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## Chapter 12

# Physical Properties of Solutions

## **Solutions**

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 12.1** Types of Solutions

Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO <sub>2</sub> in water)
Gas	Solid	Solid	H <sub>2</sub> gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

## Saturation

A *saturated solution* contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An *unsaturated solution* contains less solute than the solvent has the capacity to dissolve at a specific temperature.

A *supersaturated solution* contains more solute than is present in a saturated solution at a specific temperature.

Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.









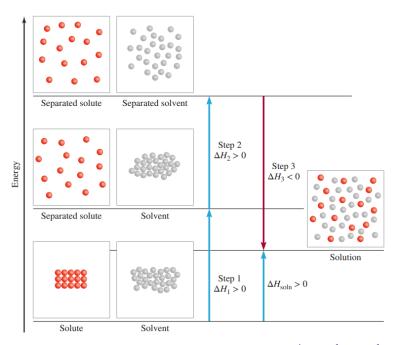
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## Formation of a Solution

Three types of interactions in the solution process:

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

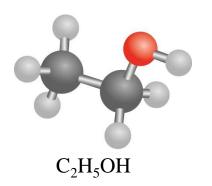
#### Molecular view of the formation of solution

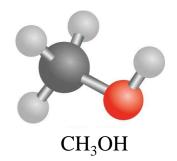


$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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## "Like Dissolves Like"





Two substances with similar *intermolecular* forces are likely to be soluble in each other.

non-polar molecules are soluble in non-polar solvents

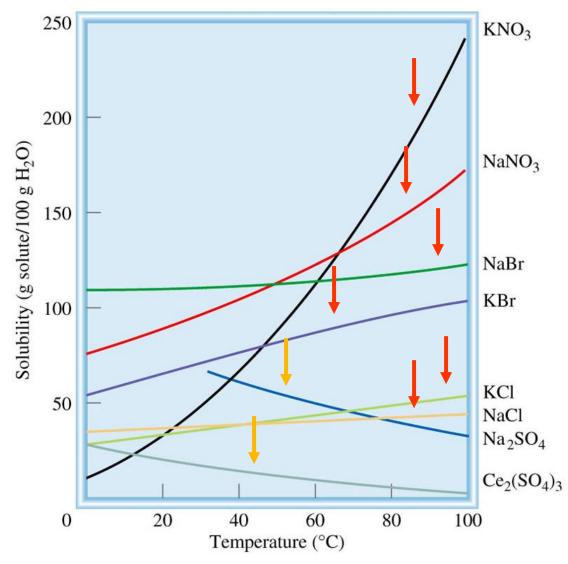
polar molecules are soluble in polar solvents

ionic compounds are more soluble in polar solvents

NaCl in H<sub>2</sub>O or NH<sub>3</sub> (*I*)

## **Temperature and Solubility**

## Solid solubility and temperature

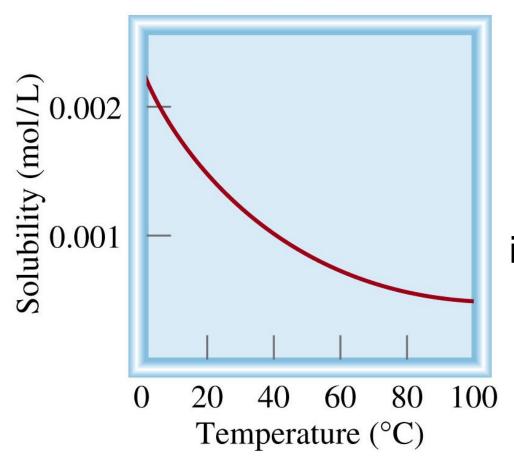


solubility increases with increasing temperature

solubility decreases with increasing temperature

## **Temperature and Solubility**

O<sub>2</sub> gas solubility and temperature



Gas solubility usually decreases with increasing temperature

### **Concentration Units**

The *concentration* of a solution is the amount of solute present in a given quantity of solvent or solution.

