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:

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

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

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

And we have:

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

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

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

ΔS_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, ΔG is associated with $\Delta\sigma$:

$\Delta\sigma > 0 \Rightarrow$ Spontaneous reaction

$\Delta\sigma = 0 \Rightarrow$ Reversible transformation,

$\Delta\sigma < 0 \Rightarrow$ Impossible transformation

So, we can relate ΔG to Δσ and summarize this in the following table:

Type of reaction	***ΔG = -T Δσ***	***Δσ***
Transformation at equilibrium	ΔG = 0	Δσ = 0 Equilibrium
Transformation impossible	ΔG > 0	Δσ < 0 Impossible
Spontaneous transformation	ΔG < 0	Δσ > 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:

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

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

For ideal gases : at constant temperature (T Cst)

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

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

And if the initial pressure is :. $P_i = 1$ 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 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:

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

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

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

$$\Delta G = \;148{,}46\,J$$

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 Joul

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

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

$$\Rightarrow \Delta G_{\text{gas mixture}} = G^P{}_{T\,\text{gas mixture}} - G^0{}_{T\,\text{gas mixture}} = RT \sum n_i Ln x_i$$

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 (ΔG_f°):

Consider the following chemical reaction:

$$aA + bB \xrightarrow{\Delta G_R} cC + dD$$

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

According to Hess's law :

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

α_i , β_i **: Stoichiometric coefficients**

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

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

Notes :

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

$$\Delta G^0_{f,298}(O_2)_g = 0 \,;\, \Delta G^0_{f,298}(H_2)_g = 0 \,;\, \Delta G^0_{f,298}(C_S)_{graphite} = 0$$
$$\Delta G^0_{f,298}(I_2)_S = 0; \Delta G^0_{f,298}(Mg)_S = 0; \Delta G^0_{f,298}(Fe)_S = 0$$
$$\Delta G^0_{f,298}(Zn)_S = 0 \,;\, \Delta G^0_{f,298}(Ne)_g = 0 \,;\, \Delta G^0_{f,298}(Na)_S = 0$$

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

$$\Delta G^0_{R,T} = \Delta H^0_{R,T} - T\,\Delta S^0_{R,T}$$

Where according to Kirchhoff's law :

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

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

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

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

Example :

Let the following chemical reaction occur at P = 1 atm and T = 298 K

$$C_{S(graphite)} + 2H_{2(g)} \xrightarrow{\Delta G_R^0} CH_{4(g)}$$

$$\Delta G_{R,298}^0 = \Delta G_{f,298}^0\left(CH_{4(g)}\right) - \Delta G_{f,298}^0\left(C_{S(graphite)}\right) - 2\Delta G_{f,298}^0\left(H_{2(g)}\right)$$

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

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

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

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

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

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

Practical example :

Let the following chemical reaction :

$$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$$

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

P = 1 atm و T = 298 K

The element	ΔH_f°(KJ/mol)	S_f°(J/K.mol)	ΔG_f°(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 K, P = atm) :

$$\frac{1}{2}N_{2(g)} + O_{2(g)} \xrightarrow{\Delta H_{R1}^0} NO_{2(g)}$$

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

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

$$\Longrightarrow \Delta H^0_{R1} = \Delta H^0_f\left(NO_{2(g)}\right)$$

We have :

$$\Delta G^0_{R1} = \Delta H^0_{R1} - T\,\Delta S^0_{R1} = \Delta H^0_{R1} - 298\,\Delta S^0_{R1}$$
$$\Delta G^0_{R1} = \Delta H^0_f\left(NO_{2(g)}\right) - 298\,\Delta S^0_{R1}$$
$$\Delta S^0_{R1} = S^0\left(NO_{2(g)}\right) - \frac{1}{2}S^0\left(N_{2(g)}\right) - S^0\left(O_{2(g)}\right)$$
$$\Delta S^0_{R1} = 240,45 - \frac{1}{2}(191,49) - (205,03) = -60,325J.K^{-1}.mol^{-1}$$
$$\Delta G^0_{R1} = \Delta G^0_f\left(NO_{2(g)}\right) - \frac{1}{2}\Delta G^0_f\left(N_{2(g)}\right) - \Delta G^0_f\left(O_{2(g)}\right)$$
$$\Delta G^0_f\left(N_{2(g)}\right) = 0\ ;\ \Delta G^0_f\left(O_{2(g)}\right) = 0$$
$$\Longrightarrow \Delta G^0_{R1} = \Delta G^0_f\left(NO_{2(g)}\right) = 51,84\ KJ/mol$$

