

Vapour pressure :

- Liquids having low boiling points are called volatile liquids.
Ex: Ether, acetone, benzene, carbondisulphide, carbon tetrachloride are volatile liquids.
- Liquids having high boiling points are called non volatile liquids.
Ex: Aniline, Nitrobenzene, Con.H₂SO₄, water are non volatile liquids.
- Volatile liquids have
 - i) Weak intermolecular forces
 - ii) High vapour pressure
 - iii) Low boiling point
- Non – volatile liquids have
 - i) Strong intermolecular forces
 - ii) Low vapour pressure
 - iii) High boiling point
- When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.
- The vapour pressure of the liquid must be called as saturated vapour pressure, because actually the atmosphere over the liquid, which is saturated with the vapour of the liquid, exerts the pressure on the liquid.
- The vapour pressure of the liquid is represented by P.
- The vapour pressure of water is known as aqueous tension.
- The vapour pressure of the liquid is directly proportional to the temperature of the liquid.
- The vapour pressure of a liquid is independent of shape of the vessel.
- Vapour pressure of liquid increases exponentially with increase in temperature.
- $\log P \text{ Vs } \frac{1}{T}$ gives a straight line with – ve slope. This is called Clausius – clapeyron curve.
- The temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure is known as the boiling point of the liquid.
- Boiling point of a liquid can be changed by changing the external pressure. If external pressure is increased, the boiling point of a liquid is increased and vice- versa.

Lowering of vapour pressure :

- When a non – volatile solute is added to a solvent, the vapour pressure of pure solvent decreases. This is called lowering of vapour pressure.
- With increase in the concentration of solution, the lowering of vapour pressure further decrease.

$P_s < P^\circ$ P_s = vapour pressure of solution

P° = vapour pressure of pure solvent

$P^\circ - P_s$ = lowering of vapour pressure

- The ratio of lowering of vapour pressure to the vapour pressure of pure solvent is called relative lowering of vapour pressure.

$$\frac{P^\circ - P_s}{P^\circ} = \text{Relative lowering of vapour pressure.}$$

Raoult's law :

- I) For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law :

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A} \text{ (for dilute solutions, } n_B \text{ is very small and it can be neglected)}$$

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

P^0 = Vapour pressure of pure solvent

P_s = Vapour pressure of solution

X_B = mole fraction of solute

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute W = weight of solvent

Relation between Raoult's law and molality :

$$\frac{P^0 - P_s}{P^0} = \frac{\text{molality} \times M}{1000} \text{ (M = mol.wt. of solvent)}$$

- II) Raoult's law for solution containing two or more miscible liquids is "the partial vapour pressure of a liquid component in the solution is directly proportional to its mole fraction".
- If solution contains two miscible liquids A and B , then

$$P_A \propto X_A \quad P_B \propto X_B$$

$$P_A = P_A^0 \cdot X_A \quad P_B = P_B^0 \cdot X_B$$

$$P_{\text{total}} = P_A + P_B$$

$$P_{\text{total}} = P_A^0 \cdot X_A + P_B^0 \cdot X_B$$

Ideal solutions: The solutions which obey Raoult's law at all concentrations of temperatures are called ideal solutions.

- In case of ideal solutions,
 - i) $\Delta V_{\text{mixing}} = 0$
 - ii) $\Delta H_{\text{mixing}} = 0$
 - iii) No change in interactions
- Solutions behave ideally at infinite dilution.
- Raoult's law is applicable to
 - i) Ideal solutions
 - ii) dilute solutions
 - iii) solutions containing non volatile solute
 - iv) no change in the interactions before and after mixing of liquid components in case of solution containing miscible liquids.
 - v) Solute which neither dissociate nor associate.