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. increasing the temperature.
   c. transferring the mixture to a 10.0 L container.   Answer ____**N/A**_____
   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 ____**A**_____
   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   Answer ____**D**_____
      high temperatures.
   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)

   Must discuss how tendency is indicated by the relative energies of reactants and products and how rate information comes from the central portion of the coordinate diagram relating to activation energy and mechanism..

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 $\Delta G°$ at 298K? At what temperature, if any, does spontaneity of the reaction change? Is the reaction more or less spontaneous at high temperatures?

Species	$\Delta G°_f$ (kJ/mol)	$\Delta H°_f$ (kJ/mol)	$S°_f$ (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

Start with a balanced reaction:
$$NH_4NO_3 \ (s) \rightarrow N_2O \ (g) + 2 \ H_2O \ (\ell)$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta H° = \Delta H°_f(N_2O) + 2\Delta H°_f(H_2O)] - [\Delta H°_f(NH_4NO_3)]$$
$$\Delta H° = [(+82.05) + 2(-285.8)] - [(-365.6)]kJ$$
$$\Delta H° = -123.95 \ kJ$$

$$\Delta S° = \Delta S°_f(N_2O) + 2\Delta S°_f(H_2O)] - [\Delta S°_f(NH_4NO_3)]$$
$$\Delta S° = [(219.9) + 2(69.91)] - [(151.1)]J/K$$
$$\Delta S° = +208.6 \ J/K$$

$$\Delta G° = -123.95 \ kJ/mol - 298 \ K(0.2086 \ kJ/mol \ K) = \textbf{-186.1 kJ}$$

Since $\Delta H°$ is negative and $\Delta S°$ is positive and since $\Delta G° = \Delta H° - T\Delta S°$, there is no temperature where the reaction is nonspontaneous. Since T is always positive, $\Delta G° = \Delta H° - T\Delta S°$ will be negative at all temperatures when $\Delta H°$ is negative and $\Delta S°$ is positive.

Since $\Delta S°$ is positive, the reaction will be more spontaneous at higher temperatures.

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:

$$C_6H_4(OH)_2 \text{ (aq)} + H_2O_2 \text{ (aq)} \rightarrow C_6H_4O_2 \text{ (aq)} + 2 H_2O \text{ } (\ell) \qquad \Delta H^o_{rxn} = -202.6 \text{ kJ}$$

   hydroquinone   hydrogen   benzoquinone   water
                   peroxide
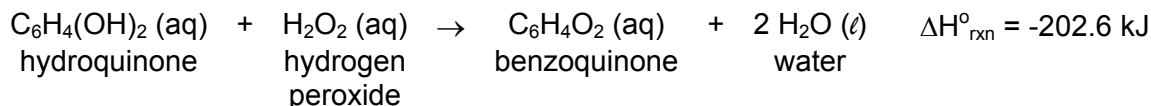
When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, and sprays the mixture (which is near its boiling point) onto the predator. Assume a beetle emits 0.90 mL of 3.0 M hydroquinone and 1.10 mL of 3.0 M peroxide. If the initial temperature of this solution is 25.0^oC, 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.

Limiting reagent is hydroquinone (0.90 mL * 3.0 mol/L = 0.0027 mol)

$$q_{rxn} = -q_{solution}$$
$$n_{LR}\Delta H_{rxn} = -mC\Delta T$$

$$\Delta T = \frac{n_{LR}\Delta H_{rxn}}{-mC} = \frac{0.0027 \text{ mol} \times (-202,600 \text{ J/mol})}{2.0 \text{ g} \times 4.184 \text{ J/gK}} = 65.4 \text{ K} = 65.4^oC$$

$$\Delta T = T_{final} - T_{initial}$$

$$\textbf{T}_{\textbf{final}} = \Delta\textbf{T} + \textbf{T}_{\textbf{initial}} = \textbf{65.4}^o\textbf{C} + \textbf{25.0}^o\textbf{C} = \textbf{90.4}^o\textbf{C}$$

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.

Your answer should discuss how ΔH^o, ΔS^o and ΔG^o are related. Since $\Delta G^o = \Delta H^o - T\Delta S^o$, as long as $T\Delta S^o$ is greater than ΔH^o, the reaction will be product favored. This can occur if ΔS^o is very large or at increased temperature.

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

Free energy changes are thermodynamic quantities that tell us about the tendency for a reaction to proceed, they tell us nothing about the rate of the reaction. We need information about kinetics to do that.

