

S2.C. Osmotic Pressure in Dilute Solutions

Osmosis is demonstrated by the setup shown in Fig.2.16.

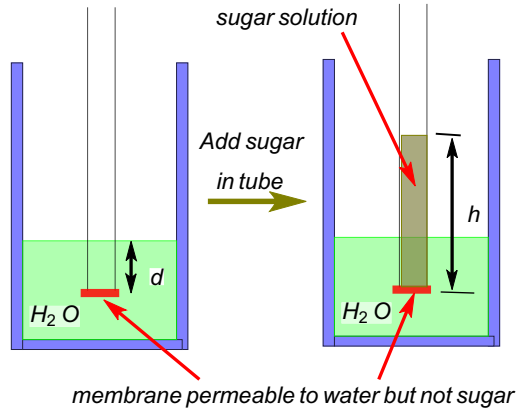


Fig.2.16.

To begin, a tube with one end closed with a membrane permeable only to water is immersed into a beaker of water. The water levels in and outside the tube are equal. If sugar is added inside the tube, level of the sugar solution will rise. The phenomenon is called **osmosis**.

With reference to Fig.2.16, the pressures at the membrane after equilibrium is established are

$$P_{\text{inside}} = P_{\text{atm}} + \rho_s h g = P_{\text{outside}} = P_{\text{atm}} + \rho_w d g \quad (2.219a)$$

where

P_{atm} = atmospheric pressure

ρ_s = density of sugar solution

ρ_w = density of water

g = acceleration of gravity

h = height of sugar solution

d = depth of membrane

The **osmotic pressure** is the excess pressure caused by the sugar solute,

$$\begin{aligned} \pi &= P_{\text{inside}} - P_{\text{outside}} \\ &= (\rho_s h - \rho_w d) g \\ &\approx \rho_s (h - d) g \quad \text{for dilute solution } (\rho_s \approx \rho_w) \end{aligned} \quad (2.219b)$$

An equivalent setup of the phenomenon is shown in Fig.2.17, where the role of π is depicted more clearly.

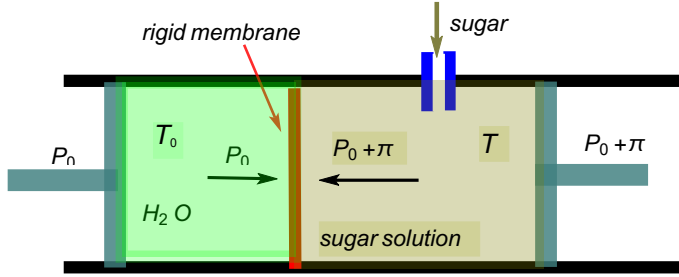


Fig.2.17.

The Gibbs free energy for pure water is defined as

$$dG_{H_2O} = -SdT + VdP + \mu_w^{(0)} dn_w \tag{2.219b}$$

For the sugar solution,

$$dG_{sol} = -SdT + VdP + \mu_w dn_w + \mu_s dn_s \tag{2.219}$$

where the subscripts w & s denote the water and sugar components, respectively.

From the Gibbs-Duhem equation [see (2.62) of §2.E], we see that the chemical potentials are intensive variables that depend only on T, P , & the **molar fractions** [see (2.65)].

$$x_j = \frac{n_j}{n} \quad n = \sum_k n_k \tag{2.220a}$$

$$\rightarrow \sum_j x_j = 1 \tag{2.220b}$$

Owing to (2.220b), only one molar fraction is independent in a two-component system.

Consider now the setup in Fig.2.17. Since the membrane is rigid and impermeable to sugar, the conditions for thermodynamic equilibrium are

$$T = T_0 \quad \text{and} \quad \mu_w^{(0)}(T_0, P_0) = \mu_w(T, P_0 + \pi, x_s) \tag{2.221}$$

where we have chosen x_s as the independent molar fraction.

Using the results of Ex.2.9 in §2.H.2, we set

$$G_{sol} = n_w \mu_w^{(0)}(T, P) + n_s \mu_s^{(0)}(T, P) + RT n_w \ln x_w + RT n_s \ln x_s + \lambda \frac{n_w n_s}{n} \tag{2.222}$$

where $\mu_s^{(0)}$ is the chemical potential for pure sugar. We shall assume $\lambda < 0$ (i.e., attractive interactions)

so that the condition $T > \frac{\lambda}{2R}$ for a single phase (i.e., no sugar precipitation) is satisfied for all T [see Figure in Ex.2.9].

Note: By definition, μ_j is the increase of the system energy if we add 1 mole of the type j molecules into the system. If $\lambda < 0$, then (2.222) shows that this energy change is reduced if $n_k \neq 0$ for $k \neq j$. Therefore, the interaction between types j & k molecules must be attractive.

