Chem 130		Name	
Exam 3 100 Points		November 8, 2017	
Please follow the instructions problems. Provide answers with discussion questions. Point va	for each section of th the correct units ar les are in parenthese	e exam. Show your work on all mand significant figures. Be concise in s by each problem.	thematical your answers to
Part I: Complete all of probl1. The heat of solution of Na the solution temperature: (ems 1-9 OH(s) in water is -41 4)	.6 kJ/mol NaOH. When NaOH is	dissolved in water,
a. increases.b. decreases.c. remains constant.d. either increases or de	creases depending or	n the amount of NaOH dissolved.	Answer_A
2. A spontaneous process (4)a. happens quickly.b. has a small activation	c. 1 barrier. d.	continues on its own once begun. is never endothermic.	AnswerC
3. The reaction $A + B \rightarrow C + 0.012 \text{ M}^{-1}\text{min}^{-1}$. What is the set of $6 \times 10^{-4} \text{ M min}^{-1}$.	D is second order in he rate of this reaction	A and zero order in B. The value on when $[A] = 0.125$ M and $[B] = 0$	of k is .235 M? (4)
b. $2.8 \times 10^{-3} \text{ M min}^{-1}$	c. d.	$1.5 \times 10^{-3} \text{ M min}^{-1}$	Answer <u>C</u>

- 4. For each of the statements below, indicate whether the statement is CORRECT or INCORRECT and justify your choice in no more than two sentences for each item. (6)
 - a. As two gases mix, ΔS is positive.

CORRECT: As gases mix, the "disorder" or number of microstates with the same energy increases. As a result, entropy increases as well.

b. Molecules in a liquid state have higher entropy than molecules in the gaseous state.

INCORRECT: As we go from a liquid to a gas, the number of microstates with the same energy increases, leading to an increase in entropy

5. For the reaction, $2 \operatorname{NO}(g) + \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{NOCl}(g)$, $\Delta H^\circ = -40.9 \text{ kJ}$. Is the reaction to be spontaneous at high temperature, low temperature, all temperatures, or no temperatures? Justify your answer in no more than three sentences. No calculations are necessary. (6)

If we look at the reaction, there are three moles of gas on the reactant side and only two moles of gas on the product side, therefore, we expect the ΔS for this process to be negative. So, we will have a situation where we have a negative ΔH and a negative ΔS . Since $\Delta G = \Delta H - T\Delta S$, the spontaneity of the reaction will depend on temperature. In order for ΔG to be negative and have a spontaneous reaction, temperature must be low in order for ΔH - T ΔS to remain negative. Therefore, we expect this reaction to be spontaneous at low temperatures.

6. 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*. (8)



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:

$$\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$$

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 = 5.000M⁻¹ and at t = 1 sec, 1/[L] = 1/0.173M = 5.780M⁻¹
slope = m =
$$\frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{(5.780 - 5.000)M^{-1}}{(1.00 - 0.00) \sec} = 0.780M^{-1} \sec^{-1} = k$$

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

 Sketch a generic reaction coordinate diagram below for a reaction that is <u>nonspontaneous</u> and <u>slow</u>. Be sure to label the diagram. Describe how information related to the tendency and rate of the reaction can be extracted from such a diagram (10)

Your diagram for the nonspontaneous and slow reaction should bear some resemblance to the picture below and meet the following requirements: 1) the axes must be labeled, 2) the free energy for the reactants must be lower than the free energy of the products so that ΔG is negative (spontaneous), 3) the size of the activation barrier (hill) must be present, and relatively large to indicate a slow reaction. Your discussion should point out these items.



8. 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. (10)

$$A + B \xrightarrow{k_1} W \text{ (slow)}$$
$$W + B \xrightarrow{k_2} C + D \text{ (fast)}$$

To confirm the stoichiometry, we add the two reactions together to get: $A + B + W + B \rightarrow W + C + D$. This simplifies to $A + 2B \rightarrow C + D$, 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.

9. In a constant-pressure calorimeter, 65.0 mL of 0.790 M H_2SO_4 was added to 65.0 mL of 0.310 M NaOH. The reaction caused the temperature of the solution to rise from 21.22°C to 23.33°C. If the solution has the same density and specific heat as water (1.00 g/mL and 4.184 J/g·K, respectively), what is ΔH for this reaction (per mole of H_2O produced)? Assume that the total volume is the sum of the individual volumes. (10)

Start with a balanced reaction: $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ $n_{HCl}\Delta H_{rxn} = -mc\Delta T$

We need to find the limiting reactant. If H₂SO₄ is the limiting reagent,

$$65 \text{ mLH}_2\text{SO}_4 \text{ x } \underline{0.790 \text{ mol H}_2\text{SO}_4}_{1 \text{ L}} \text{ x } \underline{2 \text{ mol H}_2\text{O}}_{1 \text{ mol H}_2\text{SO}_4} = 102.7 \text{ mmol H}_2\text{O is produced}$$