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).

$$2\ HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$$
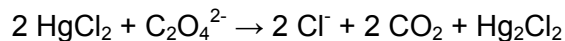
Experiment	[HgCl$_2$], M	[C$_2$O$_4^{2-}$], M	Initial Rate, M min^{-1}
1	0.105	0.300	7.18×10^{-5}
2	0.052	0.300	3.56×10^{-5}
3	0.105	0.900	6.46×10^{-4}

Comparing experiments 1 and 2: [C$_2$O$_4^{2-}$] is constant, while [HgCl$_2$] doubles. As a result the rate of the reaction doubles.

$$\frac{Rate_1}{Rate_2} = \frac{k[HgCl_2]^x[C_2O_4^{2-}]^y}{k[HgCl_2]^x[C_2O_4^{2-}]^y} = \frac{7.18\times10^{-5}}{3.56\times10^{-5}} = 2 = \frac{k[0.105]^x\cancel{[0.300]^y}}{k[0.052]^x\cancel{[0.300]^y}} = 2^x \quad x = 1$$

Now examining the other pair of data sets will allow us to find the order for C$_2$O$_4^{2-}$.

$$\frac{Rate_3}{Rate_1} = \frac{k[HgCl_2]^1[C_2O_4^{2-}]^y}{k[HgCl_2]^1[C_2O_4^{2-}]^y} = \frac{6.46\times10^{-4}}{7.18\times10^{-5}} = 9$$

$$9 = \frac{[0.900]^y}{[0.300]^y} \quad y = 2$$
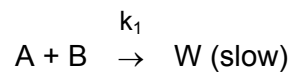
$$\mathbf{Rate = k[HgCl_2]^1[C_2O_4^{2-}]^2}$$

Use any single data set to calculate k.

$$k = \frac{Rate}{[HgCl_2]^1[C_2O_4^{2-}]^2} = \frac{7.18\times10^{-5}\ \cancel{mol/L}min}{(0.105\ \cancel{mol/L})(0.300\ mol/L)^2} = \mathbf{7.6\times10^{-3}\ L^2mol^{-1}min^{-1}}$$

So,

$$\mathbf{Rate = 7.6\times10^{-3}\ M^{-2}min^{-1}\ [HgCl_2][C_2O_4^{2-}]^2}$$

9. Consider the reaction: A + 2B → 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.

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

$$W + B \quad \xrightarrow{k_2} \quad C + D \text{ (fast)}$$
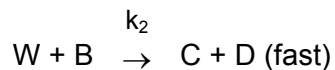
To confirm the stoichiometry, we add the two reactions together to get: A + B + W + B → W + C + D. This simplifies to A+ 2B → C + D, corresponding to the known reaction stoichiometry.

The rate law is governed by the rate-determining step. Since this is the first step, we can write the rate law based on this elementary step alone. In this case, **rate = k[A][B]**, which **does not** correspond to the experimental rate law. Since the rate law for the proposed mechanism does not match the experimentally determined rate law, the propose mechanism is not valid.

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
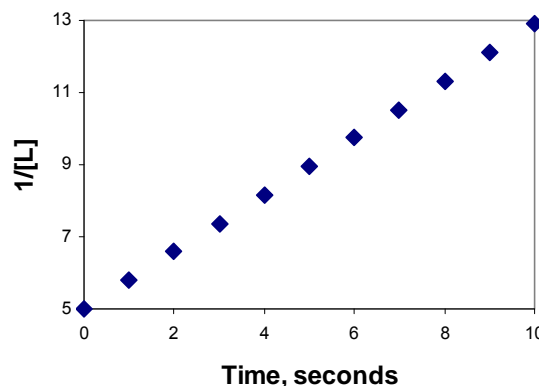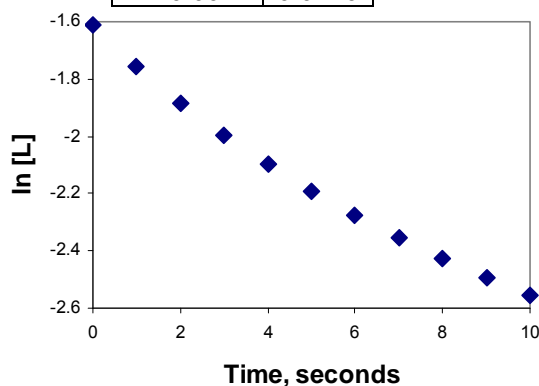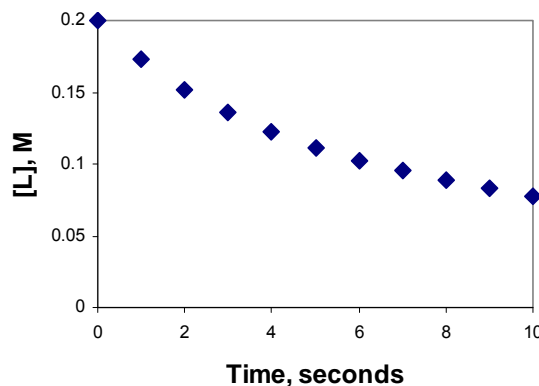
Since the plot of 1/[L] versus time is linear, the reaction must be second order in L, since this relationship corresponds to a second order rate law in the form:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

