

## (7)

### Chemical Potential in Ideal Liquid Solution

Let us consider a liquid solution with a non volatile solute. In vapour phase there will be only solvent molecule.

At a particular T & P, there exist an equilibrium bet<sup>n</sup> vapour and liquid phases of the solvent. At equilibrium  $P_{\text{vapour}} = P_i$  — (A)

chemical pot. of solvent must be equal in 2 phases (liquid)

The chemical potential of the solvent in the vapour phase

$$\mu_i(\text{vapour}) = \mu_i^{\circ}(\text{vapour}) + RT \ln P_i \quad — (1)$$

where

$\mu_i^{\circ}$  = std. chemical potential of the solvent vapour

$P_i$  = Partial Vapour Pressure of the solvent

$$\text{At equilibrium } \mu_i(\text{liq}) = \mu_i^{\circ}(\text{vapour}) + RT \ln P_i. \quad — (2)$$

Partial v. P<sub>i</sub>(P<sub>i</sub>) of solvent in the solution is related to v. P. of pure solvent and its mole fraction x<sub>i</sub> in the solution by Raoult's law

$$P_i = P_i^* x_i \quad \text{eq A becomes}$$

$$\mu_i(\text{liq}) = \underbrace{\mu_i^{\circ}(\text{vapour}) + RT \ln P_i^*}_{+ RT \ln x_i} \quad — (3)$$

These two terms of are independent of mole fraction & hence can be taken as chemical potential of pure solvent

$$\mu_i^{\circ}(\text{vapour}) + RT \ln P_i^* = \mu_i^{\circ}(\text{vapour}) \quad — (4)$$

In case of eq<sup>n</sup> bet<sup>n</sup> pure solvent & pure vapour solvent.

$$\mu_i^{\circ}(\text{liq}) = \mu_i^{\circ}(\text{vapour}) \quad — (5)$$

eq (3) becomes

$$\mu_i(\text{liquid}) = \mu_i^*(\text{pure}) + RT \ln x_i \quad - (6) \quad (5)$$

$\mu_i(\text{ly})$  = Chemical Potential of the solvent in solution

$\mu_i^*$  = " " " " pure liquid

$x_i$  = Mole fraction of solvent in the solution

Eq. (6) is valid for solutions whose vapour phase behaves as an ideal gas. Two solutions obey (6) at all conc' with accuracy.

At high Pressure and temp. is increased the deviations of the vapour form occur from ideal behaviour becomes more predominant. Here the Pressure is replaced with fugacity

$$f_i = f_i^* x_i = f_i^* (1-x_2) \quad \text{Acc to Raoult's law}$$

then chemical potential becomes

$$\text{Chemical pot. } \mu_i = \mu_i^* + RT \ln f_i \quad - (7)$$

### Mixing Properties of Ideal liquid solutions

The chemical potential in an ideal liquid mixture

$$\mu_i = \mu_i^* + RT \ln x_i$$

$$\Delta G_{\text{mix}} = RT \sum n_i \ln x_i$$

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i$$

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

$$\Delta V_{\text{mix}} = 0$$

If a solution is ideal,  $\Delta H_{\text{mix}} = \Delta V_{\text{mix}} = 0$

The reverse is not always true i.e if  $\Delta H_{\text{mix}} = \Delta V_{\text{mix}} = 0$ , then the solution may or may not be ideal.

Calculate the  $\Delta H_{\text{mix}}$ ,  $\Delta G_{\text{mix}}$ ,  $\Delta S_{\text{mix}}$  of mixing of  
 1 mole of  $C_6H_5CH_3$  (toluene) and 2 moles of  
 $C_6H_6$  (Benzene) at  $25^\circ C$  (9)

If mixture is ideal then  $\Delta H_{\text{mix}} = 0$

$$\Delta G_{\text{mix}} = 2303 \times 8.314 \text{ J/k mole} \times 298 \text{ K} \left( 1 \text{ mole log } \frac{1}{3} + 2 \text{ moles log } \frac{2}{3} \right)$$

$$= -4732 \text{ J}$$

$$\Delta S_{\text{mix}} = -\frac{\Delta G_{\text{mix}}}{T} = \frac{4732 \text{ J}}{298 \text{ K}} = 15.8 \text{ J/K}$$

### Henry law

If a very small amt of substance (2) is added  
 isothermally to a liquid (1) with which  
 the substance (2) doesn't react chemically,  
 don't undergo association or dissociation  
 The partial Pressure of component (2) in  
 an equilibrium vapour phase increases  
 linearly with mole fraction  $x_2$

$$P_2 = k_2(T) x_2$$

$k_2$  is const & depends on T & on nature  
 of solute & solvent. This is Henry law and  
 is perfect provided mole fraction of  
 solute is very low  $x_2 \approx 0.02$  and the  
 pressure is low for the V.P. to be  
 regarded as perfect

To evaluate  $k_2$  a graph is plotted

between  $(\frac{P_2}{x_2})$  VS  $x_2$  and the curve is extrapolated at  $x_2 = 0$ ,  $k_2$  is obtained from the intercept.

The unit of Henry law ( $k_2$ ) is same as that of pressure. But  $k_2$  is not same as V.P. of pure component 2 because Henry law is valid only a very dilute solution of component 2 and not for pure substance.

