

Gibbs Free Energy and Equilibrium

For a system in equilibrium $\Delta G = 0$, therefore the free energy change can be used to evaluate the equilibrium state for a chemical reaction. The free energy of a substance in a state other than the standard state G is related to its free energy G° by the following

$$G = G^\circ + RT \ln(a) \quad (1)$$

where

R = ideal gas constant 8.3143 J/K mol

T = absolute temperature

$\ln a$ = natural log of activity of the system

(I.B. will not require you to know much about activity. Activity is the "effective concentration" for now think of it as concentration.)



$$\Delta G = \Delta G^\circ + RT \ln \frac{[Y]^y [Z]^z}{[W]^w [X]^x} \quad (3)$$

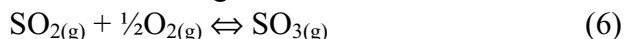
The stuff at the end should be recognizable as the expression for the equilibrium constant; therefore,

$$\Delta G = \Delta G^\circ + RT \ln k \quad (4)$$

At equilibrium $\Delta G = 0$, thus

$$\Delta G^\circ = -RT \ln K \quad (5)$$

For example, calculate the K_p for the following reaction at 25°C



The type of K obtained depends on the definition of the standard states and in the values for the Gibbs free energy used.



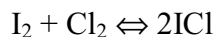
As the ΔG° is positive, you would think that $\text{N}_2\text{O}_{4(g)}$ would not dissociate under standard conditions and that the reverse reaction would take place. Both predictions are incorrect. If you calculate the K from the equation $K = 0.113$, you would find that some $\text{N}_2\text{O}_{4(g)}$ does dissociate.

You must be careful when using ΔG° to predict spontaneity.

A **large -ive** ΔG° means that K for the reaction is a **large +ive** value, indicating that the reaction goes left to right. A **large +ive** ΔG° means that K for the reaction is a **very small** value, indicating that the reverse reaction is predominant.

If ΔG° is neither small nor large, more of an "equilibrium" situation exists.

Example



we have 0.2 mol I_2 , 0.2 mol Cl_2 in 2 L. At equilibrium there is 0.05 mol/L present. Calculate K_c at 550 K. What is ΔG° at this temperature?

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \quad (8)$$

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT} \quad (9)$$

$$= \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

Since ΔH° and ΔS° do not vary significantly over T, then we may take the previous equation to be of the form.

$$y = mx + b \quad (11)$$

where

$$m = -\frac{\Delta H^\circ}{R}$$

$$b = +\frac{\Delta S^\circ}{R}$$

This is useful in two ways:

1. We can calculate ΔH° for reactions where it cannot be determined directly.
2. We can calculate K for temperatures other than those determined.

Note:

$$\ln K_2 - \ln K_1 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1} \quad (12)$$

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (13)$$

So we can calculate 1 of 5 quantities: ΔH° , T_1 , T_2 , K_2 and K_1 .

Example



$\Delta G^\circ = 23.7\text{kJ}$ at 25°C . What is the K_p (K_c ?) for this reaction? Comment upon the spontaneity of this reaction.

$$\Delta G^\circ = -(8.314)(298) \ln K = -23.7$$

Then,

$$\ln K = \frac{23.7}{(8.314)(298)} = 0.009566$$

Thus,

$$K = e^{-K} = 0.9904$$

so the reaction is at equilibrium.

Electromotive Force

The potential of a cell is related to the change in free energy that accompanies the cell reaction

$$\Delta G = -nF\varepsilon \quad (14)$$

where

F is the value of the Faraday constant (96 487 C)

ε is the emf in volts

Similarly,

$$\Delta G^\circ = -nF\varepsilon^\circ \quad (15)$$

Recall that for a spontaneous reaction the free energy decreases or ΔG is negative. Therefore ε must be positive, as we learned before. Also note that

$$\Delta G^\circ = -nF\varepsilon^\circ = -RT \ln K \quad (16)$$

These equations are given to you in the I.B. exam.