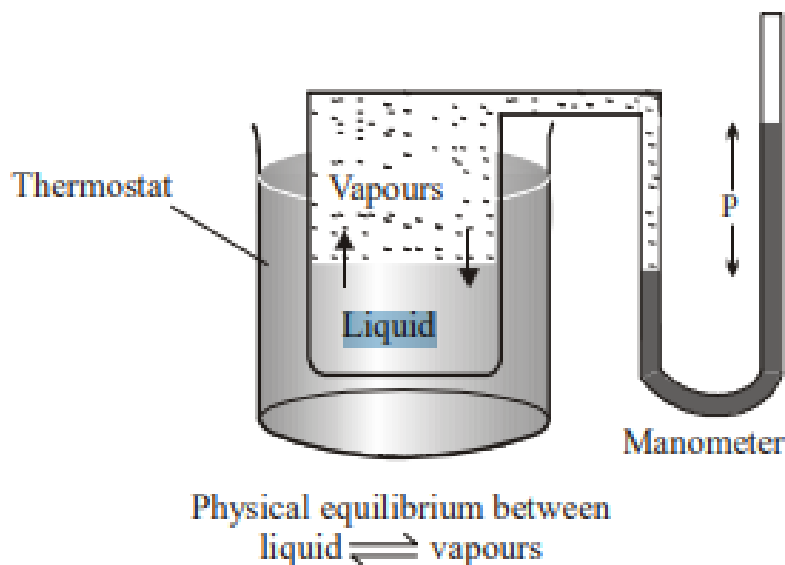


1. Vapor pressure

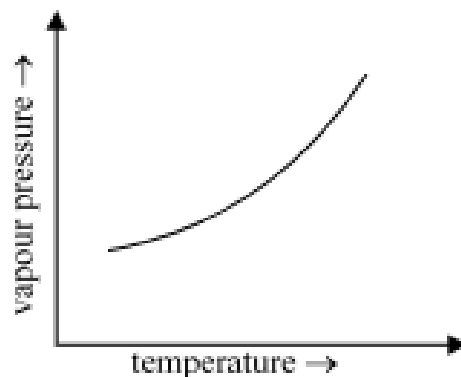
The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.



2. Factors affecting vapour pressure

1. Temperature : Vapour pressure \propto Temperature

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its boiling point.





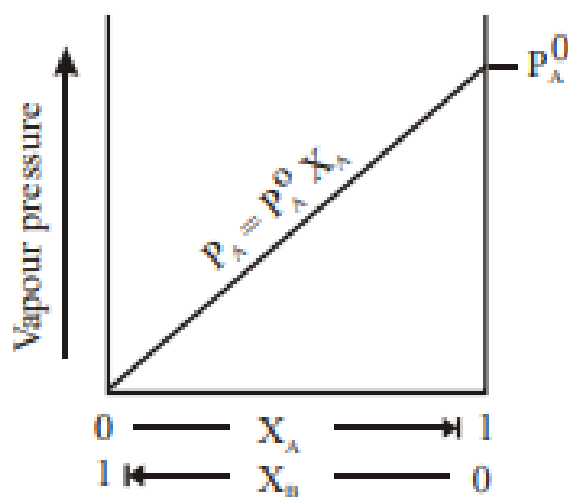
2. Nature of liquid: vapour pressure of liquid \propto (1/acting between molecules
The strength of intermolecular forces)

For example, ethyl alcohol has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

Vapour Pressure of a Solution Containing Non Volatile Solute - Raoult's Law

Raoult's Law : According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

$$P_A \propto X_A \Rightarrow P_A = P_A^0 X$$



Relative Lowering of vapour pressure: For a solution of a non-volatile solute in a liquid, the vapour pressure contribution by the non-volatile solute is negligible. Therefore, the partial vapour pressure of a solution containing a non-volatile solute is equal to the product of vapour pressure of the pure liquid (solvent P_A^0) and its mole fraction in the solution.



