* Volume change and Enthalpy change of mixing for an ideal soln. :-

We know that —

The change in free energy w.r.t Temperature at constant P is —

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S \quad \text{——} (1)$$

and the change in free energy w.r.t Pressure at constant T is —

$$\left[\frac{\partial(\Delta G)}{\partial P}\right]_T = -\Delta V \quad \text{——} (2)$$

for free energy of mixing, eqs —(1) and eqn -(2) are written in the ~~form~~ —

$$\left[\frac{\partial(\Delta G_{mix})}{\partial T}\right]_P = -\Delta S_{mix} \quad \text{——} (3)$$

and

$$\left[\frac{\partial(\Delta G_{mix})}{\partial P}\right]_T = -\Delta V_{mix} \quad \text{——} (4)$$

Since, $\left[\frac{\partial(\Delta G_{mix})}{\partial P}\right]_T = 0.$

$\therefore \quad \Delta V_{mix} = 0.$

Thus, if two pure liquid constituents are mixed together in any proportion to give an ideal soln, there is no change in volume.

The free energy of mixing of an ideal soln is given as —

$$\Delta G_{mix} = n_A RT \ln x_A + n_B RT \ln x_B \quad \text{—— (1)}$$

or

$$\frac{\Delta G_{mix}}{T} = n_A R \ln x_A + n_B R \ln x_B \quad \text{—— (2)}$$

now, differentiating eqn —(2) w.r.t T at constant P; $\left[\frac{\partial(\Delta G_{mix})/T}{\partial T}\right]_P = 0$ —(3)

$$\left[\frac{\partial(\Delta G_{mix})/T}{\partial T}\right]_P = \frac{T\left[\frac{\partial(\Delta G_{mix})}{\partial T}\right]_P - \Delta G_{mix}}{T^2} \quad \text{—(4)}$$

on applying well known Gibb's Helmholtz eqn —

$$\Delta G - \Delta H = T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

thus eqn —(4) becomes —

$$\left[\frac{\partial(\Delta G_{mix}/T)}{\partial T}\right]_P = \frac{\cancel{\Delta G_{mix}} - \Delta H_{mix} - \cancel{\Delta G_{mix}}}{T^2}$$

$$= \frac{-\Delta H_{mix}}{T^2} \quad \text{—— (5)}$$

on combining eqn —(3) and eqn —(5) we get —

$$\frac{-\Delta H_{mix}}{T^2} = 0.$$

$$\therefore \quad \Delta H_{mix} = 0.$$

Thus, if two pure liquids are mixed together in any proportion to give an ideal soln, there is no change in enthalpy.

* Entropy change of mixing for an Ideal Solution

Let us consider entropy change of mixing in case of an ideal solution, which is written as –

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

or $$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad \text{——} \quad (1)$$

Since, for an ideal soln –

$$\Delta H_{mix} = 0$$

$$\therefore \quad \Delta G_{mix} = -T\Delta S_{mix} \quad \text{——} \quad (2)$$

We know that –

free energy change of mixing in terms of mole fraction –

$$\Delta G_{mix} = n_A RT \ln X_A + n_B RT \ln X_B \quad \text{——} \quad (3)$$

$$\therefore \quad \Delta S_{mix} = -\left[n_A R \ln X_A + n_B R \ln X_B\right] \quad \text{——} \quad (4)$$

for more than two components –

$$\Delta S_{mix} = -R \sum n_i \ln X_i \quad \text{——} \quad (5)$$

Since, X_i is always less than unity.

$\therefore$ ΔS_{mix} is always positive quantity.

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