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The molecular speed of all molecules in a liquid is not same. Some molecules move with a very high velocity and few move with a very low velocity. Majority of the molecules move with a fixed speed known as most probable speed.

The molecules which move with high speed will have high kinetic energy which is sufficient to overcome the attractive forces holding the molecules together and is sufficient to overcome escape from the bulk liquid. This is known as vaporization. These molecules in the vapor may collide with each other and with the walls of the container where they can exchange momentum. Some molecules will lose momentum and will come back to the surface of the liquid. This is known as condensation. The two phenomena continue and a dynamic equilibrium is attained when $\text{vapourization} \rightleftharpoons \text{condensation}$.

Weaker is attractive force b/w liquid molecules greater is escaping tendency. The Escaping tendency is increased by increasing the kinetic energy or raising temperature because Kinetic Energy is directly proportional to Temperature. During vaporization molecules strike with the wall of vessel and impart momentum on it. on attaching a manometer on the side of

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Then, 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

$$P_1 \propto x_1$$

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

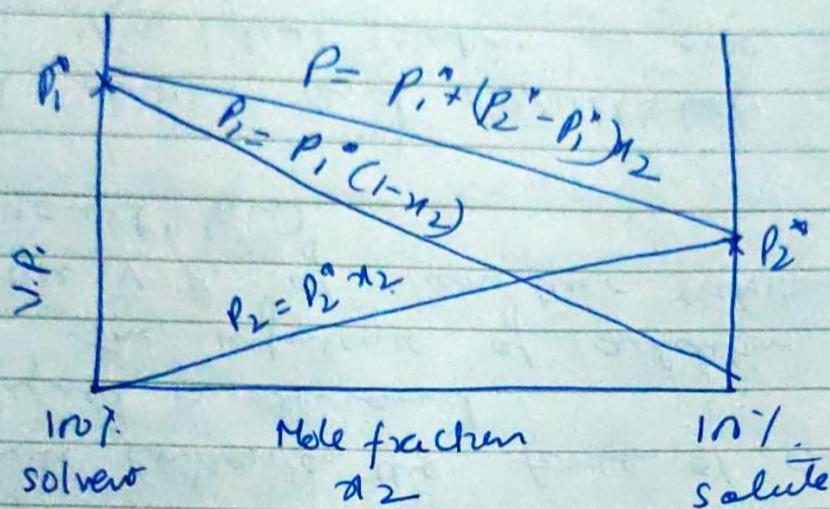
where P_1^* is the V.P. of pure liquid, x_1 is mole fraction of solvent, x_2 is mole fraction of solute

For the solute $P_2 = P_2^* \pi_2$ where P_2^* is v.p. of pure component 2. (3)

i.e. Total v.p. of solution is

$$\begin{aligned} P &= P_1 + P_2 = P_1^* \pi_1^* + P_2^* \pi_2^* \\ &= P_1^* \pi_1 + P_2^* \pi_2 \\ &= P_1^* (1 - \pi_2) + P_2^* \pi_2 \\ &= P_1^* - P_1^* \pi_2 + P_2^* \pi_2 \\ P &= P_1^* + (P_2^* - P_1^*) \pi_2 \quad \text{--- (1)} \end{aligned}$$

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

Coleton & Raoult law $P_1 = P_1^* \pi_1 = P y_1$

$P_2 = P_2^* \pi_2 = P y_2$

$$\text{eq } ① \quad x_2 = \frac{P - P_i^*}{P^* - P_i^*}$$

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$$Py_2 = P_2^* x_2 = P_2^* \left(\frac{P - P_i^*}{P^* - P_i^*} \right)$$

$$Py_2 (P^* - P_i^*) = P_2^* P - P_2^* P_i^*$$

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

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

$$P = \frac{P_2^* P_i^*}{P_2^* + (P_i^* - P_2^*) y_2} \longrightarrow ②$$

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.

$$\begin{aligned} \frac{1}{P} &= \frac{P_2^* + (P_i^* - P_2^*) y_2}{P_2^* P_i^*} \\ &= \frac{1}{P_i^*} + \frac{P_i^*}{P_i^* P_2^*} y_2 - \underbrace{\frac{P_2^* y_2}{P_2^* P_i^*}}_{\text{cancel}} \end{aligned}$$

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

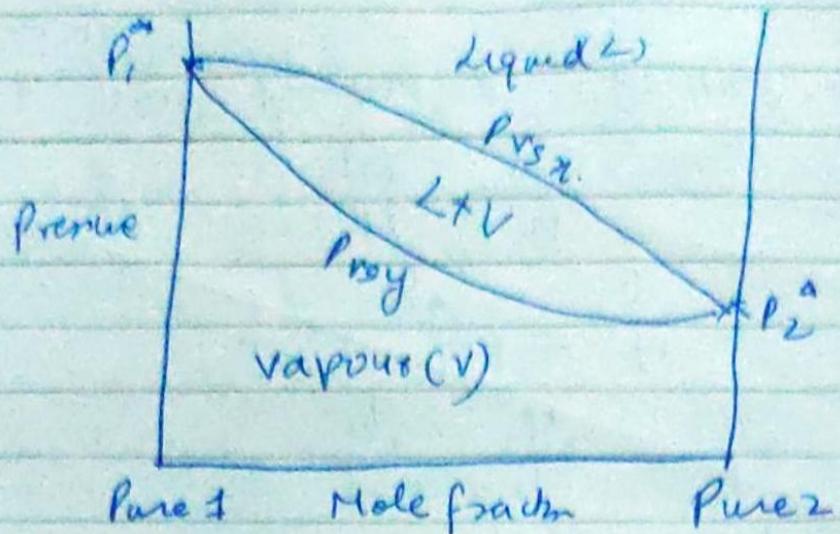
$$= \frac{1}{P_i^*} - \frac{y_2}{P_i^*} + \frac{y_2}{P_2^*}$$

$$= \underbrace{\left(1 - \frac{y_2}{P_i^*}\right)}_{P_i^*} + \frac{y_2}{P_2^*}$$

$$\frac{1}{P} = \frac{y_1}{P_i^*} + \frac{y_2}{P_2^*} \longrightarrow ③$$

If total pressure P is plotted against the mole fraction

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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
 equilibria

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
 \rightarrow 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