Chem 130   **Name**_____

Exam 3, Ch 7, 19, 14   **November 9, 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.

Part 0: Warmup. 4 points each

1. Reactions with a positive ΔH^o and a negative ΔS^o are
    a. spontaneous at all temperatures.
    b. non-spontaneous at all temperatures.
    c. spontaneous at low temperatures but non-spontaneous at   Answer ____B_____
        high temperatures.
    d. non-spontaneous at low temperatures but spontaneous at
        high temperatures.
2. Which of the processes below DOES NOT result in an increase in entropy?
    a. $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$
    b. $H_2O(s) \rightarrow H_2O(\ell)$ (The melting of ice.)
    c. $CO_2(s) \rightarrow CO_2(g)$ (The sublimation of dry ice.)   Answer ____A_____
    d. $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(\ell)$
3. Consider the reaction below. If hydrogen chloride gas is being produced at 1.2 moles per liter per minute (M min^{-1}), at what rate is hydrogen gas being consumed
    $$2ICl(g) + H_2(g) \rightarrow I_2(g) + 2HCl(g)$$
    a. 1.2 M min^{-1}
    b. 0.60 M min^{-1}
    c. 2.4 M min^{-1} Answer ____B_____
    d. Not enough information to determine.

Part I: Complete all of problems 4-8

4. Describe what is meant when we call something a "state function". How do the properties of a state function aid us in determining thermodynamic parameters and in predicting thermodynamic behavior? (6 points)

    Sate functions are only concerned with the starting and ending "states" or conditions of a process, but are not dependent on the pathway the process takes going from the start to the end. This allows us to model thermodynamic problems by building pathways from known components, like component reactions using Hess' law or by using enthalpies, entropies and Gibbs energies of formation.

5. Concisely discuss the validity of each of the following statements. Clearly justify your reasoning. A few sentences should be sufficient. (14 points)
   a. Reactions with a positive ΔH° and a positive ΔS° can never be product-favored.

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

6. Consider a first order reaction B → Products. An experiment is performed and it is determined that, given a starting [B] = 0.100 M, it requires 56.2 seconds for the concentration to fall to 0.029 M. What is the rate constant for the reaction? How long would it take for the concentration to fall from 0.100 M to 0.0010 M? (14 points)

The integrated rate law for a first order reaction is helpful here: $\ln[A]_t = -kt + \ln[A]_0$. From the problem, $[A]_t = 0.029$ M, $[A]_0 = 0.100$ M and t = 56.2 s

$$k = \frac{\ln[A]_t - \ln[A]_0}{-t} = \frac{\ln(0.029) - \ln(0.100)}{-56.2 \text{ s}} = \mathbf{0.022 \text{ s}^{-1} = k}$$

Now that we have k, we can use the integrated rate law to solve the second part of the problem:

$$t = \frac{\ln[A]_t - \ln[A]_0}{-k} = \frac{\ln(0.0010) - \ln(0.100)}{-0.022 \text{ s}^{-1}} = \mathbf{209 \text{ s} = 210 \text{ s (2 sig figs)}}$$

   Answer: Rate constant_____0.022 s^{-1}_____ Time to 0.0010 M_____210 s_____

7. How much heat energy is produced when 0.100 kg of gaseous ethane (C_2H_6) undergoes a combustion reaction with excess oxygen gas to produce gaseous carbon dioxide and liquid water? (14 points)

Species	$\Delta H°_f$, kJ mol^{-1}	Species	$\Delta H°_f$, kJ mol^{-1}
O(g)	+249.2	$H_2O(\ell)$	-285.8
O_2(g)	0	H_2O(g)	-241.8
H(g)	+218.0	C_2H_6(g)	-84.7
H_2(g)	0	CO_2(g)	-393.5

$$2C_2H_6(g) + 7O_2(g) \rightarrow 6H_2O(\ell) + 4CO_2(g)$$
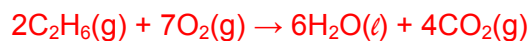
$$\Delta H°_{rxn} = (6\Delta H°_{f, H2O} + 4\Delta H°_{f,CO2}) - (2\Delta H°_{f, C2H6} + 7\Delta H°_{f, O2})$$

$$\Delta H°_{rxn} = (6(-285.8 \text{ kJ}) + 4(-393.5 \text{ kJ})) - (2(-84.7 \text{ kJ}) + 7(0 \text{ kJ}))$$

$$\Delta H°_{rxn} = -3119 \text{ kJ}$$

So, 3288 kJ of energy is released every time two moles of ethane is consumed.