Now, if NaOH is the limiting reagent,

$$65 \text{ mL-NaOH} \quad x \quad \underbrace{0.0.310 \text{ mol-NaOH}}_{1 \text{ L}} \quad x \quad \underbrace{2 \text{ mol-H}_2\text{O}}_{2 \text{ mol-NaOH}} = 20.15 \text{ mmol-H}_2\text{O} \text{ is produced}$$

So, NaOH is the limiting reactant. The total mass of solution is (65 mL + 65 mL)x1.00g/mL=130 g $(0.065 \text{ L } x \text{ } 0.310 \text{ mol NaOH/L})\Delta H_{rxn} = -(130 \text{ g})(4.184 \text{ J/g}^{\circ}\text{C})(23.33^{\circ}\text{C} -21.22^{\circ}\text{C})$

$$\Delta H_{rxn} = \frac{-(130 \text{ g})(4.184 \text{ J/g}^{\circ} \text{C})(2.11^{\circ} \text{C})}{(0.065 \text{ L x } 0.310 \text{ mol NaOH/L})} = \frac{-56956 \text{ J}}{\text{mol NaOH}} \text{ x } \frac{2 \text{ mol NaOH}}{2 \text{ mol H}_2\text{O}} = \frac{-57.0 \text{ kJ}}{\text{mol H}_2\text{O}}$$

Answer___-57.0 kJ/mol H₂O____

Part II. Answer <u>three (3)</u> of problems 10-13. Clearly mark the problems you do not want graded. 12 points each.

10. 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.

 $\begin{array}{rcl}C_{6}H_{4}(OH)_{2}\left(aq\right) &+& H_{2}O_{2}\left(aq\right) &\rightarrow& C_{6}H_{4}O_{2}\left(aq\right) &+& 2\ H_{2}O\left(l\right) & \Delta H^{o}_{rxn}=-202.6\ kJ\\ & hydrogen & benzoquinone & water\\ & peroxide\end{array}$

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° 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.

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

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

 $\Delta T = \underline{n_{LR} \Delta H_{rxn}}_{-mC} = \underline{0.0027 \text{ mol } x (-202,600 \text{ J/mol})}_{2.0 \text{ g } x \text{ 4.184 J/gK}} = 65.4 \text{ K} = 65.4^{\circ}\text{C}$

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

 $T_{\text{final}} = \Delta T + T_{\text{initial}} = 65.4^{\circ}\text{C} + 25.0^{\circ}\text{C} = 90.4^{\circ}\text{C}$

If you had your temperatures in Kelvin, this corresponds to 363.5 K

Answer_____90.4°C _____

11. Determine the standard enthalpy of formation of hexane, $C_6H_{14}(l)$, from the information below. Report your result in units of kJ per mole of hexane.

Species	ΔH [°] _f , kJ mol ⁻¹	S ^o _f , J mol ⁻¹ K ⁻¹	ΔG^{o}_{f} , kJ mol ⁻¹
$O_2(g)$	0	205.1	0
$H_2(g)$	0	130.7	0
C(s, graphite)	0	5.74	0
$CO_2(g)$	-393.5	213.7	-394.4
$H_2O(1)$	-285.8	69.91	-237.1
$H_2O(g)$	-241.8	188.8	-228.6

 $2 C_6 H_{14}(l) + 19 O_2(g) \rightarrow 12 CO_2(g) + 14 H_2O(l) \qquad \Delta H^o = -8326 \text{ kJ}$

$$\begin{split} \Delta H^{o}_{\ rxn} &= 12 \Delta H^{o}_{\ f,\ CO2} + 14 \Delta H^{o}_{\ f,\ H2O} - (2 \Delta H^{o}_{\ f,\ C6H14} + 19 \Delta H^{o}_{\ f,\ O2}) \\ -8326 \ kJ &= 12 \ \frac{\text{mol} \ CO}{2} (-393.5 \ kJ/ \ \frac{\text{mol} \ CO}{2}) + 14 \ \frac{\text{mol} \ H_2O}{142} (-285.8 \ kJ/ \ \frac{\text{mol} \ H_2O}{142}) - \\ & (2 \ mol \ C_6H_{14} \Delta H^{o}_{\ f,\ C6H14} + 19 \ \frac{\text{mol} \ O_2}{142} (0 \ kJ/ \ \frac{\text{mol} \ O_2}{142})) \end{split}$$

 $\Delta H^{o}_{f,C6H14} = -8326 \text{ kJ} - 12(-393.5 \text{ kJ}) - 14(-285.8 \text{ kJ}) = -198.6 \text{ kJ/mol } C_{6}H_{14}$