So :

$$\Delta G^0_{R1} = \Delta H^0_f\left(NO_{2(g)}\right) - 298\,\Delta S^0_{R1}$$
$$\Delta G^0_f\left(NO_{2(g)}\right) = \Delta H^0_f\left(NO_{2(g)}\right) - 298\,\Delta S^0_{R1}$$
$$\Delta H^0_f\left(NO_{2(g)}\right) = \Delta G^0_f\left(NO_{2(g)}\right) + 298\,\Delta S^0_{R1}$$
$$\Delta H^0_f\left(NO_{2(g)}\right) = 51,84 + 298\,(-60,325\,.\,10^{-3}) = 33,86315\ KJ/mol$$

Calculating $\Delta G^0_f\left(N_2O_{4(g)}\right)$ **:**

$$N_{2(g)} + 2O_{2(g)} \xrightarrow{\Delta G^0_{R2}} N_2O_{4(g)} \qquad (2)$$
$$\Delta G^0_{R2} = \Delta G^0_f\left(N_2O_{4(g)}\right) - \Delta G^0_f\left(N_{2(g)}\right) - 2\Delta G^0_f\left(O_{2(g)}\right)$$
$$\Delta G^0_f\left(N_{2(g)}\right) = 0\ ;\ \Delta G^0_f\left(O_{2(g)}\right) = 0$$
$$\Longrightarrow \Delta G^0_{R2} = \Delta G^0_f\left(N_2O_{4(g)}\right) = \Delta H^0_f\left(N_2O_{4(g)}\right) - 298\,\Delta S^0_{R2}$$
$$\Delta S^0_{R2} = S^0\left(N_2O_{4(g)}\right) - S^0\left(N_{2(g)}\right) - 2S^0\left(O_{2(g)}\right)$$
$$\Delta S^0_{R2} = 304,30 - (191,49) - 2(205,03) = -297,25J.K^{-1}.mol^{-1}$$
$$\Delta G^0_f\left(N_2O_{4(g)}\right) = \Delta H^0_f\left(N_2O_{4(g)}\right) - 298\,\Delta S^0_{R2} = 9,71 - 298(-297,25)$$
$$= 98,29\ KJ/mol$$

The nature of the reaction (3) :

$$N_2O_{4(g)} \xrightarrow{\Delta G^0_{R3}} 2NO_{2(g)} \qquad (3)$$

$$\Delta G^0_{R3} = 2\Delta G^0_f\left(NO_{2(g)}\right) - \Delta G^0_f\left(N_2O_{4(g)}\right)$$

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

$\Delta G^0_{R3} > 0 \Longrightarrow$ **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 :

$$aA + bB \rightarrow cC + dD$$

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

$$G^P_T(A) = G^0_T(A) + RTLnP_A$$
$$G^P_T(B) = G^0_T(B) + RTLnP_B$$
$$G^P_T(C) = G^0_T(C) + RTLnP_C$$
$$\Delta G^P_T(D) = G^0_T(D) + RTLnP_D$$

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

$$\Delta G^P_T = \sum n_i G^P_T(\text{Products}) - \sum n_i G^P_T(\text{Reactants})$$

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

$$\Delta G_T^P = [cG_T^0(C) + cRTLnP_C + dG_T^0(D) + dRTLnP_D] - [aG_T^0(A) + aRTLnP_A + bG_T^0(B) + bRTLnP_B]$$

$$\Delta G_T^P = [cG_T^0(C) + dG_T^0(D)] - \left[aG_T^0(A) + bG_T^0(B)\right] + RT[\left(LnP_C{}^c + LnP_D{}^d\right) - \left(LnP_A{}^a + LnP_B{}^b\right)]$$

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

Which :

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

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

In general :

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

Example 1:

Calculate the free enthalpy for the following reaction :

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

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

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

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

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

$$\Delta G^P_R = \Delta G^0_R + RTLn \frac{{P_{HCl}}^2}{P_{H_2} . P_{Cl_2}}$$

Example 2 :

Calculate the free enthalpy for the following reaction :

$$NH_4Cl_{(S)} \rightarrow NH_{3(g)} + HCl_{(g)}$$

$$\Delta G^P_R = \Delta G^0_R + RTLn(P_{NH_3} . P_{HCl})$$

$$\Delta G^0_R = \Delta G^0_f(NH_{3(g)}) + \Delta G^0_f(HCl_{(g)}) - \Delta G^0_f(NH_4Cl_{(S)})$$

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	ΔS	ΔH	$\Delta G = \Delta H - T\Delta S$	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	$\Delta S < 0$	$\Delta H < 0$	$\Delta H < T\Delta S$ $\Delta G < 0$ $\Delta H > T\Delta S$ $\Delta G > 0$	Spontaneous Impossible
4	$\Delta S > 0$	$\Delta H > 0$	$\Delta H > T\Delta S$ $\Delta G > 0$ $\Delta H < T\Delta S$ $\Delta G < 0$	Impossible Spontaneous
5	$\Delta H = T\Delta S$		$\Delta G = 0$	Equilibrium