5.1. Free energy and enthalpy:

5.1.1. Free enthalpy:

1. Definition :

According to the 2nd law of thermodynamics, a transformation is spontaneous (irreversible) if:

$$\mathbf{\Delta S_{tot} = \Delta S_{sys} + \Delta S_{ext} > 0}$$

Or: $\Delta S_{ext} = \frac{-Q_{sys}}{T}$ ($Q_{ext} = - Q_{sys}$) when the transformation is carried out at a constant temperature T.

For an isobaric transformation: $Q_{sys} = \Delta H_{sys} \Longrightarrow \Delta S_{ext} = \frac{-\Delta H_{sys}}{T}$

From where: $\Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0 \Longrightarrow T\,\Delta S_{sys} - \Delta H_{sys} > 0 \Longrightarrow \mathbf{\Delta H_{sys} - T\Delta S_{sys} < 0}$

By definition the term: **ΔH – TΔS** is called "free enthalpy" or "GIBBS function" denoted ΔG hence

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

$$\mathbf{G = H - TS}$$

$$\mathbf{dG = dH - TdS}$$

For a chemical reaction:

$$aA + bB \underset{\text{Sens 2}}{\overset{\text{Sens 1}}{\rightleftarrows}} cC + dD$$

If : $\Delta G < 0 \Longrightarrow$ the reaction takes place in the direct direction (direction 1); she is spontaneous.

If: $\Delta G > 0 \Longrightarrow$ the reaction takes place in the opposite direction (direction 2).

If : $\Delta G = 0 \Longrightarrow$ the system is in equilibrium.

2. Evolution of free enthalpy as a function of partial pressure:

$G = H - TS = U + PV - TS$

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

Or $dU = TdS - PdV$

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

$$\mathbf{dG = VdP - SdT}$$

At T = cste , $\mathbf{dG = VdP}$

For a pressure variation from P_1 to P_2

$\Delta G = G_T^{P2} - G_T^{P1} = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln \frac{P_2}{P_1}$

$G_T^{P2} = G_T^{P1} + nRT \ln \frac{P_2}{P_1}$

Under standard conditions, we define the standard molar free enthalpy at temperature T denoted $G°_T$ and the molar free enthalpy of the gas at temperature T and pressure P is given by the expression:

$$\mathbf{G_T^P = G°_T + RT\ln P}$$

In the case of a supposedly perfect gas mixture: the molar free enthalpy of each constituent i under its partial pressure Pi at temperature T is given by:

$$\mathbf{G_T^P\,(i) = G°_T\,(i) + RT\ln P_i}$$

The total free enthalpy of the mixture (G_T^P (tot)) is given by::

$$\mathbf{G_T^P\,(tot) = \sum ni\, G_T^P}$$

3. Calculation of the change in free enthalpy during a chemical reaction:

3.1. The standard free enthalpy of formation($\Delta G°_f$) :

We call the standard free enthalpy of formation of a compound ($\Delta G°_f$) the variation in free enthalpy accompanying the formation of a mole of this compound from its constituent elements under standard conditions.

Example :

$H_2 + ½\, O_2 \xrightarrow{\Delta G°_f} H_2O$

$$\mathbf{\Delta G°_f\ (Elementary\ substance) = 0}$$

$\Delta G°_f\,(O_2) = \Delta G°_f\,(N_2) = 0$

3.2. The free enthalpy of a chemical reaction:

Consider a chemical reaction taking place at P = cste and T = cste

$$aA + bB \longrightarrow cC + dD$$

$\Delta G°_R = (c\,\Delta G°_f\,(C) + d\,\Delta G°_f\,(D)) - (a\,\Delta G°_f\,(A) + b\,\Delta G°_f\,(B))$

In the general case :

$$\mathbf{\Delta G°_R = \sum \upsilon j\, \Delta G°_f\ (products) - \sum \upsilon i\, \Delta G°_f\ (reactants)}$$

Example :

Let's calculate $\Delta G°_{298}$ of the following reaction:

$$F_2\,(g) + 2\,HCl\,(g) \longrightarrow 2\,HF\,(g) + Cl_2\,(g)$$

With :

$\Delta G°_f\,(HCl) = -\ 95{,}18$ KJ/mol ; $\Delta G°_f\,(HF) = -\ 276{,}21$ KJ/mol

$\Delta G°_R = 2\Delta G°_f\,(HF) + \cancel{\Delta G°_f\,(Cl_2)} - \cancel{\Delta G°_f\,(F_2)} - 2\,\Delta G°(HCl)$

$\Delta G°_R = -\ 362{,}06\ KJ < 0 \Longrightarrow$ The reaction is spontaneous under standard conditions

5.1.2. Free energy:

For an irreversible transformation we have:

$$\mathbf{\Delta S_{tot} = \Delta S_{sys} + \Delta S_{ext} > 0}$$

Or : $\Delta S_{ext} = \frac{-Q_{sys}}{T}$ ($Q_{ext} = -\ Q_{sys}$) when the transformation is carried out at a constant temperature T.