$$100 \text{ g } C_2H_6 \ \times \ \frac{1 \text{ mol } C_2H_6}{30.07 \text{ g } C_2H_6} \ \times \ \frac{3119 \text{ kJ}}{2 \text{ mol } C_2H_6} \ = \ \textbf{5188 kJ}$$

Answer_____**5188 kJ**_____

Part II. Answer three (3) of problems 8-11. Clearly mark the problem you do not want graded. 14 points each.
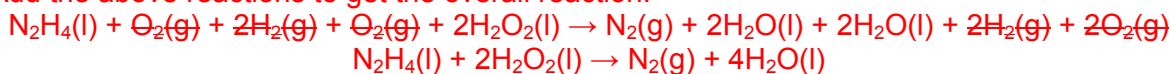
8. Determine ΔH^o for the reaction $N_2H_4(\ell) + 2H_2O_2(\ell) \rightarrow N_2(g) + 4H_2O(\ell)$ from these data:

Reaction	ΔH^o
$N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2H_2O(\ell)$	-622.2 kJ
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$	-285.8 kJ
$N_2(g) + O_2(g) \rightarrow 2NO(g)$	+173.1 kJ
$H_2(g) + O_2(g) \rightarrow H_2O_2(\ell)$	-187.8 kJ

	Reaction	ΔH^o
The first reaction is left alone:	$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$	-622.2 kJ
Double the second reaction:	$2(H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l))$	2(-285.8 kJ)
Reverse and double the fourth rxn:	$2(H_2O_2(l) \rightarrow H_2(g) + O_2(g))$	-2(-187.8 kJ)

The third reaction is not used

Add the above reactions to get the overall reaction:
$N_2H_4(l) + \cancel{O_2(g)} + \cancel{2H_2(g)} + \cancel{O_2(g)} + 2H_2O_2(l) \rightarrow N_2(g) + 2H_2O(l) + 2H_2O(l) + \cancel{2H_2(g)} + \cancel{2O_2(g)}$
$N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

ΔH^o = -622.2 kJ + (2(-285.8 kJ)) +(-2(-187.8 kJ)) = **-818.2 kJ**

Answer_____**-818.2 kJ** _____

4

9. A coffee-cup calorimeter contains 100.0 mL of 0.300 M HCl at 20.3°C. When 1.82 g zinc metal also at 20.3°C is added and is allowed to react via the net ionic equation below, the temperature rises to 30.5°C. What is the heat of reaction per mole of Zn? Assume no heat is lost to the environment during the course of the reaction and that the heat capacity and the density of the solution is the same as that of pure water (1.00 g/mL and 4.184 J/g°C, respectively).

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$
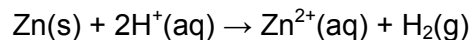
We first need to determine if all of the zinc will react. How many mL HCl will we need?

$$1.82 \text{ g Zn} \quad \times \quad \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \quad \times \quad \frac{2 \text{ mol H}^+}{1 \text{ mol Zn}} \quad \times \quad \frac{1000 \text{ mL}}{0.300 \text{ mol H}^+} \quad = \quad 185 \text{ mL}$$

So, HCl is the limiting reagent:

$$q_{reaction} = {}^-q_{calorimeter}$$
$$n_{HCl}\Delta H_{rxn} = -mc\Delta T$$

$$(0.100 \text{ L} \times 0.300 \text{ mol HCl/L})\Delta H_{rxn} = -(101.82 \text{ g})(4.184 \text{ J/g°C})(30.5°C - 20.3°C)$$

$$\Delta H_{rxn} = \frac{-(101.82 \text{ g})(4.184 \text{ J/g°C})(10.2°C)}{(0.100 \text{ L} \times 0.300 \text{ mol HCl/L})} = \frac{144.8 \text{ kJ}}{\text{mol HCl}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Zn}} = \mathbf{\frac{-289.7 \text{ kJ}}{\text{mol Zn}}}$$

(If you make the incorrect assumption that Zn is the limiting reagent, you find ΔH = -156 kJ/mol Zn.)

