

## Chapter 5: Chemical Reactions Energetically

**1- Introduction:** In transformations, the first law of thermodynamics only provides the energy balance for all energy exchanges, while the second principle predicts the direction of the transformation, but its application is not straightforward. Therefore, we define two new functions:

Free energy, denoted by F (Helmholtz function at constant volume)

Where:  $F = U - TS$

Free enthalpy, denoted by G (Gibbs function at constant pressure)

Where:  $G = H - TS$

Functions F and G are state functions, and dF and dG are two exact differential equations:

$$dF = dU - TdS - SdT$$

$$dG = dH - TdS - SdT$$

Thus, for a chemical reaction occurring at constant T and P:

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

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

And we have:

$$\Delta U = Q + W = Q - P\Delta V$$

$$\Delta G = Q - P\Delta V + P\Delta V - T\Delta S = Q - T\Delta S$$

$$\Delta S = \Delta S_e + \Delta\sigma$$

$\Delta S_e$ : The entropy gained from the external environment

$\Delta\sigma$ : The entropy generated within the system

$$\Delta S_e = \frac{Q}{T} \Rightarrow \Delta S = \frac{Q}{T} + \Delta\sigma$$
$$\Delta G = Q - T \left[ \frac{Q}{T} + \Delta\sigma \right] = -T\Delta\sigma \Rightarrow \Delta G = -T\Delta\sigma$$

So,  $\Delta G$  is associated with  $\Delta\sigma$  :

$$\Delta\sigma > 0 \Rightarrow \text{Spontaneous reaction}$$

$$\Delta\sigma = 0 \Rightarrow \text{Reversible transformation}$$

$$\Delta\sigma < 0 \Rightarrow \text{Impossible transformation}$$

So, we can relate  $\Delta G$  to  $\Delta\sigma$  and summarize this in the following table:

<i>Type of reaction</i>	$\Delta G = -T \Delta\sigma$	$\Delta\sigma$
Transformation at equilibrium	$\Delta G = 0$	$\Delta\sigma = 0$ Equilibrium
Transformation impossible	$\Delta G > 0$	$\Delta\sigma < 0$ Impossible
Spontaneous transformation	$\Delta G < 0$	$\Delta\sigma > 0$ Spontaneous

### 1- Free enthalpy as a function of T and P:

$$G = H - TS$$

$$H = U + PV$$

$$G = U + PV - TS \Rightarrow dG = dU + PdV + VdP - TdS - SdT$$

$$U = Q + W \Rightarrow dU = dQ - PdV$$

$$dS = \frac{dQ}{T} \Rightarrow dQ = TdS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT \Rightarrow$$

$$dG = VdP - SdT$$

### Notes:

$$\Delta G = \int VdP \Leftarrow dG = VdP \Leftarrow T \text{ Cst} \quad (1)$$

$$\Delta G = \int -SdT \Leftarrow dG = -SdT \Leftarrow P \text{ Cst} \quad (2)$$

For ideal gases : at constant temperature (T Cst)

$$\Delta G = \int dG = \int VdP \quad ; \quad PV = nRT \Rightarrow V = \frac{nRT}{P}$$

$$\Rightarrow \Delta G = nRT \int_{P_i}^{P_f} \frac{dP}{P} = nRTLn\left(\frac{P_f}{P_i}\right)$$

And if the initial pressure is :  $P_i = 1 \text{ atm}$  so :

$$\Delta G = G_T^P - G_T^0 = nRTLnP$$

### Note:

We use the relationship  $G = V\Delta P$  in the case of a system transformation in the solid or liquid phase as follows:

$$\Delta G = V (P_f - P_i)$$

**Example:** Let's consider the transformation of 1 mole of mercury with a volume of  $14.8 \text{ cm}^3$  from a pressure of 1 atm to a pressure of 100 atm. Calculate the change in free enthalpy for this system.

