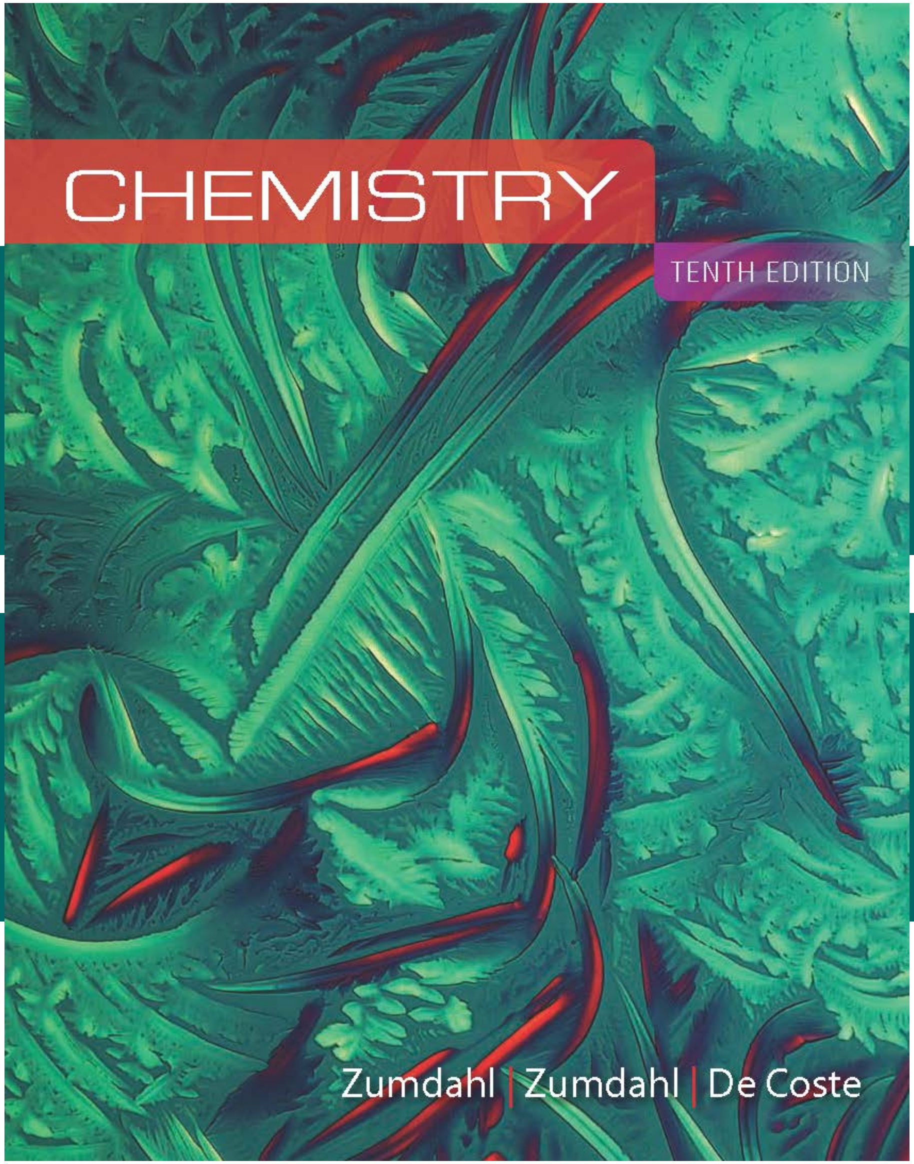


Chapter 11

Properties of Solutions

Chapter 11

Table of Contents

Colligative Properties

- Depend on the number of the solute particles in an ideal solution
  - Do not depend on the identity of the solute particles
- Include boiling-point elevation, freezing-point depression, and osmotic pressure
- Help determine:
  - The nature of a solute after it is dissolved in a solvent
  - The molar masses of substances

Boiling-Point Elevation

- Nonvolatile solute elevates the boiling point of the solvent
  - Magnitude of the boiling-point elevation depends on the concentration of the solute
  - Change in boiling point can be represented as follows:

$$\Delta T = K_b m_{\text{solute}}$$

    - ΔT - Boiling-point elevation
    - K_b - **Molal boiling-point elevation constant**
    - m_{solute} - Molality of the solute

Figure 11.15 - Phase Diagrams for Pure Water and for an Aqueous Solution Containing a Nonvolatile Solute

