

Chem 130
Exam 3, Ch 7, 19, and a little 14
100 Points

Name _____
November 11, 2011

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

- A spontaneous process:
 - will happen quickly.
 - releases large amounts of energy.
 - will continue on its own once begun.
 - is never endothermic.

Answer C
- Reactions with a positive ΔH° and a negative ΔS° are:
 - spontaneous at all temperatures.
 - non-spontaneous at all temperatures.
 - spontaneous at low temperatures but non-spontaneous at high temperatures.
 - non-spontaneous at low temperatures but spontaneous at high temperatures.

Answer B
- The reaction $A + B \rightarrow C + D$ is second order in A and zero order in B. The value of k is $0.012 \text{ M}^{-1}\text{min}^{-1}$. What is the rate of this reaction when $[A] = 0.235 \text{ M}$ and $[B] = 0.125 \text{ M}$?
 - $6.6 \times 10^{-4} \text{ M min}^{-1}$
 - $2.8 \times 10^{-3} \text{ M min}^{-1}$
 - $1.9 \times 10^{-4} \text{ M min}^{-1}$
 - $1.5 \times 10^{-3} \text{ M min}^{-1}$

Answer A

Part I: Complete all of problems 3-8. 12 points each.

- 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.
 - As temperature in a gas decreases, ΔS is positive.

INCORRECT: As T decreases, the gas particles have less kinetic energy and therefore less freedom of movement. This leads to less "disorder" and a decrease in entropy, or negative ΔS .

- 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.

- 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.

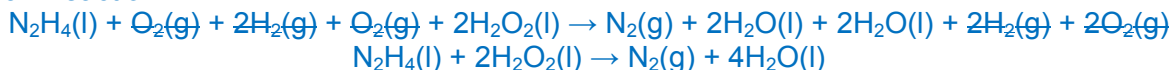
Form B

5. Determine ΔH° for the reaction $\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ from these data:

Reaction	ΔH°
$\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-622.2 kJ
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285.8 kJ
$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l})$	-187.8 kJ

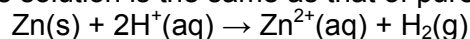
The first reaction is left alone:	$\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-622.2 kJ
Double the second reaction	$2(\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}))$	2(-285.8 kJ)
Reverse and double the third rxn:	$2(\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2(\text{g}) + \text{O}_2(\text{g}))$	-2(-187.8 kJ)

Overall Reaction:



$$\Delta H^\circ = -622.2 \text{ kJ} + (2(-285.8 \text{ kJ})) + (-2(-187.8 \text{ kJ})) = \mathbf{-818.2 \text{ kJ}}$$

6. 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, the temperature rises to 30.5°C. What is the heat of reaction per mole of Zn? Assume no heat is lost 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.



We first need to determine if all of the zinc will react. How many mL HCl will we need?

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

So, HCl is the limiting reagent:

$$n_{\text{HCl}} \Delta H_{\text{rxn}} = -mc\Delta T$$

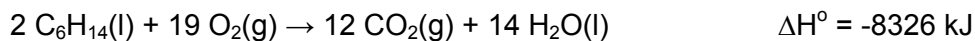
$$(0.100 \text{ L} \times 0.300 \text{ mol HCl/L}) \Delta H_{\text{rxn}} = -(101.82 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(30.5^\circ\text{C} - 20.3^\circ\text{C})$$

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

(If you make the incorrect assumption that Zn is the limiting reagent, you find $\Delta H = -156 \text{ kJ/mol Zn}$.)

Form B

7. 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	$\Delta H^\circ_f, \text{kJ mol}^{-1}$	$S^\circ_f, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\circ_f, \text{kJ mol}^{-1}$
$O_2(g)$	0	205.1	0
$H_2(g)$	0	130.7	0
$C(s, \text{graphite})$	0	5.74	0
$CO_2(g)$	-393.5	213.7	-394.4
$H_2O(l)$	-285.8	69.91	-237.1
$H_2O(g)$	-241.8	188.8	-228.6

$$\Delta H^\circ_{\text{rxn}} = 12\Delta H^\circ_{f, CO_2} + 14\Delta H^\circ_{f, H_2O} - (2\Delta H^\circ_{f, C_6H_{14}} + 19\Delta H^\circ_{f, O_2})$$

$$-8326 \text{ kJ} = 12(-393.5 \text{ kJ}) + 14(-285.8 \text{ kJ}) - (2\Delta H^\circ_{f, C_6H_{14}} + 19(0 \text{ kJ}))$$

$$\Delta H^\circ_{f, C_6H_{14}} = \frac{-8326 \text{ kJ} - 12(-393.5 \text{ kJ}) - 14(-285.8 \text{ kJ})}{-2} = -198.6 \text{ kJ/mol } C_6H_{14}$$

