Physical Properties of Solutions

Chapter 12

1

A **solution** is a homogenous mixture of 2 or more substances

The **solute** is(are) the substance(s) present in the smaller amount(s)

The **solvent** is the substance present in the larger amount

Table 13.1	Types of Solutions		
Solute	**Solvent**	**State of Resulting Solution**	**Examples**
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

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Three types of interactions in the solution process:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction

Molecular view of the formation of solution

Step 1
ΔH_1

Solvent

Step 2
ΔH_2

Solute

Step 3 ΔH_3

$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Solution

3
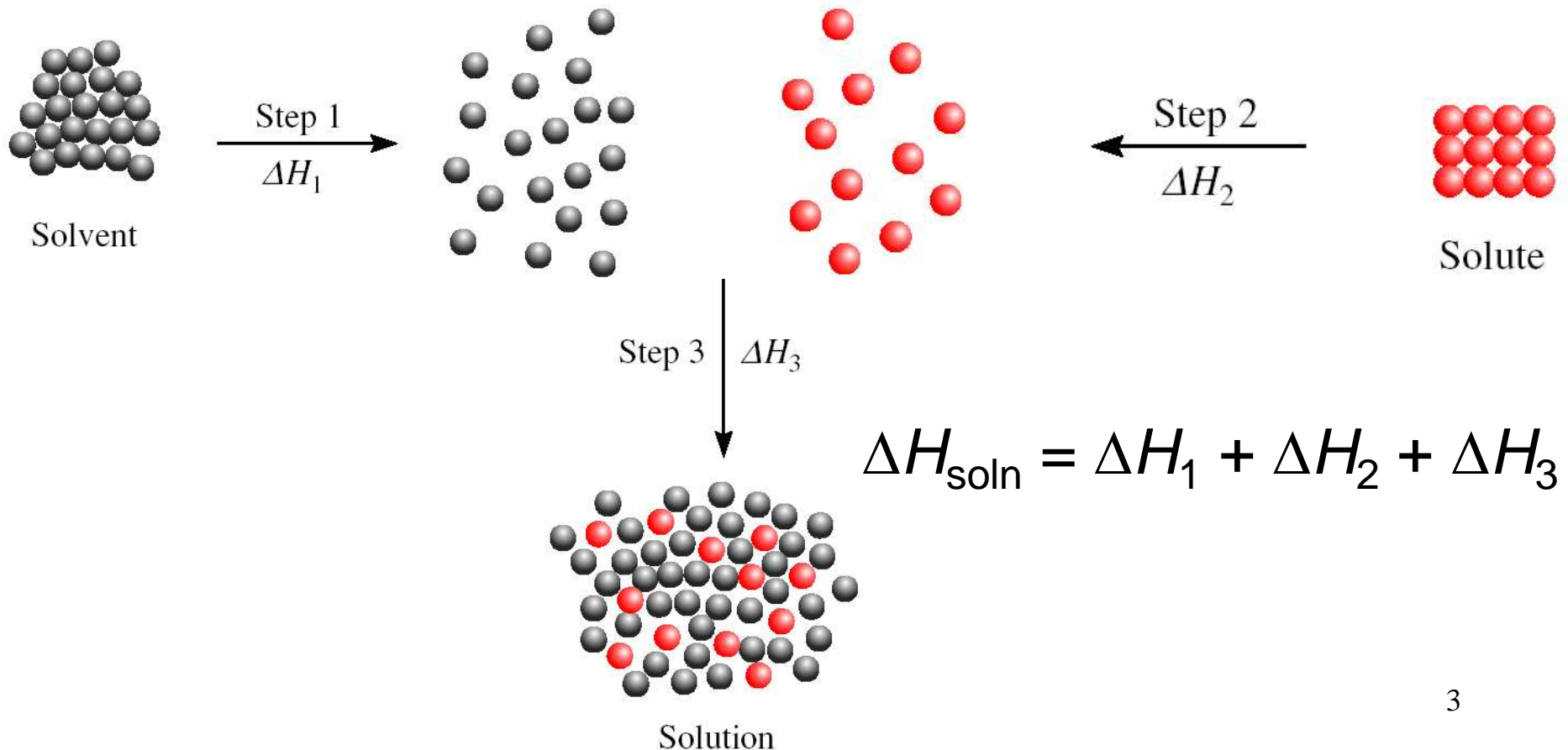
Concentration Units Continued

Molarity *(M)*

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$
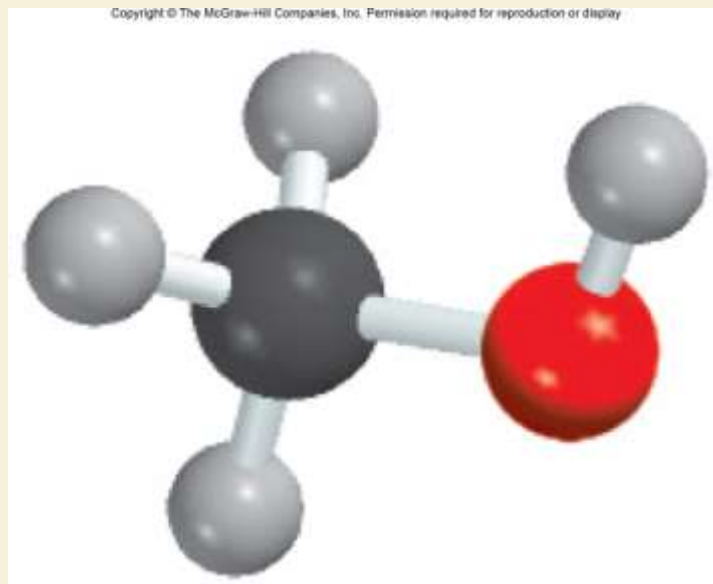
Molality *(m)*

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Example 13.2

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water.