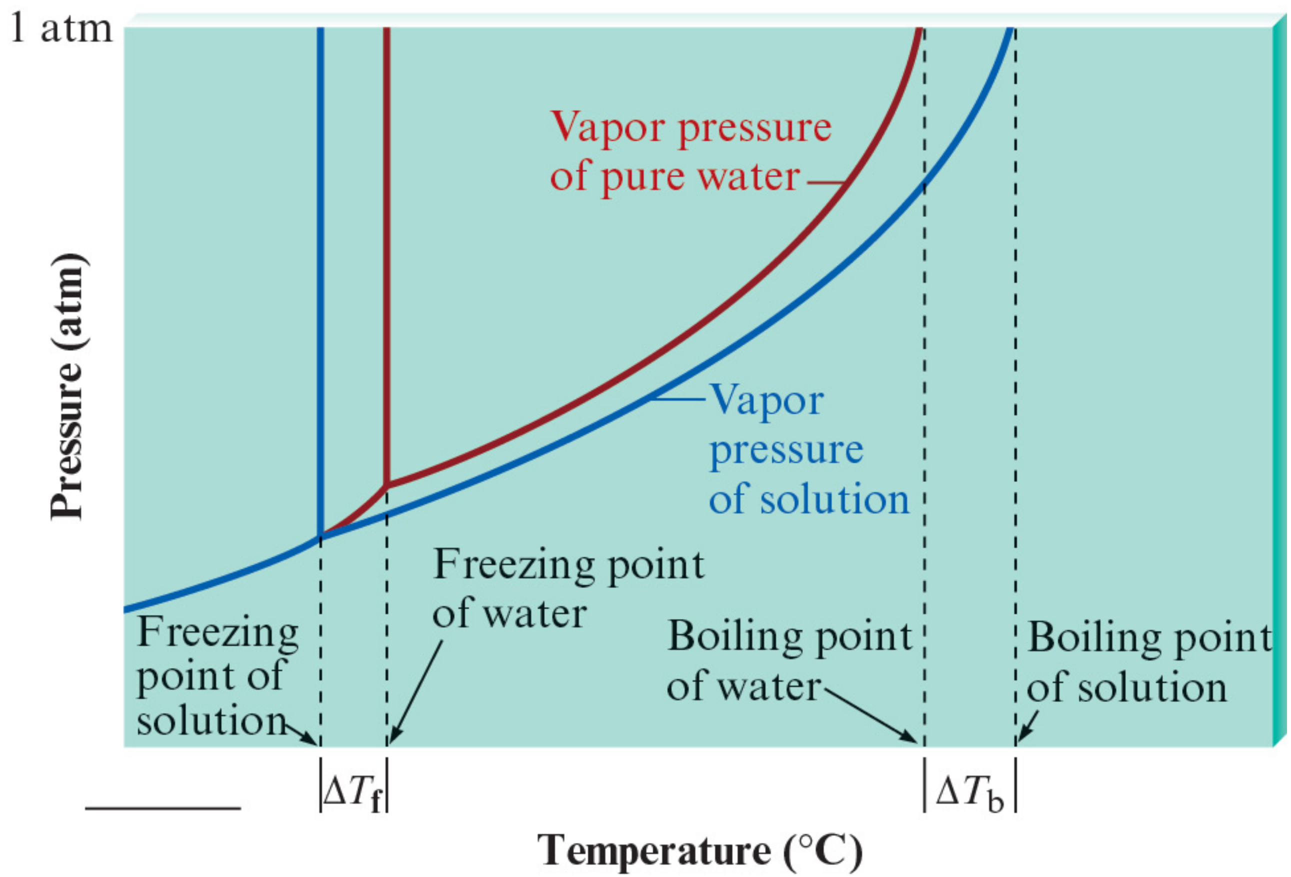


Table 11.5 - Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	−22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	−63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

Interactive Example 11.8 - Calculating the Molar Mass by Boiling-Point Elevation

- A solution was prepared by dissolving 18.00 g glucose in 150.0 g water, and the resulting solution was found to have a boiling point of 100.34° C
  - Calculate the molar mass of glucose
    - Glucose is a molecular solid that is present as individual molecules in solution

Interactive Example 11.8 - Solution

- We make use of the following equation:

$$\Delta T = K_b m_{solute}$$

  - Where $\Delta T = 100.34^\circ\text{C} - 100.00^\circ\text{C} = 0.34^\circ\text{C}$
  - For water, $K_b = 0.51$
- The molality of this solution then can be calculated by rearranging the boiling-point elevation equation

Interactive Example 11.8 - Solution (Continued 1)

$$m_{\text{solute}} = \frac{\Delta T}{K_{\text{b}}} = \frac{0.34°\text{C}}{0.51°\text{C} \cdot \text{kg/mol}} = 0.67 \text{ mol/kg}$$

- The solution was prepared using 0.1500 kg water
  - Using the definition of molality, we can find the number of moles of glucose in the solution

$$m_{\text{solute}} = 0.67 \text{ mol/kg} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{n_{\text{glucose}}}{0.1500 \text{ kg}}$$

Interactive Example 11.8 - Solution (Continued 2)

