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COLLIGATIVE PROPERTIES

There are certain physical properties of the solutions which depend only upon the number of particles in solution and are independent of nature of particles. These properties are called Colligative properties of the solutions.

Some most common Colligative properties of the solutions are as under-

(1) Relative lowering in vapour pressure

(2) Elevation in boiling point

(3) Depression in freezing point

(4) Osmotic pressure

(1) RELATIVE LOWERING IN VAPOUR PRESSURE-

When a nonvolatile solute is added to a volatile solvent, the partial vapour pressure of solvent in solution (vapour pressure of solution) gets decreased. This is called lowering in vapour pressure of solution.

Let, vapour pressure of a pure volatile solvent A is p^0_A and that of solution containing nonvolatile solute B is p_A, then,

$$\text{Lowering in Vapour Pressure} = (p^0_A - p_A)$$

"The ratio of the lowering in vapour pressure of solution to the vapour pressure of pure solvent is called relative lowering in vapour pressure of solution."

Mathematically,

$$\text{Relative lowering in vapour pressure} = \frac{p0_A - p_A}{p0_A}$$

Relative lowering in vapour pressure is a colligative property which depends only upon the number of particles in solution and is independent of nature of particles. It is used in experimental determination of molecular masses of different non-volatile solutes.

RAOULT'S LAW ABOUT RELATIVE LOWERING IN VAPOUR PRESSURE-

Let, W_B g of a non volatile solute B having molecular mass M_B is present in W_A g of a volatile solvent A having molecular mass M_A. The vapour pressure of pure solvent is p^0_A and that of solution containing nonvolatile solute B is p_A, then,

$$\text{Lowering in vapour pressure} = p^0_A - p_A$$

$$\text{and Relative lowering in vapour pressure} = \frac{p0_A - p_A}{p0_A} \qquad \text{----- (1)}$$

From Raoult's law,

$$p_A = p^0_A X_A \qquad \text{------ (2)}$$

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$$\because \quad X_A + X_B = 1$$

$$\therefore \quad X_A = 1 - X_B$$

Putting this value of X_A in eq. (2), we get,

$$p_A = p^0_A (1 - X_B)$$

$$\text{or} \quad p_A = p^0_A - p^0_A X_B$$

$$\text{or} \quad p^0_A X_B = p^0_A - p_A$$

$$\text{or} \quad \frac{p0_A - p_A}{p0_A} = X_B \quad \text{-------} \quad (3)$$

Thus, "At constant temperature, the relative lowering in vapour pressure of a solution containing non-volatile solute is equal to the mole fraction of solute in solution."

This is Raoult's law about relative lowering in vapour pressure of the solutions.

DETERMINATION OF MOLECULAR MASS OF SOLUTES ON THE BASIS OF RELATIVE LOWERING IN VAPOUR PRESSURE OF SOLUTION-

Let, W_B g of a non volatile solute B having molecular mass M_B is present in W_A g of a volatile solvent A having molecular mass M_A. The vapour pressure of pure solvent is p^0_A and that of solution containing nonvolatile solute B is p_A, then,

From Raoult's law,

$$\frac{p0_A - p_A}{p0_A} = X_B \quad \text{-------} \quad (1)$$

$$\because \quad X_B = \frac{n_B}{n_B + n_A}$$

$$\text{or} \quad X_B = \frac{W_B/M_B}{W_B/M_B + W_A/M_A} \quad \text{-------} \quad (2)$$

Raoult's law is applicable only for very dilute solutions, where small amount of solute is present in large excess of solvent. Hence, for these solutions, the number of moles of solute can be neglected as compared to that of solvent in denominator of eq. (2). Thus,

$$\frac{W_B}{M_B} + \frac{W_A}{M_A} \approx \frac{W_A}{M_A}$$

$$\therefore \quad X_B = \frac{W_B/M_B}{W_A/M_A} \quad \text{----------} \quad (3)$$

From eq. (1) and (3), we get,

$$\frac{p0_A - p_A}{p0_A} = \frac{W_B/M_B}{W_A/M_A} \quad \text{----------} \quad (4)$$

$$\text{or} \quad \frac{p0_A - p_A}{p0_A} = \frac{W_B M_A}{M_B W_A} \quad \text{----------} \quad (5)$$

$$\text{or} \quad M_B = \frac{W_B M_A}{W_A} \left(\frac{p0_A}{p0_A - p_A}\right) \quad \text{--------} \quad (6)$$

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If other parameters are known, the molecular mass of the non-volatile solute can be calculated using this expression.

From this expression it is clear that the molecular mass of the non-volatile solute is inversely proportional to the relative lowering in vapour pressure of the solution.

(2) ELEVATION IN BOILING POINT-

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

When a nonvolatile solute is added to a volatile solvent, the partial vapour pressure of solvent in solution (vapour pressure of solution) gets decreased. Hence, to equate the vapour pressure of solution to that of pure solvent, the solution required to be heated to a relatively higher temperature. Thus, when a nonvolatile solute is added to a volatile solvent, the boiling point of solution gets increased. This is called elevation in boiling point of solution.