The molar mass of sulfuric acid is 98.09 g.

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Example 13.2

Strategy To calculate the molality of a solution, we need to know the number of moles of solute and the mass of the solvent in kilograms.

Solution The definition of molality (m) is

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor.

$$\text{moles of } H_2SO_4 = 24.4 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4}$$
$$= 0.249 \text{ mol } H_2SO_4$$

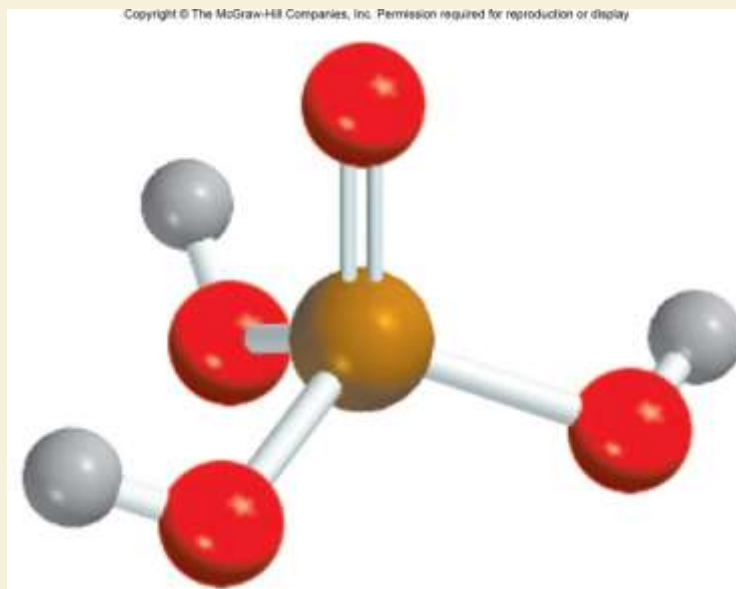# Example 13.2

The mass of water is 198 g, or 0.198 kg. Therefore,

$$m = \frac{0.249 \text{ mol } H_2SO_4}{0.198 \text{ kg } H_2O}$$

$$= 1.26 \; m$$

Example 13.3

The density of a 2.45 *M* aqueous solution of methanol (CH$_3$OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

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Example 13.3

Strategy To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

given

want to calculate

need to find

Example 13.3

Solution Our first step is to calculate the mass of water in 1 L of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 *M* solution of methanol is

$$1 \text{ L soln} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL soln}} = 976 \text{ g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

$$\text{mass of } H_2O = \text{mass of soln} - \text{mass of solute}$$
$$= 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right)$$
$$= 898 \text{ g}$$

Example 13.3

The molality of the solution can be calculated by converting 898 g to 0.898 kg:

$$\text{molality} = \frac{2.45 \text{ mol } CH_3OH}{0.898 \text{ kg } H_2O}$$

$$= 2.73 \; m$$

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

X_1 = mole fraction of the solvent

If the solution contains only one solute:
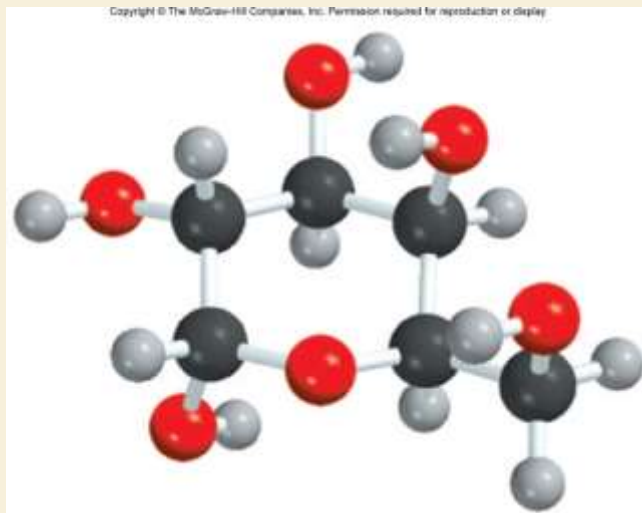
$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0 \qquad X_2 = \text{mole fraction of the solute}$$

Example 13.6

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C.

What is the vapor-pressure lowering?

The vapor pressure of pure water at 30°C is given in Table 5.2 (p. 157). Assume the density of the solvent is 1.00 g/mL.

Example 13.6

Strategy We need Raoult's law [Equation (13.6)] to determine the vapor pressure of a solution. Note that glucose is a nonvolatile solute.