Answer_____

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

Species	$\Delta G^{o}_{f}(kJ/mol)$	$\Delta H^{o}_{f}(kJ/mol)$	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 ₂ O (<i>l</i>)	-237.1	-285.8	69.91

Start with a balanced reaction:

 $NH_4NO_3 (s) \rightarrow N_2O (g) + 2 H_2O (\ell)$

 $\Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S^{\rm o}$

$$\begin{split} \Delta H^{o} &= \Delta H^{o}{}_{f}(N_{2}O) + 2\Delta H^{o}{}_{f}(H_{2}O)] - [\Delta H^{o}{}_{f}(NH_{4}NO_{3})] \\ \Delta H^{o} &= [(+82.05) + 2(-285.8)] - [(-365.6)]kJ \\ \Delta H^{o} &= -123.95 \text{ kJ} \end{split}$$

$$\begin{split} \Delta S^{\circ} &= \Delta S^{\circ}{}_{f}(N_{2}O) + 2\Delta S^{\circ}{}_{f}(H_{2}O)] - [\Delta S^{\circ}{}_{f}(NH_{4}NO_{3})] \\ \Delta S^{\circ} &= [(219.9) + 2(69.91)] - [(151.1)]J/K \\ \Delta S^{\circ} &= +208.6 \text{ J/K} \end{split}$$

 $\Delta G^{\circ} = -123.95 \text{ kJ/mol} - 298 \text{ K}(0.2086 \text{ kJ/mol} \text{ K}) = -186.1 \text{ kJ}$ You can also calculate ΔG° using the ΔG°_{f} and will arrive at the same result.

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

Since ΔS° is positive, the reaction will be more spontaneous at higher temperatures. That is, higher temperatures lead to a larger negative ΔG° .

Answer_____

Experiment	[A], M	[B], M	Initial Rate (Ms ⁻¹)
1	0.0133	0.0370	6.75 x 10 ⁻⁴
2	0.0266	0.0370	2.70 x 10 ⁻³
3	0.0200	0.0200	8.24 x 10 ⁻⁴

13. The initial rate of the reaction $A + B \rightarrow C + D$ is determined for different initial conditions, with the results listed in the table below. Determine the rate law and the rate constant for the reaction.

Comparing reactions 1 and 2: [B] remains constant, but [A] changes by (0.0266/0.0133) = 2 times. The rate changes by $(2.70 \times 10^{-3}/6.75 \times 10^{-4}) = 4$ times $= 2^2$. Since the change in rate is the same as the change in concentration squared, the reaction must be **second order in A**.

Since we do not have another pair of experiments where one concentration stays the same while the other changes, we have a little more work to do to find the order for B

$\frac{2.70 \text{ x } 10^{-3} \text{ Ms}^{-4}}{8.24 \text{ x } 10^{-4} \text{ Ms}^{-4}} = \frac{\text{k}(0.0266)^2 (0.0370)^{\text{x}}}{\text{k}(0.0200)^2 (0.0200)^{\text{x}}}$
$3.277 = \frac{1.769(0.0370)^{x}}{(0.0200)^{x}}$
$1.85 = (0.0370)^{x} = (1.85)^{x}$ (0.0200) ^x
log(1.85) = xlog(1.85) x = log(1.85)/log(1.85) = 1
Therefore, the rate law must be: $Rate = k[A]^{2}[B]$

We can use any experiment to find the value of the rate constant. Let's use experiment 3:

k = Rate = $8.24 \times 10^{-4} \text{ Ms}^{-1}$ = $103 \text{ M}^{-2}\text{s}^{-1}$ (0.0200M)²(0.0200M)

So, the overall rate law is: Rate = $103 \text{ M}^{-2}\text{s}^{-1} [\text{A}]^{2}[\text{B}]$

Answer___Rate = $103 \text{ M}^{-2} \text{s}^{-1} [\text{A}]^2 [\text{B}]___$

Possibly Useful Information

$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	$K = {}^{\circ}C + 273.15$	slope = m = $\frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$
q=mc\DeltaT	$q=n_{LR}\Delta H_{rxn}$	q=m∆H
$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$	$\Delta G = \Delta H - T \Delta S$	$\Delta S_{surr} = -\Delta H_{sys}/T$
$rate = k[A]^0$	$[\mathbf{A}]_{t} = -\mathbf{k}\mathbf{t} + [\mathbf{A}]_0$	$t_{1/2} = [A]_0/2k$
$rate = k[A]^1$	$\ln[A]_{t} = -kt + \ln[A]_{0}$	$t_{1/2} = 0.693/k$
$rate = k[A]^2$	$\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$	$t_{1/2} = 1/(k[A]_0)$

1																	18
1A																	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	З 3В	4 4B	5 5B	6 6B	7 7B	8	9 	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)							
*Lar	nthanid	e 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
[†] Act	inide s	eries		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)

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