Vapour pressure :-

The pressure exerted by the vapours in equilibrium with the liquid at a constant temperature is called vapour pressure of the liquid.

i.e. Liquid ⇌ Vapour.

Vapour pressure of solutions and Rault's law :-

1). Rault's law is applicable to :

(A) Solutions containing two or more volatile liquids -

When a solution contains two volatile liquids A & B, both the liquids form vapours. In such a case, the vapour pressure of the solution is equal to the sum of the partial vapour pressure of the individual liquids.

$$P_S = P_A + P_B \quad \text{---} \quad (1)$$

Where, P_S = total vapour pressure of the solution.

P_A & P_B = Partial vapour pressure of two liquids.

Rault's law :-

The partial vapour pressure of each components (P_A & P_B) is proportional to their respective mole fractions (χ_A & χ_B) in the solution.

If χ_A & χ_B are the mole fractions of liquid A & B in the solution respectively. Then,

$P_A \propto x_A$ and $P_B \propto x_B$

or $P_A = P_A^\circ x_A$ & $P_B = P_B^\circ x_B$

Where, P_A° and P_B° are the vapour pressure of pure liquids A & B respectively.

Now putting these values in eqn-(1) we get

$$P_s = P_A^\circ x_A + P_B^\circ x_B \quad \text{——} \quad (2)$$

Since, $x_A + x_B = 1$.

or $x_B = 1 - x_A$

on substituting this value in eqn-(2) we get

$$P_s = P_A^\circ x_A + P_B^\circ (1 - x_A)$$

or $P_s = P_A^\circ x_A + P_B^\circ - P_B^\circ x_A$

or $P_s = P_B^\circ + x_A (P_A^\circ - P_B^\circ) \quad \text{——} \quad (3)$

Similarly we can write-

$$P_s = P_A^\circ + x_B (P_B^\circ - P_A^\circ) \quad \text{——} \quad (4)$$

This law is applicable only when the two liquids are miscible and form homogeneous solution.

Conclusions:-

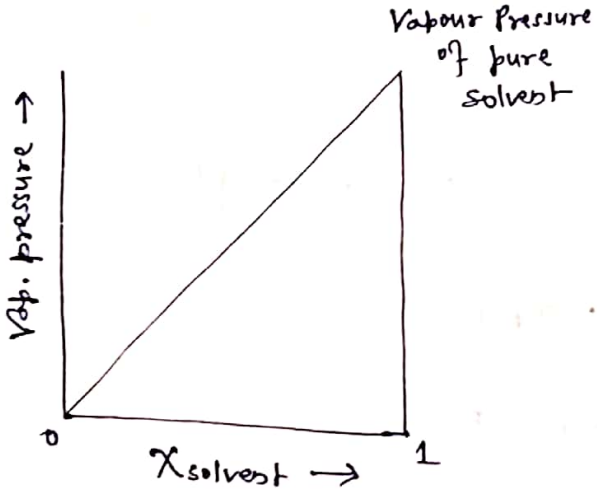
(i) Total vapour pressure of the solution can be related to the mole fraction of any one component (x_A or x_B).

(ii) Total vapour pressure over the solution varies linearly with

the mole fraction (χ_A) of the Component A or mole fraction (χ_B) of Component B.

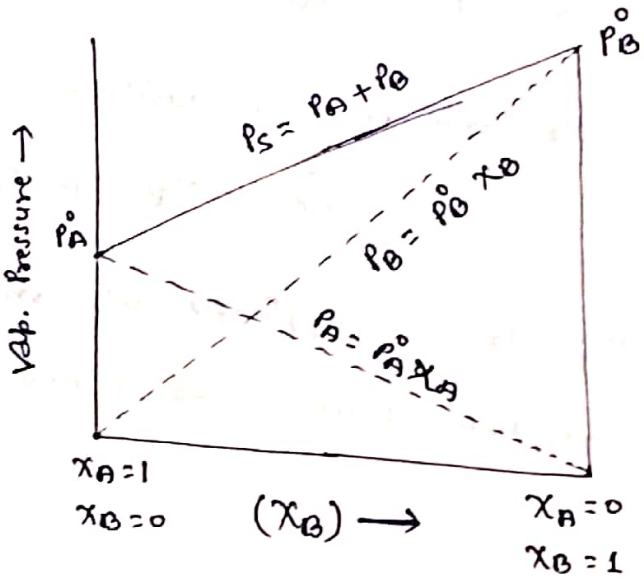
(iii) The total vapour pressure over the solution decreases or increases with the increase in the mole fraction (χ_A) of Component A. Same is true for the mole fraction (χ_B) of Component B.

Plot :— (1)



Vapour pressure of an ideal solution varies from 0 to v.p of pure solvent.

Plot -(2)



Relation b/n vapour pressure & mole fraction of an ideal solution at Const T.

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