Chem 120 **Name**_____
Exam 3, Ch 7, 19 **November 7, 2008**
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. I have intentionally left a great deal of space for each problem. I do not expect each problem to take up all of the space provided!

Part 0: Warmup. 4 points each

1. The heat of solution of NaOH(s) in water is -41.6 kJ/mol NaOH. When NaOH is dissolved in water, the solution temperature

   a. increases.
   b. decreases.
   c. remains constant.
   d. either increases or decreases depending on the amount of NaOH dissolved.

   Answer ____**A**_____

2. A plausible final temperature when 75.0 mL of water at 80.0^{o}C is added to 100.0 mL of water at 20.0^{o}C is

   a. 28^{o}C.
   b. 40^{o}C.
   c. 46^{o}C.
   d. 50^{o}C.

   Answer ____**C**_____

3. For a process to occur spontaneously,

   a. the entropy of the system must increase.
   b. both the entropy of the system and surroundings must increase.
   c. the net change of the entropy of the system and surroundings must be a positive quantity.
   d. the entropy of the universe must remain constant.

   Answer ____**C**_____

4. Reactions with a positive ΔH^{o} and a positive ΔS^{o} are

   a. spontaneous at all temperatures.
   b. nonspontanteous at all temperatures.
   c. spontaneous at low temperatures but nonspontaneous at high temperatures.
   d. nonspontaneous at low temperaures but spontaneous at high temperatures.

   Answer ____**D**_____

5. 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.)
   d. $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(\ell)$

   Answer _____**A**_____

Part I: Complete all of problems 6-9.

6. Concisely discuss the validity of each of the following statements. Clearly justify your reasoning. A few sentences should be sufficient. (12 points)
   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.

7. An ice cube weighing 5.63 g originally at 0.0°C was dropped into an insulated cup. After a short period of time, the ice had all melted and the temperature of the remaining liquid water had reached 25.2°C. How much heat energy, in kJ, did the water lose to the surroundings as it melted and warmed? (For water, ΔH^o_{fusion} = 333 J/g, $\Delta H^o_{vaporization}$ = 2256 J/g) (12 points)

   The intent here was to calculate the quantity of heat (q) transferred when the ice undergoes the phase change and warms up.

$$q_{total} = q_{melting} + q_{temperature\ change}$$
$$q_{total} = n\Delta H^o_{fus} + mc\Delta T$$
$$q_{total} = (5.63\ \cancel{g} \times 333 J/\cancel{g}) + [5.63\cancel{g} \times 4.184 J/\cancel{g}\cancel{K} \times (25.2-0.0)\cancel{K}]$$
$$q_{total} = 2468.4\ J$$
$$\mathbf{q_{total} = 2.47\ kJ}$$

   The work above corresponds to what I had intended the problem to lead you towards. However, the problem asks "how much heat did the water **lose**…". Besides the fact that I had misspelled lose as *loose*, as the ice melts and the water warms, it **gains** heat, it doesn't lose it. So an acceptable answer would be that is loses no heat, since the melting and warming are endothermic!

8. For the following processes, give the algebraic sign for ΔH^o, ΔS^o, and ΔG^o. No calculations are necessary, use your common sense and briefly justify your decisions. A few sentences should be sufficient. (12 points)

   a. The splitting of liquid water to give gaseous oxygen and gaseous hydrogen, a process that requires a considerable amount of energy.

Parameter	Expected Sign	Justification
ΔH^o	+	Experience tells us that when hydrogen and oxygen react, a great deal of heat is evolved (think Hindenberg). Therefore, the reverse process would require the addition of heat (energy).
ΔS^o	+	Converting a liquid to gas leads to an increase in entropy.
ΔG^o	depends	Depends on temperature, but at room temperature, experience tells us that water does not spontaneously convert to hydrogen and oxygen, so at room temperature, ΔG^o is positive.

   b. The explosion of dynamite, a mixture of solid nitroglycerine and solid diatomaceous earth. The explosive decomposition gives gaseous products such as water, CO_2 and others and much heat is evolved.

Parameter	Expected Sign	Justification
ΔH^o	-	The sentence says “and much heat is evolved”. The evolution of heat corresponds to a negative ΔH^o.
ΔS^o	+	Converting a solid to gas leads to an increase in entropy.
ΔG^o	-	Since ΔH^o is negative and ΔS^o is positive, ΔG^o must be negative since $\Delta G^o = \Delta H^o - T\Delta S^o$.