Let, the boiling point of a volatile solvent A is T^0_b and that of solution containing nonvolatile solute B is T_b, then,

Elevation in boiling point of solution, $\Delta T_b = (T_b - T^0_b)$

If vapour pressure of pure solvent A and that of solution containing nonvolatile solute B are plotted against absolute temperature (T), then following curves are obtained-

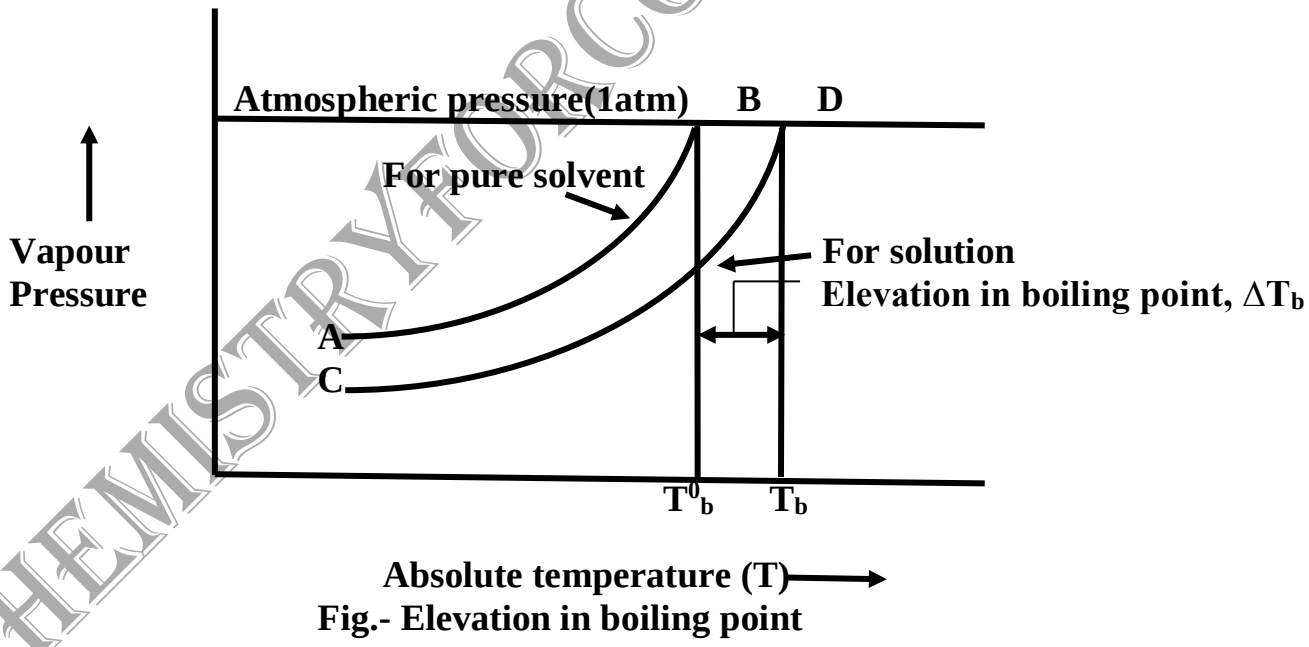


Fig.- Elevation in boiling point

Here, vapour pressure of both solvent and solution increases with increase of temperature. At temperature corresponding to point B (T^0_b), the vapour pressure of pure solvent becomes equal to the atmospheric pressure. Hence, it corresponds to the boiling point of pure solvent. Similarly, at temperature corresponding to point D (T_b), the vapour

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pressure of solution becomes equal to the atmospheric pressure. Hence, it corresponds to the boiling point of solution. It is clear that, the boiling point of solution is more than that of pure solvent.

Elevation in boiling point is a colligative property, which depends only upon the number of particles in solution and is independent of nature of particles. It is used in experimental determination of molecular masses of different non-volatile solutes.

DETERMINATION OF MOLECULAR MASS OF SOLUTES ON THE BASIS OF ELEVATION IN BOILING POINT

Let, W_B g of a non volatile solute B having molecular mass M_B is present in W_A g of a volatile solvent A having molecular mass M_A. The boiling point of pure volatile solvent A is T^0_b and that of solution containing nonvolatile solute B is T_b, then-

Elevation in boiling point of solution, $\Delta T_b = (T_b - T^0_b)$

Experimentally, it has been found that, the elevation in boiling point is directly proportional to the molal concentration of solution. Thus,

$$\Delta T_b \ \alpha \ m$$

$$\text{or} \quad \Delta T_b = K_b m \quad \text{---------- (1)}$$

where, K_b is a proportionality constant called molal boiling point elevation constant or ebullioscopic constant.

