

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 :

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

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

* $\Delta G < 0$ \rightarrow The system evolves in the forward direction (towards the products). The reaction is spontaneous.

* $\Delta G > 0$ \rightarrow The system evolves in the reverse direction (towards the reactants). The reaction is non-spontaneous.

* $\Delta G = 0$ \rightarrow The system is in equilibrium.

5.1.3. Relationship between G and F:

In the expression: $G = H - T.S$, we can replace the enthalpy function with its expression:

$H = U + P.V$. 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 ; $H = U + P.V$

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

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

$$\text{So : } dG = V.dP - S.dT$$

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

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

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

$$\mathbf{G_T = G_T^\circ + nRT \ln P}$$

$$\text{For } n=1 \text{ mol} \rightarrow \mathbf{G_T = G_T^\circ + RT \ln P}$$

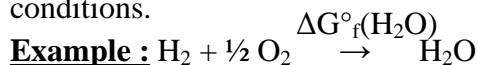
G_T : Free enthalpy at temperature T under pressure P.

G_T° : Free enthalpy at temperature T under pressure ($P^\circ = 1 \text{ bar}$).

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.



Note :

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

Examples: $\Delta G^\circ_f(\text{O}_2(\text{g}))=0$, $\Delta G^\circ_f(\text{H}_2(\text{g}))=0$

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:

$$\Delta G^\circ_R = \Delta H^\circ_R - T \cdot \Delta S^\circ_R$$

With:

ΔG°_R : standard free enthalpy change of the reaction.

ΔH°_R : standard enthalpy change of the reaction.

ΔS°_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:

$$\Delta G^\circ_R = \sum(\gamma_j \cdot \Delta G^\circ_{f(j)}\text{products}) - \sum(\gamma_i \cdot \Delta G^\circ_{f(i)}\text{reactants})$$

With:

γ_j : Stoichiometric coefficients of the products.

γ_i : Stoichiometric coefficients of the reactants.

ΔG°_f : Standard free enthalpy change of formation.

Example :

Calculate at 298K, ΔG°_R of the following reaction : $\text{CO}_2(\text{g}) + \text{C}_{(\text{graphite})} \rightarrow 2\text{CO}(\text{g})$

substance	$\text{CO}(\text{g})$	$\text{CO}_2(\text{g})$	$\text{C}_{(\text{graphite})}$
$\Delta G^\circ_{f, 298}$ (KJ/mol)	-137.1	-393.5	0

$$G_{R, 298}^\circ = 2 \Delta G^\circ_{f,298}(\text{CO},\text{g}) - \Delta G^\circ_{f,298}(\text{CO}_2,\text{g}) - \Delta G^\circ_{f,298}(\text{C}, \text{graphite}) = 119.3 \text{ KJ}$$

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 : $aA + bB \leftrightarrow cC + dD$

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

$$\Delta G = c(G_C^\circ + RT \ln P_C) + d(G_D^\circ + RT \ln P_D) - a(G_A^\circ + RT \ln P_A) - b(G_B^\circ + RT \ln P_B)$$

$$\Delta G = (c \cdot G_C^\circ + d \cdot G_D^\circ - a \cdot G_A^\circ - b \cdot G_B^\circ) + RT (\ln P_C^c + \ln P_D^d - \ln P_A^a - \ln P_B^b)$$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right)$$

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

$$\text{So : } \Delta G = \Delta G^\circ + RT \ln K_P$$

$$\text{At equilibrium, } \Delta G = 0 \text{ and consequently, } \Delta G^\circ + RT \ln K_P = 0 \rightarrow \ln K_P = \frac{-\Delta G^\circ}{RT}$$

$$K_P = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad (\text{Guldberg and Waage's Law})$$

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

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

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

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}; \text{ and ; } (c + d) - (a + b) = \Delta n$$

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

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

We have : $P_i = x_i \cdot P_t$

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

$$K_x = \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}, \text{ and, } (c + d) - (a + b) = \Delta n$$

$$\text{So: } k_P = k_x \cdot P_t^{\Delta n} \rightarrow k_x = k_P \cdot P_t^{-\Delta n} \quad (3^{\text{rd}} \text{ law of mass action})$$

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

$$\Delta G^\circ + RT \ln K_P = 0 \rightarrow \ln K_P = \frac{-\Delta G^\circ}{RT}$$

$$\frac{d}{dT} (\ln K_P) = \frac{d}{dT} \left(\frac{-\Delta G^\circ_T}{R \cdot T} \right) = -\frac{1}{R} \frac{d}{dT} \left(\frac{\Delta G^\circ_T}{T} \right)$$

$$\frac{d}{dT} (\ln K_P) = -\frac{1}{R} \left(\frac{\frac{d\Delta G^\circ_T}{dT} \cdot T - \Delta G^\circ_T}{T^2} \right) = -\frac{1}{R} \left(\frac{1}{T} \frac{d\Delta G^\circ_T}{dT} - \frac{\Delta G^\circ_T}{T^2} \right)$$

