

Colligative Properties

OSMOSIS AND OSMOTIC PRESSURE

Abbe' Nollet in 1748 observed an important colligative property known as osmotic pressure. He observed that when a solution is separated from a pure solvent by a semipermeable membrane, (which allows through it the flow of solvent molecules only), there is spontaneous flow of solvent into the solution. This phenomenon of spontaneous flow of a solvent through a semi permeable membrane into a solution or from a dilute solution to a concentrated one is termed as osmosis. By applying a certain pressure to the solution, osmosis can be prevented. The minimum pressure required to prevent osmosis is known as the osmotic pressure. Osmotic pressure of a solution is a colligative property and at a given temperature its magnitude depends only on the concentration of the solute. The nature of the membrane used in osmosis depends on the nature of the solvent and solute. Some common membranes include animal membranes, cellulose and a film of cupric ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ etc.

Osmosis differs from diffusion in the following respects:

Osmosis	Diffusion
1. There is a flow of solvent into the solution through a semipermeable membrane.	1. There is a flow of both the solvent and the solute and no semipermeable membrane is required.
2. Solvent flows from the solution of lower concentration to solution of higher concentration.	2. Solution flows from higher concentration to lower concentration until an equilibrium in concentration is achieved.

Osmosis can be easily understood with the help of an apparatus shown in Fig. 4. A semipermeable membrane (SPM) of pig bladder is tied over the end of a thistle funnel. It is then filled with a solution of sugar and is dipped into a beaker containing water (solvent). Due to osmosis, water will pass through the membrane and the level of sugar solution will rise until the hydrostatic pressure of the liquid column equalizes the osmotic pressure of the solution. This hydrostatic pressure of the liquid column is a measure of osmotic pressure and is equal to $h\rho g$ where h is the height upto which the solution level rises in the funnel and d is the density of the solution.

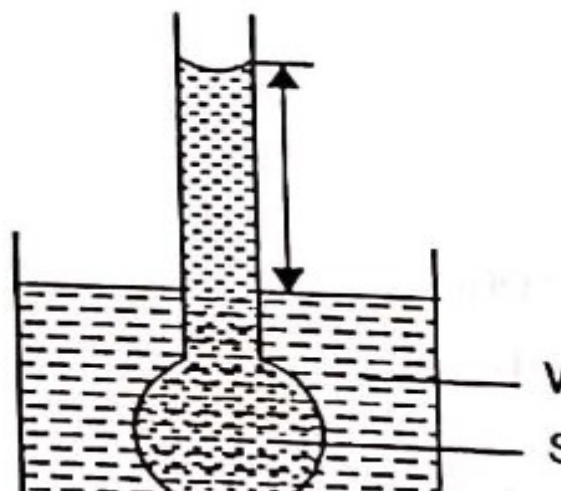


Fig. 4: Osmosis through a semipermeable membrane

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Another example may be given to illustrate the phenomenon of osmosis and osmotic pressure. Chamber A, The chamber is divided by a semipermeable membrane into two compartments. The left compartment is filled with the solution and the right one with the pure solvent. The solvent will pass through the semipermeable membrane into the solution compartment due to osmosis and will push the piston upward. The upward movement of the piston can be prevented by applying pressure on the piston to keep it in the original position. The mechanical pressure that must be applied on the solution side in order to prevent osmosis is the osmotic pressure of the solution. It is denoted by π . If the solvent in the above experiment is replaced by a solution of different concentration, osmosis will still occur from dilute solution towards concentrated solution. If the solutions have same concentration, no osmosis will occur and the solutions are said to be isotonic.

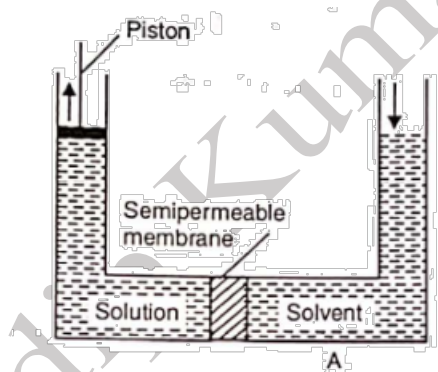


Fig. 5 Osmotic pressure of solutions

THERMODYNAMIC DERIVATION OF OSMOTIC PRESSURE OF A SOLUTION

When a solution separated from the pure solvent by a semipermeable membrane is at equilibrium, the chemical potential of the solvent must be the same on both sides of the membrane. If $\mu_A^0(P)$ is the chemical potential of pure solvent and $\mu_A(P + \pi, X_1)$ the chemical potential of the solvent in the solution at a given temperature the equilibrium condition is

$$\mu_A^0(P) = \mu_A(P + \pi, X_1)$$

$$\text{For ideal solution} \quad \mu_A(P + \pi, X_1) = \mu_A^0(P + \pi) + RT \ln X_1$$

$$\text{So} \quad \mu_A^0(P) = \mu_A^0(P + \pi) + RT \ln X_1 \quad \dots\dots\dots(35)$$

