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Fundamentals of Chemistry

CHEM 101

Colligative Properties

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Colligative Properties



A colligative property may be defined as one which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles.

Four properties of dilute solutions

Lowering of the Vapour Pressure
Elevation of the Boiling Point
Depression of the Freezing Point
Osmotic Pressure

The term "colligative" originates from the Latin word "colligatus," which means "bound together" or "connected."

Related properties;
if one can be measured;
others can be calculated

- ✓ Valuable methods for finding the molecular weights of dissolved substances

Lowering of Vapour Pressure

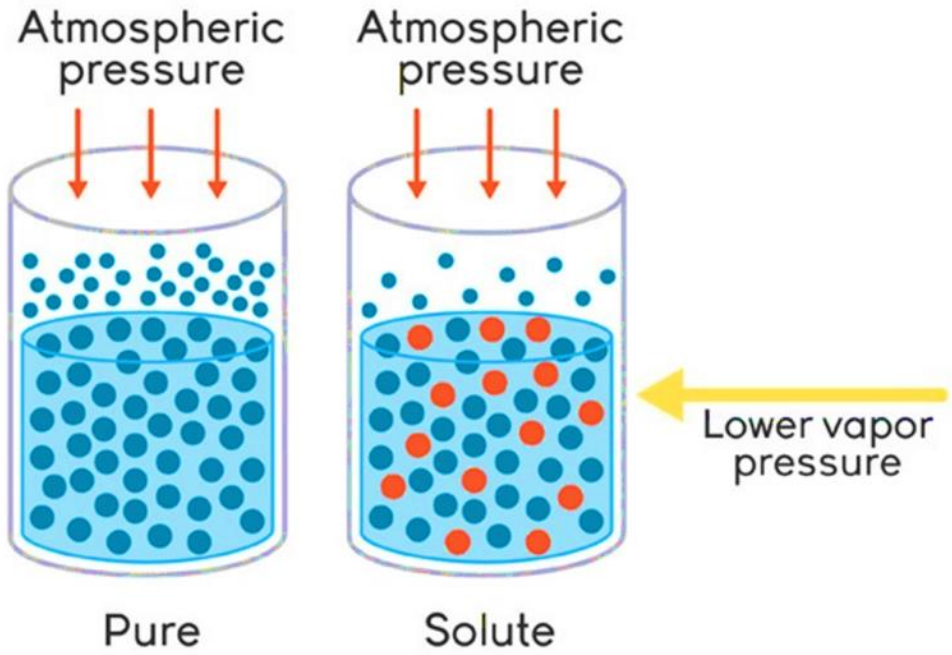
The vapour pressure of a pure solvent decreases when a non-volatile solute is dissolved in it.

Sucrose, Glucose, Urea

Raoult's Law

The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.

$$\frac{p - p_s}{p} = \frac{n}{N + n}$$



p is the vapour pressure of the solvent

p_s is the vapour pressure of the solution

n = number of moles or molecules of solute

N = number of moles or molecules of solvent.

Derivation of Raoult's Law

The vapour pressure of the solution is, therefore, determined by the number of molecules of the solvent present at any time in the surface which is proportional to the mole fraction. That is,

$$p_s \propto \frac{N}{n+N}$$

where N = moles of solvent and n = moles of solute.

or
$$p_s = k\,\frac{N}{n+N}$$

k being proportionality factor.

In case of pure solvent $n = 0$ and hence

$$\text{Mole fraction of solvent} = \frac{N}{n+N} = \frac{N}{0+N} = 1$$

Now from equation (1), the vapour pressure $p = k$

Therefore the equation (1) assumes the form

$$p_s = p\,\frac{N}{n+N}$$

or
$$\frac{p_s}{p} = \frac{N}{n+N}$$

$$1 - \frac{p_s}{p} = 1 - \frac{N}{n+N}$$

$$\frac{p - p_s}{p} = \frac{n}{n+N}$$

This is Raoult's Law.

Lowering of Vapour Pressure

The boiling point of the solution increases/elevates.

Since the vapor pressure of the solution is lower than that of the pure solvent, it will take more energy (heat) to raise the vapor pressure to the atmospheric pressure and cause the liquid to boil.

The freezing point of the solution decreases/depresses.

This is because the freezing point is the temperature at which the liquid becomes a solid. When a non-volatile solute is added to the solvent, it interferes with the formation of the crystal lattice of the solvent molecules, making it harder for them to come together and freeze.

A solution which obeys Raoult's law strictly is called an Ideal solution.

A solution shows deviations from Raoult's law is called a Nonideal or Real solution.

Lowering of Vapour Pressure

Determination of Molecular Mass from Vapour Pressure Lowering

The molecular mass of a nonvolatile solute can be determined by measuring the lowering of vapour pressure ($p - p_s$) produced by dissolving a known weight of it in a known weight of the solvent.

If in a determination w grams of solute is dissolved in W grams of the solvent, m and M are molecular masses of the solute and solvent respectively, we have :

$$\text{No. of Moles of solute } (n) = \frac{w}{m}$$

$$\text{No. of Moles of solvent } (N) = \frac{W}{M}$$

Substituting these values in the Raoult's law Equation,

$$\frac{p - p_s}{P} = \frac{n}{n + N} \qquad \text{...(Raoult's Law Eq.)}$$

$$\frac{p - p_s}{P} = \frac{w/m}{w/m + W/M} \qquad \text{...(1)}$$

Lowering of Vapour Pressure

Since for very dilute solution, the number of moles (molecules) of solute (w/m), is very small, it can be neglected in the denominator. The equation (1) can now be written as

