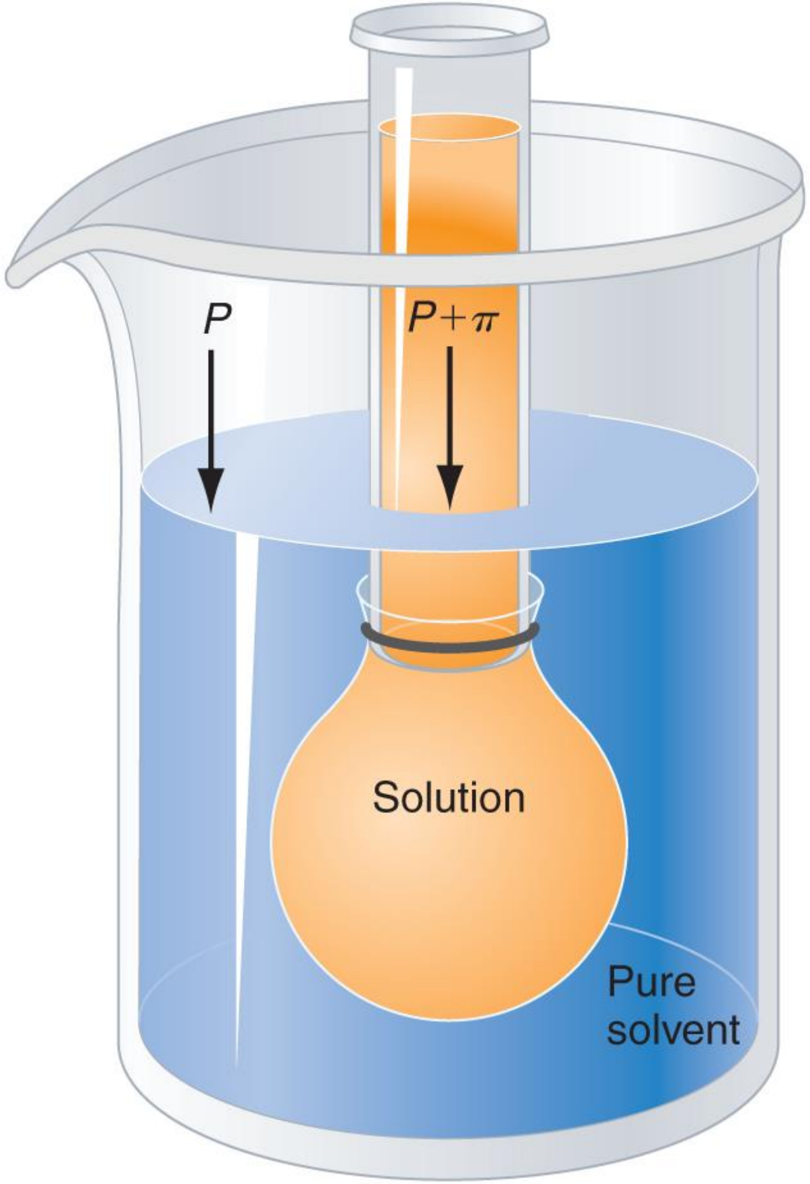
Ideal and Real Solutions

8 The Osmotic Pressure

- *Some membranes allow the passage of small molecules like water, yet do not allow larger molecules like sucrose to pass through them*
- *Such a semipermeable membrane is an essential component in medical technologies such as kidney dialysis*
- *The process in which the solvent diffuses through a membrane and dilutes a solution is known as* ***osmosis***
- *The amount by which the pressure in the solution is raised is known as the* ***osmotic pressure***



8 The Osmotic Pressure

- *To understand the origin of the osmotic pressure, denoted by π, the equilibrium condition is applied to the contents of the sac and the surrounding solvent*

$$\mu_{solvent}^{solution}(T, P + \pi, x_{solvent}) = \mu_{solvent}^{*}(T, P)$$

- *Because μ for the solvent is lower in the solution than in the pure solvent, only an increased pressure in the solution can raise its sufficiently to achieve equilibrium with the pure solvent*

$$\mu_{solvent}^{solution}(T, P + \pi, x_{solve}$$

$$\pi V_m^{*} + RT \ln x_{solvent} = 0$$

$$RT \ln x_{solvent}$$

8 The Osmotic Pressure

$$\pi V_m^* + RT \ln x_{solvent} = 0$$

$$\ln x_{solvent} = \ln(1 - x_{solute}) \approx -x_{solute} = -\frac{n_{solute}}{n_{solute} + n_{solvent}} \approx -\frac{n_{solute}}{n_{solvent}}$$