### Solution:

State of gas mixture:

$$\Delta G = V(P_f - P_i) \quad ; \quad P_f = 100 \text{ atm} \quad ; \quad P_i = 1 \text{ atm}$$

$$1 \text{ atm} = 1,01325 \times 10^5 \text{ pas} \quad ; \quad V = 14,8 \text{ cm}^3 = 14,8 \times 10^{-6} \text{ m}^3$$

$$\Delta G = V(P_f - P_i) = 14,8 \times 10^{-6} [100 - 1] \times 1,01325 \times 10^5 = 148,46 \text{ pas.m}^3$$

$$\Delta G := 148,46 \text{ J}$$

We have :

$$\Delta G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S - S\Delta T$$

At constant temperature :

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

According to the second law of Joule

$$\Delta H = 0 \Rightarrow \Delta G = -T\Delta S_{\text{gas mixture}}$$

$$\Delta S_{\text{gas mixture}} = -R \sum n_i \ln x_i$$

$$\Rightarrow \Delta G_{\text{gas mixture}} = G_{\text{gas mixture}}^P - G_{\text{gas mixture}}^0 = RT \sum n_i \ln x_i$$

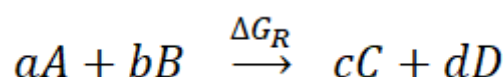
$x_i$  : The molar fraction of the i gas in the mixture

$n_i$  : Number of moles of the i gas in the mixture

### 3- Application of free enthalpy to chemical reactions:

#### 3-1- Standard free enthalpy of formation ( $\Delta G_f^\circ$ ):

Consider the following chemical reaction:



$$\Delta G_R = G_f - G_i = c\Delta G_f(C) + d\Delta G_f(D) - a\Delta G_f(A) - b\Delta G_f(B)$$

According to Hess's law :

$$\Delta G_R = \sum \alpha_i \Delta G_f(\text{Products}) - \sum \beta_i \Delta G_f(\text{Reactants})$$

$\alpha_i, \beta_i$  : Stoichiometric coefficients

at standard conditions (P = 1 atm ; T = 298 K) we have :

$$\Delta G_{R,298}^0 = \sum \alpha_i \Delta G_{f,298}^0(\text{Products}) - \sum \beta_i \Delta G_{f,298}^0(\text{Reactants})$$

**Notes :**

- $\Delta G_{f,298}^0$  for pure simple substances at standard conditions is zero

$$\Delta G_{f,298}^0(O_2)_g = 0 ; \Delta G_{f,298}^0(H_2)_g = 0 ; \Delta G_{f,298}^0(C_s)_{\text{graphite}} = 0$$

$$\Delta G_{f,298}^0(I_2)_s = 0 ; \Delta G_{f,298}^0(Mg)_s = 0 ; \Delta G_{f,298}^0(Fe)_s = 0$$

$$\Delta G_{f,298}^0(Zn)_s = 0 ; \Delta G_{f,298}^0(Ne)_g = 0 ; \Delta G_{f,298}^0(Na)_s = 0$$

- If the chemical reaction is at a temperature different from 298 K , then :

$$\Delta G_{R,T}^0 = \Delta H_{R,T}^0 - T \Delta S_{R,T}^0$$

Where according to Kirchhoff's law :

$$\Delta H_{R,T}^0 = \Delta H_{R,298}^0 + \int_{298}^T \Delta C_P$$

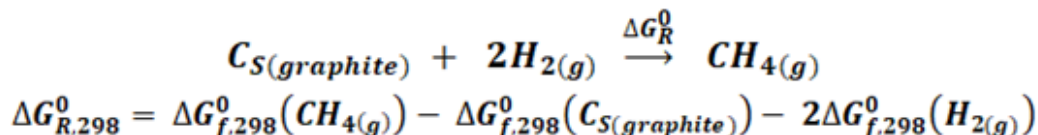
$$\Delta H_{R,298}^0 = \sum \alpha_i \Delta H_{f,298}^0(\text{Products}) - \sum \beta_i \Delta H_{f,298}^0(\text{Reactants})$$

$$\Delta S_{R,T}^0 = \Delta S_{R,298}^0 + \int_{298}^T \Delta C_P \frac{dT}{T}$$

$$\Delta S_{R,298}^0 = \sum \alpha_i S_i^0(\text{Products}) - \sum \beta_i S_i^0(\text{Reactants})$$

