

and, a change in the height of the column in manometer is observed which becomes stationary after some time at constt temp. The pressure recorded by manometer is called vapour pressure of liquid at a given temp.

Any liquid which have strong forces of attraction will have low V.P. and vice versa.

(1) V.P. can be increased with increased in temp.

(2) If a certain substance is added to a liquid which enhances the force of attraction, the V.P. of liquid is decreased.

The influence of addition of one substance on the V.P. of another substance is given by Raoult's law

Ideal Solution and Raoult's law

An ideal solution is one if the escaping tendency of each component is proportional to the mole fraction of that component in the solution.

Partial V.P. of the component is directly proportional to its mole fraction in the solution.

In a binary liquid solution, the partial vapour pressure P_1 of the solvent is

$$P_1 \propto x_1$$

$$P_1 = P_1^* x_1 = P_1^* (1 - x_2)$$

Where P_1^* is the V.P. of pure liquid, x_1 is mole fraction of solvent, x_2 is mole fraction of solute

For the solute $P_2 = P_2^* x_2$ where P_2^* is v.p. of pure component 2. (2)

$\therefore$ Total v.p. of solution is

$$P = P_1 + P_2 = P_1^* x_1 + P_2^* x_2$$

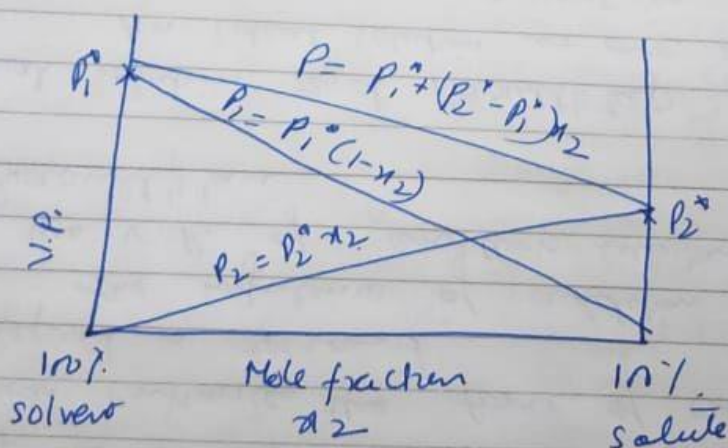
$$= P_1^* x_1 + P_2^* x_2$$

$$= P_1^* (1 - x_2) + P_2^* x_2$$

$$= P_1^* - P_1^* x_2 + P_2^* x_2$$

$$P = P_1^* + (P_2^* - P_1^*) x_2 \quad \text{--- (1)}$$

Eq. (1) suggests that total v.p. of the solution is a linear function of the mole fraction of either component in solution.



Total v.p. of solution and vapour phase composition
Let us consider a binary liquid and y_1 & y_2 are two mole fractions of two components in the vapour phase in equilibrium with liquid solution.

Dalton's law $P_1 = P y_1$, $P_2 = P y_2$

where P is total pressure

& Raoult's law $P_1 = P_1^* x_1 = P y_1$
 $P_2 = P_2^* x_2 = P y_2$

$$(1) \quad x_2 = \frac{P - P_1^*}{P_2^* - P_1^*}$$

$$P y_2 = P_2^* x_2 = P_2^* \left(\frac{P - P_1^*}{P_2^* - P_1^*} \right)$$

$$P y_2 (P_2^* - P_1^*) = P_2^* P - P_2^* P_1^*$$

$$P [y_2 (P_2^* - P_1^*) - P_2^*] = -P_2^* P_1^*$$

$$P [P_2^* + (P_1^* - P_2^*) y_2] = P_2^* P_1^*$$

$$P = \frac{P_2^* P_1^*}{P_2^* + (P_1^* - P_2^*) y_2}$$

— (2)

This relation (2) shows that P (total v.p.) varies inversely with mole fraction of component 2 in the vapour phase of an ideal solution.