$$\frac{p - p_s}{P} = \frac{wM}{mW} \qquad \ldots(2)$$

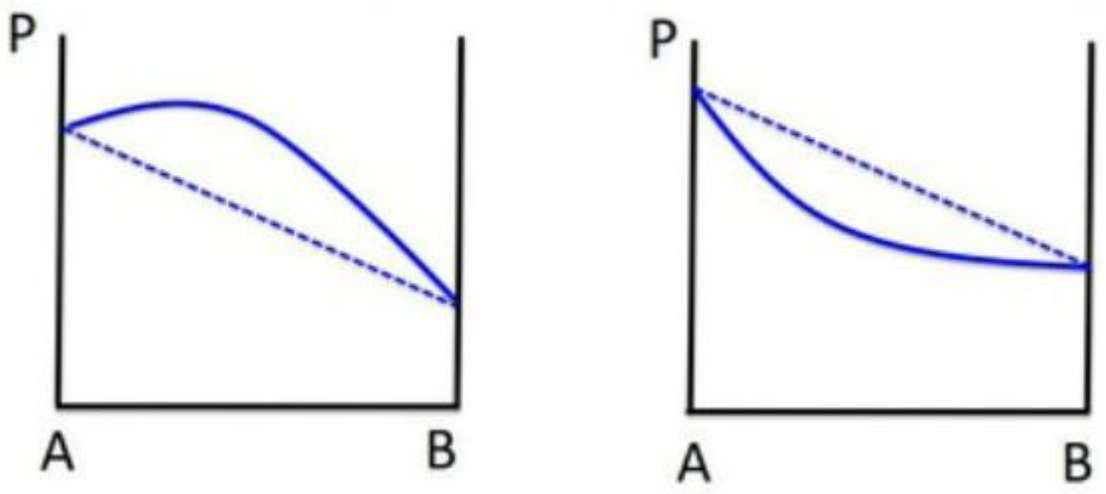
Knowing the experimental value of $p - p_s/p$, and the molecular mass of the solvent (M), the molecular weight of solute (m) can be calculated from (1) or (2).

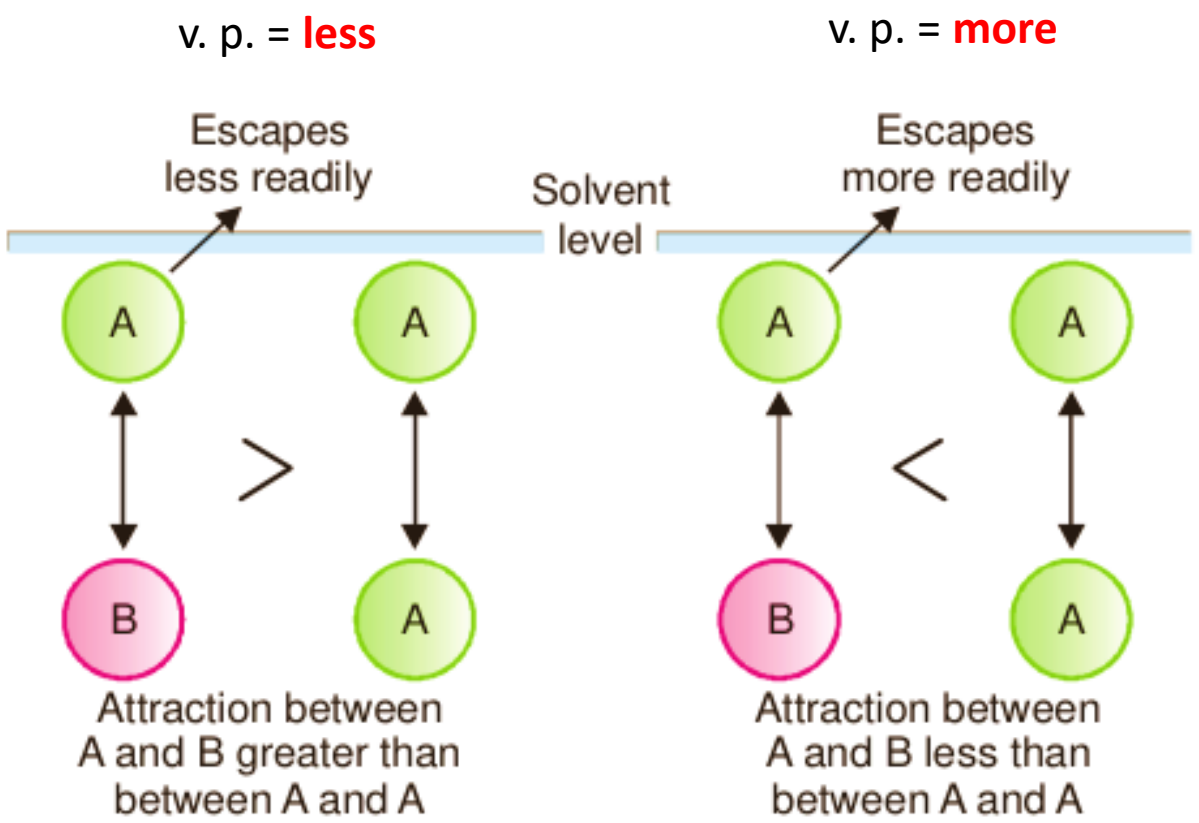
Deviations from Raoults's Law

Suppose the molecules of the solvent and solute are represented by A and B respectively. Now, let γ_{AB} be the attractive force between A and B, and γ_{AA} between A and A. If

$$\gamma_{AB} = \gamma_{AA}$$

The solution will show the same vapour pressure as predicted by Raoult's law





Negative deviation and Positive deviation.

Measurements of lowering of Vapour pressure

Barometric Method

Manometric Method

Ostwald and Walker’s Dynamic Method

Numericals

SOLVED PROBLEM 2. 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.

SOLUTION

Since the solution is not very dilute, the complete Raoult's Law Equation applied is

$$\frac{p - p_s}{p} = \frac{w/m}{W/M + w/m} \qquad \ldots(1)$$

In this case :

w, the mass of solute (urea) = 18.2 g

W, *the* mass of solvent (water) = 100 g

m, the mol mass of solute (urea) = ?

