5.1. Free Energy and Enthalpy :

5.1.1. Free Energy (F) :

We define a new function called **free energy** (or **Helmholtz function**) and denoted by **F**.

$\mathbf{F = U - T.S}$

5.1.2. Free Enthalpy (G) :

We define a state function called **free enthalpy** or **Gibbs function**, denoted as **G**.

$\mathbf{G = H - T.S}$

Its differential expression is :

$\mathbf{dG = dH - T.dS}$ → $\mathbf{\Delta G = \Delta H - T.\Delta S}$

Consider the reaction : $a\,A + b\,B \rightleftarrows c\,C + d\,D$

*Δ**G < 0** → The system evolves in the forward direction (towards the products). The reaction is spontaneous.

*Δ**G > 0** → The system evolves in the reverse direction (towards the reactants). The reaction is non-spontaneous.

*Δ**G = 0** → The system is in equilibrium.

5.1.3. Relationship between G and F:

In the expression: $\mathbf{G = H - T.S}$, we can replace the enthalpy function with its expression: $\mathbf{H = U + P.V}$.. Then it follows:

$G = U + P.V - T.S = U - T.S + P.V = F + P.V$

$\mathbf{G = F + P.V}$

5.1.4. Variation of free enthalpy with pressure at constant temperature

We have : $G = H - T.S$; and ; $H = U + P.V$

So : $G = U + P.V - T.S \rightarrow dG = dU + P.dV + V.dP - T.dS - S.dT$

We have : $dU = \partial Q + \partial W = T.dS - P.dV \rightarrow dU - T.dS + P.dV = 0$

So : $dG = V.dP - S.dT$

* $T = Cte \rightarrow dT = 0 \rightarrow dG = V.dP$

*For an ideal gas :$V = \frac{nRT}{P}$ So : $dG = nRT.\frac{dP}{P}$

$\int_{G_T^\circ}^{G_T} dG = nRT\int_{P^\circ}^{P}\frac{dP}{P} \rightarrow G_T - G_T^\circ = nRT\,LnP$

$\mathbf{G_T = G_T^\circ + nRT\,LnP}$

For n=1 mol → $\mathbf{G_T = G_T^\circ + RT\,LnP}$

G_T : Free enthalpy at temperature T under pressure P.

G_T°: Free enthalpy at temperature T under pressure (P° = 1 bar).

5.1.5. Free enthalpy change of a chemical reaction:

1. Standard free enthalpy of formation :

The standard free enthalpy of formation of a compound, ΔG°_f, is the free enthalpy change that accompanies the formation of one mole of that compound from its elements under standard conditions.

Example : $H_2 + \frac{1}{2} O_2 \xrightarrow{\Delta G^\circ_f(H_2O)} H_2O$

Note :

By convention, standard free enthalpy of formation ($\Delta G°_f$) of an ***element*** is taken as ***zero***.

Examples: $\Delta G°_f(O_2(g))=0$, $\Delta G°_f(H_2(g))=0$

2. Calculation of the free enthalpy change of a chemical reaction:

Method 1:

The standard free enthalpy change of a chemical reaction can be calculated using the equation:

$$\Delta G^{\circ}_{R} = \Delta H^{\circ}_{R} - T.\Delta S^{\circ}_{R}$$

With:

$\Delta G°_R$: standard free enthalpy change of the reaction.

$\Delta H°_R$: standard enthalpy change of the reaction.

$\Delta S°_R$: standard entropy change of the reaction.

T: temperature of the reaction (K).

Method 2:

The standard free enthalpy change of a chemical reaction can also be calculated by:

$$\Delta G^{\circ}_{R} = \sum\left(\gamma_J.\Delta G^{\circ}_{f(J)}\right)_{products} - \sum\left(\gamma_i.\Delta G^{\circ}_{f(i)}\right)_{reactants}$$

With:

γ_j: Stoichiometric coefficients of the products.

γi: Stoichiometric coefficients of the reactants.

$\Delta G_f°$: Standard free enthalpy change of formation.