For an isochoric transformation: $Q_{sys} = \Delta U_{sys} \Longrightarrow \Delta S_{ext} = \frac{-\Delta U_{sys}}{T}$

From where : $\Delta S_{sys} - \frac{\Delta U_{sys}}{T} > 0 \Longrightarrow T\,\Delta S_{sys} - \Delta\,U_{sys} > 0 \Longrightarrow \mathbf{\Delta U_{sys} - T\Delta S_{sys} < 0}$

For an isothermal transformation taking place at V = cst, we define a state function denoted “F” called “Free energy” or “Helmholtz function” such that:

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

$$\mathbf{F = U - TS}$$

$$\mathbf{dF = dU - TdS}$$

If : $\Delta F < 0 \Longrightarrow$ the transformation is spontaneous (direct direction of the reaction).
If : $\Delta F < 0 \Longrightarrow$ the transformation cannot be spontaneous (opposite direction of the reaction).
If : $\Delta F = 0 \Longrightarrow$ the system is in equilibrium.

Relationship between G and F:

We have : F = U – TS, G = H – TS et H = U + PV
G = U + PV – TS = U – TS + PV

$$\mathbf{G = F + PV}$$

5.2. Chemical equilibrium:

5.2.1. Definition :

In chemical equilibrium, concentration of the reactants and products do not change with time and the system does not show any further change in properties.
In case of chemical equilibrium, rate of forward reaction becomes equal to the rate of backward reaction. i.e. Rate (forward reaction) = Rate (backward reaction)

5.2.2. Law of Mass Action:

Consider the reaction

$$aA + bB \underset{2}{\overset{1}{\rightleftarrows}} cC + dD$$

Let's calculate ΔG of the reaction

$\Delta G_R = (cG(C) + d\,G(D)) - (aG(A) + b\,G(B))$

We know that: $\mathbf{G_T^P (i) = G°_T (i) + RT\ln P_i}$

So $\Delta G_R = [c(G°_C + RT\ln P_C) + d(G°_D + RT\ln P_D)] - [a(G°_A + RT\ln P_A) + b(G°_B + RT\ln P_B)]$

$\Delta G_R = cG°_C + dG°_D - aG°_A - bG°_B + cRT\ln P_C + dRT\ln P_D – aRT\ln P_A - bRT\ln P_B$

$\Delta G_R = \Delta G° + RT(c\ln P_C + d\ln P_D – a\ln P_A - b\ln P_B)$

$\Delta G_R = \Delta G° + RT(\ln P_C{}^C + \ln P_D{}^D – \ln P_A{}^A - \ln P_B{}^B)$

$\Delta G_R = \Delta G° + RT \ln\frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$

$$\mathbf{\Delta G_T = \Delta G° + RT \ln \ln K_P}$$

At equilibrium $\Delta G_T = 0 \Longrightarrow \Delta G° + RT \ln \ln K_P = 0$

So $\Delta G° = -RT \ln \ln K_P \Longrightarrow \mathbf{K_P = \exp(\frac{-\Delta G°}{RT})}$

$$\left.\begin{array}{l} \mathbf{K_P = \exp(\frac{-\Delta G°}{RT})} \\ \mathbf{K_P = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}} \end{array}\right\} \quad \textbf{1}^{\textbf{st}}\textbf{ law of mass action - law of Guldberg and waage}$$

a, b, c and d are the stoichiometric coefficients. P_A, P_B, P_C et P_D are the partial pressures of the reactants and products.

