(1.60 \times 10^{-5})$ = 0.0586_5 M

Plugging in to K_c:

$$K_c = \frac{[H_2S]^2}{[H_2]^2[S_2]} = \frac{(0.0586_5)^2}{(0.992_2)^2(1.60 \times 10^{-5})} = \mathbf{218}$$

$$\mathbf{K_p = K_c(RT)^{\Delta n} = 218(0.08206 \times 1670)^{-1} = 1.59}$$

Answer____K_c=218, K_p = 1.59____

7. At a certain temperature, the equilibrium constant, K_c, for this reaction is 53.3. At this temperature, 0.800 mol of H_2 and 0.400 mol of HI were placed in a 0.50 L container to react. What concentration of HI is present at equilibrium?

$$H_2\,(g) + I_2\,(g) \rightleftarrows 2HI\,(g)$$

The ICE table approach works well here. First we need to get things in terms of concentration:

$$\frac{0.800 \text{ mol } H_2}{0.5L} = 1.60 \text{ M } H_2 \quad \text{and} \quad \frac{0.400 \text{ mol HI}}{0.5L} = 0.800 \text{ M HI}$$

	H_2	+	I_2	$\rightleftarrows$	2HI
I	1.60		0		0.800
C	+x		+x		-2x
E	1.60+x		x		0.800-2x

Inserting into K_c gives:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.800\text{-}2x)^2}{(1.60+x)(x)}$$

Now some algebra:

$$(1.60x+x^2)K_c = 0.640–3.2x+4x^2$$
$$53.3x^2 + 85.28x = 0.640–3.2x+4x^2$$
$$0 = 49.3x^2 + 88.48x – 0.64$$

From the quadratic formula, we find x = 0.00720 or -1.802
Since x represents the equilibrium concentration of I_2, a negative value makes no chemical sense, therefore, the value x = 0.00720is the reasonable result and [HI]=0.800-2x=0.786M

Answer____[HI]=0.786M _____

8. At equilibrium, the concentrations in this system were found to be $[N_2]=[O_2]=0.100$ M and [NO]=0.500 M. If more NO is added, bringing its concentration to 0.800 M, what will the final concentration of NO be after equilibrium is re-established?

$$N_2\,(g) + O_2\,(g) \rightleftarrows 2NO\,(g)$$

First we need to find K using the given equilibrium concentrations:

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.500)^2}{(0.100)(0.100)} = 25$$

Now the ICE table using the "new", non-equilibrium conditions:

	N_2	+	O_2	$\rightleftarrows$	2NO
I	0.100		0.100		0.800
C	+x		+x		-2x
E	0.100+x		0.100+x		0.800-2x

Inserting into K_c gives:

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.800\text{-}2x)^2}{(0.100+x)(0.100+x)} = \frac{0.640\text{-}3.20x+4x^2}{0.0100+0.200x+x^2}$$

Now some algebra:

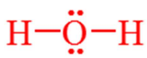
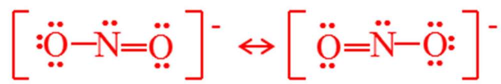
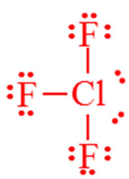
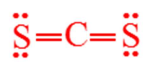
$$(0.0100+0.200x+x^2)K_c = 0.640–3.2x+4x^2$$
$$25x^2 + 5x + 0.250 = 0.640–3.20x+4x^2$$
$$0 = 21x^2 + 8.20x – 0.390$$

From the quadratic formula, we find x = 0.0429 or -0.433
Since x represents an expected increase in N_2 and O_2 concentrations, a negative value makes no chemical sense, therefore, the value x = 0.0429 is the reasonable result and [NO]=0.800-2x=0.714M.

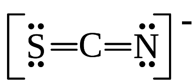
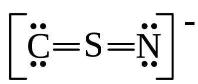
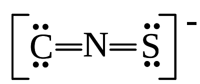
Answer___[NO]=0.714M __________

Part III. <u>Bonding</u>. Answer <u>two (2)</u> of problems 9-11. Clearly mark the problem you do not want graded. 15 points each.

9. Complete the table for **<u>three (3)</u>** of the species below.

Species	Lewis Structure (indicate resonance if necessary)	Species	Lewis Structure (indicate resonance if necessary)
H_2O		NO_2^-	
ClF_3		CS_2	

10. The Lewis structure for the thiocyanate ion (a polyatomic anion comprised of one atom each of C, N, and S) could be drawn in several ways, three of which are shown below. Which of these structures is more likely to be representative of the real structure of thiocyanate? Justify your answer.

 OR  OR 

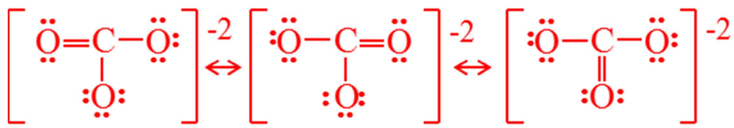
I II III

To begin, we need to calculate the formal charges on each atom in each structure.

Structure	Formal Charge on S	Formal Charge on C	Formal Charge on N
I	0	0	-1
II	+2	-2	-1
III	0	-2	+1

Since a goal in the drawing of Lewis Structures (and in the formation of compounds) is to minimize formal charge on atoms in the compound, structure I appears most favored. Structures II and III each have atoms with large formal charge, while structure I has only one atom with a nonzero formal charge.

11. Drawing the Lewis structure for carbonate ion (CO_3^{2-}) requires the use of the concept of *resonance*. Draw Lewis structures of carbonate and explain why resonance is necessary and how multiple resonance structures can be a better representation of the true structure than a single Lewis structure alone.



You should talk about the idea that the purpose of a model is to represent real life and that resonance is a modification to the Lewis model to account for some situations where the model doesn't represent real life.

When resonance is used, such as in the carbonate structure above, we recognize that the real structure is a hybrid of the resonance forms. The structure does not oscillate between the forms, but is more of an "average" of the structures.

Possibly Useful Information

$R = 0.08206\ L\ atm\ mol^{-1}\ K^{-1}$ $R = 8.314\ J\ mol^{-1}\ K^{-1}$	$K = {}^{o}C + 273.15$	$slope = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$
$\Delta G = \Delta H - T\Delta S$	${}^{o}C = K - 273.15$	$K_p = K_c(RT)^{\Delta n}$
$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$	$pV = nRT$	$\Delta G = -RTlnK$

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)