9. Answer the following questions regarding the decomposition of sulfur trioxide to sulfur dioxide and oxygen. (16 points)

$2\ SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g)$

Species	ΔH_f^o (kJ/mol)	S^o (J/mol K)
O (g)	249.170	161.055
O_2 (g)	0	205.138
S (s)	0	31.80
S (g)	278.805	167.821
SO_2 (g)	-296.830	248.22
SO_3 (g)	-395.72	256.76

a. Calculate the ΔG^o for this reaction at 298K. (10 points)

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta H^o = 2\Delta H^o_f(SO_2) + \Delta H^o_f(O_2) - 2\Delta H^o_f(SO_3) = [2(-296.8) + 0 - 2(-395.7)]kJ/mol$$
$$\Delta H^o = 197.8\ kJ/mol$$

$$\Delta S^o = 2S^o(SO_2) + S^o(O_2) - 2S^o(SO_3) = [2(248.22) + 205.13 - 2(256.76)]kJ/mol\ K$$
$$\Delta S^o = 188.1\ J/mol\ K$$

$$\Delta G^o = 197.8\ kJ/mol - 298\ K(0.1881\ kJ/mol\ K) = \mathbf{+141.8\ kJ/mol}$$

b. Calculate the minimum temperature required for the reaction to be product-favored. (6 points).

For a favorable reaction ($\Delta G < 0$), $|\Delta H|$ must be smaller than $|T\Delta S|$, or ΔG must go through zero. So the temperature where ΔG is zero is the temperature where the spontaneity changes.

$$\Delta G = \Delta H - T\Delta S$$
$$0 = \Delta H - T\Delta S$$
$$\Delta H/\Delta S = T$$
$$T = 197.9\ kJ/mol/(0.1881\ kJ/mol\ K) = 1051\ K$$

So, T must be greater than 1051 K

Part II. Answer two (2) of problems 10-13. Clearly mark the problems you do not want graded. 14 points each.

10. 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

Start with a balanced reaction:

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

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

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

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

$$\Delta G^o = -123.95\ kJ/mol - 298\ K(0.2086\ kJ/mol\ K) = \mathbf{-186.1\ kJ}$$

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

For problems 11-13, 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:

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2\,(aq)} + \underset{\text{hydrogen peroxide}}{H_2O_2\,(aq)} \rightarrow \underset{\text{benzoquinone}}{C_6H_4O_2\,(aq)} + \underset{\text{water}}{2\,H_2O\,(\ell)}$$

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.

11. Calculate the ΔH^o for the Bombardier Beetle reaction using the following data:

Reaction	**ΔH^o**
$C_6H_4(OH)_2\,(aq) \rightarrow C_6H_4O_2\,(aq) + H_2\,(g)$	+177.4 kJ
$H_2\,(g) + O_2\,(g) \rightarrow H_2O_2\,(aq)$	-191.2 kJ
$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$	-483.6 kJ
$H_2O\,(g) \rightarrow H_2O\,(\ell)$	-43.8 kJ

OK as given	$C_6H_4(OH)_2\,(aq) \rightarrow C_6H_4O_2\,(aq) + H_2\,(g)$	177.4 kJ
reverse	$H_2O_2\,(aq) \rightarrow H_2\,(g) + O_2\,(g)$	-(-191.2 kJ)
OK as given	$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$	-483.6 kJ
need 2x	$2[H_2O\,(g) \rightarrow H_2O\,(\ell)]$	2(-43.8 kJ)
Net Rxn	**$C_6H_4(OH)_2\,(aq) + H_2O_2\,(aq) \rightarrow C_6H_4O_2\,(aq) + 2\,H_2O\,(\ell)$**	**-202.6 kJ**

12. Using the table of ΔH^o_f below and your result from number 11, calculate the ΔH^o_f ,of hydroquinone, $C_6H_4(OH)_2$., in kJ/mol. (Note: if you did not get an answer to number 11, you may use -200 kJ as a reasonable estimate for ΔH^o_{rxn}).

$$\underset{\text{hydroquinone}}{C_6H_4(OH)_2\ (aq)} + \underset{\text{hydrogen peroxide}}{H_2O_2\ (aq)} \rightarrow \underset{\text{benzoquinone}}{C_6H_4O_2\ (aq)} + \underset{\text{water}}{2\ H_2O\ (\ell)}$$