8. For the reaction, $2 NO(g) + Cl_2(g) \rightarrow 2 NOCl(g)$, $\Delta H^\circ = -40.9 \text{ kJ}$. At what temperatures do you expect the reaction to be spontaneous: high, low, all, or none? Justify your answer.

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 $\Delta H - T\Delta S$ to remain negative. Therefore, we expect this reaction to be spontaneous at low temperatures.

Part II. Answer two (2) of problems 9-11. Clearly mark the problems you do not want graded. 15 points each.

9. 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.

Experiment	[A], M	[B], M	Initial Rate (Ms^{-1})
1	0.0133	0.0185	3.35×10^{-4}
2	0.0133	0.0370	6.75×10^{-4}
3	0.0266	0.0370	2.70×10^{-3}
4	0.0266	0.0185	1.35×10^{-3}

Comparing reactions 1 and 2: [A] remains constant, but [B] changes by $(0.0370/0.0185) = 2$ times. The rate changes by $(6.75 \times 10^{-4}/3.35 \times 10^{-4}) = 2.01$ times. Since the change in rate is the same as the change in concentration, the reaction must be **first order in B**.

Now comparing reactions 2 and 3: [B] remains constant, but [A] changes by $(0.0266/0.0133) = 2$ times. The rate changes by $(2.70 \times 10^{-3}/6.75 \times 10^{-4}) = 4.00$ times. Since the change in rate is the same as the change in concentration squared, the reaction must be **second order in A**.

Therefore, the rate law must be: $\text{Rate} = k[\text{A}]^2[\text{B}]$

We can use any experiment to find the value of the rate constant. Let's use experiment 4:

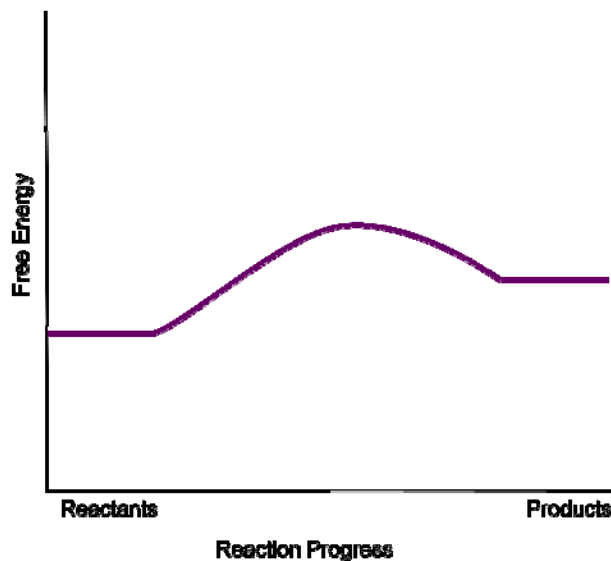
$$k = \frac{\text{Rate}}{[\text{A}]^2[\text{B}]} = \frac{1.35 \times 10^{-3} \text{ Ms}^{-1}}{(0.0266\text{M})^2(0.0185\text{M})} = 103 \text{ M}^{-2}\text{s}^{-1}$$