M, the mol mass of solvent (water) = 18

$p - p_s$, the lowering of vapour pressure = 5mm

p, the vapour pressure of solvent (water) = 92mm

Substituting these values in equation (1),

$$\frac{5}{92} = \frac{18.2/m}{18.2/m + 100/18}$$

Hence m, the molecular mass of urea = **57.05**

Elevation of Boiling Point

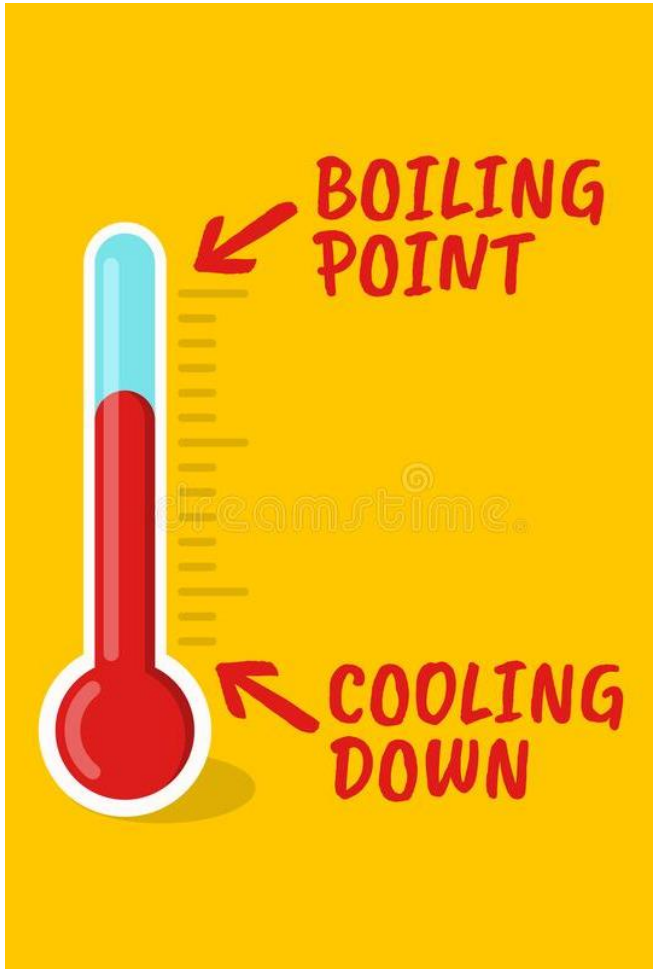


Boiling Point!!

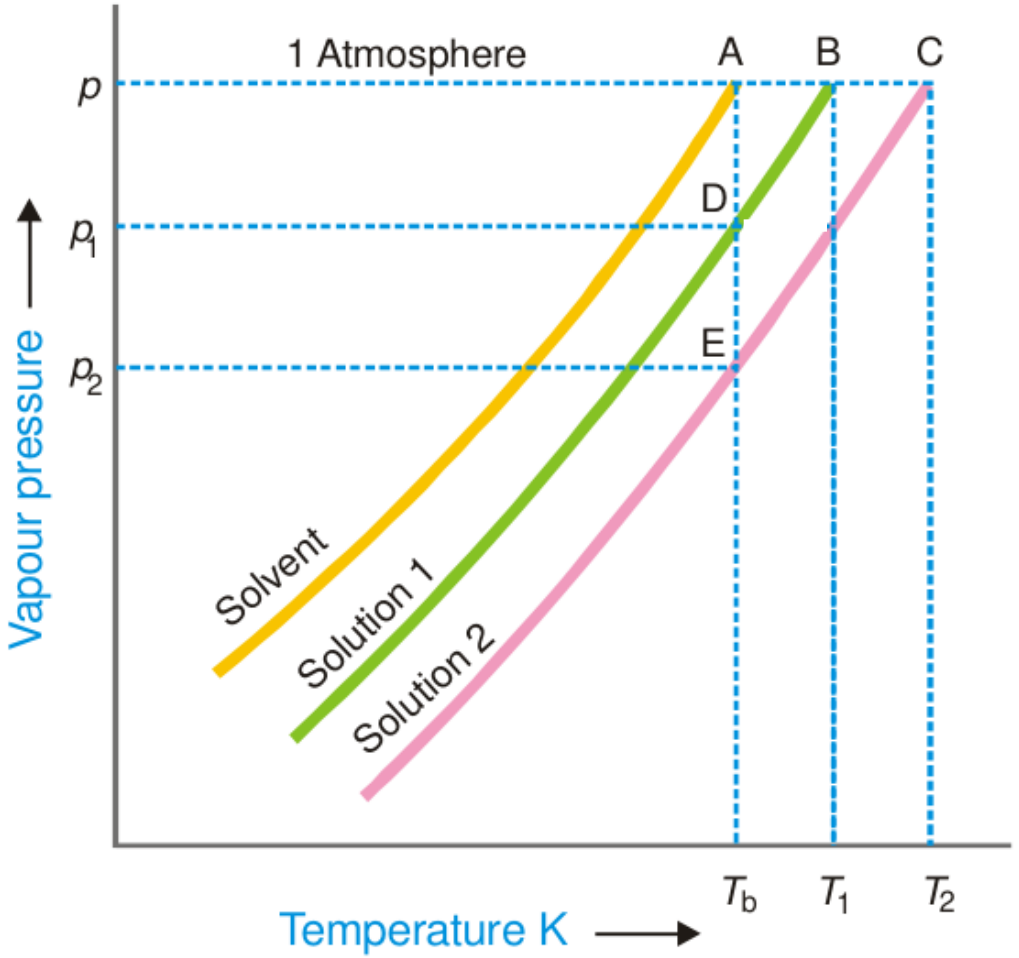


If T_b is the boiling point of the solvent and T is the boiling point of the solution, the difference in the boiling points (ΔT) is called the **elevation of boiling point.**

$$T - T_b = \Delta T$$



Elevation of Boiling Point



The vapour pressure curves of pure solvent, and solutions (1) and (2) with diff. concentrations of solute

For dilute solutions, the curves BD and CE are parallel and straight lines approximately. Therefore, for similar triangles ACE and ABD,

$$\frac{AB}{AC} = \frac{AD}{AE}$$

$$\frac{T_1 - T_b}{T_2 - T_b} = \frac{p - p_1}{p - p_2}$$

where $p - p_1$ and $p - p_2$ are lowering of vapour pressure for solution (1) and solution (2), respectively.

$$\Delta T \propto p - p_s$$

The elevation of boiling point is directly proportional to the lowering of vapour pressure.

Elevation of Boiling Point

Determination of Molecular Mass from Elevation of Boiling Point

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \qquad \ldots(2)$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} \propto \frac{wM}{Wm} \qquad \ldots(3)$$

Since M (mol mass of solvent) is constant, from (3)

$$\frac{p - p_s}{p} \propto \frac{w}{Wm} \qquad \ldots(4)$$

From (2) and (4)

$$\Delta T \propto \frac{w}{m} \times \frac{1}{W}$$

Elevation of Boiling Point

$$\Delta T = K_b \times \frac{w}{m} \times \frac{1}{W}$$

$$\boxed{\Delta T_b = K_b \,.\, m}$$

where K_b is a constant called Boiling point constant or Ebulioscopic constant of molal elevation constant.

If w/m = 1, W = 1, $K_b = \Delta T$. Thus,

Molal elevation constant may be defined as the boiling-point elevation produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent.