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The chemical potential of the solvent under a pressure of $P + \pi$ is now expressed in terms of the chemical potential under a pressure P . From the fundamental equation at constant temperature, we have $d\mu_A^0 = V_A^0 dP$

Integrating, we get
$$\int_P^{P+\pi} \mu_A^0(P + \pi, X_1) - \mu_A^0(P) = \int_P^{P+\pi} V_A^0 dP \quad \dots\dots\dots(36)$$

Hence, from equation (34), we obtain

$$\int_P^{P+\pi} V_A^0 dP + RT \ln X_1 = 0 \quad \dots\dots\dots(37)$$

In Eq. (37), V_A^0 is the molar volume of the pure solvent. If the solvent is incompressible, then V_A^0 is independent of pressure.

Then from Eq. (37), we get $V_A^0 \pi = -RT \ln X_1 = -RT \ln(1 - X_2) = RT X_2$ (as $\ln(1-X_2) \approx -X_2$)

where X_2 is the mole fraction of the solute in the solution.

For dilute solutions

$$X_2 = \frac{n_2}{n_1} \quad \text{(As } n_1 \gg n_2 \text{)}$$

Hence
$$\pi V_A^0 = n_2 \quad \dots\dots\dots(38)$$

n_1 and n_2 being the number of moles of the solvent and solute in the solution respectively. Equation (38) can also be expressed as

$$\pi = \left(\frac{n_2}{V_A^0} \right) RT = CRT \quad \dots\dots\dots(39)$$

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where $C (=n_2/ V^0_A)$ is the molar concentration of the solute in the solution.

From the above experimental results it is clear that osmotic pressure of a solution depends both on temperature and the concentration.

From Eqs. (38) and (39) one can say that the osmotic pressure of a solution is equal to the pressure it would exert if it were a gas occupying the same volume as that occupied by the solution at the same temperature.

The van't Hoff Eqs. (38) and (39) clearly show that the osmotic pressure of a solution at a given temperature depends only on concentration of the solute and is independent of its nature.

Problem : An aqueous solution contains $2 \times 10^{-2} \text{ kg}$ of glucose per dm^3 . Assuming the solution to be ideal, calculate its osmotic pressure at 298 K.

Solution: We know, $\pi = n RT /V$

where n is the number of moles of solute in $V \text{m}^3$ of the solution.

$$\text{Therefore } n = \frac{2.0 \times 10^{-2} \text{ kg}}{1.80 \times 10^{-1} \text{ kg mol}^{-1}} = \frac{1}{9} \text{ mol}$$

$$\text{Hence, } \pi = \left(\frac{1}{9} \text{ mol} \right) \frac{(0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}) (298 \text{ K})}{(1 \text{ dm}^3)}$$

$$= 2.718 \text{ atm}$$

Problem Calculate the osmotic pressure of an aqueous solution containing 1g each of sucrose and glucose per dm^3 at 300 K. If this pressure were measured and it were not known that the solute was a mixture, what molar mass would be expected?

Solution: We know that, $\pi = CRT$

$$\text{Here } C = C_1 + C_2$$

$$C_1 = 1/342$$

$$C_2 = 1/180$$

$$\pi = (1/180 + 1/342) RT = 0.2087 \text{ atm}$$



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$$\pi = (2/M) RT$$

$$M = (2RT)/\pi = (2 \times 0.0821 \times 300) / 0.2087 = 235.75 \text{ kgmol}^{-1}$$

The molar mass would be average molar mass depending upon their concentrations.

RELATIONSHIP BETWEEN DIFFERENT COLLIGATIVE PROPERTIES

The expressions of colligative properties, viz, the relative lowering of vapour pressure, the elevation of boiling point, the depression of freezing point and osmotic pressure are expressed in a common term, mole fraction of the solute i.e.,

$$X_2 = \frac{P^0 - P_s}{P^0} = \frac{\Delta H_{\text{vap}, m} \Delta T_b}{RT_0^2} = \frac{\Delta H_{\text{fus}, m} \Delta T_f}{RT_0^2} = \frac{\pi \bar{V}_A}{RT} \dots\dots\dots(40)$$

Equation (40) can be used to find the value of a colligative property if the value of any other colligative property is known.