Chem 130 **Name**_____
Exam 3, Ch 7,13,14,19 **July 26, 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.

Complete Problems 1-4

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, (4 points)
   a. adding a catalyst.
   b. decreasing the temperature.
   c. transferring the mixture to a 10.0 L container. Answer _____
   d. Decreasing the pressure

2. The heat of solution of NaOH(s) in water is -41.6 kJ/mol NaOH. When NaOH is dissolved in water, the solution temperature (4 points)
   a. increases.
   b. decreases.
   c. remains constant. Answer _____
   d. either increases or decreases depending on the amount of NaOH dissolved.

3. Reactions with a positive ΔH^o and a positive ΔS^o are (4 points)
   a. spontaneous at all temperatures.
   b. nonspontanteous at all temperatures.
   c. spontaneous at low temperatures but nonspontaneous at high temperatures. Answer _____
   d. nonspontaneous at low temperaures but spontaneous at high temperatures.

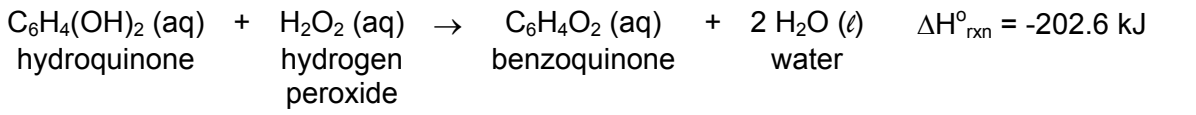
4. Consider a reaction coordinate diagram. Describe how information related to the tendency and rate of the reaction can be extracted from such a diagram. (10 points)

Thermodynamics. Answer two (2) of problems 5-7. Clearly mark the problem you do not want graded. 13 points each.

5. Solid ammonium nitrate can decompose to dintrogen oxide gas and liquid water. What is the ΔG^o at 298K? At what temperature, if any, does spontaneity of the reaction change? Is the reaction more or less spontaneous at high temperatures?

Species	ΔG^o_f (kJ/mol)	ΔH^o_f (kJ/mol)	S^o_f (J/mol)
NH_4NO_3 (s)	-183.9	-365.6	151.1
N_2O (g)	+104.2	+82.05	219.9
H_2O (ℓ)	-237.1	-285.8	69.91

6. Consider the Bombardier Beetle, who defends itself by spraying nearly boiling water on its predators. It has two glands on the tip of its abdomen, with each gland containing two compartments. The inner compartment holds an aqueous solution of hydroquinone and hydrogen peroxide. The outer compartment holds a mixture of enzymes that catalyze the following reaction:



When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, and sprays the mixture (which is near its boiling point) onto the predator. Assume a beetle emits 0.90 mL of 3.0 M hydroquinone and 1.10 mL of 3.0 M peroxide. If the initial temperature of this solution is 25.0^{O}C, what will the solution temperature be after the reaction? Assume the specific heat of the solution is 4.184 J/gK and that the density of solution is 1.00 g/mL.

7. Concisely discuss the validity of each of the following statements. Clearly justify your reasoning. A few sentences should be sufficient.
   a. Reactions with a positive ΔH^o and a positive ΔS^o can never be product-favored.

   b. Free energy changes provide a good indication of which reactions are favorable and fast, as well as those that are unfavorable and slow.

Kinetics. Answer two (2) of problems 8-10. Clearly mark the problem you do not want graded. 13 points each.

8. 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	0.105	0.900	6.46×10^{-4}

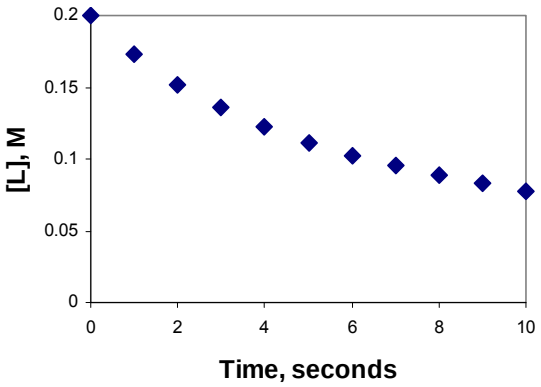
9. Consider the reaction: $A + 2B \rightarrow C + D$, the rate law is: rate = $k[A][B]^2$. Is the mechanism below valid for this reaction and rate law? Clearly justify your assertion.

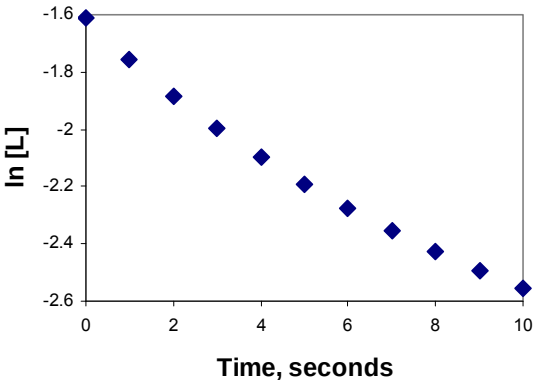
$$A + B \xrightarrow{k_1} W \text{ (slow)}$$

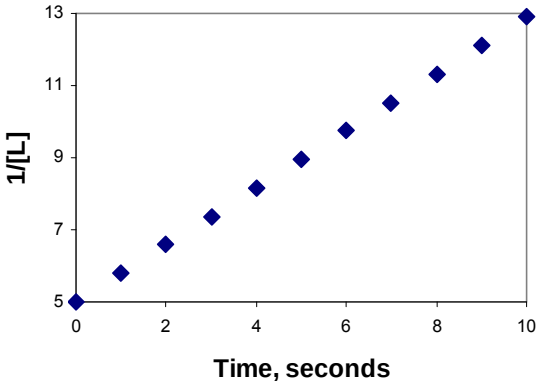
$$W + B \xrightarrow{k_2} C + D \text{ (fast)}$$

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







Equilibrium. Answer two (2) of problems 11-13. Clearly mark the problem you do not want graded. 13 points each.

11. 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?

$$2CO_2\,(g) \rightleftarrows 2CO\,(g) + O_2\,(g)$$

12. 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:

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

a. raising the temperature of the mixture.

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

c. introducing more $C_5H_6(g)$.

13. 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.*

Possibly Useful Information

$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$	$y = mx + b$	$R = 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}$ $R = 8.31441\ \text{J mol}^{-1}\text{K}^{-1}$
$\Delta G = \Delta H - T\Delta S$	$^{o}C = K - 273.15$	$K_p = K_c(RT)^{\Delta n}$
$q_{rxn} = n\Delta H_{rxn}$	$q = mc\Delta T$	$q_{released} = -q_{absorbed}$
$\text{rate} = k[A]^1$	$[A]_t = -kt + [A]_0$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\text{rate} = k[A]^2$	$\ln[A]_t = -kt + \ln[A]_0$	$k = Ae^{-E_a/RT}$
$\text{rate} = k[A]^0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$

1 1A																	18 8A
1 H 1.00794	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	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	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	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)