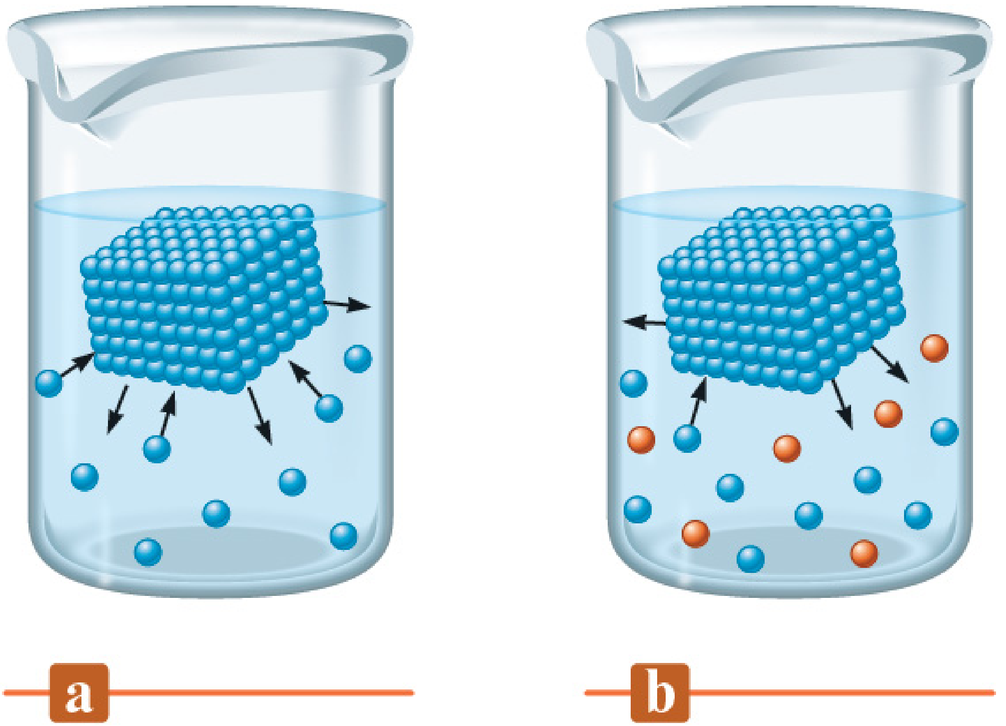
$$n_{\text{glucose}} = (0.67\ \text{mol/kg})(0.1500\ \text{kg}) = 0.10\ \text{mol}$$

- Thus, 0.10 mole of glucose has a mass of 18.00 g, and 1.0 mole of glucose has a mass of 180 g (10 × 18.00 g)
- The molar mass of glucose is 180 g/mol

Freezing-Point Depression

- When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent
- Water in a solution has lower vapor pressure than that of pure ice
  - As the solution is cooled, the vapor pressure of ice and that of liquid water will become equal
    - Temperature at this point is below 0° C, and the freezing point has been depressed

Figure 11.16 - Model of Freezing-Point Depression



Ice in equilibrium with liquid water

Ice in equilibrium with liquid water containing a dissolved solute

Equation for Freezing-Point Depression

$$\Delta T = K_{\mathrm{f}} m_{\mathrm{solute}}$$

- ΔT - Freezing-point depression
- K_{f} - **Molal freezing-point depression constant**
- m_{solute} - Molality of solute

- Used to:
  - Ascertain molar masses
  - Characterize solutions

Exercise

- Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($HOCH_2CH_2OH$) in water
  - Ethylene glycol is a nonelectrolyte

$$T_f = 229.9^\circ\ \mathrm{C}$$

$$T_b = 108.2^\circ\ \mathrm{C}$$

Interactive Example 11.10 - Determining Molar Mass by Freezing-Point Depression

- A chemist is trying to identify a human hormone that controls metabolism by determining its molar mass
  - A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240° C
  - Calculate the molar mass of the hormone

Interactive Example 11.10 - Solution

- K_f for benzene is 5.12° C · kg/mol, so the molality of the hormone is:

$$m_{\text{hormone}} = \frac{\Delta T}{K_{\text{f}}} = \frac{0.240\text{캟}}{5.12\text{캟}\,\text{kg/mol}}$$

$$= 4.69 \times 10^{-2} \text{ mol/kg}$$

Interactive Example 11.10 - Solution (Continued 1)

- The moles of hormone can be obtained from the definition of molality:

$$4.69 \times 10^{-2}\ \text{mol/kg} = m_{\text{solute}} = \frac{\text{mol hormone}}{0.0150\ \text{kg benzene}}$$

Or

$$\text{mol hormone} = \left(4.69 \times 10^{-2}\ \frac{\text{mol}}{\text{kg}}\right)(0.0150\ \text{kg}) = 7.04 \times 10^{-4}\ \text{mol}$$

Interactive Example 11.10 - Solution (Continued 2)

- Since 0.546 g hormone was dissolved, 7.04×10^{-4} mole of hormone has a mass of 0.546 g, and

$$\frac{0.546 \text{ g}}{7.04 \times 10^{-4} \text{ mol}} = \frac{x}{1.00 \text{ mol}}$$