Solution The vapor pressure of a solution (P_1) is

$$\overset{\text{want to calculate}}{\underset{}{P_1}} = \overset{}{X_1} \overset{\text{need to find}}{\underset{\text{given}}{P_1^\circ}}$$

First we calculate the number of moles of glucose and water in the solution

$$n_1(\text{water}) = 460 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 25.5 \text{ mol}$$

$$n_2(\text{glucose}) = 218 \text{ g} \times \frac{1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol}$$
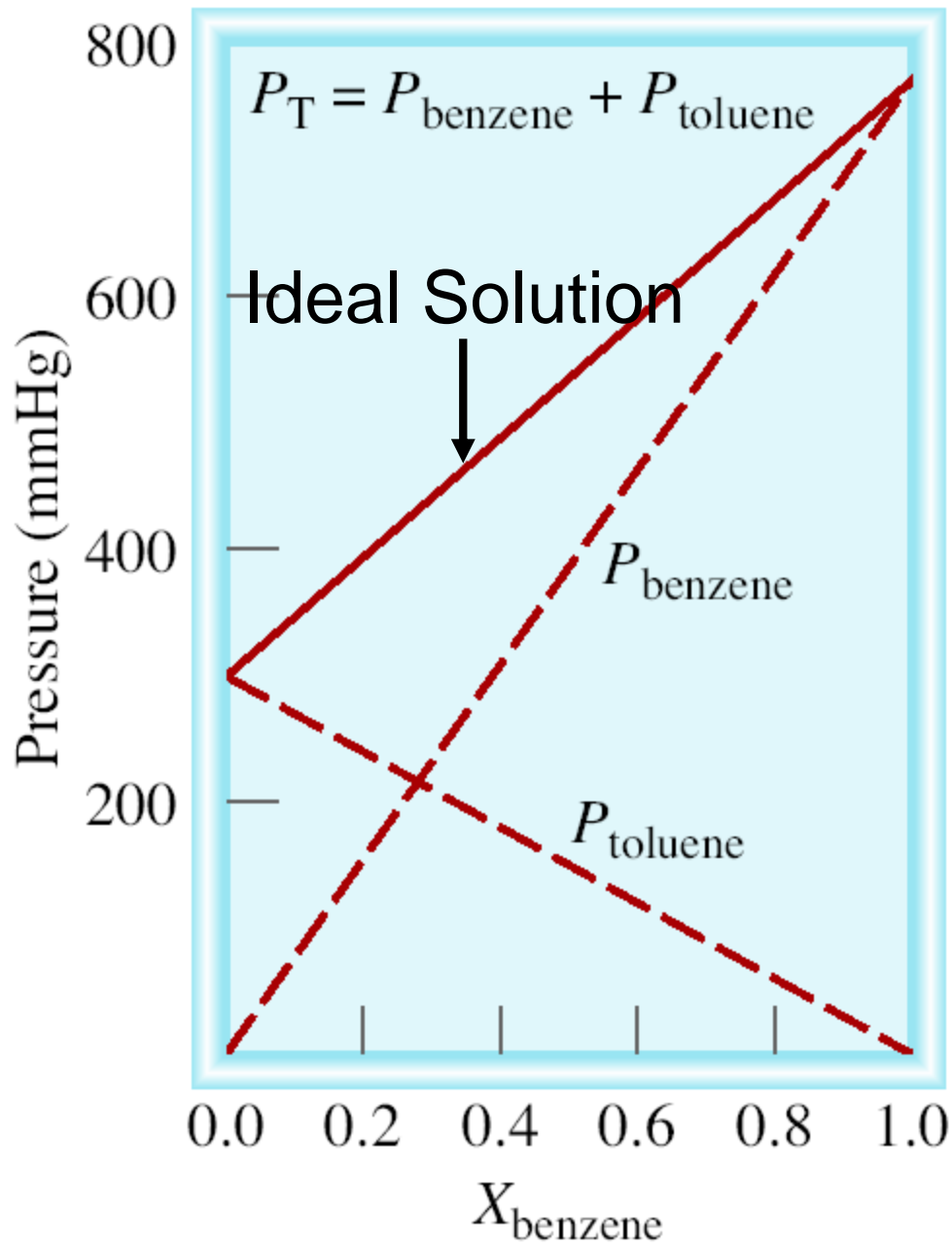
Example 13.6

The mole fraction of water, X_1, is given by

$$X_1 = \frac{n_1}{n_1 + n_2}$$
$$= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955$$

From Table 5.2, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

$$P_1 = 0.955 \times 31.82 \text{ mmHg}$$
$$= 30.4 \text{ mmHg}$$

Finally, the vapor-pressure lowering (ΔP) is (31.82 − 30.4) mmHg, or 1.4 mmHg.