If $m = 1$

Then, $\Delta T_b = K_b$ --------- (2)

Thus, "The elevation in boiling point of a molal solution is called molal boiling point elevation constant or ebullioscopic constant of the solvent."

or

"The elevation in boiling point observed when one mole of a nonvolatile solute is added to 1000 g of a volatile solvent is called molal boiling point elevation constant or ebullioscopic constant of the solvent."

$$\because \quad \text{Molality, } m = \frac{Mass\ of\ solute\ (g) \times 1000}{\text{GMM of Solute} \times \text{Mass of Solvent (g)}}$$

$$= \frac{W_B\ (g) \times 1000}{M_B \times W_A\ (g)}$$

$$\therefore \quad \Delta T_b = \frac{1000 K_b . W_B\ (g)}{M_B . W_A\ (g)} \quad \text{---------- (3)}$$

$$\text{or} \quad M_B = \frac{1000 K_b . W_B\ (g)}{\Delta Tb . W_A\ (g)} \quad \text{---------- (4)}$$

If other parameters are known, the molecular mass of the non-volatile solute can be calculated using this expression.

From this expression it is clear that, the molecular mass of the non-volatile solute is inversely proportional to the elevation in boiling point of the solution.

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(2) DEPRESSION IN FREEZING POINT-

The temperature at which the vapour pressure of a liquid becomes equal to the vapour pressure of its solid phase is called freezing point of the liquid.

When a nonvolatile solute is added to a volatile solvent, the partial vapour pressure of solvent in solution (vapour pressure of solution) gets decreased. Hence, to equate the vapour pressure of solution to that of solid solvent, the solution is required to be cooled further to a relatively lower temperature. Thus, when a nonvolatile solute is added to a volatile solvent, the freezing point of solution gets decreased. This is called depression in freezing point of solution.

Let, the freezing point of a volatile solvent A is T^0_f and that of solution containing nonvolatile solute B is T_f, then ,

Depression in freezing point of solution, $\Delta T_f = (T^0_f - T_f)$

If vapour pressure of pure solid solvent, liquid solvent and solution containing nonvolatile solute are plotted against absolute temperature (T), then following curves are obtained-

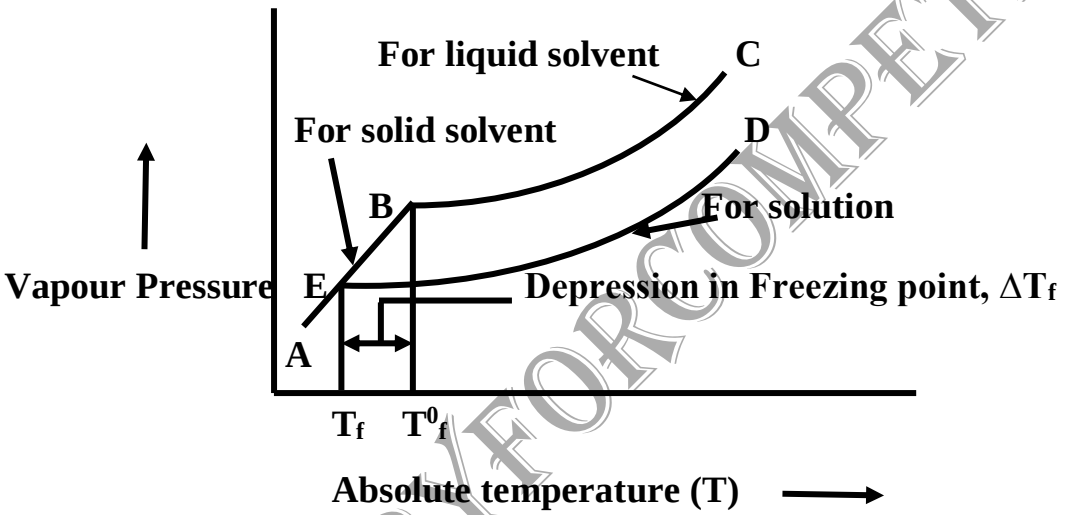


Fig.- Depression in Freezing point

Here, vapour pressure of both liquid solvent and solution decreases with decrease of temperature. At temperature corresponding to point B (T^0_f), the vapour pressure of pure liquid solvent becomes equal to the solid solvent. Hence, it corresponds to the freezing point of pure solvent (T^0_f). Similarly, at temperature corresponding to point E (T_f), the vapour pressure of solution becomes equal to the solid solvent. Hence it corresponds to the freezing point of solution. It is clear that, the freezing point of solution is lesser than that of pure solvent.

Depression in freezing point is a colligative property, which depends only upon the number of particles in solution and is independent of nature of particles. It is used in experimental determination of molecular masses of different non-volatile solutes.