$$\frac{1}{P} = \frac{P_2^* + (P_1^* - P_2^*) y_2}{P_2^* P_1^*}$$

$$= \frac{1}{P_1^*} + \frac{P_1^*}{P_1^* P_2^*} y_2 - \frac{P_2^* y_2}{P_2^* P_1^*}$$

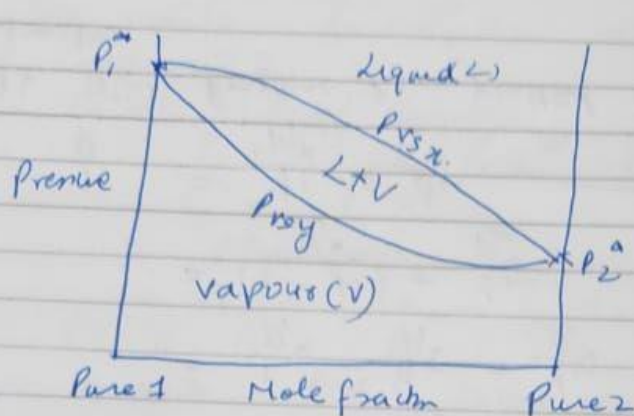
$$= \frac{1}{P_1^*} + \frac{y_2}{P_2^*} - \frac{y_2}{P_1^*}$$

$$= \frac{1}{P_1^*} - \frac{y_2}{P_1^*} + \frac{y_2}{P_2^*}$$

$$= \frac{(1 - y_2)}{P_1^*} + \frac{y_2}{P_2^*}$$

$$\frac{1}{P} = \frac{y_1}{P_1^*} + \frac{y_2}{P_2^*} \quad \text{— (3)}$$

9. total Pressure P is plotted against the mole fraction



The upper curve indicates variation of P with x_2 i.e. mole fraction of component 2 in the liquid phase. This shape is predicted by Raoult law.

Above this curve the region shows the existence of liquid state.

The lower curve represents the variation of P with y_2 , the mole fraction of component 2 in the vapour phase. Below this curve the system is in vapour phase. The region enclosed by these two curves represents liquid-vapour equilibrium.

Q1 100g each of ethanol and methanol are mixed at 20°C to prepare an ideal mixture. The vapour pressure of pure methanol is 88.7 mm Hg that of ethanol is 44.5 mm Hg at 20°C . Calculate (1) the vapour pressure of solution (2) Partial vapour pressure of ethanol & methanol in solution (3) The vapour phase composition.

$$P_{C_2H_5OH}^* = 44.5 \text{ mm Hg}$$

$$m(C_2H_5OH) = w_1 = 100 \text{ g}$$

$$m(CH_3OH) = w_2 = 100 \text{ g}$$

$$P_{CH_3OH}^* = 88.7 \text{ mm Hg}$$

$$n_{C_2H_5OH} = 100 \text{ g} / 46 \text{ g mol}^{-1} = 2.17 \text{ mole}$$

$$n_{CH_3OH} = 100 \text{ g} / 32 \text{ g/mole} = 3.12 \text{ mole}$$

(6)

$$x_{C_2H_5OH} = x_1 = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{CH_3OH}} = \frac{2.17}{2.17 + 3.12} = \frac{2.17}{5.29} = 0.41$$

$$x_{CH_3OH} = 1 - 0.41 = 0.59$$

Partial Pressure of $C_2H_5OH = P_1 = P_1^* x_1$
 $= 44.5 \text{ mmHg} \times 0.41$
 $= 18.2 \text{ mmHg}$

Partial Pressure of Methanol $P_2 = P_2^* x_2$
 $= 88.7 \times 0.59$
 $= 52.3 \text{ mmHg}$

Total Pressure of Solution $P = P_1 + P_2$
 $= 18.2 \text{ mmHg} + 52.3 \text{ mmHg} = 70.5 \text{ mmHg}$