Ideal Solution

Graph axes: Pressure (mmHg) vs $X_{benzene}$

$$P_T = P_{benzene} + P_{toluene}$$

$P_{benzene}$

$P_{toluene}$
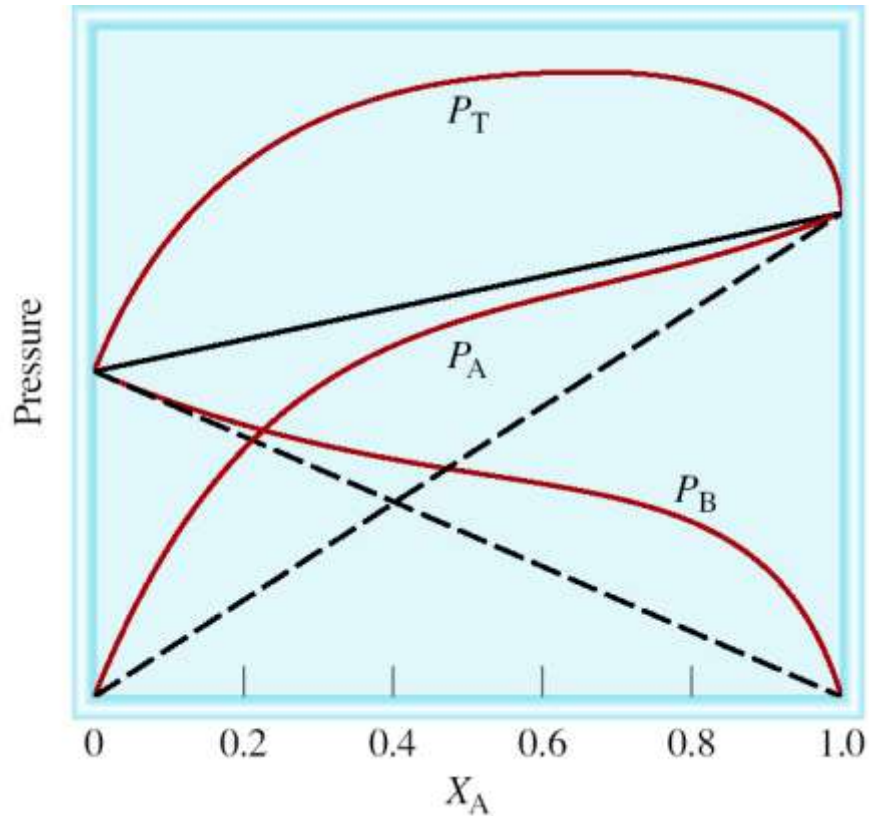
$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = P_A + P_B$$

$$P_T = X_A P_A^0 + X_B P_B^0$$
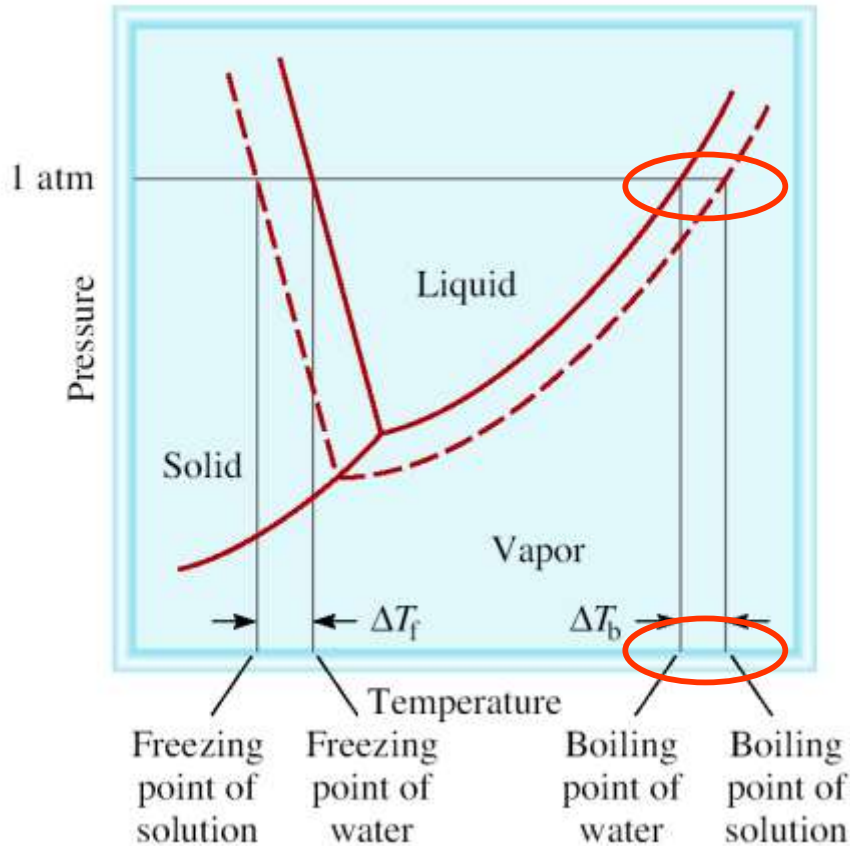
P_T is greater than predicted by Raoult's law

P_T is less than predicted by Raoult's law

Force A-B $<$ Force A-A & Force B-B
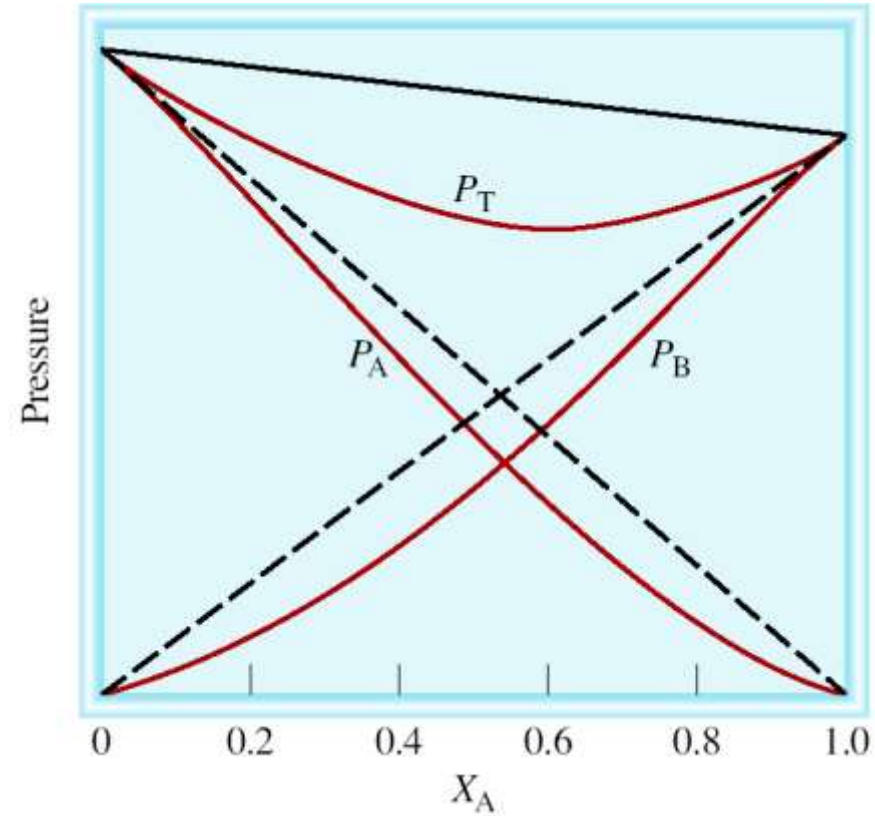
Force A-B $>$ Force A-A & Force B-B