Converted into kg

$$\Delta T = K_b \times \frac{w}{m} \times \frac{1}{W/1000}$$

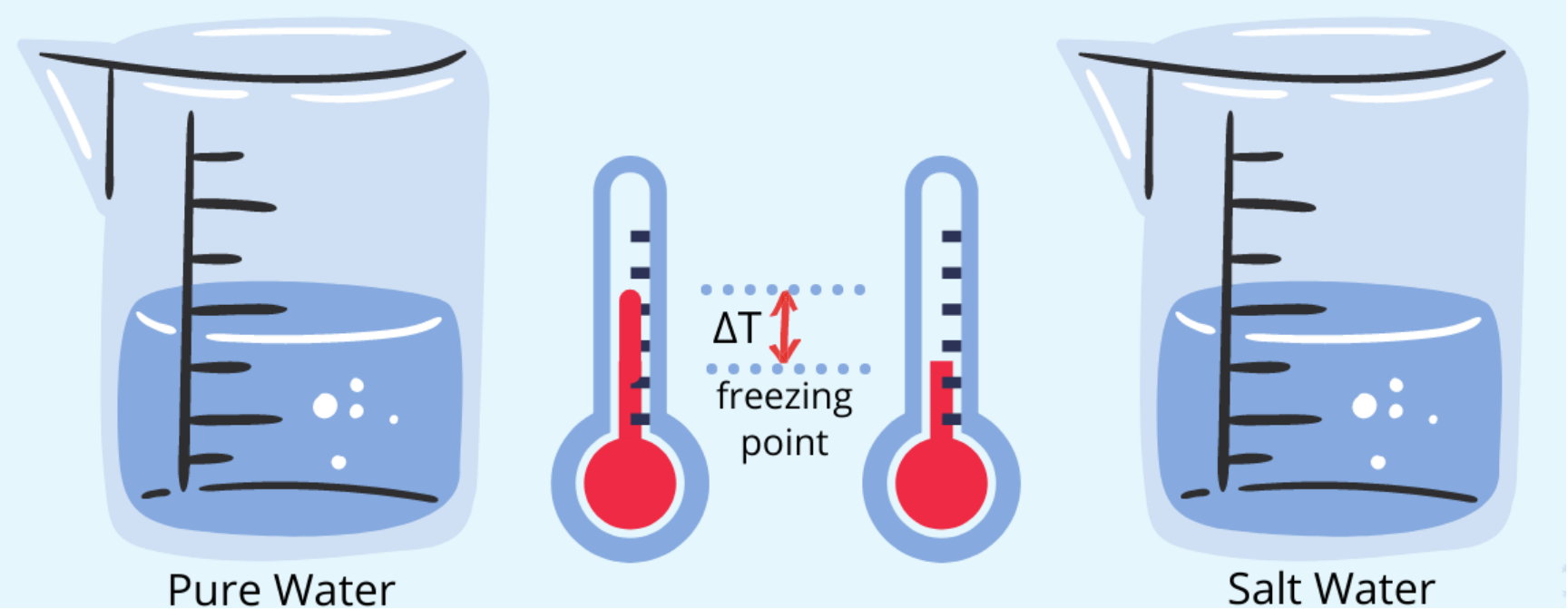
$$m = \frac{1000 \times K_b \times w}{\Delta T \times W}$$

MEASUREMENT

- Landsberger-Walker Method
- Cottrell's Method

Depression of Freezing Point

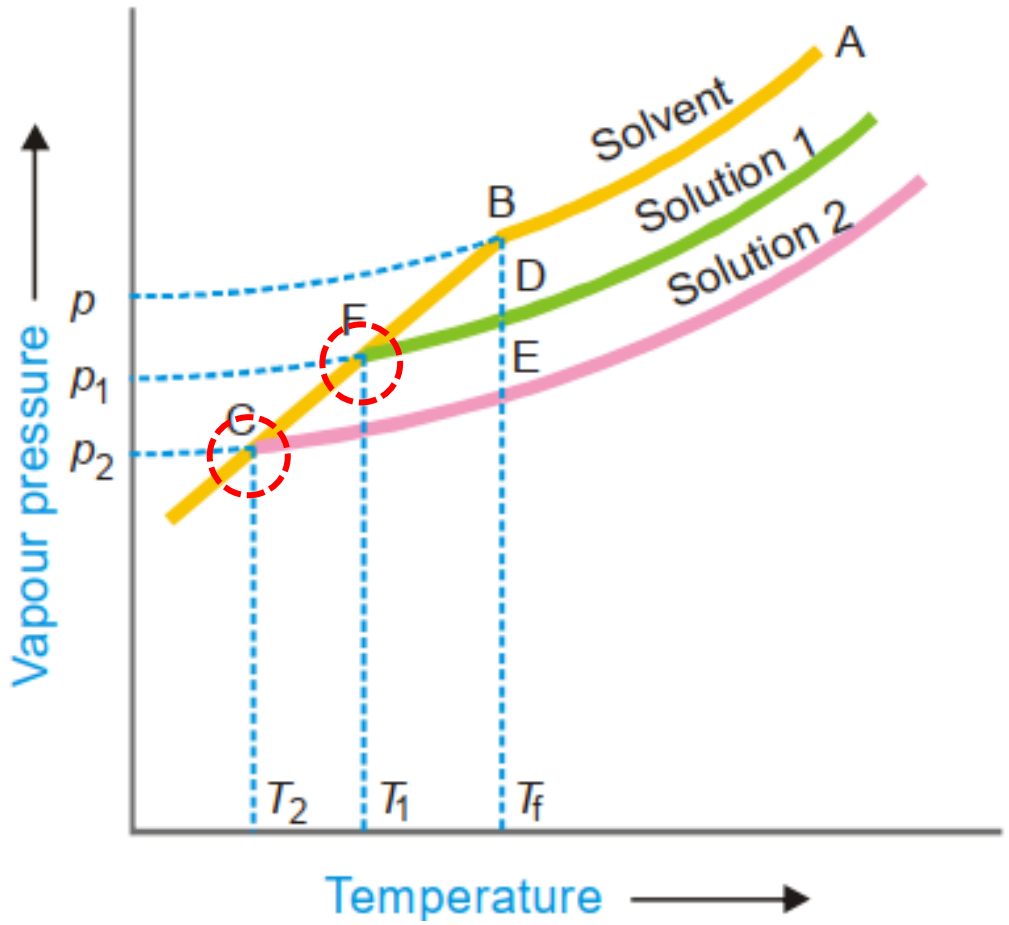
Lowers the freezing point of a liquid when another substance is dissolved in it



- **Salting of icy roads**

Vodka: Why it does not freeze in the freezer?

Depression of Freezing Point



T_f Equilibrium between the **liquid state** and the **solid state** of the solvent

The difference of the freezing point of the pure solvent and the solution is referred to as the Depression of freezing point.

$$T_f - T_1 = \Delta T$$

When more of the solute is added to the solution 1, we get a more concentrated solution (solution 2.) The vapour pressure of solution 2 meets the freezing-point at C, indicating a further lowering of freezing point to T_2.