Let y_1 be mole fraction of C_2H_5OH in the vapour phase above the liquid mixture. Dalton's Law of partial pressure

$$P_1 = P y_1 \Rightarrow y_1 = \frac{P_1}{P} = \frac{18.2 \text{ mmHg}}{70.5 \text{ mmHg}} = 0.258$$

Mole fraction of Methanol $y_2 = 1 - y_1 = 1 - 0.258 = 0.742$

The vapour phase is enriched in with more volatile component (methanol) than in the liquid phase

Chemical Potential in Ideal Liquid Solution (7)

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 exists an equilibrium betⁿ vapour and liquid phases of the solvent. At equilibrium $\mu_{\text{vapour}} = \mu_{\text{liquid}}$

The chemical potential of the solvent in the vapour phase
 $\mu_{\text{liquid}} = \mu_{\text{liquid}}^{\circ} + RT \ln P_1$ — (1)

μ_1° = std. chemical potential of the solvent vapour

P_1 = Partial Vapour Pressure of the solvent

At equilibrium $\mu_{\text{liquid}} = \mu_{\text{liquid}}^{\circ} + RT \ln P_1$ — (2)

Partial v. p. (P_1) of solvent in the solution is related to v. p. of pure solvent and its mole fraction x_1 in the solution by Raoult's law

$$P_1 = P_1^* x_1$$

$$\mu_{\text{liquid}} = \underbrace{\mu_{\text{liquid}}^{\circ} + RT \ln P_1^*}_{\text{These two terms are independent of mole fraction}} + RT \ln x_1 \text{ — (3)}$$

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

$$\mu_{\text{liquid}}^{\circ} + RT \ln P_1^* = \mu_{\text{liquid}}^* \text{ — (4)}$$

In case of eqⁿ betⁿ pure solvent & pure vapour of solvent.

$$\mu_1^{\circ}(\text{liquid}) = \mu_1^{\circ}(\text{vapour}) \text{ — (5)}$$

eg (3) becomes

$$\mu_1(\text{liquid}) = \mu_1^*(\text{liquid}) + RT \ln x_1 \quad \text{--- (6)} \quad (5)$$

$\mu_1(\text{liq})$ = Chemical potential of the solvent in solution

μ_1^* = " " " " " pure liquid

x_1 = Mole fraction of solvent in the solution

Eq (6) is valid for solutions whose vapour phase behaves as an ideal gas

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

$$f_1 = f_1^* x_1 = f_1^* (1 - x_2)$$

Then chemical potential becomes

$$\mu_1 = \mu_1^* + RT \ln f_1 \quad \text{--- (7)}$$

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 ΔH_{mix} , ΔG_{mix} , ΔS_{mix} of mixing of ⑨
1 mole of $C_6H_5CH_3$ (Toluene) and 2 moles of
 C_6H_6 (Benzene) at $25^\circ C$

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

$$\Delta G_{mix} = 2.303 R \cdot 298 K \left(1 \text{ mole } \log \frac{1}{3} + 2 \text{ moles } \log \frac{2}{3} \right)$$

$$= -4732 J$$

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

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 constt & 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 $\left(\frac{P_2}{x_2}\right)$ 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_2

solute	H ₂	N ₂	O ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₂
$k_2 / 10^9 \text{ Pa}$	7.12	8.68	4.40	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.

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

$$\begin{aligned} P_2 &= k_2 x_2 & P_4 &= k_4 x_4 \\ P_3 &= k_3 x_3 & & \vdots \end{aligned}$$

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

Henry 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

$$f_2 = k_2(T, P) x_2 \quad \text{--- (1)}$$

k_2 is function of Temp & Pressure

A small amount of a solute (2) is added externally & continuously 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.

Eq (1) gives the fugacity of solute in a liquid at const T & P & liquid is not in eqⁿ with vapour phase

Validity of Raoult's law & Henry's law

If in a binary solution, the solvent molecules obey 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 law 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.