Using (2.111) of §2.F.4 and

$$\frac{\partial x_k}{\partial n_j} = \frac{\partial}{\partial n_j} \left(\frac{n_k}{n} \right) = \frac{\delta_{jk}}{n} - \frac{n_k}{n^2} = \frac{\delta_{jk} - x_k}{n}$$

we have

$$\mu_w(T, P, x_s) = \left(\frac{\partial G_{sol}}{\partial n_w} \right)_{T, P, n_s}$$

$$\begin{aligned}
&= \mu_W^{(0)}(T, P) + RT \left[\ln x_W + \frac{n_W}{x_W} \left(\frac{1 - x_W}{n} \right) \right] + RT \frac{n_s}{x_s} \left(-\frac{x_s}{n} \right) + \lambda \left(\frac{n_s}{n} - \frac{n_W n_s}{n^2} \right) \\
&= \mu_W^{(0)}(T, P) + RT \ln x_W + \lambda (x_s - x_W x_s) \\
&= \mu_W^{(0)}(T, P) + RT \ln (1 - x_s) + \lambda x_s^2 \tag{2.223}
\end{aligned}$$

$$= \mu_W^{(0)}(T, P) - x_s RT + O(x_s^2) \quad [\text{For dilute solution.}] \tag{2.224}$$

Using the Maxwell relation (2.114) of §2.F.4, we have, for pure water,

$$\begin{aligned}
\left(\frac{\partial \mu_W^{(0)}}{\partial P} \right)_{T, n_W} &= \left(\frac{\partial V}{\partial n_W} \right)_{T, P} \\
&= v_W^{(0)} = \text{molar volume of pure water.}
\end{aligned}$$

$$\rightarrow \mu_W^{(0)}(T, P) = \int dP v_W^{(0)} + c(T) \quad [c(T) = \text{arbitrary function of } T.]$$

Since water is highly incompressible, $v_W^{(0)}$ is nearly independent of P . Hence,

$$\begin{aligned}
\mu_W^{(0)}(T, P) &\approx \mu_W^{(0)}(T, P_0) + v_W^{(0)}(P - P_0) \\
&= \mu_W^{(0)}(T, P_0) + v_W^{(0)} \pi \tag{2.225}
\end{aligned}$$

so that (2.224) becomes

$$\mu_W(T, P, x_s) \approx \mu_W^{(0)}(T, P_0) + v_W^{(0)} \pi - x_s RT$$

Putting in the equilibrium condition (2.221), we have

$$\begin{aligned}
\pi &= \frac{x_s}{v_W^{(0)}} RT \\
&= \frac{n_s}{V^{(0)}} RT \tag{2.225a}
\end{aligned}$$

where

$$V^{(0)} = n v_W^{(0)}$$

For a dilute solution,

$$V = n_W v_W^{(0)} + n_s v_s^{(0)} \approx n v_W^{(0)}$$

so that (2.225a) becomes

$$\pi \approx \frac{n_s}{V} RT \tag{2.226}$$

which is known as the **van't Hoff's law**. Thus, the solute acts like an ideal gas inside the solution with a partial pressure π . This is to be expected since the interactions between the solute and the solvent can be ignored for dilute solutions [see (2.223-4)].

Ex.2.10.

The osmotic pressure π of a solution containing n_{suc} moles of **sucrose** ($C_{12}H_{22}O_{11}$) and 1 kg of water (H_2O) is measured at $T = 303 \text{ K}$ (30°C). The following result was obtained:

n_{suc} [mole]	π_{exp} [10^5 Pa]
0.1	2.53
0.2	5.17
0.3	7.81

(1)

Compute π using van't Hoff's law and compare the result with experiment.

Answer

The molecular weight of water (H_2O) is

$$M_w = (2 \times 1 + 16) \text{ g/mol} = 18 \text{ g/mol}$$

Therefore, 1 kg of water contains

$$n_w = \frac{1000}{18} \text{ mols} \approx 55.6 \text{ mols}$$

Since the density of water is

$$\rho_w \approx 1 \text{ g/cm}^3 = 10^6 \text{ g/m}^3$$

so that its molar volume is

$$v_w = \frac{M_w}{\rho_w} \approx 18 \times 10^{-6} \text{ m}^3/\text{mol}$$

The van't Hoff's law (2.226) then becomes

$$\begin{aligned} \pi &= \frac{n_{\text{suc}}}{n_w v_w} R T && (T = 303 \text{ K}, R \approx 8.31 \text{ J/K} \cdot \text{mol}) \\ &\approx \frac{n_{\text{suc}}}{55.6 \times 18 \times 10^{-6}} \times 8.31 \times 303 \\ &\approx 2.52 \times 10^6 n_{\text{suc}} \text{ [Pa]} \end{aligned} \quad (2)$$

which gives

n_{suc} [mole]	π_{vH} [10^5 Pa]	$\frac{\pi_{\text{vH}} - \pi_{\text{exp}}}{\pi_{\text{vH}}} \times 100\%$
0.1	2.52	-0.56%
0.2	5.03	-2.7%
0.3	7.55	-3.5%

Excellent agreements are found.

Code

$$a = \frac{8.31 \times 303}{55.6 \times 18 \times 10^{-6}}$$

$$\pi_{\text{vH}} = \{.1, .2, .3\} a$$

$$\pi_{\text{exp}} = \{2.53, 5.17, 7.81\} 10^5$$

$$2.51592 \times 10^6$$

$$\{251592., 503183., 754775.\}$$

$$\{253000., 517000., 781000.\}$$

$$\pi_{\text{vH}} - \pi_{\text{exp}}$$

$$\{-1408.27, -13816.5, -26224.8\}$$

$$\frac{\pi_{\text{vH}} - \pi_{\text{exp}}}{\pi_{\text{vH}}} 100$$

$$\{-0.559746, -2.74583, -3.47452\}$$