For dilute solutions FD and CE are approximately parallel straight lines and BC is also a straight line. Since the triangles BDF and BEC are similar,

$$\frac{DF}{EC} = \frac{BD}{BE}$$

$$\frac{T_f - T_1}{T_f - T_2} = \frac{p - p_1}{p - p_2}$$

$$\Delta T \propto p - p_s$$

Depression of Freezing Point

Determination of Molecular Weight from Depression of Freezing point

Since p is constant for the same solvent at a fixed temperature, from (1) we can write

$$\Delta T \propto \frac{p - p_s}{p} \qquad \ldots(2)$$

But from Raoult's Law for dilute solutions,

$$\frac{p - p_s}{p} \propto \frac{wM}{Wm} \qquad \ldots(3)$$

Since M (mol mass of solvent) is constant, from (3)

$$\frac{p - p_s}{p} \propto \frac{w}{Wm} \qquad \ldots(4)$$

From (2) and (4)

$$\Delta T \propto \frac{w}{m} \times \frac{1}{W}$$

Depression of Freezing Point

Determination of Molecular Weight from Depression of Freezing point

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1}{W}$$

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

where K_f is a constant called Freezing-point constant or Cryoscopic constant or Molal depression constant.

Converted into kg

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1}{W/1000}$$

$$\Delta T = K_f \times \frac{w}{m} \times \frac{1000}{W}$$

Depression of Freezing Point

SOLVED PROBLEM 1. 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C. Calculate the molecular mass of the substance. ($K_f = 5.12°C\ mol^{-1}$)

SOLUTION

We can find the molecular mass by applying the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

In this case :

$$w = 0.440\,g$$
$$\Delta T = 0.567°C$$
$$W = 22.2\,g$$
$$K_f = 5.12°C\,mol^{-1}$$

Substituting the values, $$m = \frac{1000 \times 5.12 \times 0.440}{0.567 \times 22.2} = 178.9$$

$\therefore$ Molecular mass of substance = **178.9**

Depression of Freezing Point

SOLVED PROBLEM 2. 1.250 g of naphthalene was dissolved in 60 cm^3 of benzene and freezing point of the solution was found to be 277.515 K, while that of benzene 278.495 K. Density of benzene =0.880 g cm^{-3}, K_f=5.1 K per 1000 g benzene. Calculate the molecular mass of naphthalene.

SOLUTION

Let us apply the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

In this case

$$K_f = 5.1\,\text{K}$$
$$w = 1.250\,\text{g}$$
$$W = 60 \times 0.880\,\text{g} \qquad [\,W = d * V\,]$$
$$\Delta T = 278.495 - 277.515 = 0.980\,\text{K}$$

Substituting the values,

$$m = \frac{1000 \times 5.1 \times 1.250}{0.980 \times 60 \times 0.880} = 123$$

Thus the molecular weight of naphthalene is **123**.

Osmosis

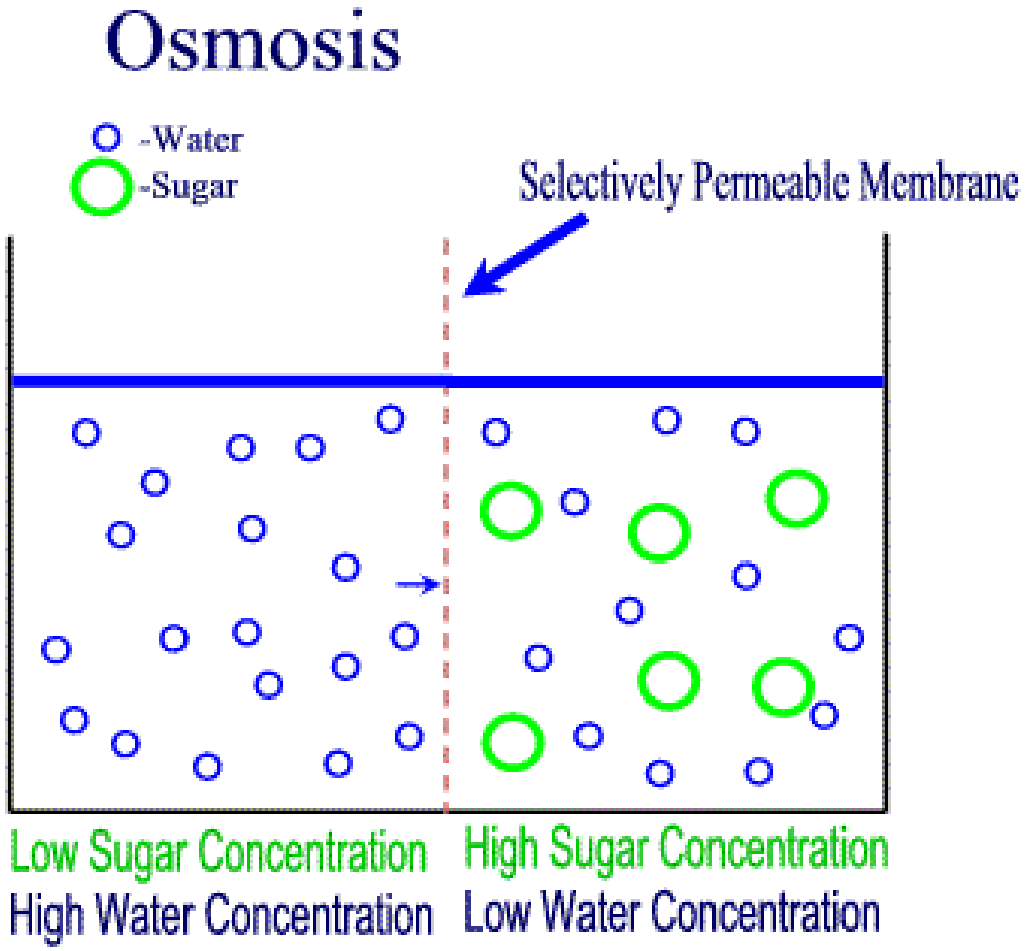
‘Osmos’ = to push



Osmosis is the movement of solvent molecules, usually water, across a semipermeable membrane from a region of lower solute concentration to a region of higher solute concentration, in order to equalize the concentration on both sides of the membrane.