**Molarity** (M) or molar concentration, which is the number of moles of solute per liter of solution.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molality (m) is the number of moles of solute dissolved in 1 kg (1000 g) of solvent

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

## **Comparison of Concentration Units**

- The advantage of molarity is that it is generally easier to measure the volume of a solution.
   For this reason, molarity is often preferred over molality.
- Molality is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent.
- The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 M at 25 °C may become 0.97 M at 45 °C because of the increase in volume on warming.
- This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

## What mass of KI is required to make 500 mL of a 2.80 *M* KI solution?

volume of KI solution 
$$\xrightarrow{M \text{ KI}}$$
 moles KI  $\xrightarrow{M \text{ KI}}$  grams KI

500 mL x 
$$\frac{11}{1000 \text{ mL}}$$
 x  $\frac{2.80 \text{ mol KI}}{1 \text{ LeoIn}}$  x  $\frac{166 \text{ g KI}}{1 \text{ mol KI}}$  = **232** g KI

#### **EXAMPLE 4.6**

How many grams of potassium dichromate ( $K_2Cr_2O_7$ ) are required to prepare a 250-mL solution whose concentration is 2.16 M?

**Strategy** How many moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> does a 1-L (or 1000 mL) 2.16 *M* K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution contain? A 250-mL solution? How would you convert moles to grams?

**Solution** The first step is to determine the number of moles of  $K_2Cr_2O_7$  in 250 mL or 0.250 L of a 2.16 M solution. Rearranging Equation (4.1) gives

moles of solute = molarity  $\times$  L soln

Thus,

$$\begin{aligned} \text{moles of } K_2 \text{Cr}_2 \text{O}_7 &= \frac{2.16 \text{ mol } K_2 \text{Cr}_2 \text{O}_7}{1 \text{ L soln}} \times 0.250 \text{ L soln} \\ &= 0.540 \text{ mol } K_2 \text{Cr}_2 \text{O}_7 \end{aligned}$$

The molar mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is 294.2 g, so we write

grams of 
$$K_2Cr_2O_7$$
 needed = 0.540 mol  $K_2Cr_2O_7 \times \frac{294.2 \text{ g } K_2Cr_2O_7}{1 \text{ mol } K_2Cr_2O_7}$   
= 159 g  $K_2Cr_2O_7$ 

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#### **EXAMPLE 4.7**

In a biochemical assay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

**Strategy** We must first determine the number of moles contained in 3.81 g of glucose and then use Equation (4.2) to calculate the volume.

**Solution** From the molar mass of glucose, we write

$$3.81 \text{ g C}_6 \text{H}_{12} \text{O}_6 \times \frac{1 \text{ mol C}_6 \text{H}_{12} \text{O}_6}{180.2 \text{ g C}_6 \text{H}_{12} \text{O}_6} = 2.114 \times 10^{-2} \text{ mol C}_6 \text{H}_{12} \text{O}_6$$

Next, we calculate the volume of the solution that contains  $2.114 \times 10^{-2}$  mole of the solute. Rearranging Equation (4.2) gives

$$V = \frac{n}{M}$$
=  $\frac{2.114 \times 10^{-2} \text{ mol C}_6 \text{H}_{12} \text{O}_6}{2.53 \text{ mol C}_6 \text{H}_{12} \text{O}_6 / \text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}}$ 
= 8.36 mL soln

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.

**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.

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 mol  $H_2SO_4$ 

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

$$m = \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}}$$
$$= 1.26 m$$

### **Concentration Units**

The Percent by Mass: (also called percent by weight or weight percent) is the ratio of the mass of a solute to the mass of the solution, multiplied by 100 percent:

% by mass = 
$$\frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solute}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

**Mole Fraction** (X): The **mole fraction** of a component of a solution, say, component A, is written  $X_A$  and is defined as

$$X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in the solution?

**Solution** We write

percent by mass of KCl = 
$$\frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$
  
=  $\frac{0.892 \text{ g}}{0.892 \text{ g} + 54.6 \text{ g}} \times 100\%$   
=  $1.61\%$ 

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). The molar mass of phosphoric acid is 97.99 g.