Example :

Calculate at 298K, $\Delta G°_R$ of the following reaction : $CO_{2(g)} + C_{(graphite)} \rightarrow 2CO_{(g)}$

substance	$CO_{(g)}$	$CO_{2(g)}$	$C_{(graphite)}$
$\Delta G_{f,\,298}$ (KJ/mol)	-137.1	-393.5	0

$G_{R,\,298}° = 2\,\Delta G°_{f,298}(CO,g) - \Delta G°_{f,298}(CO_2,g) - \Delta G°_{f,298}(C, graphite) = 119.3$ KJ

5.2. Chemical Equilibria:

5.2.1. Definition :

A chemical reaction is in a state of equilibrium when the concentrations of reactants and products do not change over time at equilibrium

5.2.2. Laws of Mass Action:

5.2.2.1. Equilibrium Constant (K_P) Relative to Partial Pressures (Guldberg and Waage Law):

For the chemical reaction : $aA + bB \leftrightarrow cC + dD$

$$\Delta G = (c.G_C + d.G_D) - (a.G_A + b.G_B)$$

$$\Delta G = c(G^{\circ}_C + RT\,LnP_C) + d\left(G^{\circ}_D + RT\,LnP_D\right) - a(G^{\circ}_A + RT\,LnP_A) - b(G^{\circ}_B + RT\,LnP_B)$$

$$\Delta G = \left(c.G^{\circ}_C + d.G^{\circ}_D - a.G^{\circ}_A - b.G^{\circ}_B\right) + RT\,(LnP^c_C + LnP^d_D - LnP^a_A - LnP^b_B)$$

$$\Delta G = \Delta G^{\circ} + RT\,Ln\left(\frac{P^c_C.P^d_D}{P^a_A.P^b_B}\right)$$

$\mathbf{K_P = \frac{P_C^c . P_D^d}{P_A^a . P_B^b}}$ **(1st law of mass action)**

So : $\mathbf{\Delta G = \Delta G^\circ + RTLnK_P}$

At equilibrium, ΔG = 0 and consequently, $\Delta G^\circ + RTLnK_P = 0 \rightarrow LnK_P = \frac{-\Delta G^\circ}{RT}$

$\mathbf{K_P = \exp(-\frac{\Delta G^\circ}{RT})}$ **(Guldberg and Waage's Law)**

5.2.2.2. Equilibrium Constant (K_C) Relative to Molar Concentrations:

According to the ideal gas law : $P = \frac{n}{v} . R . T = C . R . T \rightarrow \mathbf{P_i = [i] . R . T}$

$$K_p = \frac{P_C^c .\ P_D^d}{P_A^a .\ P_B^b} = \frac{[C]^c .\ [D]^d}{[A]^a .\ [B]^b}\ (R . T)^{(c+d)-(a+b)}$$

$\mathbf{K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$; and ; **(c + d) – (a + b) = Δn**

So : $k_P = k_C . (R . T)^{\Delta n} \rightarrow \mathbf{k_C = k_P . (R . T)^{-\Delta n}}$ **(2nd law of mass action)**

5.2.2.3. Equilibrium Constant (K_x) Relative to Mole Fractions:

We have : $\mathbf{P_i = x_i . P_t}$

$$K_P = \frac{P_C^c . P_D^d}{P_A^a . P_B^b} = \frac{x_C^c . x_D^d}{x_A^a . x_B^b}\ P_t^{(c+d)-(a+b)}$$

$\mathbf{K_x = \frac{x_C^c . x_D^d}{x_A^a . x_B^b}}$, and, **(c + d) – (a + b) = Δn**

So: $k_P = k_x . P_t^{\Delta n} \rightarrow \mathbf{k_x = k_P . P_t^{-\Delta n}}$ **(3rd law of mass action)**

5.2.3. Influence of Temperature on Equilibrium Constants (Van't Hoff Equation):

$$\Delta G^\circ + RTLnK_P = 0 \rightarrow LnK_P = \frac{-\Delta G^\circ}{RT}$$

$$\frac{d}{dT}(LnK_P) = \frac{d}{dT}\left(\frac{-\Delta G^\circ{}_T}{R.T}\right) = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G^\circ{}_T}{T}\right)$$

$$\frac{d}{dT}(LnK_P) = -\frac{1}{R}\left(\frac{\frac{d\Delta G^\circ{}_T}{dT}.T - \Delta G^\circ{}_T}{T^2}\right) = -\frac{1}{R}\left(\frac{1}{T}\frac{d\Delta G^\circ{}_T}{dT} - \frac{\Delta G^\circ{}_T}{T^2}\right)$$