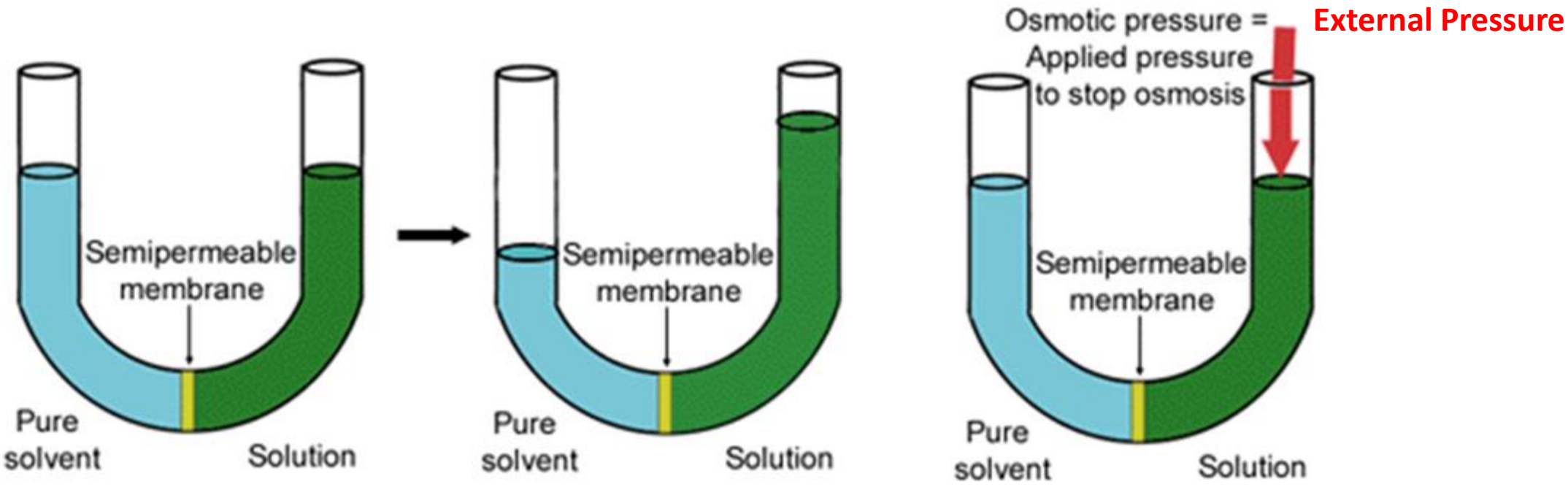
A membrane which is permeable to solvent and not to solute, is called a **semipermeable membrane**.

[Cupric Ferrocyanide Membrane]