Let X_A be the mole fraction of solvent A, then (Here $p_B^0 = \text{negligible}$ as solute is non-volatile)

$$P_A = P_A^0 X_A$$

If X_B be the mole fraction of the solute B, then

$$X_A + X_B = 1 \Rightarrow X_A = 1 - X_B$$

$$\text{hence } P_A = P_A^0 (1 - X_B) = P_A^0 - P_A^0 X_B \Rightarrow P_A^0 X_B = P_A^0 - P_A$$

($P_A - P$ is known as lowering of vapour pressure)

$$\frac{P_A^0 - P_A}{P_A^0} = X_B \quad \left(\frac{P_A^0 - P_A}{P_A^0} \text{ is called relative lowering of vapour pressure, (RLVP)} \right) \quad \left(\frac{P_A^0 - P_A}{P_A^0} \right)$$

Therefore, Raoult's law states that the relative lowering of vapour pressure

, for a non-volatile solute is equal to the mole fraction of the solute when the solvent alone is volatile.

Example: The vapour pressure of pure water at 37°C is 47.1 torr. What is the vapour pressure of an aqueous solution at 37°C containing 20 g of glucose dissolved in 500 gm of water. Also calculate vapour pressure lowering.

$$\text{Solution: } n_{\text{H}_2\text{O}} = \frac{500}{18} = 27.78 \text{ mol}, \quad n_{(\text{glucose})} = \frac{20}{180} = 0.11 \text{ mol}$$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{(\text{glucose})}} = \frac{27.78}{27.78 + 0.11} = \frac{27.78}{27.89} = 0.996$$

According to Raoult's law,

$$\text{Vapour pressure of solution } P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^0 X_{\text{H}_2\text{O}} = 47.1 \times 0.996 = 46.9 \text{ torr}$$

$$\text{Lowring of vapour pressure } P_{\text{H}_2\text{O}}^0 - P_{\text{H}_2\text{O}} = 47.1 - 46.9 = 0.2 \text{ torr}$$



Problems

1. Calculate the vapor pressure of a mixture containing 252 g of n-pentane ($M_w = 72$) and 1400 g of n-eptane ($M_w = 100$) at 20°C. The vapor pressure of n-pentane and n-eptane are 420 mm Hg and 36 mm Hg respectively.

Solution

According to Raoult's law, the vapor pressure exercised by a component of a mixture can be calculated as follows

$$P = P^0 x$$

Where:

P is the vapor pressure of the component in the mixture.

P^0 is the vapor pressure of the pure component.

x is the molar fraction of the component in the mixture.

Calculation of molar fractions (x)

$$\text{moles n-pentane} = 252/72 = 3.5$$

$$\text{moles n-eptano} = 1400/100 = 14$$

$$\text{Totals} = 3.5 + 14 = 17.5 \text{ moles}$$

$$x_{\text{n-pentane}} = 3.5/17.5 = 0.2$$

$$x_{\text{n-eptane}} = 14/17.5 = 0.8$$

Thus

$$P_{\text{n-pentane}} = 0.2 \times 420 = 84 \text{ mm Hg}$$

$$P_{\text{n-eptane}} = 0.8 \times 36 = 28.8 \text{ mm Hg}$$

$$\text{and the vapor pressure of mixture is } P_{\text{mixture}} = 84 + 28.8 = 112.8 \text{ mm}$$

Note: Although the Raoult's law is valid for diluted (ideal) solution, its application to concentrated (non-ideal) solutions does not lead to variation of the order of magnitude of the calculated vapor pressure.



2. Calculate the boiling point (at 1 atm) of a solution containing 116 g of acetone (Mw = 58) and 72 g of water (Mw = 18) by using the following table:

Temperature °C	Vapor pressure (atm) Acetone	Vapor pressure (atm) Water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

A liquid starts to boil when its vapor pressure matches the atmospheric pressure (1 atm in this case). Thus, according to Raoult's law

$$P = x_{\text{acetone}} P^{\circ}_{\text{acetone}} + x_{\text{water}} P^{\circ}_{\text{water}} = 1 \text{ atm}$$

From the given data we can calculate the molar fractions

$$\text{moles}_{\text{acetone}} = 116/58 = 2$$

$$\text{moles}_{\text{water}} = 72/18 = 4$$

$$\text{total moles} = 6$$

$$x_{\text{acetone}} = 2/6 = 1/3$$

$$x_{\text{water}} = 4/6 = 2/3$$

thus,

$$P = 2/3 P^{\circ}_{\text{acetone}} + 1/3 P^{\circ}_{\text{water}} = 1 \text{ atm}$$