We have : $dG = V . dP - S . dT \rightarrow \frac{dG}{dT}|P = -S \rightarrow \frac{d\Delta G^\circ{}_T}{dT} = -\Delta S^\circ{}_T$

So : $\frac{d}{dT}(LnK_P) = -\frac{1}{R}\left(\frac{-\Delta S^\circ{}_T}{T} - \frac{\Delta G^\circ{}_T}{T^2}\right)$

We have: $G = H - T . S \rightarrow \Delta G^\circ{}_T = \Delta H^\circ{}_T - T . \Delta S^\circ{}_T$

$$\frac{d}{dT}(LnK_P) = -\frac{1}{R}\left(\frac{-\Delta S^\circ{}_T}{T} - \frac{\Delta H^\circ{}_T}{T^2} + \frac{\Delta S^\circ{}_T}{T}\right)$$

$\mathbf{\frac{d}{dT}(LnK_P) = \frac{\Delta H^\circ{}_T}{R.T^2}}$ **(Van't Hoff equation)**

*Equilibrium at variable temperature :

For each temperature, the chemical reaction has an equilibrium state:

At temperature T_1, we have an equilibrium defined by K_{P1}.

At temperature T_2, we have an equilibrium defined by K_{P2}.

$$\int_{K_{P1}}^{K_{P2}} dLnK_P = \int_{T_1}^{T_2} \frac{\Delta H^\circ_T}{R.T^2}.dT \rightarrow LnK_{P2} - LnK_{P1} = \frac{\Delta H^\circ_T}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\boldsymbol{Ln\left(\frac{K_{P2}}{K_{P1}}\right) = \frac{\Delta H^\circ_T}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

***Gibbs-Helmholtz Relation:**

$$\frac{d}{dT}(LnK_P) = \frac{d}{dT}\left(\frac{-\Delta G^\circ_T}{R.T}\right) \quad ; \text{and;} \quad \frac{d}{dT}(LnK_P) = \frac{\Delta H^\circ_T}{R.T^2}$$

$$\text{So : } \frac{d}{dT}\left(\frac{-\Delta G^\circ_T}{R.T}\right) = \frac{\Delta H^\circ_T}{R.T^2}$$

$$\boldsymbol{\frac{d}{dT}\left(\frac{\Delta G^\circ_T}{T}\right) = -\frac{\Delta H^\circ_T}{T^2}} \qquad \textbf{(Gibbs-Helmholtz Relation)}$$

5.2.4. Laws of Shifting Equilibrium (Le Chatelier's Principle):

The principle of Le Chatelier allows predicting the direction of shifting of the equilibrium when a factor is varied (temperature, total pressure, and partial pressure (concentration)).

Statement of Le Chatelier's principle :

"Any change in one of the factors of equilibrium induces a shift in the equilibrium in a direction that opposes this change."

a) Influence of temperature :

"An increase in temperature shifts the equilibrium in the endothermic direction."

Example : $N_{2(g)} + 3H_{2(g)} \underset{2}{\overset{1}{\rightleftarrows}} 2NH_{3(g)}$ $\Delta H^\circ_R = -22$ Kcal

The reaction is exothermic ($\Delta H^\circ_R < 0$); an increase in temperature favors the reaction in direction (2); that is, the dissociation of NH_3.

b) Influence of total pressure :

"An increase in total pressure shifts the equilibrium in the direction that reduces the number of gaseous moles."

Example : $N_{2(g)} + 3H_{2(g)} \underset{2}{\overset{1}{\rightleftarrows}} 2NH_{3(g)}$

If the total pressure is increased, the reaction is favored in direction (1) because the number of gaseous moles decreases.

c) Influence of partial pressure (concentration) :

"The equilibrium shifts in the direction of the disappearance of the component whose concentration is increased."

Example : $H_{2(g)} + I_{2(g)} \underset{2}{\overset{1}{\rightleftarrows}} 2HI_{(g)}$

If the partial pressure (concentration) of H_2 is increased, the equilibrium shifts in direction (1).

d) Effect of inert gas :

**** « The addition of an inert gas at constant volume (isochoric system) has no effect on the equilibrium »***

**** « The addition of an inert gas at constant pressure (isobaric system) shifts the equilibrium in the direction that increases the number of gaseous moles »***

Example : $N_{2(g)} + 3H_{2(g)} \underset{2}{\overset{1}{\rightleftarrows}} 2NH_{3(g)}$

Adding an inert gas at constant pressure shifts the equilibrium in direction (2) because the number of gaseous moles increases.

e) Case of heterogeneous reactions:

"In the case of heterogeneous systems, only the concentrations (partial pressures) that appear in the law of mass action are equilibrium factors."