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DETERMINATION OF MOLECULAR MASS OF SOLUTES ON THE BASIS OF DEPRESSION IN FREEZING POINT-

Let, W_B g of a non volatile solute B having molecular mass M_B is present in W_A g of a volatile solvent A having molecular mass M_A. The freezing point of pure volatile solvent A is T^0_f and that of solution containing nonvolatile solute B is T_f, then-

Depression in freezing point of solution, $\Delta T_f = (T^0_f - T_f)$

Experimentally it has been found that, the depression in freezing point is directly proportional to the molal concentration of solution. Thus,

$$\Delta T_f \quad \alpha \quad m$$

$$\text{or} \qquad \Delta T_f = K_f m \qquad \text{---------- (1)}$$

where, K_f is a proportionality constant called molal freezing point depression constant or cryoscopic constant.

$$\text{If} \qquad m = 1$$

$$\text{Then,} \qquad \Delta T_f = K_f \qquad \text{---------- (2)}$$

Thus, "The Depression in freezing point of a molal solution is called molal freezing point depression constant or cryoscopic constant of the solvent."

or

"The depression in freezing point observed when one mole of a nonvolatile solute is added to 1000 g of a volatile solvent is called molal freezing point depression constant or cryoscopic constant of the solvent."

$$\because \qquad \text{Molality,} \quad m = \frac{Mass\ of\ solute\ (g) \times 1000}{\text{GMM of Solute} \times \text{Mass of Solvent (g)}}$$

$$= \frac{W_B\ (g) \times 1000}{M_B \times W_A\ (g)}$$

$$\therefore \qquad \Delta T_f = \frac{1000 K_f . W_B\ (g)}{M_B . W_A\ (g)} \qquad \text{-------- (3)}$$

$$\text{or} \qquad M_B = \frac{1000 K_f . W_B\ (g)}{\Delta T_f . W_A\ (g)} \qquad \text{------- (4)}$$

If other parameters are known, the molecular mass of the non-volatile solute can be calculated using this expression.

From this expression it is clear that, the molecular mass of the non-volatile solute is inversely proportional to the depression in freezing point of the solution.

OSMOSIS

The movement of solvent molecules from high solvent concentration (low solute concentration) to low solvent concentration (high solute concentration) through a semi-permeable membrane is called osmosis.

For example- if a solution is separated from its solvent through a semi-permeable membrane the solvent molecules start moving from solvent to solution through semi-permeable membrane due to osmosis.

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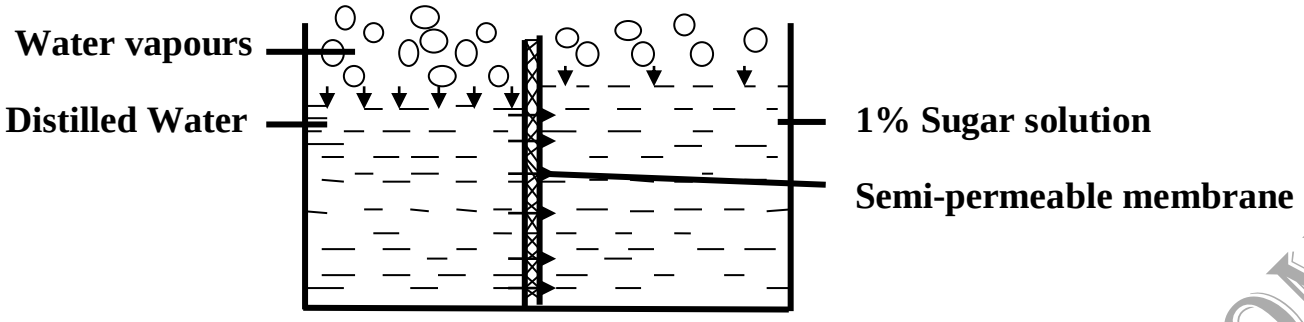


Fig.- Expression of osmosis

Osmosis is special case of diffusion, where the movement of solute molecules is checked using semipermeable membrane.

Osmosis is caused by difference in vapour pressure of pure solvent and solution.

TYPES OF OSMOSIS-

Osmosis may be of following two types-

(1) ENDO-OSMOSIS- When an animal cell is placed in distilled water, the water molecules start entering into the cell through cell membrane due to endo-osmosis, so that the cell swells up and finally get ruptured.

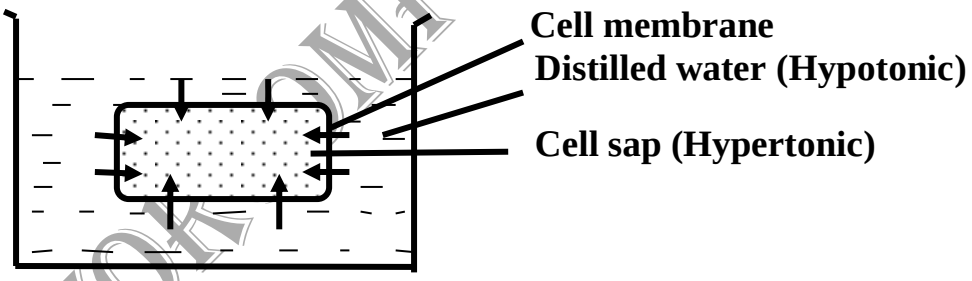


Fig.- Expression of Endo-osmosis

Here, cell sap is hypertonic to distilled water. Hence, water molecules enter into the cell through cell membrane due to endo-osmosis.

(2) EXO-OSMOSIS- When an animal cell is placed in concentrated solution of NaCl, the water molecules start coming out of the cell due to exo-osmosis and therefore the cell gets flaccid.

