Form A

**Chem 130** **Name**______________________________

**Exam 3, Ch 7, 19, and a little 14** **November 11, 2011**

**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 $\Delta H^o$ and a negative $\Delta S^o$ are:
   a. spontaneous at all temperatures.
   b. non-spontaneous at all temperatures.
   c. spontaneous at low temperatures but non-spontaneous at high temperatures.
   d. non-spontaneous at low temperatures but spontaneous at high temperatures.

   Answer ____B_______

2. A spontaneous process:
   a. will happen quickly.
   b. releases large amounts of energy.
   c. will continue on its own once begun.
   d. is never endothermic.

   Answer ____C_______

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

   Answer _____C______

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

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.
   a. As two gases mix, $\Delta S$ 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. As temperature in a gas decreases, $\Delta S$ 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 $\Delta S$.

   c. 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. 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.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

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

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

So, HCl is the limiting reagent:

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

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

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

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

6. Determine $\Delta H^o$ for the reaction $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$ from these data:

| Reaction | $\Delta H^o$ |
|---|---|
| $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$ | -622.2 kJ |
| $H_2(g) + ½ O_2(g) \rightarrow H_2O(l)$ | -285.8 kJ |
| $H_2(g) + O_2(g) \rightarrow H_2O_2(l)$ | -187.8 kJ |

| | | |
|---|---|---|
| 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 | $2(H_2(g) + ½ O_2(g) \rightarrow H_2O(l))$ | 2(-285.8 kJ) |
| Reverse and double the third rxn: | $2(H_2O_2(l) \rightarrow H_2(g) + O_2(g))$ | -2(-187.8 kJ) |

Overall Reaction:

$$N_2H_4(l) + \cancel{O_2(g)} + \cancel{2H_2(g)} + \cancel{O_2(g)} + 2H_2O_2(l) \rightarrow N_2(g) + 2H_2O(l) + 2H_2O(l) + \cancel{2H_2(g)} + \cancel{2O_2(g)}$$

$$N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$$

$\Delta H^o$ = -622.2 kJ + (2(-285.8 kJ)) +(-2(-187.8 kJ)) = **-818.2 kJ**

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.

$$2\ C_6H_{14}(l) + 19\ O_2(g) \rightarrow 12\ CO_2(g) + 14\ H_2O(l) \qquad \Delta H^o = -8326\ kJ$$

| **Species** | **$\Delta H^o_f$, kJ mol$^{-1}$** | **$S^o_f$, J mol$^{-1}$ K$^{-1}$** | **$\Delta G^o_f$, 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 |
| $H_2O(l)$ | -285.8 | 69.91 | -237.1 |
| $H_2O(g)$ | -241.8 | 188.8 | -228.6 |

$$\Delta H^o_{rxn} = 12\Delta H^o_{f,\ CO2} + 14\Delta H^o_{f,H2O} - (2\Delta H^o_{f,C6H14} + 19\Delta H^o_{f,O2})$$
$$-8326\ kJ = 12(-393.5\ kJ) + 14(-285.8\ kJ) - (2\Delta H^o_{f,C6H14} + 19(0\ kJ))$$

$$\Delta H^o_{f,C6H14} = \frac{-8326\ kJ - 12(-393.5\ kJ) - 14(-285.8\ kJ)}{-2} = \mathbf{-198.6\ kJ/mol\ C_6H_{14}}$$

8. For the reaction, $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$, $\Delta H^o = -40.9$ 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 $\Delta S$ for this process to be negative. So, we will have a situation where we have a negative $\Delta H$ and a negative $\Delta S$. Since $\Delta G = \Delta H - T\Delta S$, the spontaneity of the reaction will depend on temperature. In order for $\Delta G$ 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 <u>two (2)</u> 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 → 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 | $3.35 \times 10^{-4}$ |
| 2 | 0.0133 | 0.0370 | $6.75 \times 10^{-4}$ |
| 3 | 0.0266 | 0.0370 | $2.70 \times 10^{-3}$ |
| 4 | 0.0266 | 0.0185 | $1.35 \times 10^{-3}$ |