**Strategy** In solving this type of problem, it is convenient to assume that we start with a 100.0 g of the solution. If the mass of phosphoric acid is 35.4 percent, or 35.4 g, the percent by mass and mass of water must be 100.0% - 35.4% = 64.6% and 64.6 g.

**Solution** From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

moles of 
$$H_3PO_4 = 35.4 \text{ g } H_3PO_4 \times \frac{1 \text{ mol } H_3PO_4}{97.99 \text{ g } H_3PO_4}$$
  
= 0.361 mol  $H_3PO_4$ 

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

molality = 
$$\frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}}$$
  
=  $5.59 \text{ m}$ 

## To convert one concentration unit of a solution to another

#### **Example:**

Express the concentration of a 0.396 m glucose ( $C_6H_{12}O_6$ ) solution in molarity? (density of solution = 1.16 g/mL)

0.396 *m* glucose ( $C_6H_{12}O_6$ )

i.e., there is 0.396 mole of glucose in 1000 g of the solvent.

To calculate molarity; we need to determine the volume of this solution.

First, we calculate the mass of the solution from the molar mass of glucose:

$$\left(0.396 \text{ mol } C_6 H_{12} O_6 \times \frac{180.2 \text{ g}}{1 \text{ mol } C_6 H_{12} O_6}\right) + 1000 \text{ g H}_2 O = 1071 \text{ g}$$

### The density of the solution is 1.16 g/mL

#### We can now calculate the volume of the solution in liters

volume = 
$$\frac{\text{mass}}{\text{density}}$$
= 
$$\frac{1071 \text{ g}}{1.16 \text{ g/mL}} \times \frac{1 \text{ L}}{1000 \text{ mL}}$$
= 
$$0.923 \text{ L}$$

#### The molarity of the solution is given by

molarity = 
$$\frac{\text{moles of solute}}{\text{liters of soln}}$$
  
=  $\frac{0.396 \text{ mol}}{0.923 \text{ L}}$   
=  $0.429 \text{ mol/L} = 0.429 \text{ M}$ 



## What is the molality of a 5.86 M ethanol (C<sub>2</sub>H<sub>5</sub>OH) solution whose density is 0.927 g/mL?

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

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol927 g of solution (1000 mL x 0.927 g/mL)

mass of solvent = mass of solution – mass of solute = 927 g - 270 g = 657 g = 0.657 kg

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92 \text{ m}$$

The density of a 2.45 M aqueous solution of methanol (CH<sub>3</sub>OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

**Solution** Our first step is to calculate the mass of water in one liter 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

mass of H<sub>2</sub>O = mass of soln - mass of solute  
= 976 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 g

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

molality = 
$$\frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}}$$
$$= 2.73 \text{ m}$$

## Pressure and Solubility of Gases

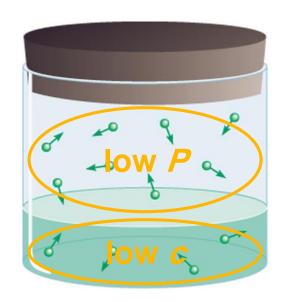
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (*Henry's law*).

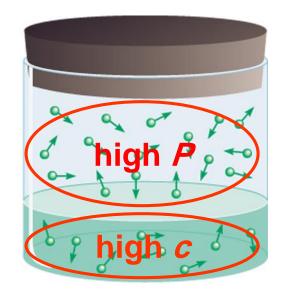
$$c = k_H P$$

c is the concentration (M) of the dissolved gas

**P** is the pressure of the gas over the solution

 $k_H$  is a constant for each gas (mol/L•atm) that depends only on temperature





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Most gases obey Henry's law, but there are some important exceptions:

For **example**, if the dissolved gas <u>reacts</u> with water, higher solubilities can result.