Species	ΔH^o_f (kJ/mol)	Species	ΔH^o_f (kJ/mol)
H_2O_2 (*aq*)	-191.2	H_2O (*g*)	-241.8
H_2O_2 (ℓ)	-187.8	H_2O (ℓ)	-285.8
$C_6H_4O_2$ (*aq*)	-50.4		

$\Delta H^o_{rxn} = \Delta H^o_f(C_6H_4O_2\ (aq)) + 2\Delta H^o_f(H_2O\ (\ell)) - [\Delta H^o_f(C_6H_4(OH)_2\ (aq)) + \Delta H^o_f(H_2O_2\ (aq))$

To save some writing, let x = $\Delta H_f^o(C_6H_4(OH)_2\ (aq))$

ΔH^o_{rxn} = (-50.4 kJ) + 2(-285.8 kJ) – [x + (-191.2 kJ)]

$\Delta H^o_f(C_6H_4(OH)_2\ (aq))$ = -228.2 kJ

13. 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. (Note: if you did not get an answer to number 11, you may use -200 kJ as a reasonable estimate for ΔH^{o}_{rxn}).

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

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

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

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

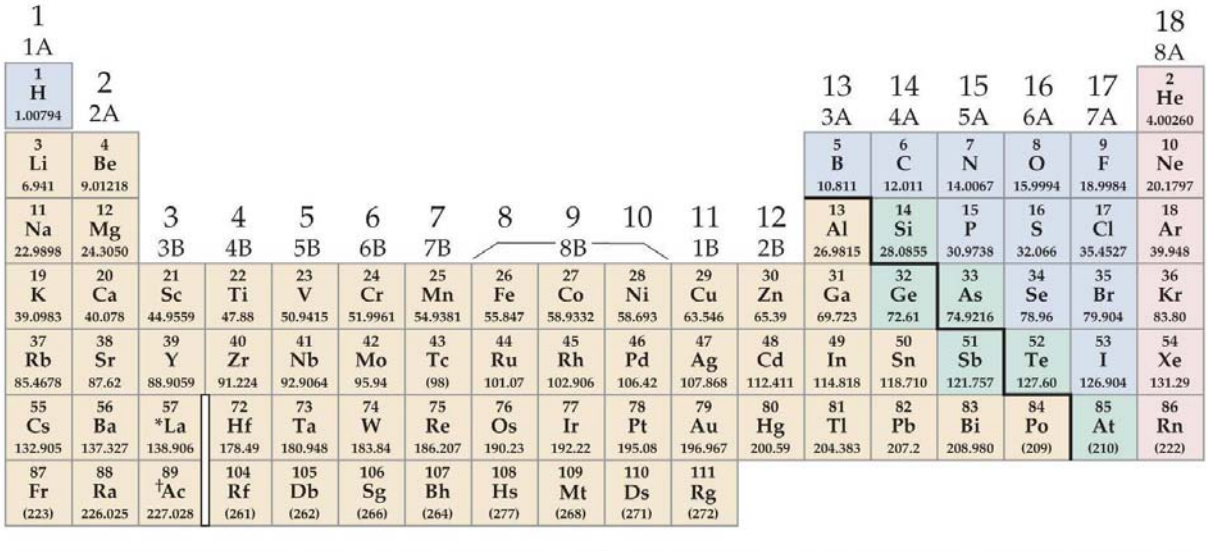
$T_{final} = \Delta T + T_{initial} = 65.4^{o}C + 25.0^{o}C = 90.4^{o}C$

Possibly Useful Information

$\Delta G = \Delta H - T\Delta S$	$^{o}C = K - 273.15$
$q_{rxn} = n\Delta H_{rxn}$	$q = mc\Delta T$
henway = ~5-6 lbs	$q_{released} = -q_{absorbed}$

Compound	Molar Mass (g/mol)	Compound	Molar Mass (g/mol)
H_2O	18.0153	SO_2	64.065
H_2O_2	34.0147	SO_3	80.064
$C_6H_4O_2$	108.097	NH_4NO_3	80.0434
$C_6H_4(OH)_2$	110.112	N_2O	44.0129
H_2	2.01588	CO_2	44.010
O_2	31.9988		

Material	Specific Heat Capacity (J/gK)
H_2O (s)	2.050
H_2O (l)	4.184
H_2O (g)	2.080



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