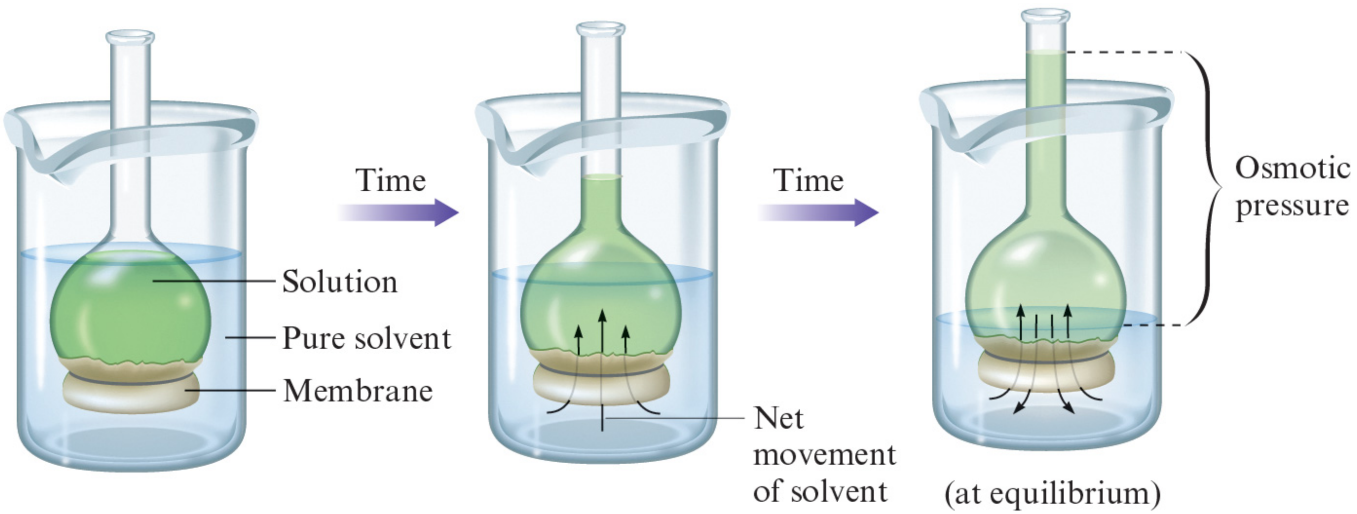
$$x = 776$$

- Thus, the molar mass of the hormone is 776 g/mol

Osmosis

- Flow of solvent into solution through a **semipermeable membrane**
  - **Semipermeable membrane**: Permits solvent but not solute molecules to pass through
- **Osmotic pressure**: Result of increased hydrostatic pressure on the solution than on the pure solvent
  - Caused by the difference in levels of the liquids at equilibrium

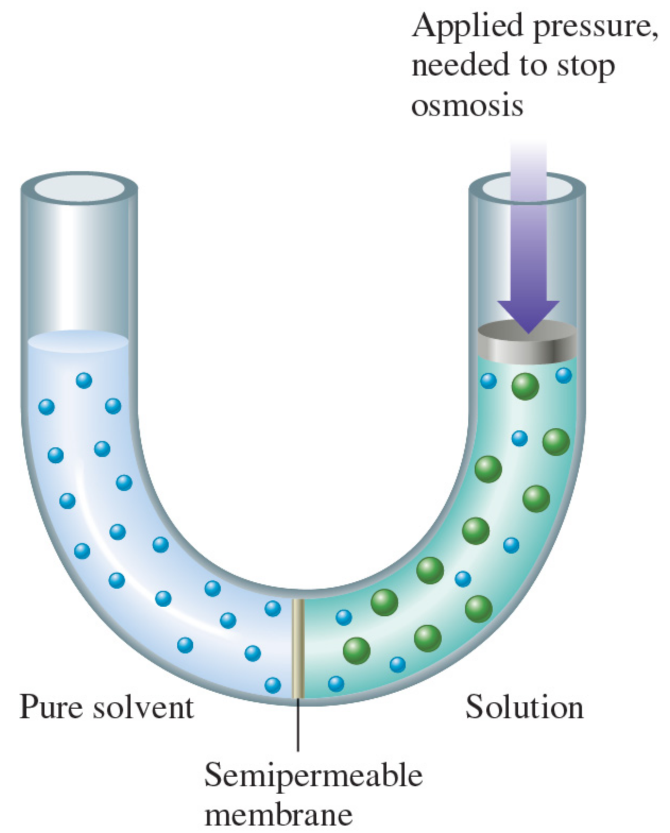
Figure 11.17 - Process of Osmosis



A tube with a bulb on the end that is covered by a semipermeable membrane and the solution is inside the tube and is bathed in the pure solvent; there is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions

Preventing Osmosis

- Apply pressure to the solution
  - Minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution



Uses of Osmotic Pressure

- Characterizes solutions
- Determines molar masses
- A small concentration of solute produces a relatively large osmotic pressure