By trials, using the table, we can find the values of vapor pressure which satisfies the above equation. The best result is obtained by using the values at 80°C :

$$P = 2/3 \cdot 0.456 + 1/3 \cdot 2.12 = 1.01 \text{ atm then the boiling point is about } 80^{\circ}\text{C}.$$



3. A mixture of water and acetone at 756 mm boils at 70°C. Calculate the percentage composition of the mixture using the following table:

Temperature °C	Vapor pressure (atm) Acetone	Vapor pressure (atm) Water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

According to Raoult's law

$$P = x_{\text{acetone}} P^{\circ}_{\text{acetone}} + x_{\text{water}} P^{\circ}_{\text{water}} = 756/760 = 0.995 \text{ atm}$$

by substituting the values at 70°C we have

$$P = x_{\text{acetone}} 1.58 + x_{\text{acqua}} 0.312 = 0.995$$

and remembering that the sum of molar fractions is 1

$$x_{\text{acetone}} + x_{\text{acqua}} = 1 \quad x_{\text{acqua}} = 1 - x_{\text{acetone}}$$

thus

$$x_{\text{acetone}} 1.58 + 0.312 (1 - x_{\text{acetone}}) = 0.995$$

$$x_{\text{acqua}} 1.58 + 0.312 - 0.312 x_{\text{acetone}} = 0.995$$

$$x_{\text{acetone}} 1.26 + 0.312 = 0.995$$

$$x_{\text{acetone}} = (0.995 - 0.312) / 1.26 = 0.54$$

from which

$$x_{\text{water}} = 1 - 0.54 = 0.46$$



considering 100 moles of solution we have 54 moles of acetone corresponding to $54 \times 58 = 3132$ grams and 46 moles of water corresponding to $46 \times 18 = 828$ grams. Eventually,

$$\% \text{ water} = (828)(100)/(3132 + 828) = 21\%$$

$$\% \text{ acetone} = 100 - 21 = 79\%$$

4. The addition of 114 grams of sucrose to 1000 grams of water lowers the vapor pressure of water from 17.540 to 17.435. Calculate the molecular weight of sucrose.

The variation in pressure is $17.540 - 17.435 = 0.105$ then

$$0.105 = 17.540 \times_2 = n_{\text{solute}}/(n_{\text{solvent}} + n_{\text{solute}})$$

$$n_{\text{solvent}} = 1000/\text{mw}_{\text{water}} = 1000/18 = 55.55 \text{ moles}$$

$$0.105 = 17.540 \times_2 = 17.540 n_{\text{solute}}/(55.55 + n_{\text{solute}})$$

by solving this equation we obtain $n_{\text{solute}} = 0.335$ moles and thus

$$\text{MW} = 114/0.335 = 340$$

The calculated molecular weight (340) is very close to the true molecular weight of sucrose (342).

5. Calculate the osmotic pressure at 20° of a suspension containing 60g/l of solid particles each particle having a mass of 10^{-9} grams (1 nanogram).

$$p = MRT$$

$$T = 273 + 20 = 293 \text{ } ^\circ\text{K}$$

$$R = 0.0823$$

The number of particles in one liter of solution is

$60/10^{-9} = 6 \times 10^{10}$ Remembering that one mole contains an Avogadro number of particles (6×10^{23}), the number of moles in one liter of suspension is $6 \times 10^{10}/6 \times 10^{23} = 10^{-13}$ which corresponds to the molarity of the suspension. Thus



$$p = (0.0823)(298) (10^{-13}) = 24.5 \times 10^{-13} \text{ atm}$$

6. Calculate the osmotic pressure of a solution 0.1 molale of sucrose ($M_w = 342$) at 20°C .

To solve the problem we need to convert the molality in molarity

Molality = moles/kilogram of solvent

Molarity = moles/liter of solution

The grams of sucrose in the solutions are 34.2 and the total weight of the solution is

$$34.2 + 1000 \text{ grams of solvent} = 1034.2$$

Assuming a density = 1 for the solution we can write:

$$0.1 \text{ moles} : 1034.2 = M : 1000 \text{ grams of solution}$$

$$M = 100/1034.2 = 0.097$$

$$p = (0.097)(0.0820578 \text{ liter atm mol}^{-1} \text{ K}^{-1})(293) = 2.34 \text{ atm}$$