### Example :

Let the following chemical reaction occur at  $P = 1 \text{ atm}$  and  $T = 298 \text{ K}$



$$\Delta G_{f,298}^0(C_{S(\text{graphite})}) = 0 ; \Delta G_{f,298}^0(H_{2(g)}) = 0$$

$$\Rightarrow \Delta G_{R,298}^0 = \Delta G_{f,298}^0(CH_{4(g)})$$

If  $\Delta G_{f,298}^0(CH_{4(g)})$  is unknown, we calculate it by another method, based on the relationship :

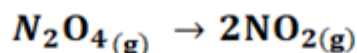
$$\Delta G_{R,298}^0 = \Delta H_{R,298}^0 - 298 \Delta S_{R,298}^0$$

$$\Delta H_{R,298}^0 = \Delta H_{f,298}^0(CH_{4(g)})$$

$$\Delta S_{R,298}^0 = S^0(CH_{4(g)}) - S^0(C_{S(\text{graphite})}) - 2S^0(H_{2(g)})$$

### Practical example :

Let the following chemical reaction :



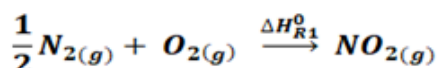
1- Complete the following table with the thermodynamic data given at

$P = 1 \text{ atm}$  ,  $T = 298 \text{ K}$

The element	$\Delta H_f^\circ (\text{KJ/mol})$	$S_f^\circ (\text{J/K.mol})$	$\Delta G_f^\circ (\text{KJ/mol})$
$N_{2(g)}$	0	191,49	0
$O_{2(g)}$	0	205,03	0
$NO_{2(g)}$	33,86315	240,45	51,84
$N_2O_{4(g)}$	9,71	304,30	98,29

Calculating  $\Delta H_f^\circ (NO_{2(g)})$  :

Let the formation reaction of  $NO_{2(g)}$  under standard conditions ( $T = 298 \text{ K}$ ,  $P = 1 \text{ atm}$ ) :



$$\Delta H_{R1}^0 = \Delta H_f^0(NO_{2(g)}) - \frac{1}{2}\Delta H_f^0(N_{2(g)}) - \Delta H_f^0(O_{2(g)})$$

$$\Delta H_f^0(N_{2(g)}) = 0 ; \Delta H_f^0(O_{2(g)}) = 0$$

$$\Rightarrow \Delta H_{R1}^0 = \Delta H_f^0(NO_{2(g)})$$

We have :

$$\Delta G_{R1}^0 = \Delta H_{R1}^0 - T \Delta S_{R1}^0 = \Delta H_{R1}^0 - 298 \Delta S_{R1}^0$$

$$\Delta G_{R1}^0 = \Delta H_f^0(NO_{2(g)}) - 298 \Delta S_{R1}^0$$

$$\Delta S_{R1}^0 = S^0(NO_{2(g)}) - \frac{1}{2}S^0(N_{2(g)}) - S^0(O_{2(g)})$$

$$\Delta S_{R1}^0 = 240,45 - \frac{1}{2}(191,49) - (205,03) = -60,325 J.K^{-1}.mol^{-1}$$

$$\Delta G_{R1}^0 = \Delta G_f^0(NO_{2(g)}) - \frac{1}{2}\Delta G_f^0(N_{2(g)}) - \Delta G_f^0(O_{2(g)})$$

$$\Delta G_f^0(N_{2(g)}) = 0 ; \Delta G_f^0(O_{2(g)}) = 0$$

$$\Rightarrow \Delta G_{R1}^0 = \Delta G_f^0(NO_{2(g)}) = 51,84 KJ/mol$$

So :