Understanding Osmotic Pressure

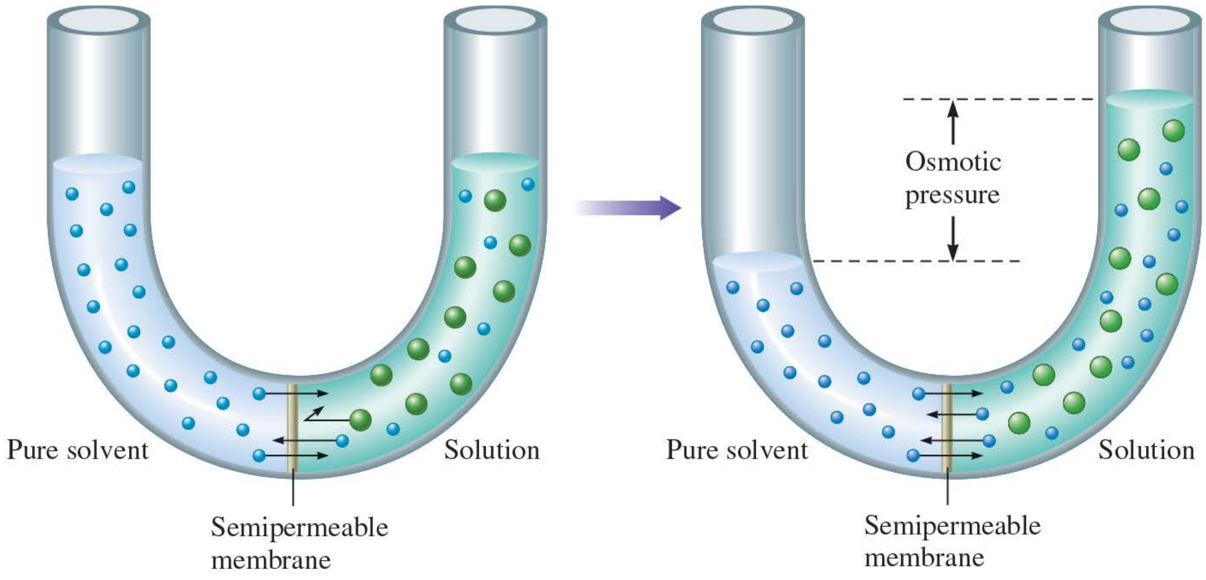
- Equation that represents the dependence of osmotic pressure on solution concentration

$$\Pi = MRT$$

  - Π - Osmotic pressure in atmospheres
  - *M* - Molarity of the solution
  - *R* - Gas law constant
  - *T* - Kelvin temperature

Critical Thinking

- Consider the following model of osmotic pressure:



Critical Thinking (continued)

- What if both sides contained a different pure solvent, each with a different vapor pressure?
  - What would the system look like at equilibrium?
  - Assume the different solvent molecules are able to pass through the membrane

Interactive Example 11.11 - Determining Molar Mass from Osmotic Pressure

- To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution
  - The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C
    - Calculate the molar mass of the protein

Interactive Example 11.11 - Solution

- We use the following equation:

$$\Pi = MRT$$

- In this case we have:

$$\Pi = 1.12 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.47 \times 10^{-3} \text{ atm}$$

  - R = 0.08206 L · atm/K · mol
  - *T* = 25.0 + 273 = 298 K

Interactive Example 11.11 - Solution (Continued 1)

- Note that the osmotic pressure must be converted to atmospheres because of the units of *R*
  - Solving for *M* gives

$$M = \frac{1.47 \times 10^{-3}\ \text{atm}}{\left(0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}\right)\left(298\ \text{K}\right)} = 6.01 \times 10^{-5}\ \text{mol/L}$$

Interactive Example 11.11 - Solution (Continued 2)

- Since 1.00×10^{-3} g protein was dissolved in 1 mL solution, the mass of protein per liter of solution is 1.00 g
  - The solution's concentration is 6.01×10^{-5} mol/L
    - This concentration is produced from 1.00×10^{-3} g protein per milliliter, or 1.00 g/L
    - Thus 6.01×10^{-5} mol protein has a mass of 1.00 g

Interactive Example 11.11 - Solution (Continued 3)

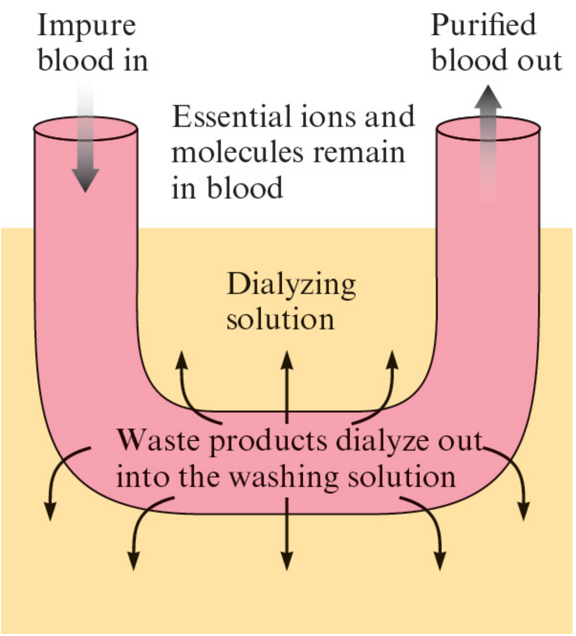
$$\frac{1.00 \text{ g}}{6.01 \times 10^{-5} \text{ mol}} = \frac{x}{1.00 \text{ mol}}$$

$$x = 1.66 \times 10^{4} \text{ g}$$

- The molar mass of the protein is 1.66×10^{4} g/mol
  - This molar mass may seem very large, but it is relatively small for a protein

Dialysis

- Occurs at the walls of most animal and plant cells
  - Membranes permit the transfer of:
    - Solvent molecules
    - Small solute molecules and ions
- Application
  - Use of artificial kidney machines to purify blood