The solubility of **ammonia** is much higher than expected because of the reaction

$$NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$$

Carbon dioxide also reacts with water, as follows:

$$CO_2 + H_2O \Longrightarrow H_2CO_3$$

Another interesting example is the dissolution of *molecular oxygen* in blood.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

The solubility of nitrogen gas at 25°C and 1 atm is  $6.8 \times 10^{-4}$  mol/L. What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

**Strategy** The given solubility enables us to calculate Henry's law constant (k), which can then be used to determine the concentration of the solution.

**Solution** The first step is to calculate the quantity k in Equation (12.3):

$$c = kP$$

$$6.8 \times 10^{-4} \text{ mol/L} = k \text{ (1 atm)}$$

$$k = 6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm}$$

Therefore, the solubility of nitrogen gas in water is

$$c = (6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm})(0.78 \text{ atm})$$
  
=  $5.3 \times 10^{-4} \text{ mol/L}$   
=  $5.3 \times 10^{-4} M$ 

## **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.

#### The colligative properties are

- vapor-pressure lowering,
- boiling-point elevation,
- freezing-point depression,
- osmotic pressure.

## Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

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

Raoult's law

 $X_1$  = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0$$

 $X_2$  = mole fraction of the solute

We see that the decrease in vapor pressure,  $\Delta P$ , is directly proportional to the solute concentration (measured in mole fraction).

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 5.3 (p. 200). Assume the density of the solution is 1.00 g/mL.

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

$$n_1(\text{water}) = 460 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 25.5 \text{ mol}$$
  
 $n_2(\text{glucose}) = 218 \text{ g} \times \frac{1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol}$ 

The mole fraction of water,  $X_1$ , is given by

$$X_1 = \frac{n_1}{n_1 + n_2}$$

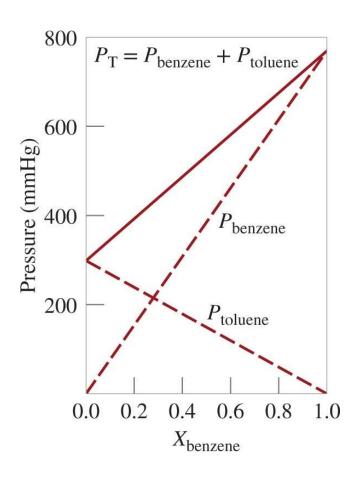
$$= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955$$

From Table 5.3, 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 mmHg

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

## Partial Pressure and Mole Fraction



$$P_{A} = X_{A}P_{A}^{0}$$

$$P_{B} = X_{B}P_{B}^{0}$$

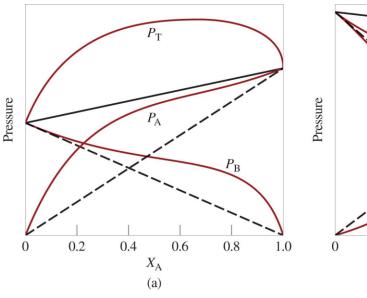
$$P_{T} = P_{A} + P_{B}$$

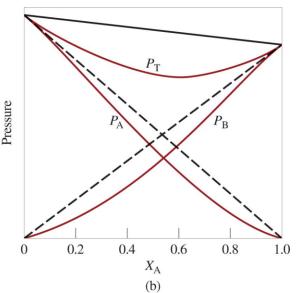
$$P_{T} = X_{A}P_{A}^{0} + X_{B}P_{B}^{0}$$

## Raoult's Law

 $P_{T}$  is greater than predicted by  $P_{T}$  is less than predicted by Raoult's law