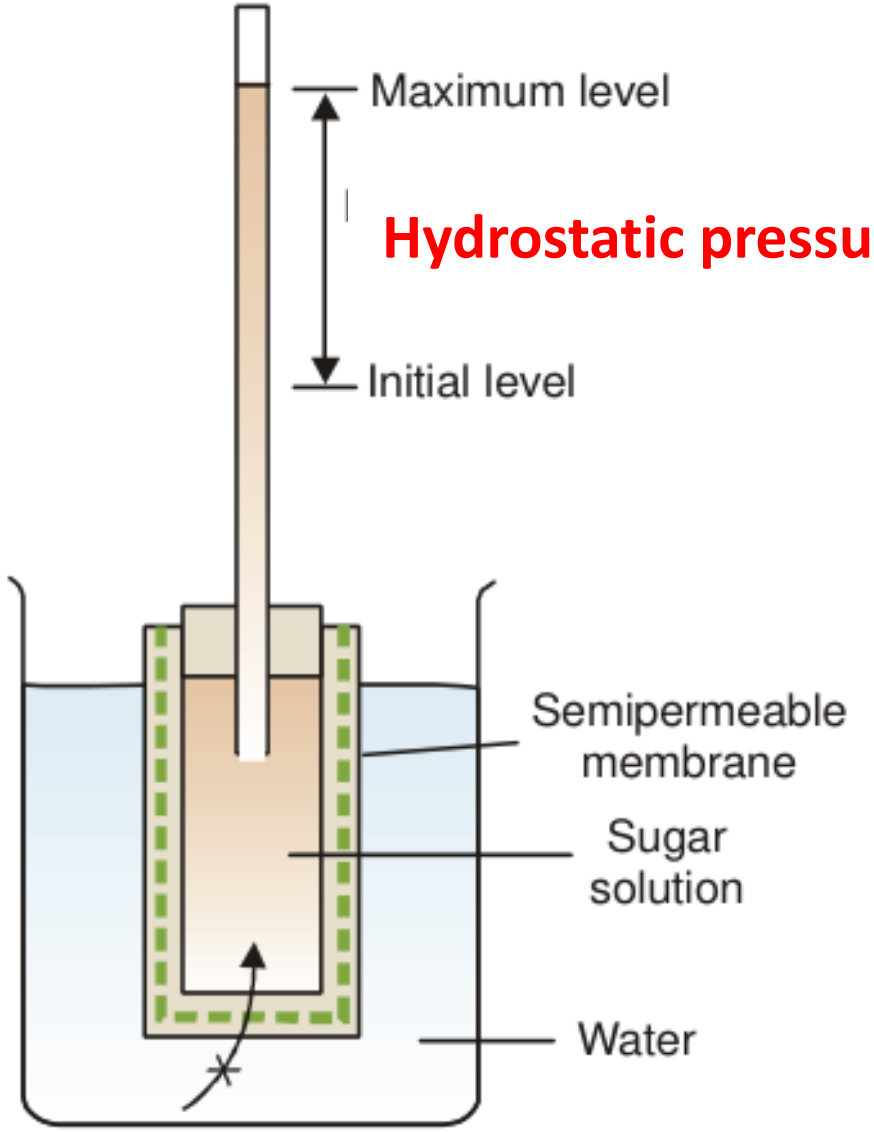
Osmotic Pressure

The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution



to arrest the movement of solvent

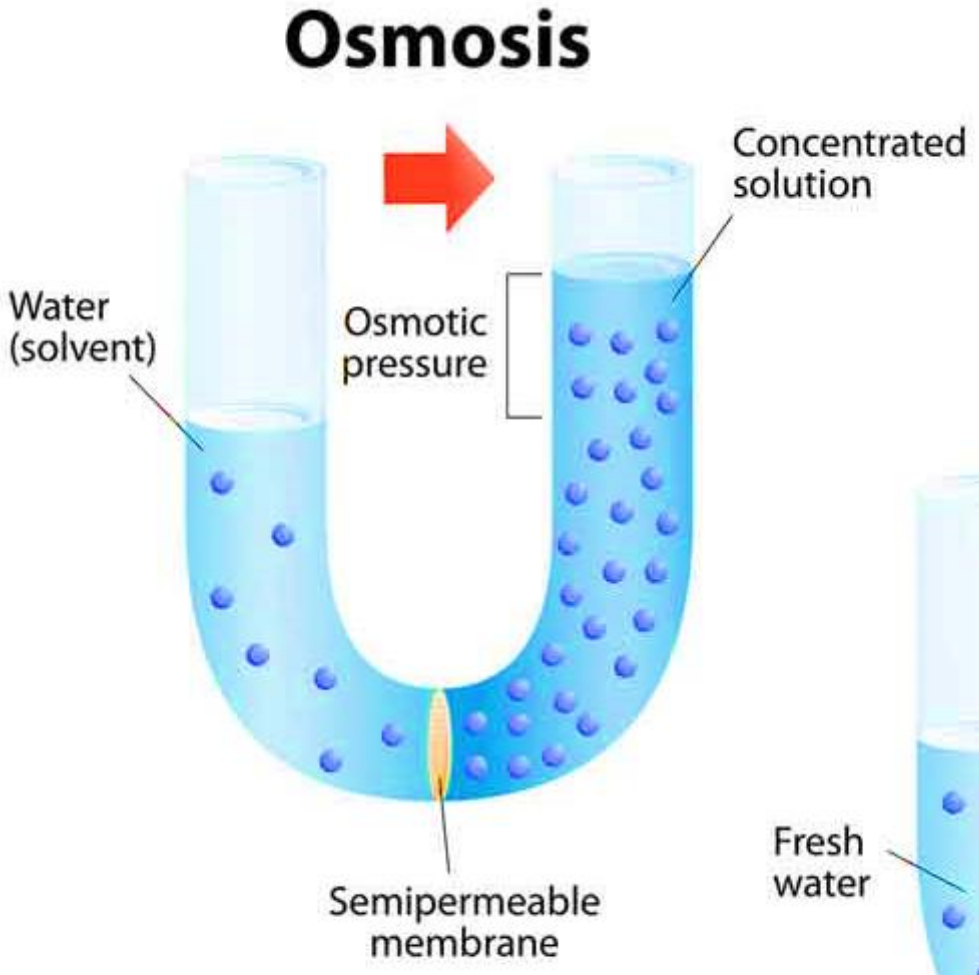
Osmotic Pressure

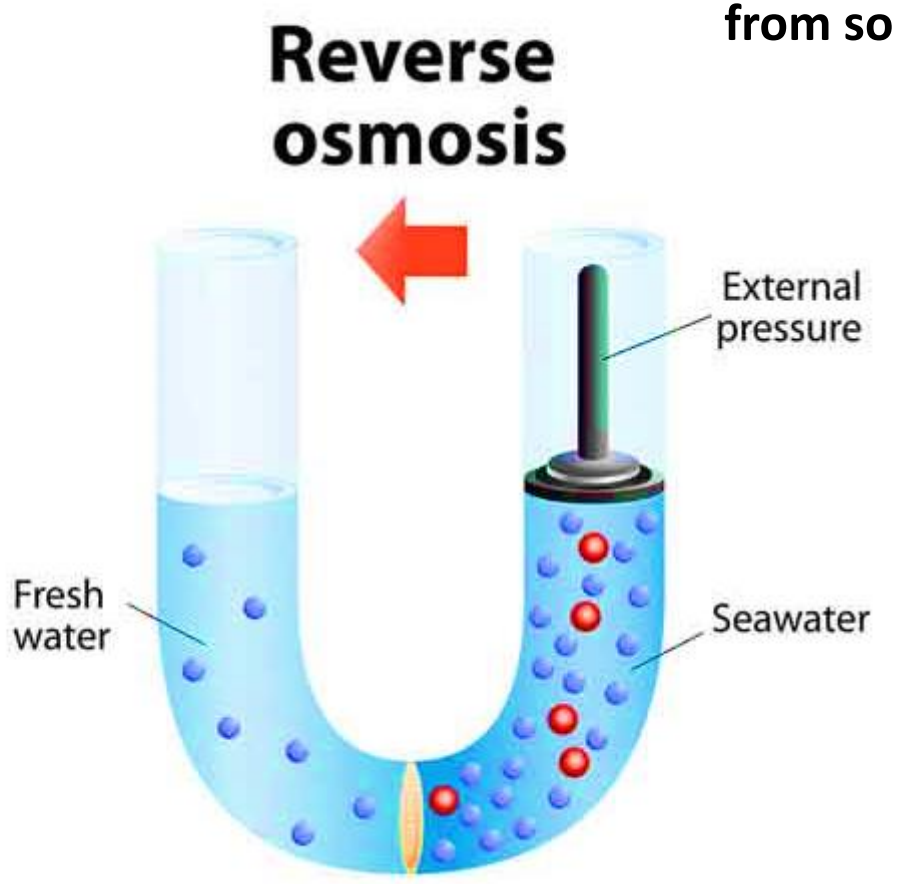


The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane, is called Osmotic Pressure.

Any real life example??

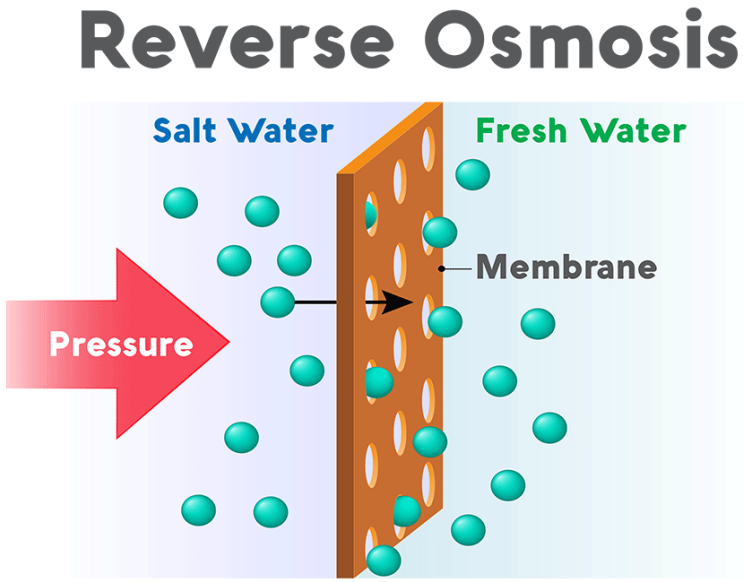
Reverse Osmosis





If pressure greater than osmotic pressure is applied, osmosis is made to proceed in the reverse direction to ordinary osmosis i.e., from solution to water.