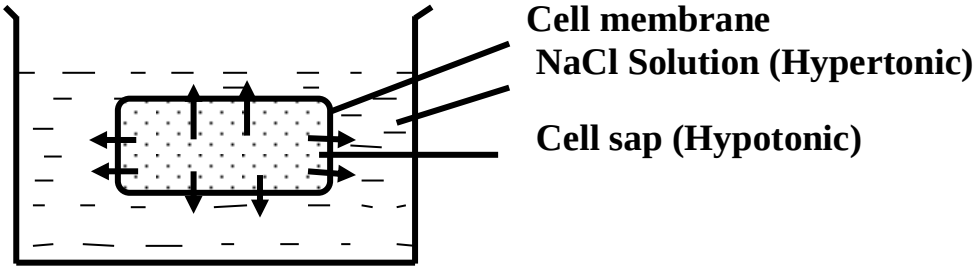


Fig.- Expression of Exo-osmosis

Here, cell sap is hypotonic to the solution. Hence, water molecules come out of the cell through cell membrane due to exo-osmosis.

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(4) OSMOTIC PRESSURE-

Osmosis is caused by difference in vapour pressure of pure solvent and solution. This difference in vapour pressure of pure solvent and solution causing osmosis is called osmotic pressure of the solution.

Osmotic pressure is defined in a number of ways-

(1) First Definition- "The hydrostatic pressure which develops due to osmosis and finally checks the osmosis is called osmotic pressure of the solution."

Let 1% aqueous solution of sugar is taken in a long neck thistle funnel provided with a semi-permeable membrane on its bottom. It is suspended in distilled water taken in a tank. Here, due to difference in vapour pressure of pure solvent and solution, the solvent molecules enter in the thistle funnel through semi-permeable membrane, so that the column of solution in the funnel rises. After some times, the osmosis gets checked and therefore, the rise of the column in funnel gets stopped. Here, due to rise of the column of solution in funnel, a hydrostatic pressure (π = hdg) gets developed, which finally checks the osmosis and is called osmotic pressure of the solution.

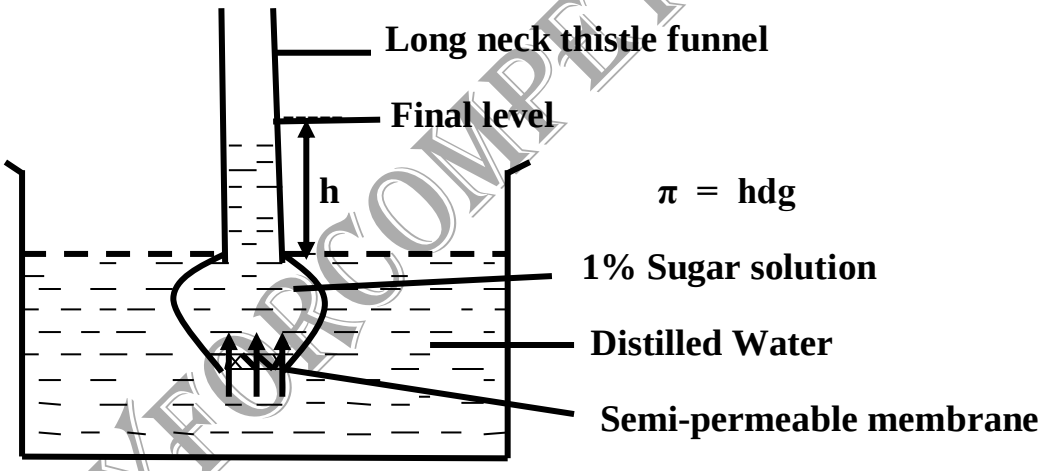


Fig.-Nollet's Experiment

(1) Second Definition- "The external pressure which when applied on the solution separated from semi-permeable membrane, the vapour pressure of solution becomes equal to that of pure solvent and osmosis gets stopped, is called osmotic pressure of the solution."

Let, a tank is divided into two equal half using a semi-permeable membrane. One part of the tank is filled with distilled water, while other part is filled with 1% aqueous solution of sugar. Here, the vapour pressure of pure solvent is more than that of solution. Hence, the solvent molecules start entering in distilled water through semi-permeable membrane.

Let, an external pressure is applied on the solution using a piston, so that the vapour pressure of solution becomes equal to that of pure solvent and therefore, osmosis gets stopped. Here, the external pressure applied corresponds to the osmotic pressure of the solution.