$$\text{We have : } dG = V \cdot dP - S \cdot dT \rightarrow \left. \frac{dG}{dT} \right|_P = -S \rightarrow \frac{d\Delta G^\circ_T}{dT} = -\Delta S^\circ_T$$

$$\text{So : } \frac{d}{dT} (\ln K_P) = -\frac{1}{R} \left(\frac{-\Delta S^\circ_T}{T} - \frac{\Delta G^\circ_T}{T^2} \right)$$

$$\text{We have: } G = H - T \cdot S \rightarrow \Delta G^\circ_T = \Delta H^\circ_T - T \cdot \Delta S^\circ_T$$

$$\frac{d}{dT} (\ln K_P) = -\frac{1}{R} \left(\frac{-\Delta S^\circ_T}{T} - \frac{\Delta H^\circ_T}{T^2} + \frac{\Delta S^\circ_T}{T} \right)$$

$$\frac{d}{dT} (\ln K_P) = \frac{\Delta H^\circ_T}{R \cdot T^2} \quad (\text{Van't Hoff equation})$$

*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} .

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

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

***Gibbs-Helmholtz Relation:**

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

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

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

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

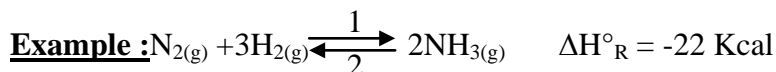
The principle of Le Chatelier allows predicting the direction of shifting of the equilibrium when a factor is varied (temperature, total pressure, and partial pressure (concentration)).

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 :

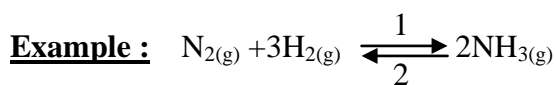
"An increase in temperature shifts the equilibrium in the endothermic direction."



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 :

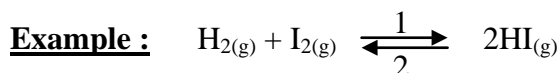
"An increase in total pressure shifts the equilibrium in the direction that reduces the number of gaseous moles."



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."

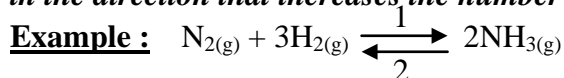


If the partial pressure (concentration) of H_2 is increased, the equilibrium shifts in direction (1).

d) Effect of inert gas :

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

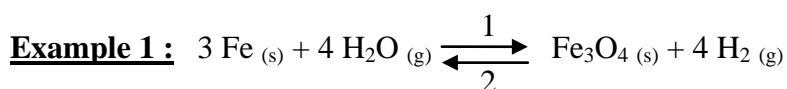
* « The addition of an inert gas at constant pressure (isobaric system) shifts the equilibrium in the direction that increases the number of gaseous moles »



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

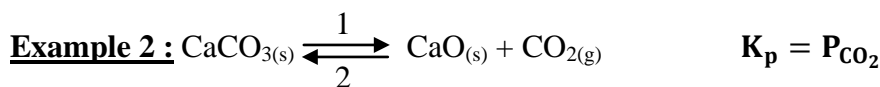
e) Case of heterogeneous reactions:

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



$$K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

Since K_p only involves H_2O and H_2 , the addition or removal of $\text{Fe}(s)$ and $\text{Fe}_3\text{O}_4(s)$ does not shift the equilibrium.



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.

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

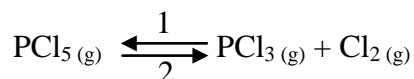
$$0 < \alpha < 1$$

Notes :

*If: $\alpha = 1$; the reaction is complete.

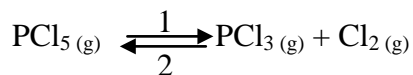
* α can be expressed as a percentage.

Example :



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 :



At t=0 n_0 0 0

At t= teq $(n_0 - \alpha n_0)$ αn_0 αn_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: $n_0(1 + \alpha) = 1.2 n_0 \rightarrow \alpha = 0.2 \rightarrow \alpha = 20\%$

b) Degree of advancement (ζ):

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

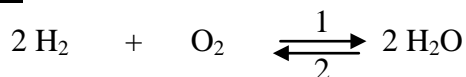
With:

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 :



At t=0 2 mol 1 mol 0 mol

At t= t 1 mol 0.5 mol 1 mol

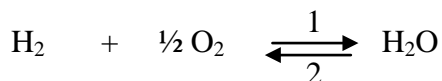
The advancement of the reaction is given by :

*H₂: $\zeta = \frac{1-2}{-2} = 0.5 \text{ mol}$

*O₂: $\zeta = \frac{0.5-1}{-1} = 0.5 \text{ mol}$

*H₂O: $\zeta = \frac{1-0}{2} = 0.5 \text{ mol}$

If we had written:



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:

*H₂: $\zeta = \frac{1-2}{-1} = 1 \text{ mol}$

*O₂: $\zeta = \frac{0.5-1}{-0.5} = 1 \text{ mol}$

*H₂O: $\zeta = \frac{1-0}{1} = 1 \text{ mol}$