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Osmosis

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The transport of solvent through a semipermeable membrane separating two solutions of different solute concentration. The solvent diffuses from the solution that is dilute in solute to the solution that is concentrated. The phenomenon may be observed by immersing in water a tube partially filled with an aqueous sugar solution and closed at the end with parchment. An increase in the level of the liquid in the solution results from a flow of water through the parchment into the solution. The process occurs as a result of a thermodynamic tendency to equalize the sugar concentrations on both sides of the barrier. The parchment permits the passage of water, but hinders that of the sugar, and is said to be semipermeable. Specially treated collodion and cellophane membranes also exhibit this behavior. These membranes are not perfect, and a gradual diffusion of solute molecules into the more dilute solution will occur. Of all artificial membranes, a deposit of cupric ferrocyanide in the pores of a fine-grained porcelain most nearly approaches complete semipermeability.

The walls of cells in living organisms permit the passage of water and certain solutes, while preventing the passage of other solutes, usually of relatively high molecular weight. These walls act as selectively permeable membranes, and allow osmosis to occur between the interior of the cell and the surrounding media.

The flow of liquid through such a barrier may be stopped by applying pressure to the liquid on the side of higher solute concentration. The applied pressure required to prevent the flow of solvent across a perfectly semipermeable membrane is called the osmotic pressure and is a characteristic of the solution.

Osmotic pressure

The driving force for osmosis is the decrease in Gibbs free energy accompanying the dilution of the solution by the transfer of solvent to the solution. With G_1^0 representing the molar free energy of the pure solvent, the molar free energy of solvent in the solution is shown in Eq. (1),

$$G_1 = G_1^0 + RT \ln a_1 \quad (1)$$

where R is the molar gas law constant, $8.314 \text{ J mole}^{-1} \text{ K}^{-1}$, and a_1 is the solvent activity in the solution. This is conventionally taken as unity for the pure solvent, and in ideal solutions, as the mole fraction, x_1 . The pressure that must be applied to the solution phase to increase the solvent free energy to that of the pure solvent is the osmotic pressure, π , of

the solution. The rate at which the free energy of a system is changed at a fixed temperature by pressure is given by the basic thermodynamic relationship (2).

$$(\delta G / \delta P)_T = V \quad (2)$$

For an incompressible liquid solution, the osmotic pressure is, then, shown in Eq. (3),

$$\pi = -(RT/V_1) \ln a_1 \quad (3)$$

where V_1 is the molar volume of solvent. Equation (3) represents the fundamental relationship between the osmotic pressure and solution thermodynamics. In an ideal solution containing n_1 moles of solvent and n_2 moles of solute, the solvent activity is $a_1 = x_1 = n_1/(n_1+n_2)$. In terms of the solute, the solvent activity is $(1 - x_2)$, where x_2 is the solute mole fraction, $n_2/(n_1 + n_2)$. For dilute solutions, $\ln a_1 = \ln (1 - x_2) \sim -x_2$ since $n_1 \gg n_2$. Then Eq. (3) becomes Eq. (4),

$$\pi = n_2 RT / (n_1 V_1) = n_2 RT / V = cRT \quad (4)$$

where $n_1 V_1$ is replaced by the total volume, V . Equation (4) is recognized as identical in form to the ideal gas law, in which c represents the solute concentration in moles L⁻¹. As applied to osmotic phenomena, Eq. (4) is called the van't Hoff equation. Measurements of osmotic pressure made early in the twentieth century on dilute sucrose solutions using copper ferrocyanide membranes confirm the applicability of (4). For example, a 0.0291 molar aqueous sucrose solution at 15.6°C exhibited an osmotic pressure of 0.684 atm compared with the calculated value of 0.689 atm.

Solution properties reflecting changes in solvent free energy caused by a nonvolatile solute include vapor-pressure lowering, boiling-point elevation, freezing-point depression, as well as osmotic pressure. Of these, the last is the most sensitive to solute concentration. Membrane requirements, however, limit its usefulness in studying solution thermodynamics.

An important application of measuring osmotic pressure is determining a polymer's molar mass. The polymer sample is dissolved in an organic solvent or in a mixture of solvents, and the osmotic pressure is measured using a pretreated cellophane film membrane. An osmometer is used in which the pressure is measured in terms of the height to which liquid rises in a solution cell capillary above that in the surrounding solvent. In accounting for nonideality, Eq. (3) is used in a modified form (5),

$$\pi/c^* = RT/M + Bc^* + Cc^{*^2} \quad (5)$$

where c^* is the concentration in g/L, and M , the molar mass in g/mole. B and C are correction terms analogous to gas-phase virial coefficients. RT/M is obtained as a limit of π/c^* as c^* approaches zero. The molar mass obtained is a number average of the polymer molar mass spectrum of the sample.

Aside from the inorganic-type membranes, which are formed by deposition of the salt in a porous matrix, membranes suitable for measurements of osmotic pressures in aqueous systems are not available. A number of synthetic polymeric films, which allow the passage of water and small ionic or molecular species, are sufficiently strong to act as selectively permeable membranes in aqueous solutions. These have been successfully used to study, for example, micellar interactions in salt and buffered media. Although the pressures measured are not true osmotic pressures, thermodynamic solute data may be obtained through a redefined G^0_1 and use of standard Gibbs-Duhem activity relationships. See also:

[Free energy \(/content/free-energy/271300\)](#)

Reverse osmosis

Just as the osmotic pressure is that pressure which when applied to the solution phase will prevent the solvent from passing through a semipermeable membrane into the solution, the application of greater pressure will cause solvent to pass from the solution into the pure solvent, or reverse osmosis. Reverse osmosis has long been considered for water purification. Home units for improving the quality of a water supply are effectively pressure filtration devices capable of removing colloidal impurities but are largely ineffective in reducing salt concentrations. On a larger scale, polymeric films or ceramic porous membranes, for example, of aluminum oxide, are described in terms of the fraction of salt rejection as a measure of efficiency. The prospect of using reverse osmosis for desalinating seawater is energetically attractive but technically difficult to realize. The osmotic pressure of seawater is approximately 23 atm. Membrane design and mechanics would have to allow for use at substantially higher pressures with large volumes of water, over long periods. With advances in membrane engineering, it is possible that reverse osmosis could be used to purify ocean water. See also: [Edema \(/content/edema/213100\)](#); [Osmoregulatory mechanisms \(/content/osmoregulatory-mechanisms/478300\)](#); [Plant-water relations \(/content/plant-water-relations/525300\)](#); [Solution \(/content/solution/635800\)](#)

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