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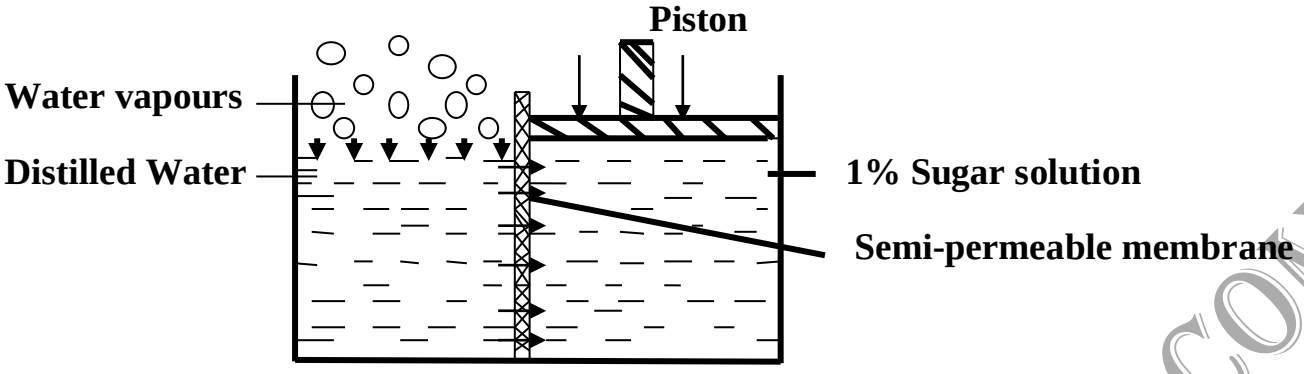


Fig.- Osmotic pressure

Osmotic pressure is a colligative property, which depends only upon the number of particles in solution and is independent of nature of particles. It is used in experimental determination of molecular masses of different non-volatile solutes.

Ideal equation of Solution-

OR

Vant Hoff equation-

On experimental basis, vant Hoff found that, in very dilute solutions, solute molecules play the same role as played by gaseous molecules in gases. Hence, all the gaseous laws are equally applicable on dilute solutions (ideal solutions). Here, osmotic pressure of solution is identical to gaseous pressure.

Identical to ideal gas equation, vant Hoff gave following equation applicable to the ideal solutions –

$$\pi V = nST$$

Where, π = osmotic pressure

n = no. of moles of solute

S = solution constant

= 8.314 $JK^{-1}mol^{-1}$

T = absolute temperature

This equation is called ideal equation for solutions.

Let, W_B g of a non volatile solute B having molecular mass M_B is present in V litre of solution, then from ideal equation for solutions-

$$\pi V = nST$$

or

$$\pi = \frac{n}{V} ST$$

or

$$\pi = \frac{W_B}{M_B V} ST$$

All these equations are called vant Hoff equations for osmotic pressure of ideal solutions.

If other parameters are known, the molecular mass of the non-volatile solute can be calculated using these expressions.

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From this expression it is clear that, the molecular mass of the non-volatile solute is inversely proportional to the osmotic pressure of the solution.

ISOTONIC SOLUTIONS-

The solutions having same osmotic pressure are called iso-osmotic or isotonic solutions.

When these solutions are separated by semi-permeable membrane, there occurs no osmosis.

Let two isotonic solutions have osmotic pressure π_1 and π_2 respectively, then-

$$\pi_1 = \pi_2$$

$$\because \quad \pi = \frac{n}{V}ST$$

$$\therefore \quad \pi = CST$$

Hence, for isotonic solutions-

$$C_1ST = C_2ST$$

$$\text{or} \quad C_1 = C_2$$

Thus, isotonic solutions have same molar concentration.

ABNORMAL MOLECULAR MASSES-

It found that, molecular mass of a solute is inversely proportional to the colligative properties.

$$\text{Molecular mass } \alpha \frac{1}{\text{colligative properties}}$$

If a molecule associate or dissociate in solution then, the number of particles in solution get changed and therefore, colligative properties get changed. Due to change in colligative properties, the molecular mass of solute determined on the basis of colligative properties is different from their real molecular mass and it is called abnormal molecular mass of the solute.

(A) Dissociation of solute in solution- If a solute undergoes dissociation in solution then, the number of particles in solution get increased and therefore, colligative properties get increased. Hence, the molecular mass of solute determined on the basis of colligative properties is lesser than their real molecular mass.

For example, KCl undergoes dissociation in solution as under-

$$KCl \rightleftharpoons K^+ + Cl^-$$

Here, number of particles in solution becomes twice and therefore, colligative properties gets twiced. Hence, the molecular mass of KCl determined on the basis of colligative properties is half of its real molecular mass i.e. (39 + 35.5)/2 = 37.25.

(B) Association of solute in solution- If a solute undergoes association in solution then, the number of particles in solution get decreased and therefore, colligative

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properties get decreased. Hence, the molecular mass of solute determined on the basis of colligative properties is more than their real molecular mass.

For example, CH_3COOH undergoes dimerization in benzene as under-

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Here, number of particles in solution becomes half and therefore, colligative properties gets halved. Hence, the molecular mass of CH_3COOH determined on the basis of colligative properties is twice of its real molecular mass i.e. 2× 60 = 120.

Vant Hoff factor (i) –

In order to express the degree of dissociation or association of solute in solution vant Hoff has introduced a factor called vant Hoff factor (i).

By definition, "the ratio of the number of particles after dissociation or association of solute in solution to the number of particles before dissociation or association is called vant Hoff factor of the solute in solution."

