Assignment III: Standard Free-Energy Changes

The change in free energy, ΔG, of a system is: $\mathbf{\Delta G = \Delta H - T\Delta S}$

Free energy is the energy available to do work. Thus, if a particular reaction is accompanied by a release of useable energy, i.e. ΔG is negative, this guarantees that the reaction will be spontaneous. The conditions for spontaneity are summarised as:

$\mathbf{\Delta G < 0}$	The reaction is spontaneous in the forward direction.
$\mathbf{\Delta G > 0}$	The reaction is non-spontaneous. (spontaneous in the opposite direction).
$\mathbf{\Delta G = 0}$	The reaction is reversible, i.e at equilibrium, there is no net change.

The standard free-energy change for a reaction is given by:

$$\Delta G^0_{rxn} = \Sigma \Delta G^0_f \text{(products)} - \Sigma \Delta G^0_f \text{(reactants)}$$

Note:

1. The term ΔG^0_f is the standard free energy of formation of a compound, i.e. the free-energy that occurs when one mole of the compound is synthesised from its elements in their standard states, (example: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta G^0_f = -394.4$ kJ mol^{-1})
2. The standard free energy of formation of any element in its stable form is zero.

Calculate the standard free-energy change for the following reactions at 25 ^{0}C:

a) $CH_{4(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)}$

b) $2\,MgO_{(s)} \longrightarrow 2\,Mg_{(s)} + O_{2(g)}$

c) $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)}$

d) $2\,NO_{(g)} + O_{2(g)} \longrightarrow N_2O_{4(g)}$

e) $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

f) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

ANSWERS

a) - 818.0 (b) + 1139 (c) - 55.2 (d) - 75.6 (e) - 92.3 (f) + 8.6 kJ mol^{-1}

Note:

In the above example the large negative value of ΔG^0_{rxn} for the combustion of methane in (a) means that the reaction is a spontaneous process under standard -state conditions, whereas the decomposition of $MgO_{(s)}$ in (b) is non-spontaneous because ΔG^0_{rxn} is a large, positive quantity. However, a large, negative, ΔG^0_{rxn} does not tell us anything about the actual ***rate*** of the spontaneous process; a mixture of $CH_{4(g)}$ and $O_{2(g)}$ at 25 ^{0}C could sit unchanged for quite some time in the absence of a spark or flame. Hence, *thermodynamics tells us nothing at all about how fast a feasible reaction will occur.*

<u>**Temperature and Spontaneous Processes**</u> : $\mathbf{\Delta G^0 = \Delta H^0 - T\Delta S^0}$

One would expect ΔG^0 to vary with temperature because of the Gibb's equation above.
This variation means that some processes which are not possible at low temperatures become feasible at higher temperatures, and vice-versa.
There are four possible outcomes for the $\Delta G = \Delta H - T\Delta S$, (see previous notes).

1. Calculate ΔG^0_{rxn} at 1000 K for the following reactions and compare with given values of ΔG^0_{rxn} at 298 K. State whether or not the reactions are feasible at each temperature.

a) $2\,NO_{(g)} + O_{2(g)} \longrightarrow N_2O_{4(g)}$ ΔG^0_{rxn} at 298 K = - 75.6 kJmol^{-1}

b) $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$ ΔG^0_{rxn} at 298 K = - 92.3 kJmol^{-1}

c) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$ ΔG^0_{rxn} at 298 K = + 8.6 kJmol^{-1}

d) $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ ΔG^0_{rxn} at 298 K = + 130.2 kJmol^{-1}

Answers: a) + 150 (b) + 108 (c) - 75 (d) + 17.5 kJ mol^{-1}

2. Predict the signs of ΔH, ΔS, and ΔG of the following processes at 101.3 kPa :
a) ammonia melts at - 60 ^{0}C, (b) ammonia melts at - 100 ^{0}C
(The normal melting point of ammonia is - 77.7 ^{0}C.)

3. (a) In what circumstances can an endothermic reaction take place spontaneously?
   (b) Explain why, in the majority of cases, ΔH^0 provides an indication of the feasibility of a reaction at 298 K.

4. Find the temperatures at which reactions with the following ΔH and ΔS values would become spontaneous:

a) $\Delta H = -126$ kJ, $\Delta S = +84\ J\ K^{-1}$ (Ans: at all temperatures)

b) $\Delta H = -11.7$ kJ, $\Delta S = -105\ J\ K^{-1}$ (Ans: below 111 K)

5. From the values of ΔH and ΔS, predict which of the following reactions would be spontaneous at $25^{O}C$:

   a. Reaction A: $\Delta H = +10.5$ kJ, $\Delta S = +30\ J\ K^{-1}$
   b. Reaction B: $\Delta H = +1.8$ kJ, $\Delta S = -113\ J\ K^{-1}$

If either of the reactions is non-spontaneous at 25 ^{0}C , at what temperature might it become spontaneous?

6. "Not all exothermic reactions are spontaneous, some endothermic changes are spontaneous."

Discuss the extent to which a knowledge of the enthalpy change for a reaction is a guide to its ability to proceed. Illustrate your answer by considering **four** reactions of varied type, **two** of which are exothermic, and **two** endothermic. You may wish to consider some or all of the following reactions or others of your own choice.

$$N_2O_{4(g)} \longrightarrow 2\ NO_{2(g)}$$
$$N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$$
$$NH_4Cl_{(s)} \longrightarrow NH_{3(g)} + HCl_{(g)}$$
$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

<u>Phase Transitions</u>

At the temperature at which a phase transition occurs (the mp, or bp) the system is at equilibrium and $\Delta G = 0$. Thus, we can write:

$$\Delta G = \Delta H - T\Delta S$$
$$0 = \Delta H - T\Delta S$$
$$\Delta S = \Delta H / T$$

ΔS is the entropy change due to the phase transition.

Example 1:

The heat of fusion of water, ΔH_{fus}, at 0 ^{0}C is 6.02 kJ mol^{-1}. What is ΔS_{fus} for 1 mol of H_2O at the melting point?

$$\Delta S = \Delta H / T$$
$$= 6.02\ kJmol^{-1} / 273\ K$$ (recall that the temperature must be in units of Kelvin)
$$= +22.1\ J\ mol^{-1}K^{-1}$$

The increase in entropy upon melting the solid corresponds to the increase in molecular disorder in the liquid state compared to the solid state.

Calculate

1. The molar heats of fusion and vapourisation of benzene are 10.9 kJ mol^{-1} and 31.0 kJ mol^{-1}, respectively. Calculate the entropy change for the solid $\longrightarrow$ liquid and liquid $\longrightarrow$ vapour transitions for benzene. At 101.3 kPa, benzene melts at 5.5 ^{0}C and boils at 80.1 ^{0}C.

(Answer: ΔS_{fus} = 39.1 J/Kmol, ΔS_{vap} = 87.8 J/K.mol)

2. The enthalpy of vapourization of mercury is 58.5 kJ mol^{-1} and the normal boiling point is 630 K. What is the entropy of vapourization of mercury.
3. The molar heat of vapourisation of ethanol is 39.3 kJ/mol and the boiling point of ethanol is 78.3 ^{0}C. Calculate ΔS for the vapourisation of 0.50 mol ethanol.
4. Explain the following nursery rhyme in terms of the second law of thermodynamics:

   Humpty Dumpty sat on a wall;
   Humpty Dumpty had a great fall.
   All the King's horses and all the King's men

Couldn't put Humpty together again.