- **For concentrations :**

For an ideal gas PV = nRT $\Longrightarrow = \frac{n}{V}RT = Crt$

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

$$K_P = K_c(RT)^{\Delta n} \text{ with } \Delta n = c+d-a-b$$

$$\left.\begin{array}{r}\mathbf{K_c = K_P(RT)^{-\Delta n}}\\ \text{et } \mathbf{K_c} = \frac{[\mathbf{C}]^{\mathbf{c}}[\mathbf{D}]^{\mathbf{d}}}{[\mathbf{A}]^{\mathbf{a}}[\mathbf{B}]^{\mathbf{b}}}\end{array}\right\} \quad \textbf{2}^{\textbf{nd}} \textbf{ law of mass action}$$

- **For the mole fractions:**

$P_i = x_i\ P_t$

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

$K_P = K_x.P_t^{\ \Delta n}$

$$\left.\begin{array}{r}\mathbf{K_x = K_P.P_t^{-\Delta n}}\\ \mathbf{K_x} = \frac{\mathbf{x_C^c \times x_D^d}}{\mathbf{x_A^a \times x_B^b}}\end{array}\right\} \quad \textbf{3}^{\textbf{rd}} \textbf{ law of mass action}$$

5.2.3. Variation of the equilibrium constant with temperature :

We have $\Delta G° = -RT \ln \ln K_P \Longrightarrow \ln K_P = \frac{-\Delta G°}{RT}$

$\frac{d(\ln K_P)}{dT} = \frac{d}{dT}(\frac{-\Delta G°}{RT}) = -\frac{1}{R}\frac{d}{dT}(\frac{\Delta G°}{T})$

$\frac{d(\ln K_P)}{dT} = -\frac{1}{R}\left[\frac{T\frac{d\Delta G°}{dT} - \Delta G°}{T^2}\right] = -\frac{1}{R}(\frac{-\Delta G°}{T^2} + \frac{1}{T}\frac{d\Delta G°}{dT})$

We have $dG = VdP - SdT \Longrightarrow \frac{dG}{dT} = -S \Longrightarrow \frac{d\Delta G°}{dT} = -\Delta S°$

$\frac{d(\ln K_P)}{dT} = -\frac{1}{R}(\frac{-\Delta G°}{T^2} + \frac{1}{T}\ (-\Delta S°))$

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

From where $\frac{d(\ln K_P)}{dT} = -\frac{1}{R}(\frac{-\Delta H°}{T^2} + \frac{\Delta S°}{T} - \frac{\Delta S°}{T})$

$$\mathbf{\frac{d(\ln K_P)}{dT} = \frac{\Delta H°}{RT^2}} \quad \textbf{Vant'Hoff equation}$$

It follows that

If ΔH > 0, K increases with temperature.

If ΔH < 0, K decreases with temperature.

At $T_1 \longrightarrow K_1$ and at $T_2 \longrightarrow K_2$

$\int_{K_1}^{K_2} d\ln K = \int_{T_1}^{T_2} \frac{\Delta H°}{RT^2} dT \Longrightarrow \ln K_2 - \ln K_1 = \frac{\Delta H°}{R}(\frac{1}{T_1} - \frac{1}{T_2})$

$$\mathbf{\ln\frac{K_2}{K_1} = \frac{\Delta H°}{R}(\frac{1}{T_1} - \frac{1}{T_2})}$$

We have $\frac{d(\ln K_P)}{dT} = \frac{d}{dT}(\frac{-\Delta G°}{RT}) = \frac{\Delta H°}{RT^2}$

$$\mathbf{\frac{d}{dT}(\frac{\Delta G°}{T}) = \frac{-\Delta H°}{T^2}} \quad \textbf{Gibbs-Helmholtz relation}$$

5.2.4. Law of equilibrium shift: Le Chatelier's principle.

Le Chatelier's principle allows us to predict the direction of equilibrium shift when a factor is varied.

The equilibrium factors are:

- Temperature T
- Total pressure P
- Partial pressure Pi (or concentrations).

Statement of Le Chatelier's principle:

"Any change in an equilibrium factor causes a shift in the equilibrium in a direction that opposes the change."

1. Influence of temperature on the shift of equilibrium:

"Increasing temperature shifts the equilibrium in the endothermic direction."

Example 1 :

$N_2\,(g) + 3\,H_2\,(g) \underset{2}{\overset{1}{\rightleftarrows}} 2NH_3\,(g) \qquad \Delta H°_{298} = -\,22$ kcal/mol

An increase in temperature favors the reaction in direction 2 (endothermic direction).

2. Influence of total pressure on the shift of equilibrium:

"An increase in total pressure causes a shift in the equilibrium in the direction that decreases the number of gas moles."

Example 1:

$CO\,(g) + 2\,H_2\,(g) \underset{2}{\overset{1}{\rightleftarrows}} CH_3OH\,(g)$

If we increase the total pressure, the reaction is favored in direction 1 since there is a reduction in the number of gas moles (from 3 to 1).

Example 2:

$Fe_3O_4\,(s) + CO\,(g) \underset{2}{\overset{1}{\rightleftarrows}} 3FeO\,(s) + CO_2\,(g)$

$\Delta n = 0$, Pressure is not an equilibrium factor.