Raoult's law

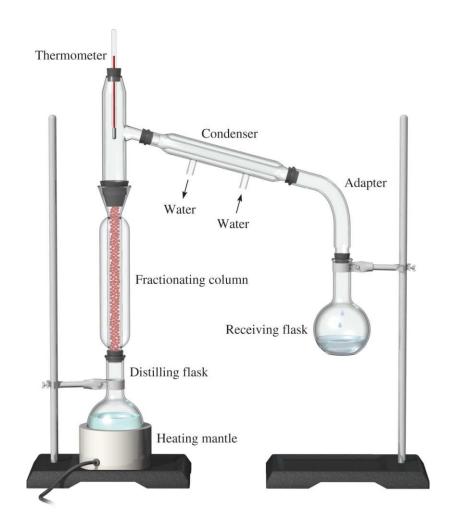




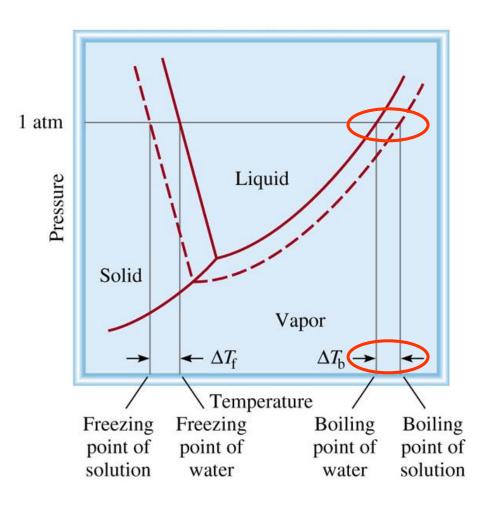
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## Fractional Distillation Apparatus



## **Boiling-Point Elevation**



$$\Delta T_{\rm b} = T_{\rm b} - T_{\rm b}^{0}$$

 $\mathcal{T}_{b}^{0}$  is the boiling point of the **pure** solvent

 $T_b$  is the boiling point of the solution

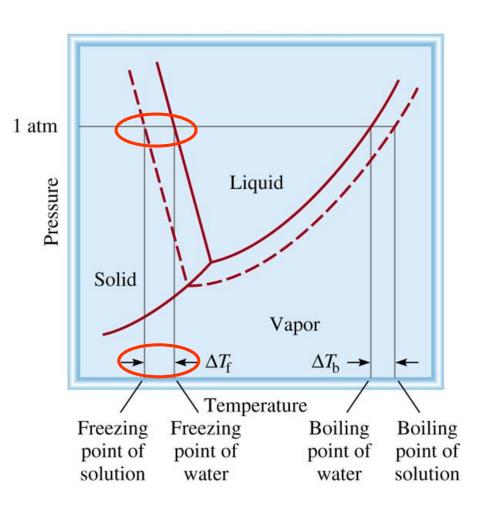
$$T_{\rm b} > T_{\rm b}^{0} \qquad \Delta T_{\rm b} > 0$$

$$\Delta T_{\rm b} = K_{\rm b} m$$

m is the molality of the solution

K<sub>b</sub> is the molal boiling-point elevation constant (°C/m) for a given solvent

## **Freezing-Point Depression**



$$\Delta T_{\rm f} = T_{\rm f}^{\rm O} - T_{\rm f}$$

7 of the freezing point of the pure solvent

 $T_f$  is the freezing point of the solution

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

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

m is the molality of the solution

K<sub>f</sub> is the molal freezing-point depression constant (°C/m) for a given solvent

#### **TABLE 12.2**

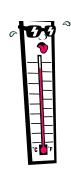
## Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)*	<i>K</i> <sub>f</sub> (°C/ <i>m</i> )	Normal Boiling Point (°C)*	<b>Κ</b> <sub>b</sub> (°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

<sup>\*</sup>Measured at 1 atm.









What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g/mol.

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

$$K_{\rm f}$$
 water = 1.86  ${}^{\circ}$ C/ $m$ 

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478 \text{ g x } \frac{1 \text{ mol}}{62.01 \text{ g}}}{3.202 \text{ kg solvent}} = 2.41 \text{ m}$$

$$\Delta T_f = K_f m = 1.86 \, {}^{\circ}\text{C}/m \, \text{x} \, 2.41 \, m = 4.48 \, {}^{\circ}\text{C}$$