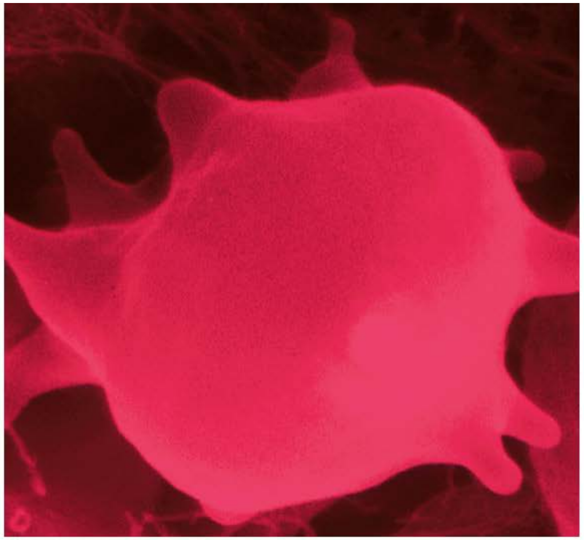
Isotonic, Hypertonic, and Hypotonic Solutions

- **Isotonic solutions**: Solutions with identical osmotic pressures
  - Intravenously administered fluids must be isotonic with body fluids
- Hypertonic solutions - Have osmotic pressure higher than that of the cell fluids
- Hypotonic solutions - Have osmotic pressure lower than that of the cell fluids

Red Blood Cells (RBCs) and Osmosis

- RBCs in a hypertonic solution undergo crenation
  - Shrivel up as water moves out of the cells

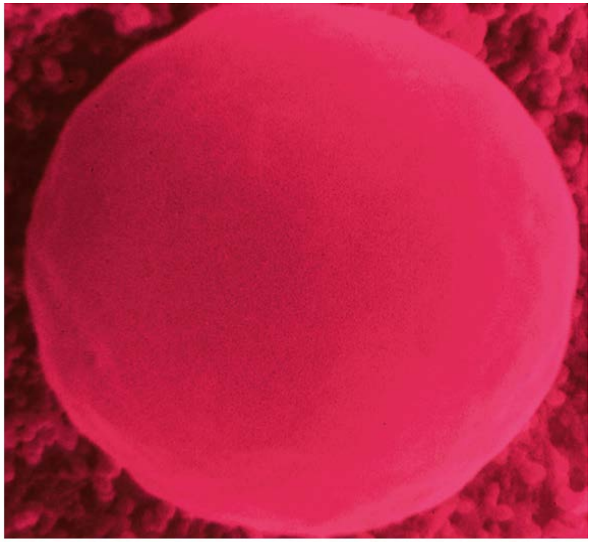
Normal



Shriveled

Red Blood Cells (RBCs) and Osmosis (continued)

- RBCs in a hypotonic solution undergo hemolysis
  - Swell up and rupture as excess water flows into the cells



Swollen

Join In (12)

- Consider a setup in which pure water is separated from an aqueous sugar solution by a semipermeable membrane, which allows water to pass freely but not sugar
  - After some time has passed, what will have happened to the concentration of the sugar solution?
    a. It will have increased
    b. It will have decreased
    c. It will not have changed

Interactive Example 11.12 - Isotonic Solutions

- What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood (Π = 7.70 atm at 25°C)?

Interactive Example 11.12 - Solution

- We can calculate the molarity of the solute from the following equation:

$$\Pi = MRT \quad \text{or} \quad M = \frac{\Pi}{RT}$$

$$M = \frac{7.70 \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.315 \text{ mol/L}$$

  - This represents the total molarity of solute particles

Interactive Example 11.12 - Solution (continued)

- NaCl gives two ions per formula unit
  - Therefore, the concentration of NaCl needed is

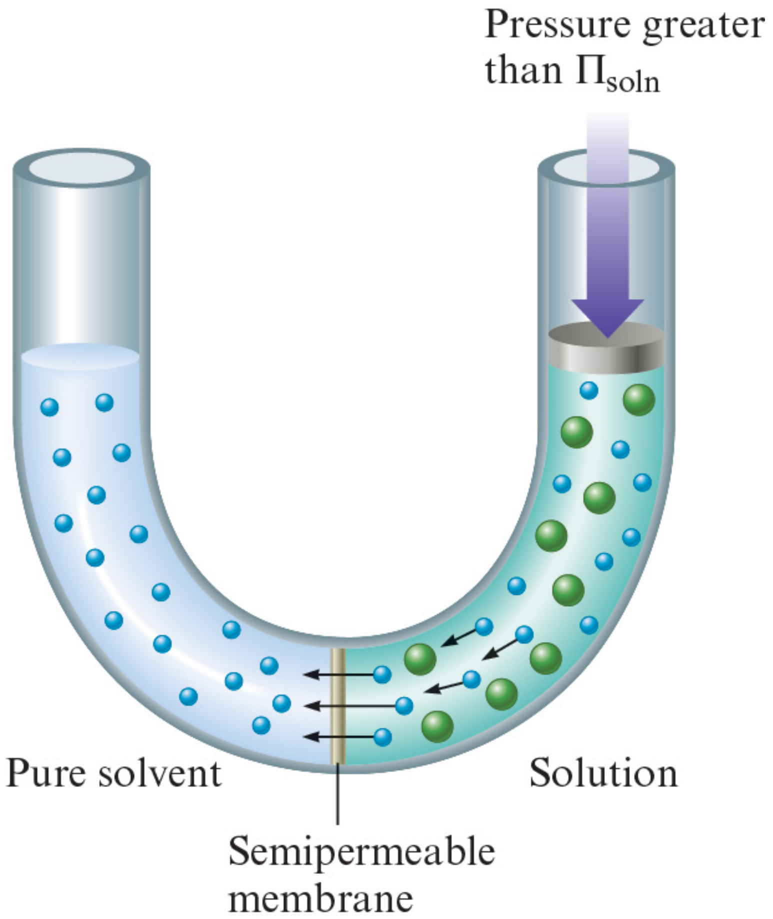
$$\frac{0.315\ M}{2} = 0.1575\ M = 0.158\ M$$

$$\underset{0.1575\ M}{\mathrm{NaCl}} \longrightarrow \underbrace{\underset{0.1575\ M}{\mathrm{Na}^{+}} + \mathrm{Cl}^{-}}_{0.315\ M}$$