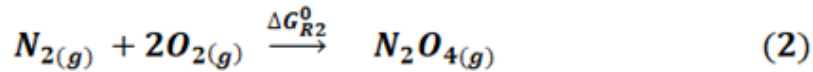
$$\Delta G_{R1}^0 = \Delta H_f^0(NO_{2(g)}) - 298 \Delta S_{R1}^0$$

$$\Delta G_f^0(NO_{2(g)}) = \Delta H_f^0(NO_{2(g)}) - 298 \Delta S_{R1}^0$$

$$\Delta H_f^0(NO_{2(g)}) = \Delta G_f^0(NO_{2(g)}) + 298 \Delta S_{R1}^0$$

$$\Delta H_f^0(NO_{2(g)}) = 51,84 + 298 (-60,325 \cdot 10^{-3}) = 33,86315 KJ/mol$$

Calculating  $\Delta G_f^0(N_2O_{4(g)})$  :



$$\Delta G_{R2}^0 = \Delta G_f^0(N_2O_{4(g)}) - \Delta G_f^0(N_{2(g)}) - 2\Delta G_f^0(O_{2(g)})$$

$$\Delta G_f^0(N_{2(g)}) = 0 ; \Delta G_f^0(O_{2(g)}) = 0$$

$$\Rightarrow \Delta G_{R2}^0 = \Delta G_f^0(N_2O_{4(g)}) = \Delta H_f^0(N_2O_{4(g)}) - 298 \Delta S_{R2}^0$$

$$\Delta S_{R2}^0 = S^0(N_2O_{4(g)}) - S^0(N_{2(g)}) - 2S^0(O_{2(g)})$$

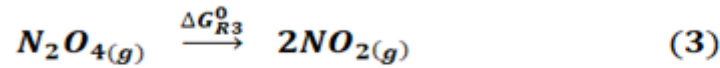
$$\Delta S_{R2}^0 = 304,30 - (191,49) - 2(205,03) = -297,25 J.K^{-1}.mol^{-1}$$

$$\Delta G_f^0(N_2O_{4(g)}) = \Delta H_f^0(N_2O_{4(g)}) - 298 \Delta S_{R2}^0 = 9,71 - 298(-297,25)$$

$$= 98,29 KJ/mol$$



The nature of the reaction (3) :



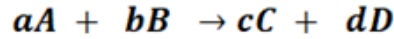
$$\Delta G_{R3}^0 = 2\Delta G_f^0(NO_{2(g)}) - \Delta G_f^0(N_2O_{4(g)})$$

$$\Delta G_{R3}^0 = 2(51,84) - (98,29) = 5,39 \text{ KJ/mol}$$

$\Delta G_{R3}^0 > 0 \Rightarrow$  the reaction is impossible under these conditions.

### 3-2-Applying Gibbs' law to a chemical reaction in the gaseous state :

Let the following reaction occur between ideal gases A, B, C and D :



$G_T^0(A)$ ,  $G_T^0(B)$ ,  $G_T^0(C)$  and  $G_T^0(D)$  are the standard free enthalpies of the gases, A, B, C and D respectively :

$$G_T^P(A) = G_T^0(A) + RT \ln P_A$$

$$G_T^P(B) = G_T^0(B) + RT \ln P_B$$

$$G_T^P(C) = G_T^0(C) + RT \ln P_C$$

$$\Delta G_T^P(D) = G_T^0(D) + RT \ln P_D$$

Where  $P_A$ ,  $P_B$ ,  $P_C$  and  $P_D$  are the partial pressures of A, B, C and D respectively

