CHE-371 Fall 2007

Homework #3

This current posting covers Chapter 19 only. This assignment is due 10/15/07 and will have Chapter 20 problems added prior to due date (probably by 10/7/07) – so check back to get the full assignment!!

Chapter 19 (and Related)

1. In class we experimented with two chemical reactions and concluded that one was endothermic and the other was exothermic. This problem steps you through the process of determining exactly how much heat was produced and helps verify these conclusions.
   a. (i) Using the table given below, calculate ΔH_{rxn} for the reaction
   $Ba(OH)_2{\cdot}8H_2O_{(s)} + 2NH_4NO_{3\,(s)} \rightarrow 2NH_{3\,(aq)} + 10H_2O_{(l)} + Ba(NO_3)_{2\,(s)}$

Substance	**ΔH_f (298K) kJ/mol**	**$S_{298\,K}$ J/mol·K**
$Ba(OH)_2{\cdot}8H_2O$ (s)	-3342	427
$Ba(NO_3)_2$ (s)	-992.07	214
NH_4NO_3 (s)	-365.6	151.1
H_2O (l)	-285.83	69.91
NH_3 (aq)	-80.29	111

   <u>Is this reaction endo or exothermic?</u>

   (ii) From general chemistry (and soon to be discussed in this class), you recall: $\Delta G = \Delta H - T\Delta S$ where ΔG is the Gibbs free energy and ΔS is the entropy. If ΔG is negative for a reaction, it will occur spontaneously. How can this happen if a reaction is *endo*thermic?

   (iii) Assuming ΔS_{rxn} can be found from $S_{298\,K}$ in the same way ΔH_{rxn} is found from ΔH_f, calculate ΔS_{rxn} and ΔG at 298 K. Does this support your answer in (ii)?

   b. (i) Calculate the enthalpy for the dehydration of sucrose (i.e., the second demo from class: $C_{12}H_{22}O_{11\,(s)} \rightarrow 12\,C(graphite) + 11\,H_2O_{(l)}$) given:
   $C_{12}H_{22}O_{11\,(s)} + 12\,O_{2\,(g)} \rightarrow 12\,CO_{2\,(g)} + 11\,H_2O_{(l)}$ $\Delta H_{comb} = -5640.9$ kJ/mol
   $C(graphite) + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H_f(CO_2) = -393.5$ kJ/mol

   <u>Is this reaction endo or exothermic?</u>

   (ii) In class, 70 g of sucrose was used. How much heat evolved from the dehydration of this amount of sugar?

   (iii) The heat of dilution of $H_2SO_4{\cdot}nH_2O$ for the reaction completed in class is -40.58 kJ/mol. We added 70 mL of 98% $H_2SO_4{\cdot}nH_2O$. How much heat was evolved from this dilution?

   (iv) What was the total heat evolved in the dehydration of sucrose demo?

2. For the two reactions given below, determine if ΔU or ΔH will be larger; assume any gases formed are <u>ideal gases</u>. (No math required!; assume ΔU is positive).
   a. $2H_2O_{(l)} \rightarrow 2H_{2\,(g)} + O_{2\,(g)}$
   b. $S_{8\,(s)} + 8\,H_{2\,(g)} \rightarrow 8\,H_2S_{(g)}$

3. One mole of monatomic ideal gas initially at pressure of 2.00 bar at temperature of 273 K is taken to a final pressure of 4.00 bar and temperature of 1092 K. Find ΔU, w, q, and ΔH for this process. Assume $\overline{C}_V$ = 12.5 J/mol·K.
4. Equation 19.22 relates temperature changes to volume changes for a reversible adiabatic expansion of an ideal monatomic gas.
   a. Show that this equation can be written as the following for any ideal gas (provided $\overline{C}_V$ is not temperature dependent):

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\overline{C}_V}$$

   b. Use your answer in part 4a) to determine the final temperature of a sample of N_2(g) being compressed reversibly and adiabatically from a volume of 20.0 dm^3 to a volume of 5.00 dm^3. Take T_1 = 298 K. Assuming that vibrational energy contributions to $\overline{C}_V$ are ***negligible***, use the diatomic ideal gas $\overline{C}_V$ determined in Ch 18 (e.g., Eq 18.41).
5. M&S Ch 19: 2,6,7,40,44 (you can do integral in Mathcad)

Chapter 20

1. a. Predict whether ΔS is positive or negative for the following reactions at 298K.
   i. $4\,Fe_{(s)} + 3O_{2(g)} \rightarrow 2\,Fe_2O_{3(s)}$
   ii. $O_{(g)} + O_{(g)} \rightarrow O_{2(g)}$
   iii. $NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$
   iv. $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

   b. Use a table of ΔS° (most gen chem. books have such a table) to find $\Delta_r S°$.

2. From the partition function for an ideal monatomic gas, you can express entropy:

$$\overline{S} = \frac{5}{2}R + R\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{\overline{V}g_{e1}}{N_A}\right]$$

   a. If you have 1 mole of He at 1 bar and 300 K in one container and 1 mole of Ar at 1 bar and 300 K in another, which will have a larger entropy?
   b. Consider (in thought) how the entropy expression would change for diatomic or polyatomic molecules. (Assume the major contributor to the entropy is the translational term.) Which molecule in the following pairs will have greater entropy under the same conditions?
      i. CO or CO_2
      ii. H_2O or D_2O
      iii. Methane or Ethane

3. M&S Ch 20: 6,8,13,18,25,29,40

For Presentation (Oct 12):

Group G: Chapter 19, #3
Group H: Chapter 20, #6
Group I: Chapter 20, #40