Answer_____-290 kJ/mol Zn_____

10. The reaction $I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$ was studied and the data below were obtained. Determine the rate law and the value of the rate constant for this reaction.

$[I^-]_0$(mol/L)	$[OCl^-]_0$(mol/L)	Initial Rate (mol/Ls)
0.12	0.18	0.0791
0.060	0.18	0.0395
0.030	0.090	0.00988
0.24	0.090	0.0791

$$\frac{Rate_1}{Rate_2} = \frac{k[I^-]^x[OCl^-]^y}{k[I^-]^x[OCl^-]^y} = 2 = \frac{\cancel{k}[0.12]^x\cancel{[0.18]^y}}{\cancel{k}[0.06]^x\cancel{[0.18]^y}} = 2^x \quad x = 1$$

Since there are no pairs or reactions in which only the OCl^- concentration changes the I^- concentration does not, we can use any of the pairs to determine the reaction order for OCl^-.

$$\frac{Rate_2}{Rate_3} = \frac{k[I^-]^x[OCl^-]^y}{k[I^-]^x[OCl^-]^y} = 4 = \frac{\cancel{k}[0.06]^1[0.18]^y}{\cancel{k}[0.03]^1[0.09]^y}$$

$$2 = \frac{[0.18]^y}{[0.09]^y} \quad y = 1$$

$$\text{Rate} = k[I^-][OCl^-] \quad k = \frac{Rate}{[I^-][OCl^-]} = \frac{0.0791\ \cancel{M}/s}{(0.12\ M)(0.18\ \cancel{M})} = 3.66\ M^{-1}s^{-1}$$

Answer____Rate = 3.7M^{-1}s^{-1}[I$^-$][OCl$^-$]_____

11. Consider the reaction $N_2O(g) + 2H_2O(\ell) \rightarrow NH_4NO_3(s)$ at 298K.

Species	ΔH°_f, kJ mol^{-1}	S°_f, J mol^{-1} K^{-1}	ΔG°_f, kJ mol^{-1}
$O_2(g)$	0	205.1	0
$H_2(g)$	0	130.7	0
$NH_4NO_3(s)$	-365.6	151.1	-183.9
$N_2O(g)$	82.05	219.9	104.2
$H_2O(\ell)$	-285.8	69.91	-237.1
$H_2O(g)$	-241.8	188.8	-228.6

a. Is the forward reaction exothermic or endothermic? (5 points)

$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_{f, NH4NO3} - (\Delta H^{\circ}_{f, N2O} + 2\Delta H^{\circ}_{f,H2O})$

ΔH°_{rxn} = -365.6 kJ – (82.05 kJ+ 2(-285.8 kJ))

ΔH°_{rxn} = +124 kJ

Since ΔH° is positive, the reaction is endothermic

b. What is the value of ΔG° at 298 K? (5 points)

$\Delta S^{\circ}_{rxn} = S^{\circ}_{f, NH4NO3} - (S^{\circ}_{f, N2O} + 2S^{\circ}_{f,H2O})$

ΔS°_{rxn} = 151.1J/K – (219.9J/K + 2(69.91J/K))

ΔS°_{rxn} = -209 J/K

$\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$ = +124kJ – 298K(0.209kJ/K) = **+186 kJ**

Alternatively:
$\Delta G^{\circ}_{rxn} = \Delta G^{\circ}_{f, NH4NO3} - (\Delta G^{\circ}_{f, N2O} + 2\Delta G^{\circ}_{f,H2O})$
ΔG°_{rxn} = -183.9 kJ – (104.2 kJ+ 2(-237.1 kJ))
ΔG°_{rxn} = +186 kJ

c. Does the reaction occur spontaneously at temperatures above 298 K, below 298 K, both, or neither? Justify your answer. (4 points)

Since ΔH°_{rxn} is positive, and ΔS°_{rxn} is negative, ΔG°_{rxn} will be positive at all temperatures, since $\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$ = (+) – (+)(+) = (+) regardless of temperature. So, the reaction is non-spontaneous at all temperatures.

(NOTE: If you did not calculate ΔS°_{rxn} in part b, you can infer that it is negative by looking at the reaction. Since there are fewer moles of gas on the products side of the reaction compared to the reactants, we expect ΔS°_{rxn} to be negative.)

Possibly Useful Information

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

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	9 8B	10	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)

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