Osmosis taking place from solution to fresh water



Reverse Osmosis

Desalination of Sea Water by Hollow-fibre Reverse Osmosis

Reverse osmosis is used for the desalination of sea water for getting fresh drinking water. This is done with the help of hollow fibres (nylon or cellulose acetate) whose wall acts as semipermeable membrane. A hollow-fibre reverse osmosis unit is shown in Fig. 16.18.

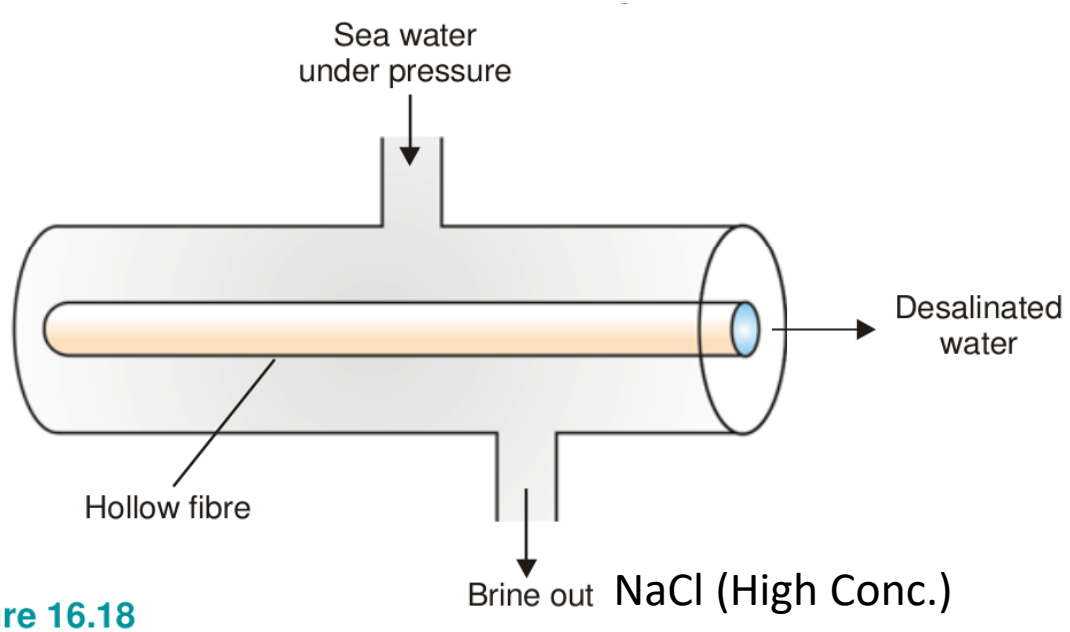


Figure 16.18
Desalination of sea water by reverse osmosis in a hollow fibre unit.

Water is introduced under pressure around the hollow fibres. The fresh water is obtained from the inside of the fibre. In actual practice, each unit contains more than three million fibres bundled together, each fibre is of about the diameter of a human hair.

Van't Hoff Laws of osmotic pressure

From a study of the experimental results obtained by Pfeffer, van't Hoff showed that for dilute solutions :

(a) The osmotic pressure of a solution at a given temp. is directly proportional to its concentration.

(b) The osmotic pressure of a solution of a given concentration is directly proportional to the absolute temp.

Boyle-van't Hoff Law for Solutions

If π is the osmotic pressure and C its concentration

we can write, **$\pi \propto C$**, if temperature is constant.

If the conc. of the solute is expressed in moles per litre and V is the vol. of the solution that contains 1 mol of solute

$$C = \frac{1}{V}$$

$$\pi \propto \frac{1}{V} \text{ at constant temperature}$$

This relationship is similar to the Boyle's law for gases and is known as the Boyle-van' t Hoff law for solutions.

Van’t hoff Laws of osmotic pressure

Charles-van’t Hoff Law for Solutions

If T is the absolute temperature, from the statement (b), we can write,

$$\pi \propto T, \text{ if concentration is constant}$$

This relationship is similar to the Charles’ Law for gases and is known as Charles-van’t Hoff law for solutions.

Van’t hoff Laws of osmotic pressure

Van’t Hoff Equation for Solutions

As shown above the osmotic pressure (π) of a dilute solution is inversely proportional to the volume (V) containing 1 mole of the solute and is directly proportional to the absolute temperature (T). This is,

$$\pi \propto \frac{1}{V} \quad \ldots(1)$$

$$\pi \propto T \quad \ldots(2)$$

Combining (1) and (2) van’t Hoff gave the general relationship

$$\pi V = R' T \quad \ldots(3)$$

where R' is a constant. He showed that this equation was parallel to the general *Gas Equation* ($PV = RT$), as the value of R' calculated from the experimental values of π, V, and T came out to be almost the same as of the *Gas constant, R*.

It is noteworthy that the *van’t Hoff Equation* (3) was derived for 1 mole of solute dissolved in V litres. If n moles of solute are dissolved in V litres of solution, this equation assumes the form

$$\pi V = n R T$$

Van’t hoff Laws of osmotic pressure

Avogadro-van’t Hoff Law for Solutions

Writing Van’t Hoff equation for two different dilute solutions,

$$\pi_1 V_1 = n_1 RT_1 \quad \ldots(1)$$

$$\pi_2 V_2 = n_2 RT_2 \quad \ldots(2)$$

where n_1 and n_2 are the number of moles (molecules) of the solute in V_1 and V_2 litres of the two solutions.

If $\pi_1 = \pi_2$ and $T_1 = T_2$, it follows from (1) and (2) that

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

Hence **when osmotic pressure and temperature are the same, equal volumes of solutions would contain equal number of moles (molecules) of the solute.** This relationship is analogous to Avogadro’s law of gases and is referred to as **Avogadro-van’t Hoff law for solutions.**

Van't hoff Laws of osmotic pressure

DETERMINATION OF MOLECULAR WEIGHT FROM OSMOTIC PRESSURE

Osmotic pressure measurements are less accurate and difficult to carry out. Therefore, this method is not widely used in the determination of molecular weights. The chief use of this method is in finding molecular weights of polymers *e.g.*, plastics, proteins, and starch, which have very high molecular weights.

Knowing the osmotic pressure of a given solution, the molecular weight of the solute can be calculated as follows from van't Hoff equation.

$$\pi V = nRT$$

$$= \frac{w}{M} RT$$

or
$$M = \frac{wRT}{\pi V}$$

where
M = molecular mass of the solute
w = amount of solute in grams
R = 0.0821 litre-atmosphere
T = $(t°C + 273)$ K
π = osmotic pressure in atmospheres
V = volume of solution in litres