$$\pi = \frac{n_{solute} RT}{V}$$

9 Real Solutions Exhibit Deviations from Raoult's Law

- *Imagine a huge volume of pure water at 25°C.*
- *When a further 1 mol H_2O is added, the volume increases by 18 cm^3. So, we can report that the molar volume of water is 18 cm^3 mol^{-1}.*
- *When we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm^3.*
- *The quantity 14 cm^3 mol^{-1} is the partial molar volume of water in pure ethanol.*
- *In general, the partial molar volume of a substance 1 in a mixture is the change in volume per mole of 1 added to a large volume of the mixture.*

$$\overline{V}_1(P, T, n_1, n_2) = \left(\frac{\partial V}{\partial n_1}\right)_{P, T, n_2}$$

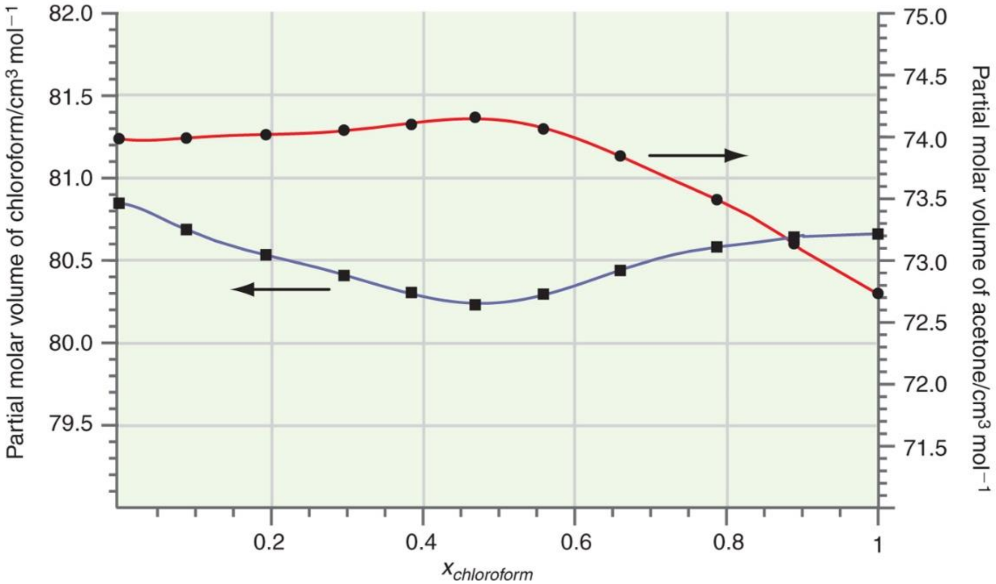
9 Real Solutions Exhibit Deviations from Raoult's Law

- *With this definition, the composition of a mixture is changed by the addition of* dn_1 *of* 1 *and* dn_2 *of* 2

$$dV = \overline{V_1} dn_1 + \overline{V_2} dn_2$$

$$V = n_1 \overline{V}_1(P, T, n_1, n_2) + n_2 \overline{V}_2(P, T, n_1, n_2)$$

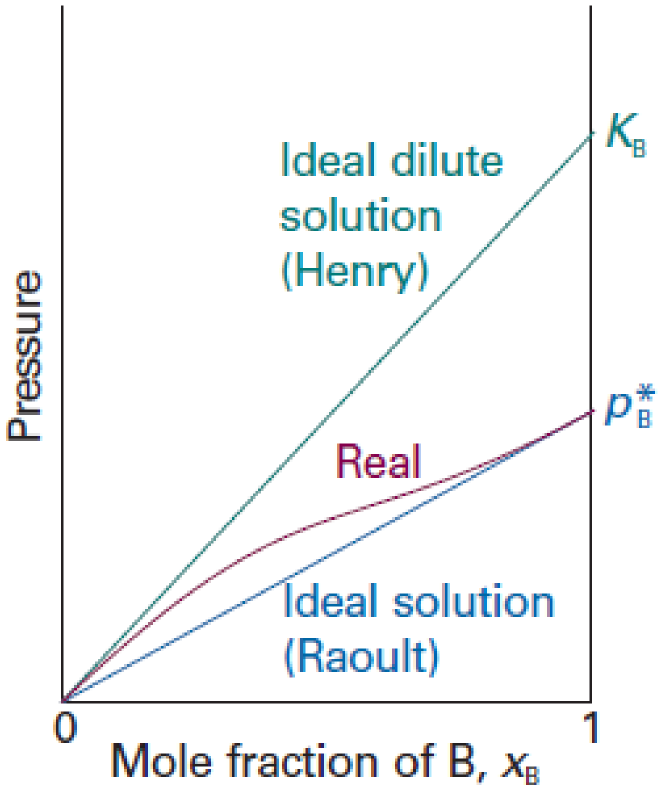
$$d\overline{V_1} = \frac{-n_2}{n_1} d\overline{V_2}$$



