* Thermodynamics of Ideal Solutions :-

* Free energy change of mixing (ΔG_{mix}) of an Ideal Soln :-

let us suppose a soln is formed by mixing n_A moles of a liquid A and n_B moles of a liquid B. i.e.

$$n_A A + n_B B \longrightarrow \text{Solution}$$

the free energy G of a solution at a given temperature and pressure is given by -

$$G = n_A \bar{G}_A + n_B \bar{G}_B \quad \text{--- (1)}$$

where, $\bar{G}_A$ and $\bar{G}_B$ are the partial molar free energies.

If G_A° & G_B° are the free energies per mole of the pure constituents A & B respectively. then, the free energy change of mixing (ΔG_{mix}) is given by -

$$\Delta G_{mix} = \left(\begin{matrix}\text{free energy of} \\ \text{solution}\end{matrix}\right) - \left(\begin{matrix}\text{Sum of free energies of} \\ \text{the pure constituents}\end{matrix}\right)$$

$$\Delta G_{mix} = G - (n_A G_A^\circ + n_B G_B^\circ) \quad \text{--- (2)}$$

Now putting the value of G from eqn -(1) in to eqn -(2),

$$\Delta G_{mix} = n_A \bar{G}_A + n_B \bar{G}_B - (n_A G_A^\circ + n_B G_B^\circ)$$

$$\Delta G_{mix} = n_A(\bar{G}_A - G_A^\circ) + n_B(\bar{G}_B - G_B^\circ) \quad \text{--- (3)}$$

The chemical potential μ_i of a component i in a given state is given by -

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad \text{--- (4)}$$

Thus,

$$\bar{G}_A = G_A^{\circ} + RT \ln a_A$$

or $$\bar{G}_A - G_A^{\circ} = RT \ln a_A$$

and $$\bar{G}_B = G_B^{\circ} + RT \ln a_B$$

or $$\bar{G}_B - G_B^{\circ} = RT \ln a_B$$

Thus from eqs— (3)

$$\Delta G_{mix} = n_A RT \ln a_A + n_B RT \ln a_B \quad \text{—— (5)}$$

If the soln is ideal, the activity of each component should be equal to its mole fraction. i.e.

$$a_A = x_A \quad \& \quad a_B = x_B$$

$$\therefore \Delta G_{mix} = n_A RT \ln x_A + n_B RT \ln x_B \quad \text{—— (6)}$$

on dividing eqs—(6) by $n_A + n_B$ we get—

$$\frac{\Delta G_{mix}}{n_A + n_B} = \frac{n_A}{n_A + n_B} RT \ln x_A + \frac{n_B}{n_A + n_B} RT \ln x_B$$

$$= x_A RT \ln x_A + x_B RT \ln x_B.$$

If $n_A + n_B = 1$ mole. then,

$$\Delta G_{mix} = RT (x_A \ln x_A + x_B \ln x_B) \quad \text{—— (7)}$$

The mole fraction is always less than unity

$\therefore \Delta G_{mix}$ is always -ve quantity