$$\Delta G_T^P = \sum n_i G_T^P(\text{Products}) - \sum n_i G_T^P(\text{Reactants})$$

$$\Delta G_T^P = cG_T^P(C) + dG_T^P(D) - aG_T^P(A) - bG_T^P(B)$$

$$\Delta G_T^P = [cG_T^0(C) + cRT\ln P_C + dG_T^0(D) + dRT\ln P_D] - [aG_T^0(A) + aRT\ln P_A + bG_T^0(B) + bRT\ln P_B]$$

$$\Delta G_T^P = [cG_T^0(C) + dG_T^0(D)] - [aG_T^0(A) + bG_T^0(B)] + RT[(\ln P_C^c + \ln P_D^d) - (\ln P_A^a + \ln P_B^b)]$$

$$\Delta G_T^P = \Delta G_T^0 + RT\ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

Which :

$$\Delta G_R^P = \Delta G_R^0 + RT\ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$\Delta G_R^P$  : It is the change in free enthalpy at pressure  $P$  (atm)

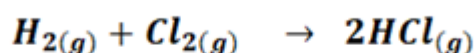
In general :

$$\Delta G_R^P = \Delta G_R^0 + RT\ln \frac{\prod P_i^i (\text{Products})}{\prod P_i^i (\text{Reactants})}$$



**Example 1:**

Calculate the free enthalpy for the following reaction :



$$\Delta G_{R,298}^0 = \sum n_i \Delta G_{f,298}^0(\text{Products}) - \sum n_i \Delta G_{f,298}^0(\text{Reactants})$$

$$\Delta G_{R,298}^0 = 2\Delta G_{f,298}^0(HCl_{(g)}) - \Delta G_{f,298}^0(H_{2(g)}) - \Delta G_{f,298}^0(Cl_{2(g)})$$

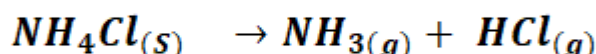
$$\Delta G_{f,298}^0(H_{2(g)}) = 0 ; \Delta G_{f,298}^0(Cl_{2(g)}) = 0$$

$$\Delta G_{R,298}^0 = 2\Delta G_{f,298}^0(HCl_{(g)})$$

$$\Delta G_R^P = \Delta G_R^0 + RT \ln \frac{P_{HCl}^2}{P_{H_2} \cdot P_{Cl_2}}$$

**Example 2 :**

Calculate the free enthalpy for the following reaction :



$$\Delta G_R^P = \Delta G_R^0 + RT \ln(P_{NH_3} \cdot P_{HCl})$$

$$\Delta G_R^0 = \Delta G_f^0(NH_{3(g)}) + \Delta G_f^0(HCl_{(g)}) - \Delta G_f^0(NH_4Cl_{(s)})$$

**1 - Predicting the evolution of a chemical reaction :**

Based on the following equation  $\Delta G = \Delta H - T\Delta S$  with constant P and T, we can predict the evolution of a chemical reaction as follows:

The state	$\Delta S$	$\Delta H$	$\Delta G = \Delta H - T\Delta S$	Type of reaction
1	$\Delta S > 0$ Increase in disorder	$\Delta H < 0$ Exothermic reaction	$\Delta G < 0$	Spontaneous
2	$\Delta S < 0$ Decrease in disorder	$\Delta H > 0$ Endothermic reaction	$\Delta G > 0$	Impossible
3	$\Delta S < 0$	$\Delta H < 0$	$\Delta H < T\Delta S$ $\Delta G < 0$	Spontaneous
			$\Delta H > T\Delta S$ $\Delta G > 0$	Impossible
4	$\Delta S > 0$	$\Delta H > 0$	$\Delta H > T\Delta S$ $\Delta G > 0$	Impossible
			$\Delta H < T\Delta S$ $\Delta G < 0$	Spontaneous
5	$\Delta H = T\Delta S$		$\Delta G = 0$	Equilibrium