Mathematically, vant Hoff factor,

$$i = \frac{\text{No.of particles after dissociation or association}}{\text{No.of particles before dissociation or association}}$$

$\because$ **Colligative properties α number of particles in solution**

$\therefore$ **vant Hoff factor,**

$$i = \frac{\text{Observed colligative properties}}{\text{Calculated colligative properties}}$$

or

$$i = \frac{\Delta P_{obs}}{\Delta P_{cal}} = \frac{\Delta T_b(obs)}{\Delta T_b(cal)} = \frac{\Delta T_f(obs)}{\Delta T_b(cal)} = \frac{\pi_{obs}}{\pi_{cal}}$$

$\because$ **Molecular mass α** $\dfrac{1}{\text{Colligative properties}}$

$\therefore$ **vant Hoff factor,**

$$i = \frac{\text{Actual molecular mass}}{\text{Observed molecular mass}}$$

Applications-

(1) For the solutes which do not associate or dissociate in solution e.g. glucose, fructose, urea etc. the number of particles after dissociation or association is equal to the number of particles before dissociation or association. Hence, vant Hoff factor,

$$i = 1$$

(2) For the solutes which dissociate in solution e.g. NaCl, KCl, Na_2SO_4 etc. the number of particles after dissociation is greater than the number of particles before dissociation. Hence, vant Hoff factor,

$$i > 1$$

For example, for NaCl

$$NaCl \rightarrow Na^+ + Cl^-$$

Considering complete dissociastion, vant Hoff factor,

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$$I = \frac{\text{No.of particles after dissociation}}{\text{No.of particles before dissociation}}$$

$$= \frac{2}{1}$$

$$= 2$$

(3) For the solutes which associate in solution, the number of particles after association is lesser than the number of particles before association. Hence, vant Hoff factor,

$$i < 1$$

For example, CH_3COOH undergoes dimerization in benzene as under-

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Considering complete dimerization, vant Hoff factor,

$$i = \frac{\text{No.of particles after association}}{\text{No.of particles before association}}$$

$$= \frac{1}{2}$$

Relation between vant Hoff factor (i) and degree of dissociation (α)-

Let, a solute X_n undergoes dissociation in its aqueous solution as under-

$$X_n \rightleftharpoons nX$$

If degree of dissociation of solute is α, then-

X_n	$\rightleftharpoons$	nX	
1		0	initial no. of moles
(1- α)		nα	no. of moles at equilibrium

∴ **Total number of moles of solute at equilibrium = (1- α) + nα**

$$= 1 + (n\text{-}1)\,\alpha$$

∵ **vant Hoff factor,**

$$i = \frac{\text{No.of particles after dissociation}}{\text{No.of particles before dissociation}}$$

or

$$i = \frac{1 + (n-1)\,\alpha}{1}$$

or

$$\alpha = \frac{(i-1)}{(n-1)}$$

This expression gives the relation between vant Hoff factor (i) and degree of dissociation of solute (α).

Relation between vant Hoff factor (i) and degree of association (α)-

Let, a solute X undergoes association in its aqueous solution as under-

$$nX \rightleftharpoons X_n$$

If degree of association of solute is α, then-

$$nX \rightleftharpoons X_n$$

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1	**0**	**initial no. of moles**
(1- α)	**α/n**	**no. of moles at equilibrium**

$\therefore$ **Total number of moles of solute at equilibrium = (1- α) + α/n**

$$= \frac{n+(1-n)\,\alpha}{n}$$

$\because$ **vant Hoff factor,**

$$i = \frac{\text{No.of particles after association}}{\text{No.of particles before association}}$$

or
$$i = \frac{\frac{n+(1-n)\,\alpha}{n}}{1}$$

or
$$\alpha = \frac{(i-1)}{\frac{1}{n}-1}$$

This expression gives the relation between vant Hoff factor (i) and degree of association (α).

MODIFICATION IN THE EQUATIONS OF COLLIGATIVE PROPERTIES

Introducing vant Hoff factor (i), the equations of different colligative properties have been modified as under-

(1) Relative lowering in vapour pressure,

$$\frac{p0_A - p_A}{p0_A} = i\,X_B$$

(2) Elevation in boiling point,

$$\Delta T_b = i\,K_b m$$

(3) Depression in freezing point,

$$\Delta T_f = i\,K_f m$$

(4) Osmotic pressure,

$$\pi = i\,CST$$

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Henry's Law-

This law gives effect of pressure on the solubility of a gas in a liquid. According to this law,

"At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution."

If m is mass of a gas dissolved in unit volume of solution and P is the pressure of the gas in equilibrium of the solution, then,

$$m \quad \alpha \quad P$$

$$m \quad = \quad KP$$

Where, K is a proportionality constant whose value depends upon the nature of gas, nature of solvent and temperature.

$$\text{If} \quad P = 1$$

$$\text{Then,} \quad m = K$$

Thus, the solubility of a gas at unit pressure is equal to constant K of the gas.

If mass m of a gas dissolved in unit volume of solution is plotted against equilibrium pressure (P), then straight line is obtained.

