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 named *osmotic pressure*.

The number density n_S of solvent in system B is assumed to be much smaller than the number and n_W of solute: $n_S \ll n_W$ (dilute solution).



Condition of chemical equilibrium for solute across membrane:

$$\mu_W^{(A)} = \mu_W^{(B)} \quad \Rightarrow \ \Delta \mu_W = 0.$$

The solute chemical potential is affected in two ways:

(1) Effect of change in solvent concentration: Use the result of [tex173].

$$\Delta \mu_W^{(1)} = RT \ln\left(\frac{n_W}{n_W + n_S}\right) = RT \ln\left(\frac{n - n_S}{n}\right) \simeq -RT \frac{n_S}{n}$$

(2) Effect of change in pressure:

Use a Maxwell relation inferred from $dG = -SdT + Vdp + \mu dn$:

$$\left(\frac{\partial \mu_W}{\partial p}\right)_{T,n_W} = \left(\frac{\partial V}{\partial n_W}\right)_{T,p} \simeq \frac{V}{n} \quad \Rightarrow \ \Delta \mu_W^{(2)} = \frac{V}{n} \Delta p.$$

At thermal equilibrium: $\Delta \mu_W^{(1)} + \Delta \mu_W^{(2)} = 0 \implies \frac{V\Delta p}{n} - RT \frac{n_S}{n} = 0.$ Van't Hoff's law for osmotic pressure: $\Delta p \doteq \pi = \frac{RTn_S}{V}.$

Application shown: $\pi = \rho g h$, where ρ is the mass density of the solution.