Reverse Osmosis

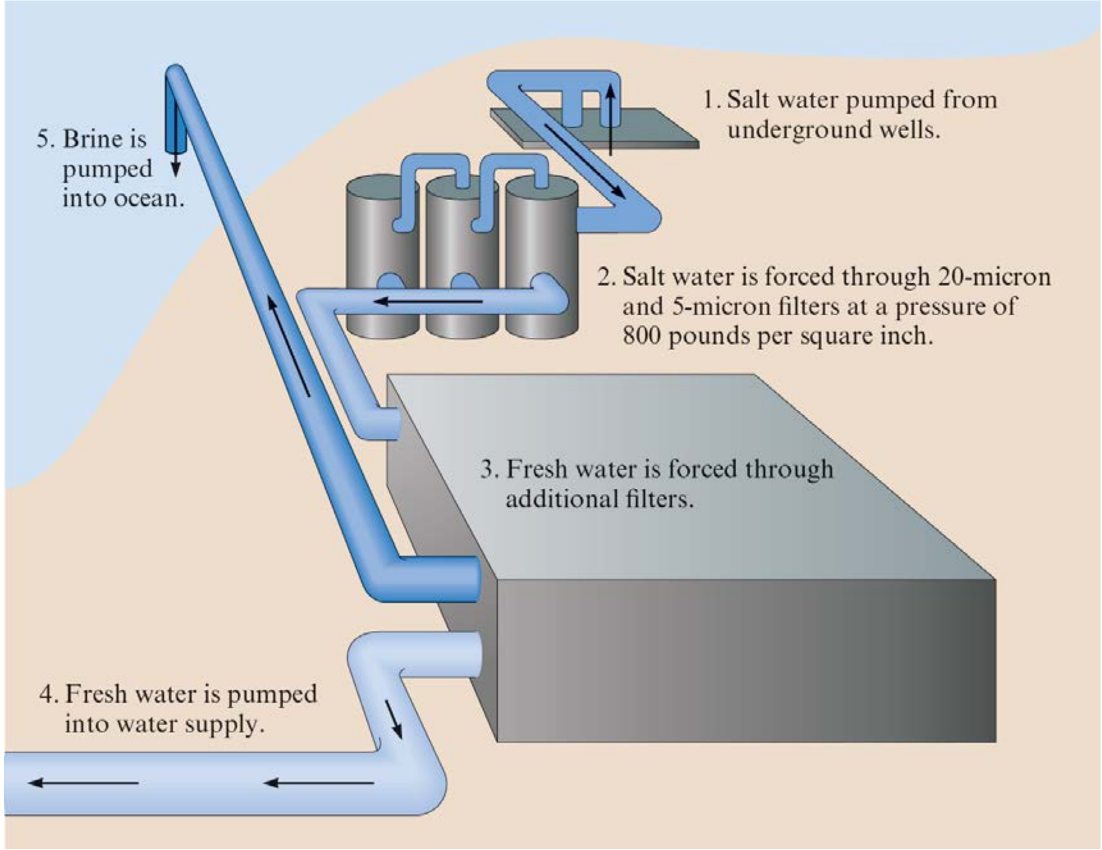
- Results when a solution in contact with a pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure
  - Pressure will cause a net flow of solvent from the solution to the solvent
  - Semipermeable membrane acts as a molecular filter
    - Removes solute particles

Figure 11.21 - Reverse Osmosis



Desalination

- Removal of dissolved salts from a solution



van’t Hoff Factor, *i*

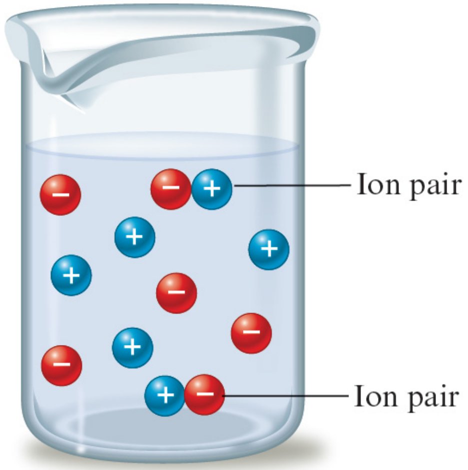
- Provides the relationship between the moles of solute dissolved and the moles of particles in solution

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

  - Expected value for *i* can be calculated for a salt by noting the number of ions per formula unit

Ion Pairing

- Oppositely charged ions aggregate and behave as a single particle
- Occurs in solutions
- Example
  - Sodium and chloride ions in NaCl