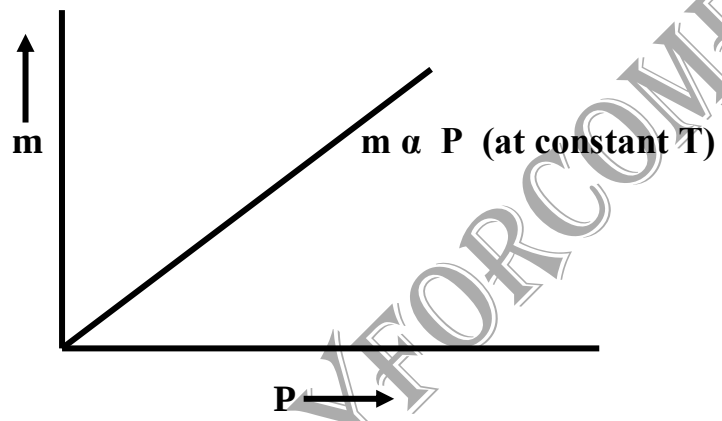


Fig. – Variation of solubility of gas against pressure

If m_1 and m_2 are the solubility of a gas in a liquid at pressure P_1 and P_2 respectively at a given temperature, then

$$\frac{m_1}{m_2} = \frac{P_1}{P_2}$$

If a mixture of two or more non- reacting gases is in contact with a liquid, then the solubility of a definite gas in a liquid is directly proportional to its partial pressure in gaseous mixture over the solution.

If mole fraction of the gas in solution is taken as a measure of its solubility in solution, then Henry's law is defined as under-

"The mole fraction of a gas in the solution is proportional to the partial pressure of the gas in gaseous mixture over the solution."

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Mathematically,

$$x \alpha p$$

$$x = K' p$$

$$\text{or} \quad p = \frac{1}{K'} x$$

$$\text{or} \quad p = K_H x$$

Where, $K_H = \frac{1}{K'}$ **is called Henry's law constant**

The value of K_H is different for different gases at a given temperature.

If partial pressure of a gas p is plotted against its mole fraction x in solution, then straight line is obtained.

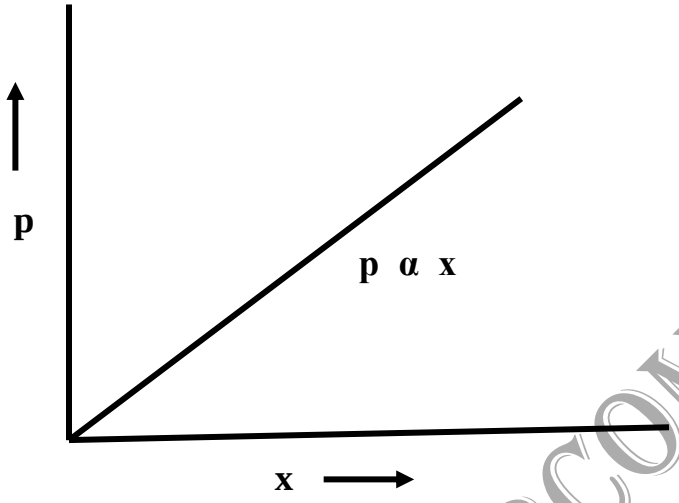


Fig.-Plot of partial pressure p against mole fraction x

From the above equation it is clear that, the higher the value of Henry's law constant K_H at a given pressure, lesser is solubility of gas in the liquid.

Limitations of Henry's Law-

Henry's law is only applicable if,

(i) The temperature is not very low

(ii) Pressure is not too high

(iii) The gas does not chemically combine to the solvent

(iv) Gaseous molecules do not associate or dissociate in solvent

- **Higher solubility is observed when the gas combines with the solvent. For example, the solubility of ammonia and CO_2 in water is much higher than expected.**

$$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

- **Normally O_2 is sparingly soluble in water, but it is highly soluble in blood because of the combination of O_2 with haemoglobin (Hb).**

$$Hb + 4O_2 \rightarrow Hb(O_2)_4$$

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Applications of Henry's law-

(1) Solubility of CO_2 in carbonated beverages-

In sealed bottle carbonated drinks more CO_2 remains dissolved at high pressure. When bottle is opened the external pressure gets decreased. Hence, solubility of gas in solution gets decreased, so that the excess of dissolved gas bubbles out with fizz.

(2) Deep Sea Diving-

Deep sea divers use air diluted with helium instead of air for breathing. It is because N_2 is highly soluble in blood and other body fluids at high pressure in deep sea. When they return back to surface, its solubility decreases rapidly with decrease of pressure. Hence, dissolved N_2 bubbles out rapidly. The formation of nitrogen bubbles in blood causes blockage of blood capillaries and is very painful. It is called Decompression sickness or Bends and may be fatal.

Hence, the scuba divers use the air tank filled with a mixture of 11.7 % helium, 56.2 % N_2 and 32.1 % O_2) for breathing. Here, solubility of He is much more lesser as compared to N_2 in blood and therefore it is safer to be used.

(3) High Altitude Sickness –

At high altitude, the partial pressure of oxygen is very low, so that the concentration of oxygen in blood and tissues of the people living these places is relatively low. Hence, these people suffer from Anoxia (High Altitude Sickness) i.e. they become weak and are unable to think properly.

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