Boiling-Point Elevation

Freezing point of solution, Freezing point of water, Boiling point of water, Boiling point of solution

$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent
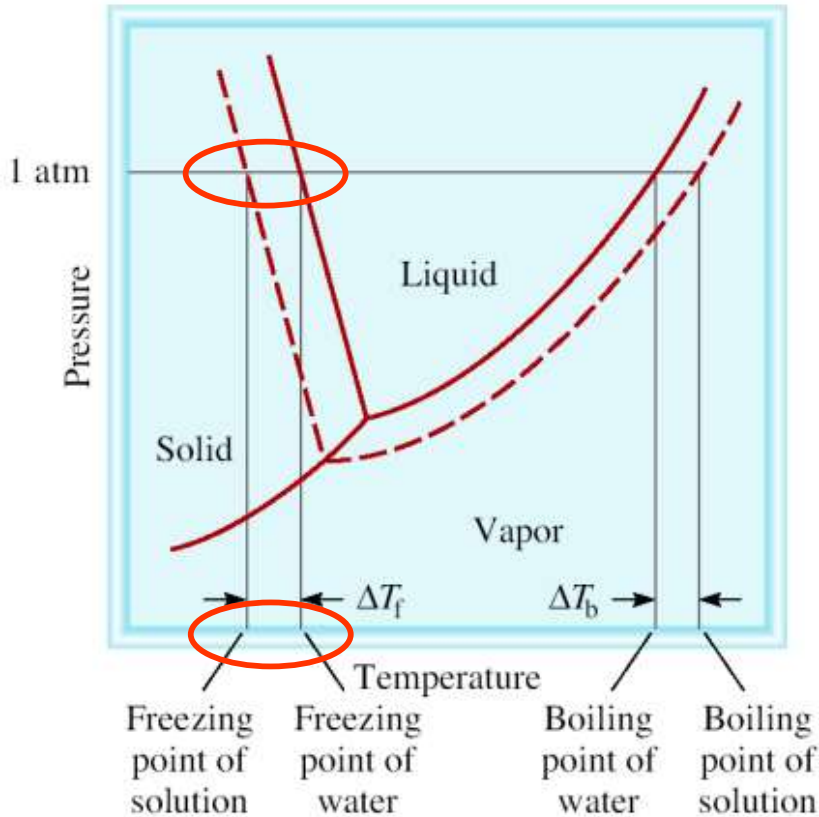
T_b is the boiling point of the solution

$$T_b > T_b^0 \qquad \Delta T_b > 0$$

$$\boxed{\Delta T_b = K_b\, m}$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant ($^0C/m$) for a given solvent

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Freezing-Point Depression

$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$$T_f^0 > T_f \qquad \Delta T_f > 0$$

$$\boxed{\Delta T_f = K_f\, m}$$

m is the molality of the solution

K_f is the molal freezing-point depression constant (^{0}C/*m*) for a given solvent

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Table 13.2 **Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids**

Solvent	Normal Freezing Point (°C)*	K_f (°C/m)	Normal Boiling Point (°C)*	K_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

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Example 13.7

Ethylene glycol (EG), $CH_2(OH)CH_2(OH)$, is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C).
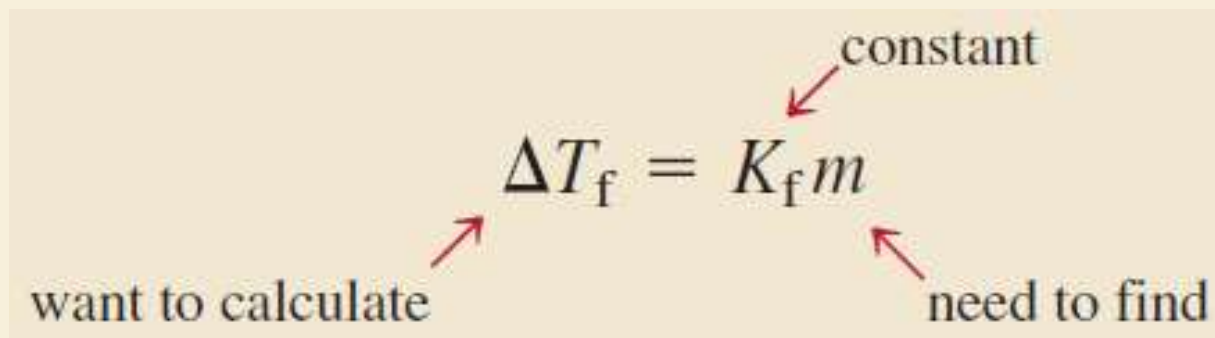
Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water.