3. Influence of concentration (or partial pressure) on the shift of equilibrium:

"The equilibrium shifts in the direction of the disappearance of a component whose concentration (or partial pressure) is increased."

Example :

$H_2 + I_2 \underset{2}{\overset{1}{\rightleftarrows}} 2\,HI$

If we increase the partial pressure of H_2 the equilibrium moves in direction 1 (direction of disappearance of H_2).

Note:

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

Exemple :

$CaCO_3\,(s) \rightleftarrows CaO\,(s) + CO_2\,(g)$

$K_P = P_{CO2}$

Only involves CO2; therefore, the introduction or removal of $CaCO_3$ or CaO does not shift the equilibrium.

4. Introduction of an inert gas:

- The addition of an inert gas at constant volume does not shift the chemical equilibrium.
- The addition of an inert gas at constant pressure shifts the equilibrium in the direction of an increase in the number of gas moles.

5.2.5. Complementary aspects of the study of equilibria :

1. Dissociation coefficient α :

The dissociation coefficient of a reactant is the ratio between the amount dissociated of that reactant and its initial amount.

$$\alpha = \frac{\textit{Number of moles of the dissociated component.}}{\textit{Initial number of moles.}} \qquad 0 < \alpha < 1$$

If α = 1 ; the reaction is total

α can be expressed %

Example :

Consider the following homogeneous gas phase equilibrium:

	$PCl_5\,(g) \rightleftarrows$	PCl_3 +	$Cl_2\,(g)$
At t = 0	n_0	0	0
At t = teq	$n_0 - \alpha n_0$	αn_0	αn_0

The initial number of moles is n_0, at equilibrium; the number of moles stabilizes at $n = 1{,}2\ n_0$

Calculate the dissociation coefficient α.

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

$n_0\,(1 + \alpha) = 1{,}2\ n_0 \Longrightarrow \alpha = 0{,}2$

So α = 20%

1. Let us relate the constant KP to the degree of dissociation of PCl_5 :

The constant K_P is given by:

$$K_P = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$$

$$P_{PCl_3} = x_{PCl_3}.P_{tot} = \frac{n_{PCl_3}}{n_{tot}}\ .\ P_{tot} = \frac{\alpha n_0}{(1+\alpha)n_0}\ .\ P_{tot} = (\frac{\alpha}{1+\alpha}).\ P_{tot}$$

$$P_{PCl_5} = x_{PCl_5}.P_{tot} = (\frac{\alpha}{1+\alpha}).\ P_{tot}$$

$$P_{Cl_2} = x_{Cl_2}.P_{tot} = (\frac{1-\alpha}{1+\alpha}).\ P_{to}\text{, d'où}$$

$$\mathbf{K_P = (\frac{\alpha^2}{1-\alpha^2})\ .\ P_{tot}}$$

2. Progress of a chemical reaction (ζ) :

Consider a chemical reaction with the overall equation:

$$a\,A + b\,B \longrightarrow cC + dD$$

The progress of this reaction at time t, denoted as "ζ" (expressed in moles), is defined by:

$$\zeta = \frac{n_i - n_{i0}}{\gamma_i}$$

n_{i0}: The initial number of moles of the species (i).

n_i: The number of moles of species (i) at time t.

$\boldsymbol{\gamma_i}$: The stoichiometric coefficient of substance i (negative if the component is a reactant, positive if it is a product of the reaction).

Example :

	$2H_2$ +	O_2 $\longrightarrow$	$2H_2O$
A t = 0	2 mol	1 mol	0 mol
A t	1 mol	0,5 mol	1 mol

The progress 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_20 : $\zeta = \frac{1-0}{2}$ = 0,5 mol

2. Variance of a system in equilibrium and phase rules:

By definition, the variance "v" of a system in equilibrium is the number of independent intensive parameters that must be known to define the equilibrium state of this system.

It can be calculated by the phase rule (GIBBS theorem):

$$\mathbf{V = C + n - \varphi}$$

V: system variance.
C: The number of independent constituents; C = N - R - S.
N: the number of constituents.
R: the number of relationships connecting them.
S: the number of special relationships.
n: the number of intensive parameters on which the equilibrium depends; typically = 2 (T and P).
φ: the number of phases.

Donc :

$$\mathbf{V = N - R - S + 2 - \varphi}$$

Example 1 :

$CaCO_3$ (s) $\rightleftarrows$ CaO (s) + CO_2 (g)

Three constituents ($CaCO_3$, CaO et CO_2) and a chemical reaction.

