Fall 2007 CH 301 Worksheet 12--Thermodynamics

1. A small (74 g) serving of French fries is burned in a bomb calorimeter containing 3 L of water. The temperature of the water increases by 82°C. The calorimeter has a heat capacity of 200 J/°C, the density of water is 1 g/mL, and the heat capacity of water is 4.18 J/g°C. How much heat is evolved per gram of french fries?

   14.1 kJ/g

2. The same calorimeter as in number 1 is used to measure the enthalpy of dissolving 2.5 mol of potassium chloride (KCl) in water. If the enthalpy of the process is $\Delta H = +15$ kJ/mol and the initial temperature of the water is 298 K, what is the final temperature of the water?

   295.1 K

3. Given

   $C_2H_2 + 5/2\ O_2 \rightarrow 2\ CO_2 + H_2O$ $\Delta H = -1300$ kJ/mol
   $C_2H_2 + H_2 \rightarrow C_2H_4$ $\Delta H = -175$ kJ/mol
   $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$ $\Delta H = -44$ kJ/mol
   $H_2 + ½\ O_2 \rightarrow H_2O$ $\Delta H = -286$ kJ/mol

   Find ΔH for the combustion of ethanol,

   $$CH_3CH_2OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$

   -1367 kJ/mol

4. Given the following information, calculate the enthalpy change for the reaction

   $$4\ HNO_3(l) + 5\ N_2H_4(l) \rightarrow 7\ N_2(g) + 12\ H_2O(l)$$

   $\Delta H_f°\ (HNO_3(l)) =$ -174.10 kJ/mol
   $\Delta H_f°\ (N_2H_4(l)) =$ +50.63 kJ/mol
   $\Delta H_f°\ (H_2O(l)) =$ -285.83 kJ/mol

   -2987 kJ/mol

5. Calculate the free energy change of the same reaction at 298 K, given

   $S_m°\ (HNO_3(l))=$ 155.60 J/K•mol $S_m°\ (N_2(g))=$ 191.61 J/K•mol
   $S_m°\ (N_2H_4(l))=$ 121.21 J/K•mol $S_m°\ (H_2O(l))=$ 69.91 J/K•mol

   -3269 kJ/mol

5. Calculate the enthalpy change for the combustion of ethanol using bond energies.

   C-H = 412 kJ/mol   C-O = 360 kJ/mol   O=O = 497 kJ/mol
   C-C = 348 kJ/mol   C=O = 743 kJ/mol   O-H = 463 kJ/mol

   -1028 kJ/mol

6. Using bond energies, calculate the enthalpy change for the reaction

   $$CH_4(g) + 4\ Cl_2(g) \rightarrow CCl_4(g) + 4\ HCl(g)$$

   C-H = 412 kJ/mol   Cl-Cl = 242 kJ/mol
   C-Cl = 338 kJ/mol   Cl-H = 431 kJ/mol

   -460 kJ/mol

7. Use enthalpies of formation to find the enthalpy change for the same reaction.

   $\Delta H_f°\ (CH_4(g)) =$ -74.81 kJ/mol
   $\Delta H_f°\ (CCl_4(g)) =$ -163.78 kJ/mol
   $\Delta H_f°\ (HCl(g)) =$ -92.31 kJ/mol

   -458.21 kJ/mol

8. Find the approximate work done for the following reaction at 400 K.

   $H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (g)$ *1.67 kJ*

9. For the reaction

$$3\ H_2\ (g) + N_2\ (g) \rightarrow 2\ NH_3\ (g)$$

how many moles of hydrogen gas must be reacted for the work to be 8 kJ at 300 K?

2.4 mol

10. A reaction occurs in a beaker. You touch the beaker and it feels cold. What is the sign of ΔH for the reaction? What can you say about the sign of ΔS?

$\Delta H > 0$, $\Delta S < 0$

11. A reaction happens in a balloon, and in the end, the volume of the balloon has doubled. What is the sign of work for the reaction?

negative

12. Give the sign of the entropy change of the system for the following processes:
    a. Dr. Laude pours hot water in a tub of liquid N2 and makes a thundercloud.
        positive
    b. Water freezes.
        negative
    c. Two cars are in a head-on collision.
        positive
    d. Sugar is dissolved in a drink.
        positive

13. For the following reaction, what happens to the entropy of the system?

$$2\ CH_4\ (g) + 3\ Cl_2\ (g) \rightarrow 2\ CHCl_3\ (l) + 3\ H_2\ (g)$$

It decreases.

14. The reaction above happens. What can you say about its enthalpy change?

It is exothermic.

15. From your knowledge of the temperature dependence of (a) water boiling and (b) water freezing, predict the sign of ΔH and ΔS.

(a) $\Delta H > 0$, $\Delta S > 0$; (b) $\Delta H < 0$, $\Delta S < 0$

16. The reaction

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (g)$$

is exothermic. Is its spontaneity temperature-dependent? In what way?

Yes. It is only spontaneous at low temperatures, where favorable decrease in enthalpy overcomes the unfavorable decrease in entropy.

17. For each of the following combinations of enthalpy and entropy change, tell whether it occurs *always*, *never*, *at high temperature*, or *at low temperature*.
    a. $\Delta H < 0$, $\Delta S < 0$ — *at low temperature*
    b. $\Delta H < 0$, $\Delta S > 0$ — *always*
    c. $\Delta H > 0$, $\Delta S < 0$ — *never*
    d. $\Delta H > 0$, $\Delta S > 0$ — *at high temperature*

18. Explain why, although water has three vibrational degrees of freedom, carbon dioxide must have four. (Hint: both molecules have 9 total degrees of freedom)

Carbon dioxide is linear. Thus, rotation around the O-C-O axis doesn't do anything to the molecule – it's not actually a degree of freedom. Thus, CO_2 has one fewer rotation degree of freedom than H_2O, so it must have one extra vibrational mode to make up for it.

19. What is the total motional (i.e. due to the motion of the atoms in the molecule) contribution to the energy of methanol, CH_3OH? Express your answer as a multiple of RT. *9RT counting translational, rotaional and vibrational. (6 atoms with 18 degrees of freedom at 3/2 RT per degree = 9RT/mole)*

20. How many translational, rotational, and vibrational degrees of freedom does ammonia have?
3 translational, 3 rotational, and 6 vibrational