9 Real Solutions Exhibit Deviations from Raoult's Law

- *Molar volumes are always positive, but partial molar quantities need not to be*
- *For example, the limiting partial molar volume of* $MgSO_4$ *in water (its partial molar volume in the limit of zero concentration) is* $-1.4\ cm^3\ mol^{-1}$
- *This means that the addition of 1 mol* $MgSO_4$ *to a large volume of water results in a decrease in volume of* $1.4\ cm^3$
- *The mixture contracts because the salt breaks up the open structure of water as the ions become hydrated, and it collapses slightly*

10 The Ideal Dilute Solution



- *An ideal dilute solution is a solution in which the solvent is described using Raoult's law and the solute is described using Henry's law.*

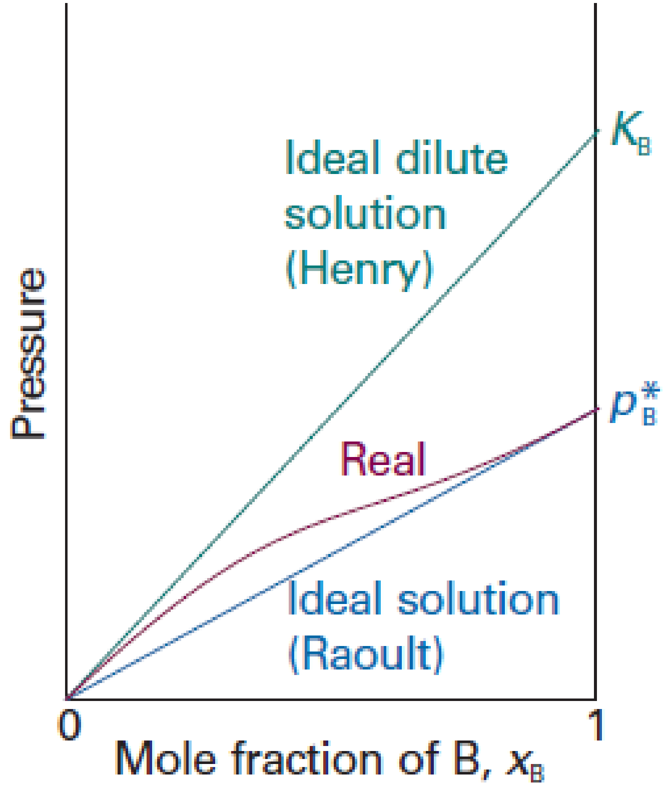
“Solvent Activity”

- *Just as for an ideal solution, at equilibrium the chemical potentials of a component in the gas and solution phase of a real solution are equal.*

$$\mu_i^{solution} = \mu_i^* + RT \ln \frac{P_i}{P_i^*} \qquad P_i \neq x_i P_i^*$$

$$a_{solvent} = \frac{P_{solvent}}{P_{solvent}^*}$$

$$\mu_i^{solution} = \mu_i^* + RT \ln a_i$$



- $a_{solvent} \rightarrow x_{solvent}$ as $x_{solvent} \rightarrow 1$

"Solvent Activity"

- *The activity and the mole fraction are related through the activity coefficient*

$$\gamma_{solvent} = \frac{a_{solvent}}{x_{solvent}}$$

- *The activity plays the same role for a component of a solution that the fugacity plays for a real gas in expressing deviations from ideal behavior*

- *In both cases, ideal behavior is observed in the appropriate limit, namely, P ⇨ 0 for the gas, and* x_{solute} ⇨ *0 or* $x_{solvent}$ ⇨ *1 for the solution*

"Solute Activity"

- *For a solute that satisfies Henry's law*

$$\mu^{solution}_{solute} = \mu^{*}_{solute} + RT \ln \frac{k^{solute}_{H} x_{solute}}{P^{*}_{solute}} = \mu^{*H}_{solute} + RT \ln x_{solute} \text{ as } x_{solute} \rightarrow 0$$

$$\overbrace{\mu^{*}_{solute} + RT \ln \frac{k^{solute}_{H}}{P^{*}_{solute}}}$$

$$a_i = \frac{P^H_i}{k^H_i} \text{ and } \gamma_i = \frac{a_i}{x_i}$$