Would you keep this substance in your car radiator during the summer?

The molar mass of ethylene glycol is 62.07 g.

Example 13.7

Strategy This question asks for the depression in freezing point of the solution.

$$\Delta T_{\mathrm{f}} = K_{\mathrm{f}} m$$

constant

want to calculate

need to find

The information given enables us to calculate the molality of the solution and we refer to Table 13.2 for the K_{f} of water.

Solution To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms.

Example 13.7

We find the molar mass of EG, and convert the mass of the solvent to 2.505 kg, and calculate the molality as follows:

$$651 \text{ g EG} \times \frac{1 \text{ mol EG}}{62.07 \text{ g EG}} = 10.5 \text{ mol EG}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

$$= \frac{10.5 \text{ mol EG}}{2.505 \text{ kg H}_2\text{O}} = 4.19 \text{ mol EG/kg H}_2\text{O}$$

$$= 4.19 \, m$$

From Equation (13.9) and Table 13.2 we write

$$\Delta T_f = K_f m$$
$$= (1.86°C/m)(4.19 \, m)$$

$$= 7.79°C$$

Example 13.7

Because pure water freezes at 0°C, the solution will freeze at (0 − 7.79)°C or 27.79°C.

We can calculate boiling-point elevation in the same way as follows:

$$\Delta T_b = K_b m$$
$$= (0.52°C/m)(4.19\ m)$$
$$= 2.2°C$$

Because the solution will boil at (100 + 2.2)°C, or 102.2°C, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

Osmotic Pressure (π)

Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A ***semipermeable membrane*** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.

Osmotic Pressure (π)

Net transfer of solvent
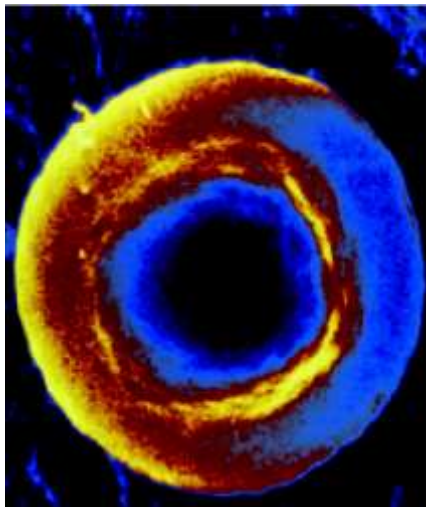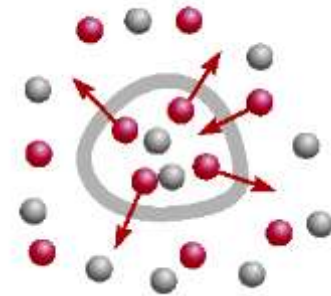
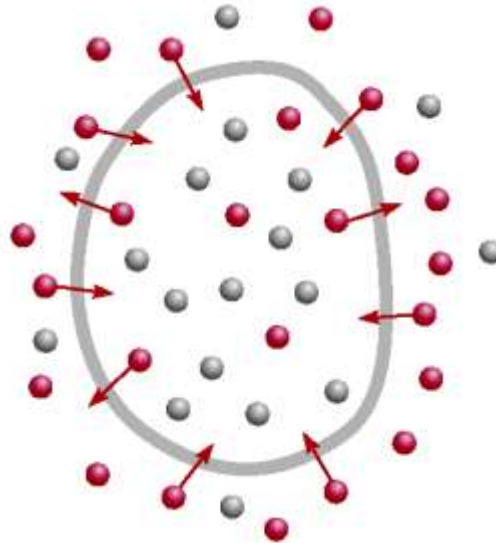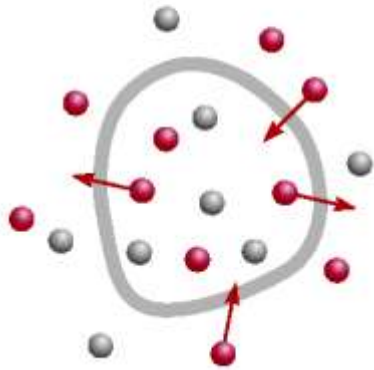solvent   solution

