Lowering of vapor pressure.

The pressure exerted by the vapors above the liquid surface in equilibrium with the liquid at a given temperature is called vapor pressure of the liquid. The vapor pressure of a liquid depends on

(1) Nature of liquid: Liquids, which have weak intermolecular forces, are volatile and have greater vapor pressure. For example, dimethyl ether has greater vapor pressure than ethyl alcohol.

(2) Temperature:Vapor pressure increases with increase in temperature. This is due to the reason that with increase in temperature more molecules of the liquid can go into vapor phase.

(3) Purity of liquid: Pure liquid always has a vapor pressure greater than its solution.

Raoult's law:When a non-volatile substance is dissolved in a liquid, the vapor pressure of the liquid (solvent) is lowered. According to Raoult's law (1887), at any given temperature the partial vapor pressure (p_A) of any component of a solution is equal to its mole fraction (X_A) multiplied by the vapor pressure of this component in the pure state (p_A^0). That is,

$$p_A = p_A^0 \times X_A$$

The vapor pressure of the solution (P_{total}) is the sum of the partial pressures of the components, i.e., for the solution of two volatile liquids with vapor pressures p_A and p_B.

$$P_{total} = p_A + p_B = (p_A^0 \times X_A) + (p_B^0 \times X_B)$$

Alternatively, Raoult's law may be stated as "the relative lowering of vapor pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution."

Relative lowering of vapor pressure is defined as the ratio of lowering of vapor pressure to the vapor pressure of the pure solvent. It is determined by Ostwald-Walker method.

Mole fraction of the solute is defined as the ratio of the number of moles of solute to the total number of moles in solution.

Thus according to Raoult's law,

$$\frac{p^0 - p}{p^0} = \frac{n}{n+N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Where, $p =$ Vapor pressure of the solution; $p^0 =$ Vapor pressure of the pure solvent

$n =$ Number of moles of the solute; $N =$ Number of moles of the solvent

w and $m =$ weight and mol. wt. of solute; W and $M =$ weight and mol. wt. of the solvent.

Limitations of Raoult's law

- Raoult's law is applicable only to very dilute solutions.
- Raoult's law is applicable to solutions containing non-volatile solute only.
- Raoult's law is not applicable to solutes which dissociate or associate in the particular solution.