The slope of this relationship gives us the value for k. We can determine the slope from any two points of the line. For example for the points at 0 and 1 seconds:

At t=0, $1/[L] = 1/0.200M = 5.000 M^{-1}$ and at t = 1 sec, $1/[L] = 1/0.173M = 5.780 M^{-1}$

$$\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{(5.780 - 5.000)M^{-1}}{(1.00 - 0.00)\,\text{sec}} = 0.780 M^{-1}\,\text{sec}^{-1} = k$$

So our rate law is: rate = 0.780 M⁻¹s⁻¹[L]²

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?

$$2CO_2 \text{ (g)} \rightleftarrows 2CO \text{ (g)} + O_2 \text{ (g)}$$

Since we have a K_c, it is useful to get all materials in terms of concentration to start with:
$$[CO_2] = 0.20 \text{ mol}/0.50 \text{ L} = 0.40 \text{ M } CO_2$$
$$[CO] = 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M CO}$$

Now we can begin to work through the equilibrium. Since we have zero O_2 intitially, we know we cannot be at equilibrium so we must use an ICE table or some other approach to find equilibrium concentrations.

	$2CO_2$	$\rightleftarrows$	$2CO$	+	O_2
I	0.40 M		0.20 M		0
C	-2x		+2x		+x
E	0.40-2x		0.20+2x		x

The equilibrium constant expression becomes:

$$K_c = \frac{[CO]^2[O_2]}{[CO_2]^2} = \frac{(0.20+2x)^2 x}{(0.40-2x)^2}$$

Without some simplification, we will need to solve a third order polynomial. Can we simplify? Since K is small, we would not expect the reaction to proceed very far to the right. Also, the presence of CO intitially will further impede the reaction. So, we expect x to be small. Lets assume x<<0.20. If this is so, the K_c expression changes.

$$K_c = \frac{(0.20+\cancel{2x})^2 x}{(0.40-\cancel{2x})^2} = \frac{(0.20)^2 x}{(0.40)^2}$$

After rearranging we find that $x = K_c(0.40)^2/(0.20)^2 = 8.0 \times 10^{-6}$.

So, **$[O_2] = 8.0 \times 10^{-6}$M.** Was our assumption OK? 0.20 – 0.0000080 = 0.1999920, which to the correct number of sig figs is indistinguishable from 0.20, so our assumption is fine.

We could have used a calculator or computer to solve the third order polynomial. Doing so on my calculator gave a value for x of 7.998×10^{-6}.

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:

$$I_2 \text{ (g)} + C_5H_8 \text{ (g)} \rightleftarrows C_5H_6 \text{ (g)} + 2 \text{ HI (g)} \qquad \Delta H^o = +92.5 \text{ kJ}$$
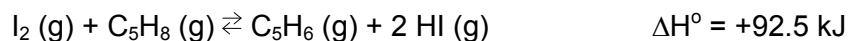
a. raising the temperature of the mixture.

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**.

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**.

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.*

Since we have a K_c, we need to begin by calculation concentrations of the species:

$$[SO_2] = 0.455 \text{ mol}/1.90 \text{ L} = 0.239_5 \text{ M}$$
$$[O_2] = 0.183 \text{ mol}/1.90 \text{ L} = 0.0963_1 \text{ M}$$
$$[SO_3] = 0.568 \text{ mol}/1.90 \text{ L} = 0.298_9 \text{ M}$$

Now we are able to calculate the reaction quotient, Q:

$$Q \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.298_9 \text{ M})^2}{(0.239_5 \text{ M})^2(0.0963_1 \text{ M})} = 16.2$$

Since Q<K, the reaction not at equilibrium and is reactant heavy. In order to reach equilibrium (Q=K), the numerator must increase while the denominator decrease. Chemically, this corresponds to increasing the concentration of products while decreasing reactants. Therefore, we would say that the reaction would proceed to the right to reach equilibrium.

Possibly Useful Information

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

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