Ion Pairing (continued)

- Essential in concentrated solutions
  - As the solution becomes more dilute, ions are spread apart leading to less ion pairing
- Occurs in all electrolyte solutions to some extent
- Deviation of *i* from the expected value is the greatest when ions have multiple charges
  - Ion pairing is important for highly charged ions

Table 11.6 - Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	*i* (expected)	*i* (observed)
NaCl	2.0	1.9
$MgCl_2$	3.0	2.7
$MgSO_4$	2.0	1.3
$FeCl_3$	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

Ion Pairing in Electrolyte Solutions

- Colligative properties are given by including the van't Hoff factor in the necessary equation
  - For changes in freezing and boiling points

$$\Delta T = imK$$

    - *K* - Freezing-point depression or boiling-point elevation constant for the solvent
  - For osmotic pressure

$$\Pi = iMRT$$

Interactive Example 11.13 - Osmotic Pressure

- The observed osmotic pressure for a 0.10-*M* solution of $Fe(NH_4)_2(SO_4)_2$ at 25°C is 10.8 atm
  - Compare the expected and experimental values for *i*

Interactive Example 11.13 - Solution

- The ionic solid $Fe(NH_4)_2(SO_4)_2$ dissociates in water to produce 5 ions:

$$Fe(NH_4)_2(SO_4)_2 \xrightarrow{H_2O} Fe^{2+} + 2NH_4^+ + 2SO_4^{2-}$$

  - Thus, the expected value for *i* is 5

Interactive Example 11.13 - Solution (Continued 1)

- We can obtain the experimental value for *i* by using the equation for osmotic pressure:

$$\Pi = iMRT \quad \text{or} \quad i = \frac{\Pi}{MRT}$$

  - Π = 10.8 atm
  - M = 0.10 mol/L
  - R = 0.08206 L · atm/K · mol
  - T = 25 + 273 = 298 K

Interactive Example 11.13 - Solution (Continued 2)

- Substituting these values into the equation gives:

$$i = \frac{\Pi}{MRT} = \frac{10.8 \text{ atm}}{(0.10 \text{ mol/L})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

$$i = 4.4$$

- The experimental value for *i* is less than the expected value, presumably because of ion pairing

Join In (13)

- As the concentration of a NaCl solution increases, ion pairing is expected to:
  a. increase
  b. decrease
  c. stay the same

Join In (14)

- Which of the following 0.05 m solutions is expected to exhibit the greatest ion pairing?
  a. NaCl
  b. MgCl
  c. $FeCl_3$

The Tyndall Effect

- Scattering of light by particles
- Used to distinguish between a suspension and a true solution
  - When a beam of intense light is projected:
    - The beam is visible from the side in a suspension
      - Light is scattered by suspended particles
    - The light beam is invisible in a true solution
      - Individual ions and molecules dispersed in the solution are too small to scatter visible light

Figure 11.24 - Tyndall Effect

Colloidal Dispersion or Colloids

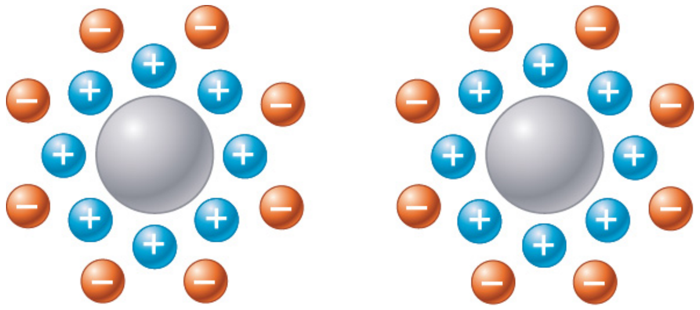
- Suspension of tiny particles in some medium
  - Can either be single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm
- Classified according to the states of the dispersed phase and the dispersing medium

Table 11.7 - Types of Colloids

Examples	Dispersing Medium	Dispersed Substance	Colloid Type
Fog, aerosol sprays	Gas	Liquid	Aerosol
Smoke, airborne bacteria	Gas	Solid	Aerosol
Whipped cream, soapsuds	Liquid	Gas	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Liquid	Solid	Sol
Marshmallow, polystyrene foam	Solid	Gas	Solid foam
Butter, cheese	Solid	Liquid	Solid emulsion
Ruby glass	Solid	Solid	Solid sol

Stabilizing Colloids

- Major factor - Electrostatic repulsions
  - A colloid is electrically neutral
    - Each particle in the center is surrounded by a layer of positive ions, with negative ions in the outer layer
    - When placed in an electric field, the center attracts from the medium a layer of ions, all of the same charge
  - Outer layer contains ions with the same charge that repel each other



Coagulation

- Destruction of a colloid
- Heating increases the velocities of the particles, causing them to collide
  - Ion barriers are penetrated, and the particles can aggregate
    - Repetition of the process enables the particle to settle out
  - Adding an electrolyte neutralizes the adsorbed ion layers

Examples of Coagulation

- Colloidal clay particles in seawater coagulate owing to high salt content
- Removal of soot from smoke
  - The suspended particles are removed when smoke is passed through an electrostatic precipitator