Number of phases (2 solids and 1 gas).

The variance is: V = 3 - 1 + 2 - 3 = 1.

To define this equilibrium, only one parameter can be chosen: either temperature or PCO2 (P and T are dependent).

Example 2 :

N_2 (g) + 3 H_2 (g) $\rightleftarrows$ 2 NH_3 (g)

N = 3, R = 1, S = 0, φ = 1

V = 3 – 1 – 0 + 2 – 1= 3

Example 3 :

H_2 (g) + I_2 (g) $\rightleftarrows$ 2 HI (g)

N = 3, R =1, S = 0, φ = 1, n = 1 (Because pressure is not an equilibrium factor, $\Delta\gamma = 0$)

V = 3 – 1 – 0 + 1 – 1 = 2

Two parameters can be chosen: for example, T and the partial pressure of one of the constituents.

Exercise :

I) We consider the following equilibrium reaction :

$$CO\,(g) + Cl_2\,(g) \underset{2}{\overset{1}{\rightleftarrows}} COCl_2\,(g)$$

$\Delta H°_{R,\,298} = - 112{,}5$ KJ ; $\Delta S°_{R,\,298} = - 131{,}6$ J/K

1) Is this reaction spontaneous at 298 K?

2) Calculate the value of the equilibrium constant K at 298K.

3) Applying Le Chatelier's principle, specify in which direction the equilibrium moves if:

a) Do we increase the temperature?

b) Do we increase the total pressure?

4) Assuming that $\Delta H°R$ remains constant in the temperature range between 298 and 630 K, calculate the value of the equilibrium constant K at 630 K.

II) In a closed container, maintained at 630 K, 2 moles of CO and 2 moles of Cl2 are introduced. When equilibrium is reached, the pressure is equal to 0.075 atm. Calculate the quantity of each of the constituents of the mixture at equilibrium.

1) To know if the reaction is spontaneous (thermodynamically possible) under standard conditions, we calculate $\Delta G°_{R,298}$

$\Delta G°_{R,298} = \Delta H°_{R,298} - T\,\Delta S°_{R,\,298} = - 112{,}5 - 298.(- 131{,}6).10^{-3} = - 73{,}283$ KJ

$\Delta G°_{R,298} < 0$; the reaction is spontaneous at T = 298 K.

2) Calculation of K_P at 298 K :

$K_P = \exp(\frac{-\Delta G°}{RT}) = 6{,}86.10^{12}$

3) Shifting the equilibrium:

a) If the temperature is increased, the equilibrium shifts in the endothermic direction, thus favoring the decomposition of COCl2 (direction 2).

b) If the pressure is increased, the equilibrium shifts in the direction of decreasing the number of gas moles, thus favoring the formation of COCl2 (direction 1).

4) K_P at 630 K :

$$\frac{\mathbf{d(\ln K_P)}}{\mathbf{dT}} = \frac{\mathbf{\Delta H°}}{\mathbf{RT^2}}$$

$$\mathbf{\ln\frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$\ln K_2 = \ln K_1 + \frac{\Delta H°}{R}(\frac{1}{T_1} - \frac{1}{T_2})$ $T_1 = 298$ K et $T_2 = 630$ K

$K_2 = K_{P(630)} = 282{,}88$.

II) The composition of the gas mixture at equilibrium:

$$CO\,(g) + Cl_2\,(g) \rightleftarrows COCl_2\,(g)$$

t = 0	2	2	0
t = teq	2 – x	2 – x	x

ntot = 4 – x

$x_{CO} = x_{Cl2} = \frac{2-x}{4-x}$; $x_{\,COCl2} = \frac{x}{4-x}$

$K_P = \frac{P_{COCl_2}}{P_{CO}P_{Cl_2}} = \frac{x_{COCl_2}.P}{x_{CO}.P.x_{Cl_2}.P} = \frac{x_{COCl_2}.P}{x_{CO}.P.x_{Cl_2}.P} = \frac{x_{COCl_2}}{x_{CO}x_{Cl_2}.P}$

We pose $K = K_P.P$

$K = \frac{4-x}{(\frac{2-x}{(4-x})^2}$

$x^2 (K + 1) – 4 (K + 1) x + 4 K = 0$

$x = 1{,}57$ mol (the other root should be rejected because it is greater than n_0)

So: the composition of the mixture is:

$n_{CO} = n_{Cl2} = 2 – x = 0{,}43$ mol.

$n_{COCl2} = 1{,}57$ mol.