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

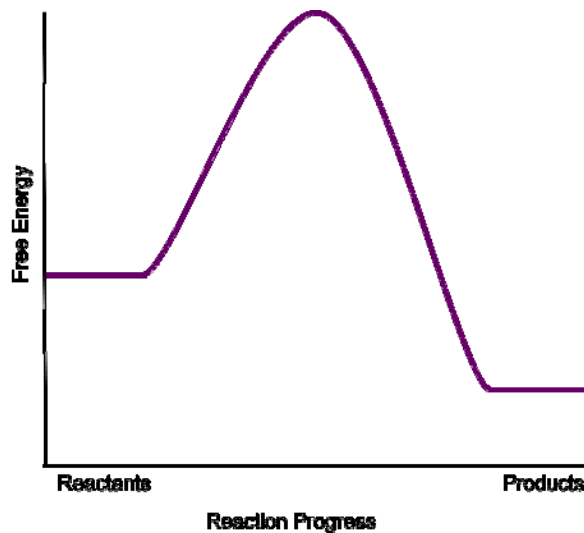
Form B

10. Sketch two reaction coordinate diagrams below. For the first diagram, illustrate a generic reaction that is non-spontaneous and fast in the forward direction. For the second, illustrate a generic reaction that is spontaneous and slow in the forward direction. Clearly label your plots. For each diagram, include a brief description of how it satisfies the spontaneity and speed of the reaction requirements.

Your diagram for the non-spontaneous and fast 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 less than the free energy of the product so that ΔG is positive (non-spontaneous), 3) the size of the activation barrier (hill) must be present, but relatively small to indicate a fast reaction. Your discussion should point out these items.



Your diagram for the spontaneous 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 higher 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.



Form B

11. Consider the reaction $\text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$ at 298K.

Species	$\Delta H^\circ_f, \text{kJ mol}^{-1}$	$S^\circ_f, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\circ_f, \text{kJ mol}^{-1}$
$\text{O}_2(\text{g})$	0	205.1	0
$\text{H}_2(\text{g})$	0	130.7	0
$\text{NH}_4\text{NO}_3(\text{s})$	-365.6	151.1	-183.9
$\text{N}_2\text{O}(\text{g})$	82.05	219.9	104.2
$\text{H}_2\text{O}(\text{l})$	-285.8	69.91	-237.1
$\text{H}_2\text{O}(\text{g})$	-241.8	188.8	-228.6

a. Is the forward reaction exothermic or endothermic?

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{f, \text{NH}_4\text{NO}_3} - (\Delta H^\circ_{f, \text{N}_2\text{O}} + 2\Delta H^\circ_{f, \text{H}_2\text{O}})$$

$$\Delta H^\circ_{\text{rxn}} = -365.6 \text{ kJ} - (82.05 \text{ kJ} + 2(-285.8 \text{ kJ}))$$

$$\Delta H^\circ_{\text{rxn}} = +124 \text{ kJ}$$

Since ΔH° is positive, the reaction is endothermic

b. What is the value of ΔG° at 298 K?

$$\Delta S^\circ_{\text{rxn}} = S^\circ_{f, \text{NH}_4\text{NO}_3} - (S^\circ_{f, \text{N}_2\text{O}} + 2S^\circ_{f, \text{H}_2\text{O}})$$

$$\Delta S^\circ_{\text{rxn}} = 151.1 \text{ J/K} - (219.9 \text{ J/K} + 2(69.91 \text{ J/K}))$$

$$\Delta S^\circ_{\text{rxn}} = -209 \text{ J/K}$$

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = +124 \text{ kJ} - 298 \text{ K}(0.209 \text{ kJ/K}) = +186 \text{ kJ}$$

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

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

Form B
Possibly Useful Information

$\Delta G = \Delta H - T\Delta S$	$^{\circ}\text{C} = \text{K} - 273.15$
$q_{\text{rxn}} = n\Delta H_{\text{rxn}}$	$q = mc\Delta T$
Don't eat the yellow snow!	$Q_{\text{released}} = -Q_{\text{absorbed}}$

Compound	Molar Mass (g/mol)	Compound	Molar Mass (g/mol)
H ₂ O	18.0153	C ₆ H ₁₄	86.177
H ₂ O ₂	34.0147	CO ₂	44.010
HCl	36.4606	N ₂ H ₄	32.0452
H ₂	2.01588	NH ₄ NO ₃	80.0434
N ₂	28.0135	N ₂ O	44.0129
O ₂	31.9988	NO	30.0061
Cl ₂	70.9054	NOCl	65.4588

Material	Specific Heat Capacity (J/gK)
H ₂ O (s)	2.050
H ₂ O (l)	4.184
H ₂ O (g)	2.080
Zn(s)	0.390

1																	18		
1A																	8A		
1 H 1.00794	2 2A													3A	4A	5A	6A	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	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	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	*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	†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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