In very dilute solutions, Raoult law holds for solvents (13) because only molecules which a solvent molecule encounters around itself are other solvent molecules. $P_1 = P_1^* x_1$. 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 $\propto$ to no. of molecules there are to escape $f_2 \propto x_2$. The proportionality constt is measure of solute-solvent interaction.

Thermodynamic Deduction

For a binary solutions having n_1 moles of solvent, n_2 moles of solute.

Gibbs Duhem Eq. $n_1 du_1 + n_2 du_2 = 0$

Dividing throughout by $(n_1 + n_2)$

$$x_1 du_1 + x_2 du_2 = 0 \quad \text{--- (1)} \quad \therefore x_1 = \frac{n_1}{n_1 + n_2} \quad x_2 = \frac{n_2}{n_1 + n_2}$$

The chemical pot $\mu_i = f(T, P, x_i)$

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T} \right)_{P, x_i} dT + \left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial \mu_i}{\partial x_i} \right)_{T, P} dx_i$$

For isothermal & isobaric process.

$$(d\mu_i)_{T, P} = \left(\frac{\partial \mu_i}{\partial x_i} \right)_{T, P} dx_i \quad \text{--- (2)}$$

$$(d\mu_i)_{T,P} = \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P} dx_i \quad \text{--- (2)}$$

From eq. (1) & (2) is sub (2) in (1) the (4)

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 = 0 \quad \text{--- (3)}$$

For a binary solution $x_1 + x_2 = 1 \Rightarrow dx_1 = -dx_2$
substitute $dx_1 = -dx_2$ in eq (3)

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} \quad \text{--- (4)}$$

The chemical potential of solvent.

$$\mu_1 = \mu_1^0 + RT \ln f_1$$

The chemical potential of solute

$$\mu_2 = \mu_2^0 + RT \ln f_2$$

For ideal solutions

$$\mu = \mu_i^0 + RT \ln P_i$$

$$\mu = \mu_i^0 + RT \ln P$$

Diff. this eqⁿ wr.t. mole fractions

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = RT \left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} \quad \text{--- (5)}$$

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = RT \left(\frac{\partial \ln f_2}{\partial x_2}\right)_{T,P} \quad \text{--- (6)}$$

Sub. 5 & 6 in eq (4)

$$x_1 RT \frac{d \ln f_1}{dx_1} = x_2 RT \frac{d \ln f_2}{dx_2}$$

$$x_1 \frac{d \ln f_1}{dx_1} = x_2 \frac{d \ln f_2}{dx_2}$$

$$x_1 \frac{d \ln f_1}{d \ln x_1} = \frac{d \ln f_2}{d \ln x_2} \quad \text{--- (7)}$$

Let solvent molecules obey Raoult law

$$f_1 = f_1^{\circ} x_1$$

$$\ln f_1 = \ln f_1^{\circ} + \ln x_1$$

Diff. w.r. x_1

$$\frac{d \ln f_1}{d x_1} = \frac{d \ln x_1}{d x_1} = \frac{1}{x_1}$$

(15)

(8)

If the vapour phase behaves as ideal gas then Raoult's law is $P_1 = P_1^{\circ} x_1$

$$\frac{d \ln P_1}{d x_1} = \frac{d \ln x_1}{d x_1} = \frac{1}{x_1}$$

Combine (7) & (8)

$$\int d \ln f_2 = \int d \ln x_2$$

$$\ln f_2 = \ln x_2 + \ln K_2$$

$$\ln f_2 = \ln K_2 x_2$$

$$f_2 = K_2 x_2 \quad \text{Henry law}$$

Similarly for ~~solvent~~ $f_2 = K_2 x_2$ (binary sol)

$$f_1 = f_1^{\circ} x_1 \quad (\text{Raoult's law})$$

$$\frac{d \ln f_2}{d x_2} = \frac{d \ln x_2}{d x_2} = \frac{1}{x_2}$$

Try as done in the previous derivation