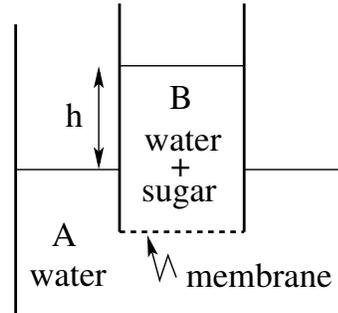


Osmotic pressure [tln26]

Consider a dilute solution. It consists of a solvent (e.g. water) and a solute (e.g. sugar). System A (pure solvent) is separated from system B (solution) by a membrane that is permeable to the solvent only. At thermal equilibrium, this causes an excess pressure in system B, which is called *osmotic pressure*.



System A: pressure p_0 , concentrations $x_S = 0$, $x_W = 1$.

System B: pressure $p = p_0 + \pi$, concentrations $x_S = 1 - x_W \ll 1$.

Observed osmotic pressure: $\pi = \rho_B g h$, where ρ_B is the mass density of B.

The osmotic pressure is a consequence of the requirement that the solvent on either side of the membrane must be in chemical equilibrium:

$$\mu_W(T, p, x_W) = \mu_W(T, p_0, 1).$$

(1) Effect of solute concentration on chemical potential:

$$\Delta\mu_W^{(1)} \equiv \mu_W(T, p, x_W) - \mu_W(T, p, 1) = RT \ln x_W = RT \ln(1 - x_S) \simeq -RT x_S.$$

(2) Effect of pressure on chemical potential: (use $n_W = n x_W$, $n_S = n x_S$)

$$\begin{aligned} \Delta\mu_W^{(2)} \equiv \mu_W(T, p, 1) - \mu_W(T, p_0, 1) &= \left(\frac{\partial \mu_W}{\partial p} \right)_{T, n_W} \Delta p = \left(\frac{\partial V}{\partial n_W} \right)_{T, p} \Delta p \\ &= \frac{V}{n_W} \Delta p \simeq \frac{V \pi}{n}. \end{aligned}$$

At thermal equilibrium: $\Delta\mu_W^{(1)} + \Delta\mu_W^{(2)} = 0 \Rightarrow \frac{V \pi}{n} - RT x_S = 0$.

Van't Hoff's law for osmotic pressure: $\pi = \frac{RT n_S}{V}$.