In case the solute being a gas then value of  $k$

solute	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>
$K_2 / 10^9 \text{ Pa}$	7.12	8.68	9.40	5.79	0.167	4.9	3.07	0.15

The solubility of a gas in a mixture is not affected by other gases, because solubility of each gas will depend on its individual partial pressure.

e.g. if two gases are dissolved in the same solvent at given temp., then Henry law is applied separately to each.

$$P_2 = k_2 x_2 \quad P_4 = k_4 x_4$$

$$P_3 = k_3 x_3$$

The solubility of a gas in a liquid is affected significantly by addition of electrolytes, solubility decreases.

Different electrolytes affect the gas solubility to different extent.

But same electrolyte decreases the solubility of different gases approximately to the same extent. (11)

For exothermic dissolution processes, the solubility of gases  $\downarrow$  (decreases) with increase of temperature.

In endothermic dissolution processes, the solubility increases with the increase of temperature.

Q Calculate the mole fraction of  $O_2$  &  $N_2$  separately dissolved in  $H_2O$  at  $25^\circ C$  & 1 atm P

$$K(O_2) = 4.34 \times 10^4 \text{ atm}, \quad K(N_2) = 8.57 \times 10^4 \text{ atm}$$

$$\text{Henry's law } x_2 = \frac{P_2}{K_2}$$

$$x_{O_2} = \frac{1.0 \text{ atm}}{4.34 \times 10^4 \text{ atm}} = 0.2304 \times 10^{-4}$$

$$x_{N_2} = \frac{1.0 \text{ atm}}{8.57 \times 10^4 \text{ atm}} = 0.1166 \times 10^{-4}$$

Exact Form of Henry Law

At higher pressures, the vapour phase shows non-ideality - then

$$f_2 = k_2(T, P) x_2 \quad (1)$$

$k_2$  is function of Temperature & Pressure

If small amt of a solute (2) is added externally & isobarily to a liquid with which solute doesn't react, the fugacity of component 2 in the liquid increases linearly with mole fraction of component 2.

Rq (1) gives the fugacity of solute in a liquid at const  $T$  &  $P$ , liquid is not in eq<sup>n</sup> with vapour phase

Validity of Raoult's law & Henry's law

If in a binary solution, the solvent molecule obeys Raoult's law and solute obeys Henry's law in the same composition range.

Conversely if one component obeys Henry's law over a given composition range, the other component must obey Henry's law & Raoult's over same range.

Eg Consider a solution of acetone & water. In first case few drops of  $H_2O$  are added to a large volume of  $CH_3COCH_3$  in a closed vessel, then partial pressure of  $H_2O$  will be given by Henry's law equation and partial pressure of  $CH_3COCH_3$  is obeyed by Raoult's law.

In second case few drops of acetone are added to large volume of  $H_2O$  in a closed vessel, then partial pressure of acetone obeys Henry's law and water obeys Raoult's law.

(3)

In very dilute solutions, Raoult law holds for solvents because only molecules which a solvent molecule encounters around itself are other solvent molecules  $P_1 = P_1^* \chi_1$ . In such dilute solutions, the solute sees only one kind neighbouring molecules is 'solvent'.

The environment of solute molecule will be affected when large quantity of solute is added that solute-solute interactions become frequent under such conditions. the escaping tendency or fugacity of solute should be  $\propto$  no. of molecules there are to escape  $f_2 \propto \chi_2$ . The proportionality const. is measure of solute-solvent interaction.

Change of Gibbs Free Energy

$$\Delta G_{\text{min}} = G_{\text{Final}} - G_{\text{Initial}}$$
$$= \sum n_i \mu_i - \sum n_i \mu_i^{\circ}$$
$$= \sum n_i (\mu_i - \mu_i^{\circ})$$

$$\therefore \mu_i = \mu_i^{\circ} + RT \ln \frac{n_i}{n_{\text{total}}}$$

$$\Delta H_{\text{min}} = \sum n_i \mu_i^{\circ} + \sum n_i RT \ln \frac{n_i}{n_{\text{total}}} - \sum n_i \mu_i^{\circ}$$

$$\Delta H_{\text{min}} = \sum n_i RT \ln \frac{n_i}{n_{\text{total}}}$$

$$\Delta S_{\text{min}} = -\frac{\partial}{\partial T} (\Delta G_{\text{min}})$$

$$= -\sum n_i R \ln \frac{n_i}{n_{\text{total}}}$$

$$\therefore \frac{n_i}{n_{\text{total}}} = x_i \quad \text{and} \quad n_i = n_{\text{total}} x_i$$

$$\therefore \Delta G_{\text{min}} = n_{\text{total}} \sum n_i x_i \ln \frac{n_i}{n_{\text{total}}} RT = +n_{\text{total}} RT \sum n_i x_i \ln x_i$$

$$\Delta G_{\text{min}} = -n_{\text{total}} RT \sum n_i x_i \ln x_i \quad \text{--- (1)}$$

$$\Delta G_{\text{min}} = \Delta H_{\text{min}} - T \Delta S_{\text{min}}$$

$$\Delta H_{\text{min}} = \Delta G_{\text{min}} + T \Delta S_{\text{min}} \quad \text{from (1) \& (2)}$$
$$= n_{\text{total}} RT \sum n_i x_i \ln x_i - n_{\text{total}} RT \sum n_i x_i \ln x_i$$
$$= 0$$

$$\Delta V_{\text{min}} = \left( \frac{\partial G_{\text{min}}}{\partial P} \right)_T$$

$$= \frac{\partial}{\partial P} [n_{\text{total}} RT \sum n_i x_i \ln x_i]$$
$$= 0$$

$\therefore \Delta G_{\text{min}}$  is independent of Pressure