time

High
P

Low
P
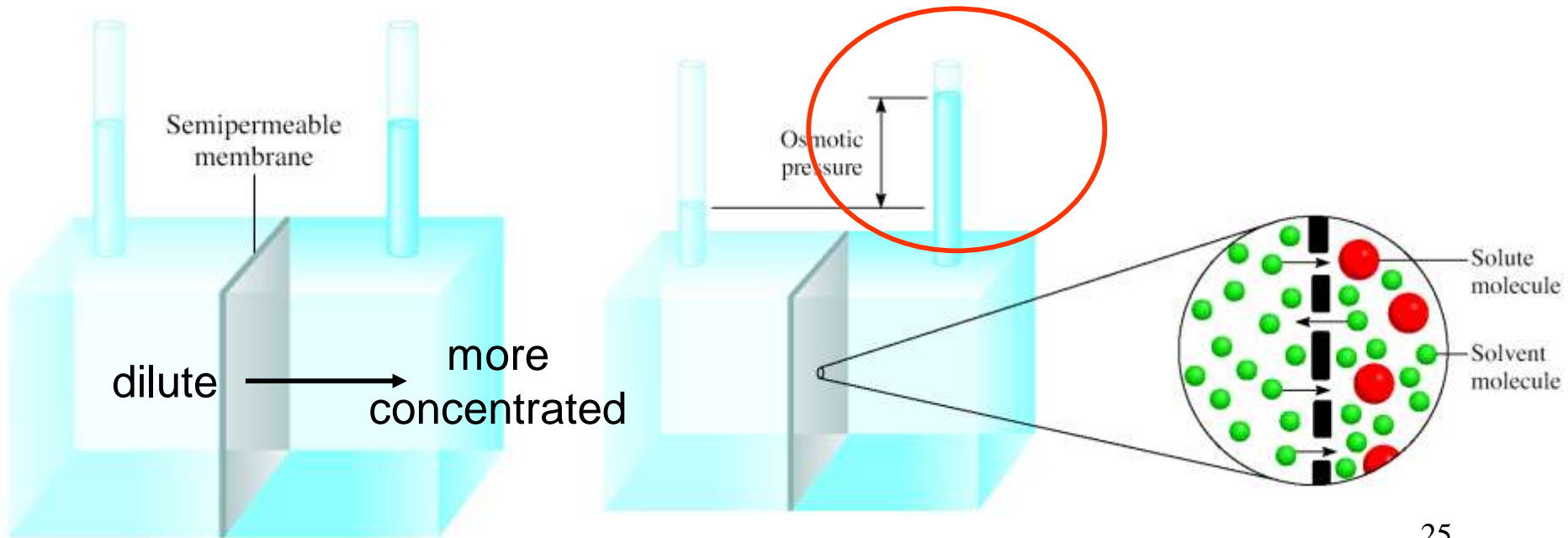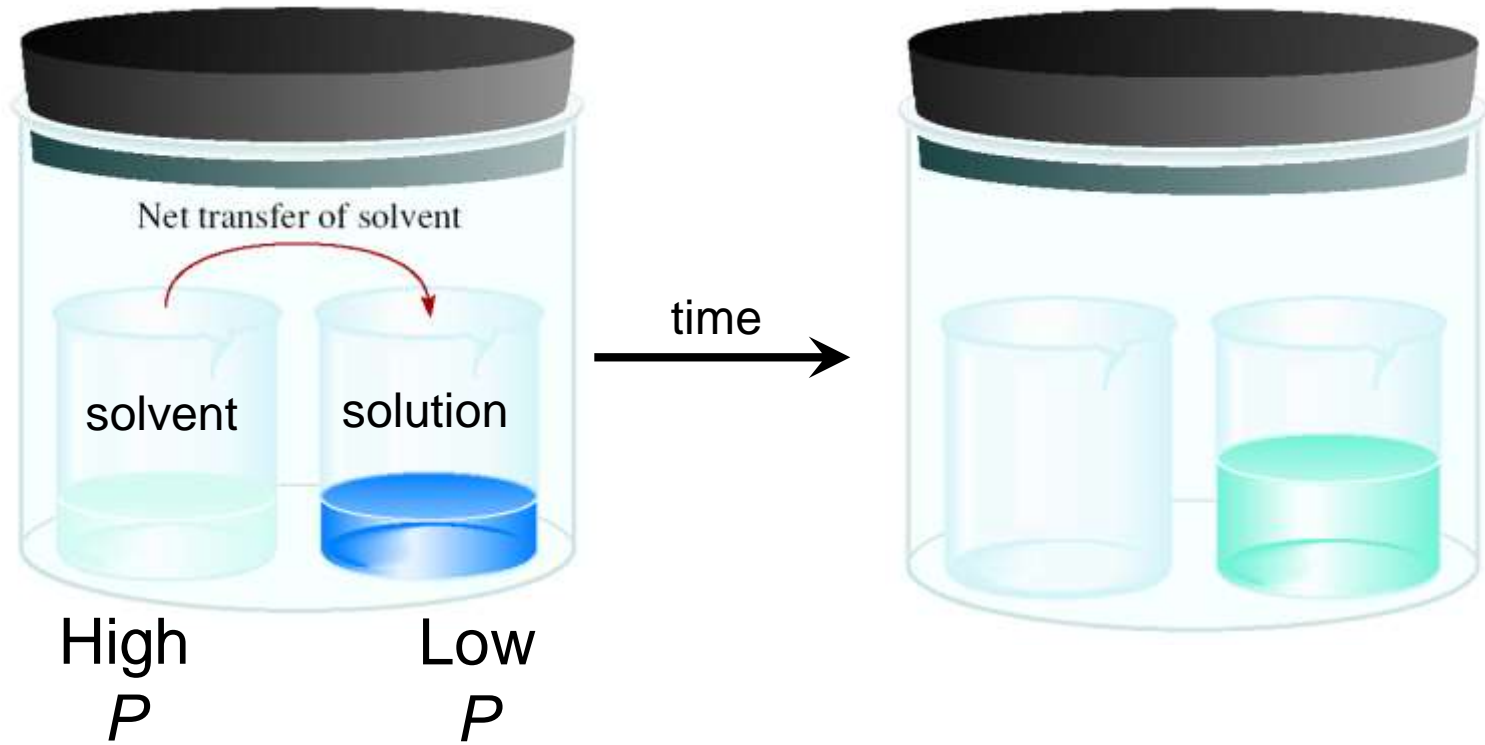
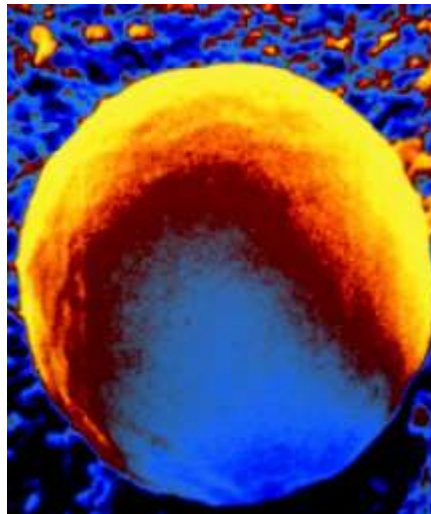$$\pi = MRT$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