$$\Delta T_{\rm f} = T_{\rm f}^{0} - T_{\rm f}$$

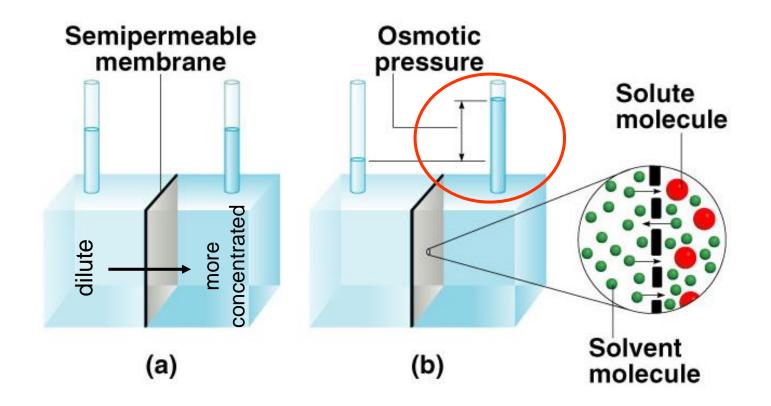
$$T_f = T_f^0 - \Delta T_f = 0.00 \, {}^{0}\text{C} - 4.48 \, {}^{0}\text{C} = -4.48 \, {}^{0}\text{C}$$

## Osmotic Pressure $(\pi)$

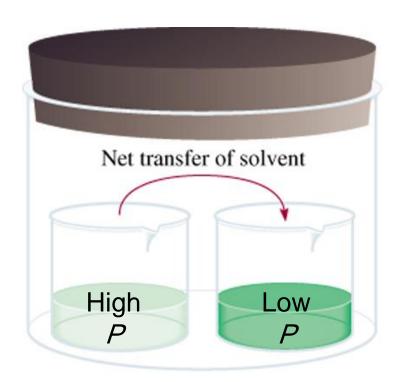
*Osmosis* is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

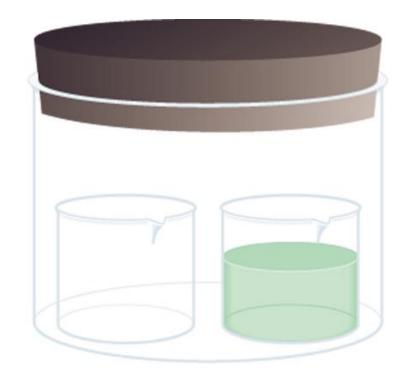
A *semipermeable membrane* allows the passage of solvent molecules but blocks the passage of solute molecules.

*Osmotic pressure* ( $\pi$ ) is the pressure required to stop osmosis.



## Osmotic Pressure $(\pi)$





 $\pi = MRT$ 

M is the molarity of the solution

**R** is the gas constant

*T* is the temperature (in K)

The average osmotic pressure of seawater, measured in the kind of apparatus shown in Figure 12.11, is about 30.0 atm at 25°C. Calculate the molar concentration of an aqueous solution of sucrose ( $C_{12}H_{22}O_{11}$ ) that is isotonic with seawater.

**Strategy** When we say the sucrose solution is isotonic with seawater, what can we conclude about the osmotic pressures of these two solutions?

**Solution** A solution of sucrose that is isotonic with seawater must have the same osmotic pressure, 30.0 atm. Using Equation (12.8).

$$\pi = MRT$$

$$M = \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$
= 1.23 mol/L
= 1.23 M

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?

**Solution** freezing-point  $\longrightarrow$  molality  $\longrightarrow$  number of  $\longrightarrow$  molar mass depression moles

molality = 
$$\frac{\Delta T_{\rm f}}{K_{\rm f}} = \frac{1.05^{\circ}\text{C}}{5.12^{\circ}\text{C/m}} = 0.205 \, m$$

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

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

Thus, the molar mass of the solute is

molar mass = 
$$\frac{\text{grams of compound}}{\text{moles of compound}}$$
 =  $\frac{7.85 \text{ g}}{0.0617 \text{ mol}}$  =  $\frac{127 \text{ g/mol}}{127 \text{ g/mol}}$ 

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).