Example 1 : $3\,Fe_{(s)} + 4\,H_2O_{(g)} \underset{2}{\overset{1}{\rightleftarrows}} Fe_3O_{4\,(s)} + 4\,H_{2\,(g)}$

$$K_p = \frac{P_{H_2}^4}{P_{H2O}^4}$$

Since K_P only involves H_2O and H_2, the addition or removal of Fe(s) and Fe_3O_4(s) does not shift the equilibrium.

Example 2 : $CaCO_{3(s)} \underset{2}{\overset{1}{\rightleftarrows}} CaO_{(s)} + CO_{2(g)}$ $\quad \mathbf{K_p = P_{CO_2}}$

Since K_P involves only CO_2, the introduction or removal of $CaCO_3$ and CaO does not shift the equilibrium.

5.2.5. Complementary aspect of studying equilibrium:

a) Dissociation coefficient (α):

It is the ratio between the number of moles dissociated from the component and the initial number of moles.

$$\alpha = \frac{\textbf{The number of moles dissociated of the component}}{\textbf{Initial number of moles of the component}}$$

$\mathbf{0 < \alpha < 1}$

Notes :

*If: **α = 1**; the reaction is complete.

***α** can be expressed as a percentage.

Example :

$$PCl_{5\,(g)} \underset{2}{\overset{1}{\leftrightarrows}} PCl_{3\,(g)} + Cl_{2\,(g)}$$

The initial number of moles is n_0. At equilibrium, the number of moles stabilizes at $n=1.2n_0$. Calculate the dissociation coefficient (α)?

Correction :

	$PCl_{5\,(g)}$	$\underset{2}{\overset{1}{\rightleftharpoons}}$	$PCl_{3\,(g)}$ +	$Cl_{2\,(g)}$
At t=0	n_0		0	0
At t= teq	$(n_0 - \alpha\, n_0)$		$\alpha\, n_0$	$\alpha\, n_0$

The total number of moles at equilibrium is : $n = n_0 - \alpha\, n_0 + \alpha\, n_0 + \alpha\, n_0 \rightarrow\; n = n_0\,(1+\alpha)$

We have : $n = n_0\,(1+\alpha)$ et $n = 1.2\, n_0$

So: $n_0\,(1+\alpha) = 1.2\, n_0 \;\rightarrow \boldsymbol{\alpha = 0.2} \;\rightarrow \boldsymbol{\alpha = 20\%}$

b) Degree of advancement (ζ):

It is given by the expression: $\boldsymbol{\zeta = \frac{n_i - n_{i0}}{\gamma_i}}$

With:

n_{i0}: Initial number of moles of substance "i".

n_i: Number of moles of substance "i" at the considered advancement state.

γ_i: Stoichiometric coefficient of substance "i" (negative for reactants, and positive for products).

Example :

	$2\,H_2$	+	O_2	$\underset{2}{\overset{1}{\rightleftharpoons}}$	$2\,H_2O$
At t=0	2 mol		1 mol		0 mol
At t= t	1 mol		0.5 mol		1 mol

The advancement of the reaction is given by :

*H_2 : $\zeta = \frac{1-2}{-2} = 0.5$ mol

*O_2 : $\zeta = \frac{0.5-1}{-1} = 0.5$ mol

*H_2O : $\zeta = \frac{1-0}{2} = 0.5$ mol

If we had written:

	H_2	+	$\frac{1}{2}\,O_2$	$\underset{2}{\overset{1}{\rightleftharpoons}}$	H_2O
At t=0	2 mol		1 mol		0 mol
At t= t	1 mol		0.5 mol		1 mol

The advancement of the reaction is:

*H_2 : $\zeta = \frac{1-2}{-1} = 1$ mol

*O_2 : $\zeta = \frac{0.5-1}{-0.5} = 1$ mol

*H_2O : $\zeta = \frac{1-0}{1} = 1$ mol