A cell in an:

Water molecules
Solute molecules

isotonic
solution

hypotonic
solution
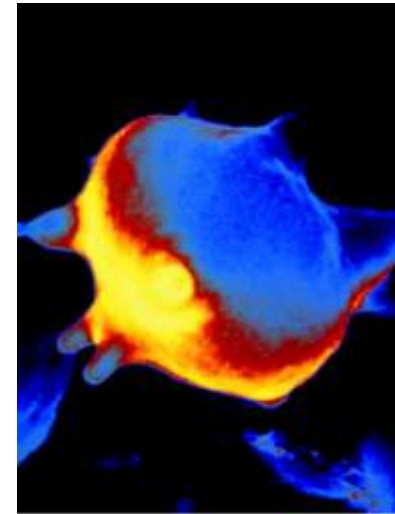
hypertonic
solution

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering $\quad P_1 = X_1 P_1^{\circ}$

Boiling-Point Elevation $\quad \Delta T_b = K_b\, m$

Freezing-Point Depression $\quad \Delta T_f = K_f\, m$

Osmotic Pressure (π) $\quad \pi = MRT$

Example 13.8

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene.

The freezing point of the solution is 1.05°C below that of pure benzene.

What are the molar mass and molecular formula of this compound?

Example 13.8

Strategy Solving this problem requires three steps. First, we calculate the molality of the solution from the depression in freezing point.

Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass.

Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

Solution The sequence of conversions for calculating the molar mass of the compound is

freezing-point ⟶ molality ⟶ number of ⟶ molar mass
depression   moles

Example 13.8

Our first step is to calculate the molality of the solution. From Equation (13.9) and Table 13.2 we write

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05°C}{5.12°C/m} = 0.205\ m$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301\ \text{kg} \times \frac{0.205\ \text{mol}}{1\ \text{kg}} = 0.0617\ \text{mol}$$

Example 13.8

Thus, the molar mass of the solute is

$$\text{molar mass} = \frac{\text{grams of compound}}{\text{moles of compound}}$$

$$= \frac{7.85 \text{ g}}{0.0617 \text{ mol}} = \boxed{127 \text{ g/mol}}$$

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127 \text{ g/mol}}{64 \text{ g/mol}} \approx 2$$

Therefore, the molecular formula is $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

Example 13.9

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume.

If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

Example 13.9

Strategy We are asked to calculate the molar mass of Hb. The steps are similar to those outlined in Example 13.8.

From the osmotic pressure of the solution, we calculate the molarity of the solution.

Then, from the molarity, we determine the number of moles in 35.0 g of Hb and hence its molar mass. What units should we use for π and temperature?

Solution The sequence of conversions is as follows:

osmotic pressure $\longrightarrow$ molarity $\longrightarrow$ number of moles $\longrightarrow$ molar mass

Example 13.9

First we calculate the molarity using Equation (13.10)

$$\pi = MRT$$

$$M = \frac{\pi}{RT}$$

$$= \frac{10.0 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

$$= 5.38 \times 10^{-4} \, M$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb.

Example 13.9

We use this quantity to calculate the molar mass:

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$

$$\text{molar mass of Hb} = \frac{\text{mass of Hb}}{\text{moles of Hb}}$$

$$= \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}}$$

$$= 6.51 \times 10^{4} \text{ g/mol}$$

Colligative Properties of Electrolyte Solutions

0.1 m NaCl solution $\longrightarrow$ 0.1 m Na$^+$ ions & 0.1 m Cl$^-$ ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 m NaCl solution $\longrightarrow$ 0.2 m ions in solution

van't Hoff factor (i) $= \dfrac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$

<u>i should be</u>

nonelectrolytes	1
NaCl	2
CaCl$_2$	3

Colligative Properties of Electrolyte Solutions

Boiling-Point Elevation $\Delta T_b = i\, K_b\, m$

Freezing-Point Depression $\Delta T_f = i\, K_f\, m$

Osmotic Pressure (π) $\pi = iMRT$

Table 13.3	The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C	
Electrolyte	*i* (measured)	*i* (calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO$_4$	1.3	2.0
MgCl$_2$	2.7	3.0
FeCl$_3$	3.4	4.0

Example 13.10

The osmotic pressure of a 0.010 *M* potassium iodide (KI) solution at 25°C is 0.465 atm.

Calculate the van't Hoff factor for KI at this concentration.

Example 13.10

Strategy Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. If so, its osmotic pressure would be

$$2(0.010\ M)(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(298\ \text{K}) = 0.489\ \text{atm}$$

However, the measured osmotic pressure is only 0.465 atm. The smaller than predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K^+ and I^- ions) in solution.

Example 13.10

Solution From Equation (13.13) we have

$$i = \frac{\pi}{MRT}$$

$$= \frac{0.465 \text{ atm}}{(0.010 \ M)(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

$$= 1.90$$