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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.

**Solution** The sequence of conversions is as follows:

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

First we calculate the molarity using Equation (12.8)

$$\pi = MRT$$

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

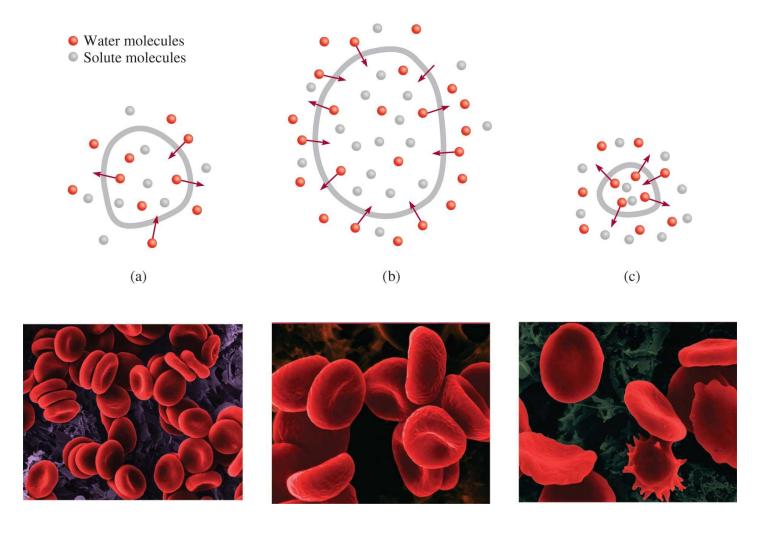
$$= \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

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

The volume of the solution is 1 L, so it must contain  $5.38 \times 10^{-4}$  mol of Hb. We use this quantity to calculate the molar mass:

moles of Hb = 
$$\frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$
  
molar mass of Hb =  $\frac{\text{mass of Hb}}{\text{moles of Hb}}$   
=  $\frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}}$   
=  $6.51 \times 10^4 \text{ g/mol}$ 

## A cell in an:



## Summary - 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** 

$$P_1 = X_1 P_1^0$$

**Boiling-Point Elevation** 

$$\Delta T_{\rm b} = K_{\rm b} m$$

**Freezing-Point Depression** 

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

Osmotic Pressure  $(\pi)$ 

$$\pi = MRT$$

#### <u>Using Colligative Properties to Determine Molar Mass</u>

From the experimentally determined freezing-point depression or osmotic pressure, We can calculate the molality or molarity of the solution. Knowing the mass of the solute, we can readily determine its molar mass.

# Colligative Properties of Electrolyte Solutions 1

 $0.1 m \text{ NaCl solution} \rightarrow 0.1 m \text{ Na}^+ \text{ ions } \& 0.1 m \text{ Cl}^- \text{ ions}$ 

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

 $0.1 \ m \, \text{NaCl solution} \rightarrow 0.2 \ m \, \text{ions in solution}$ 

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

	<u>i should be</u>
nonelectrolytes	1
NaCl	2
CaCl <sub>2</sub>	3

# Colligative Properties of Electrolyte Solutions 2

Boiling-Point Elevation 
$$\Delta T_{
m b}=iK_{
m b}m$$
Boiling-Point Depression  $\Delta T_{
m f}=iK_{
m f}m$ 
Osmotic Pressure  $(\pi)$   $\pi=iMRT$ 

**Table 12.3** The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

Electrolyte	<i>i</i> (Measured)	i(Calculated)
Surcose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
${ m MgSO_4}$	1.3	2.0
$\mathrm{MgCl}_2$	2.7	3.0
FeCl <sub>3</sub>	3.4	4.0

<sup>\*</sup>Source is a nonelectrolyte. It is listed here for comparison only.

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.

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

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

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.

**Solution** From Equation (12.12) we have

$$i = \frac{\pi}{MRT}$$
=  $\frac{0.465 \text{ atm}}{(0.010 \text{ M})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$ 
= 1.90