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: Rate = $k[A]^2[B]$

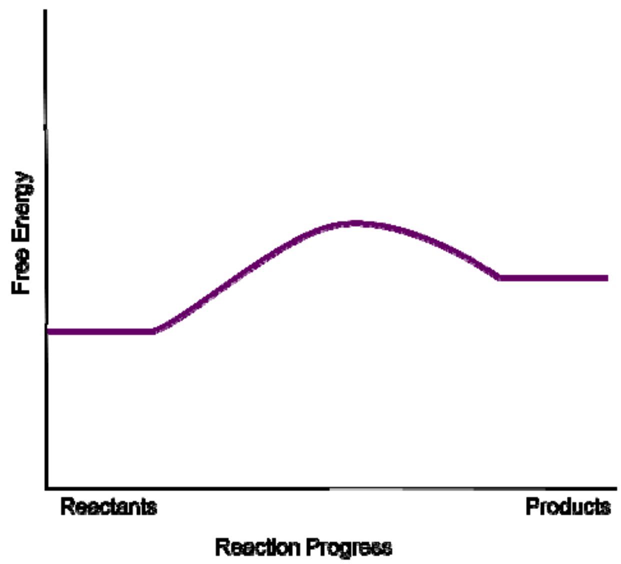
We can use any experiment to find the value of the rate constant. Let's use experiment 4:

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

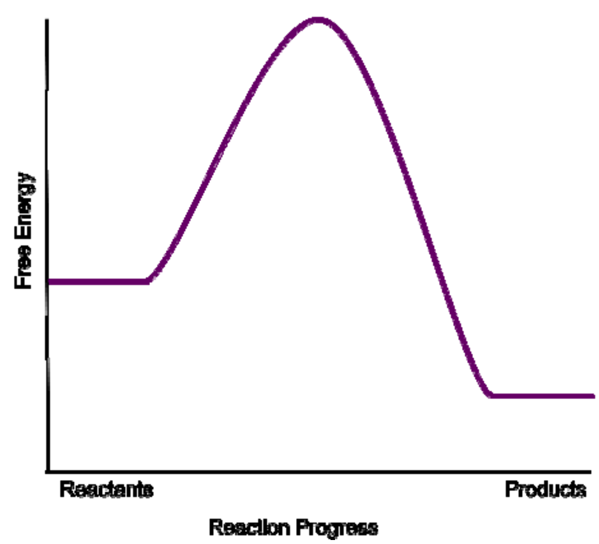
**So, the overall rate law is: Rate = 103 $M^{-2}s^{-1}$ $[A]^2[B]$**

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.



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

| **Species** | **$\Delta H^o_f$, kJ mol$^{-1}$** | **$S^o_f$, J mol$^{-1}$ K$^{-1}$** | **$\Delta G^o_f$, 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 |
| $H_2O(l)$ | -285.8 | 69.91 | -237.1 |
| $H_2O(g)$ | -241.8 | 188.8 | -228.6 |

a. Is the forward reaction exothermic or endothermic?

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

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

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

Since $\Delta H^o$ is positive, the reaction is endothermic

b. What is the value of $\Delta G^o$ at 298 K?

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

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

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

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

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

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

Form A
**Possibly Useful Information**

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

| Compound | Molar Mass (g/mol) | Compound | Molar Mass (g/mol) |
|---|---|---|---|
| $H_2O$ | 18.0153 | $C_6H_{14}$ | 86.177 |
| $H_2O_2$ | 34.0147 | $CO_2$ | 44.010 |
| HCl | 36.4606 | $N_2H_4$ | 32.0452 |
| $H_2$ | 2.01588 | $NH_4NO_3$ | 80.0434 |
| $N_2$ | 28.0135 | $N_2O$ | 44.0129 |
| $O_2$ | 31.9988 | NO | 30.0061 |
| $Cl_2$ | 70.9054 | NOCl | 65.4588 |

| Material | Specific Heat Capacity (J/gK) |
|---|---|
| $H_2O$ (s) | 2.050 |
| $H_2O$ (l) | 4.184 |
| $H_2O$ (g) | 2.080 |
| Zn(s) | 0.390 |

| 1 1A | 2 2A | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 8B | 9 8B | 10 8B | 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) |