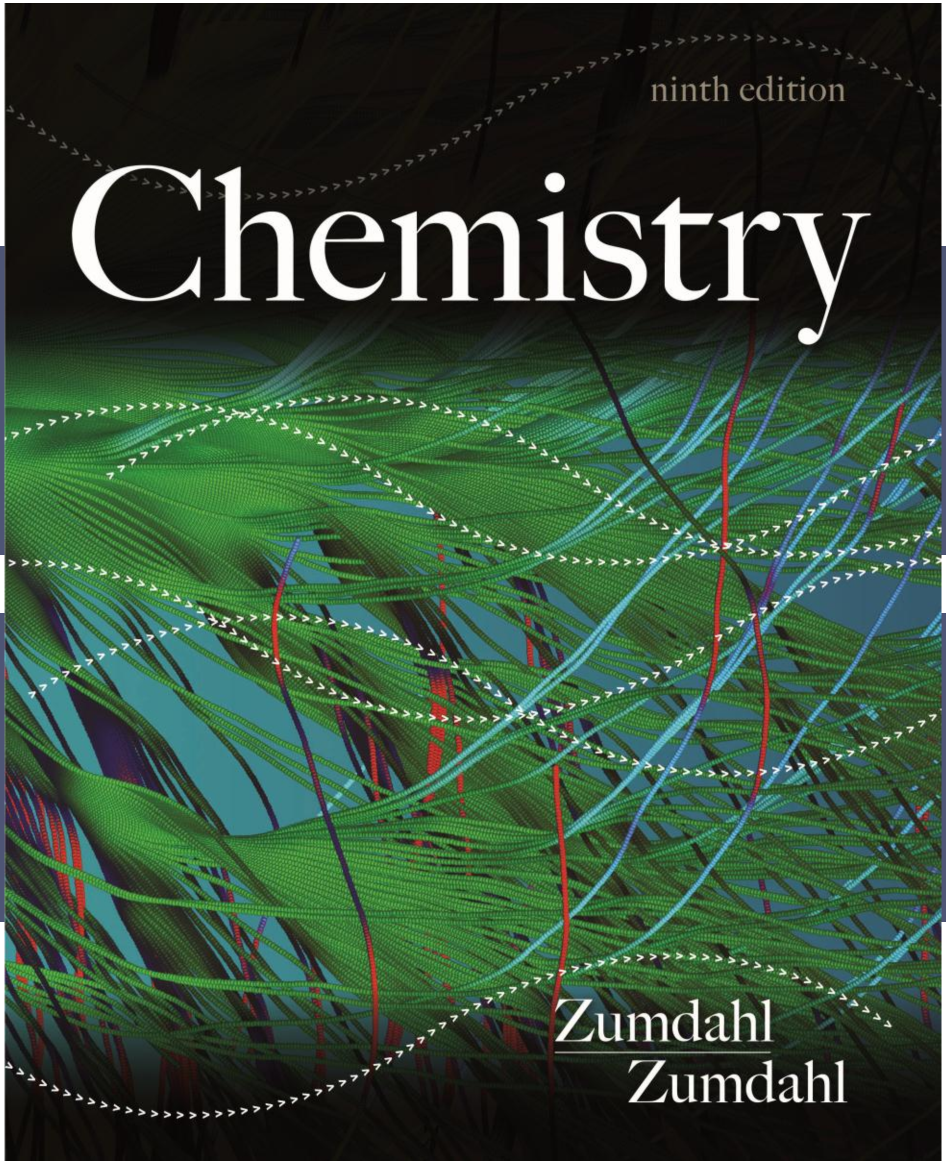


Chapter 11

Properties of Solutions

Chapter 11
Table of Contents

Table 11.1 - Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

Solution Composition

- As mixtures have variable composition, relative amounts of substances in a solution must be specified
  - Qualitative terms - Dilute and concentrated
  - **Molarity** (*M*): Number of moles of solute per liter of solution

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

Solution Composition (Continued)

- **Mass percent** (weight percent)

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}}\right) \times 100\%$$

- **Mole fraction** (χ)

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B}$$

- **Molality** (m)

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Interactive Example 11.1 - Various Methods for Describing Solution Composition

- A solution is prepared by mixing 1.00 g ethanol (C_2H_5OH) with 100.0 g water to give a final volume of 101 mL
  - Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution

Interactive Example 11.1 - Solution

- Molarity
  - The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 2.17 \times 10^{-2} \text{ mol } C_2H_5OH$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

Interactive Example 11.1 - Solution (Continued 1)

$$\text{Molarity of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}}$$

$$\text{Molarity of } C_2H_5OH = 0.215\ M$$

- Mass percent

$$\text{Mass percent } C_2H_5OH = \left(\frac{\text{mass of } C_2H_5OH}{\text{mass of solution}}\right) \times 100\%$$

$$= \left(\frac{1.00 \text{ g } C_2H_5OH}{100.0 \text{ g } H_2O + 1.00 \text{ g } C_2H_5OH}\right) \times 100\% = 0.990\%\ C_2H_5OH$$

Interactive Example 11.1 - Solution (Continued 2)

- Mole fraction

$$\text{Mole fraction of } C_2H_5OH = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{H_2O}}$$

$$n_{H_2O} = 100.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 5.56 \text{ mol}$$

$$\chi_{C_2H_5OH} = \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}} = \frac{2.17 \times 10^{-2}}{5.58} = 0.00389$$

Interactive Example 11.1 - Solution (Continued 3)

- Molality

$$\text{Molality of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{kilogram of } H_2O} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}}$$

$$= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}} = 0.217\ m$$

Critical Thinking

- You are given two aqueous solutions with different ionic solutes (Solution A and Solution B)
  - What if you are told that Solution A has a greater concentration than Solution B by mass percent, but Solution B has a greater concentration than Solution A in terms of molality?
    - Is this possible?
      - If not, explain why not
      - If it is possible, provide example solutes for A and B and justify your answer with calculations

Normality (*N*)

- Measure of concentration
- Number of equivalents per liter of solution
  - Definition of an equivalent depends on the reaction that takes place in a solution
    - For acid–base reactions, the equivalent is the mass of acid or base that can accept or provide exactly 1 mole of protons
    - For oxidation–reduction reactions, the equivalent is the quantity of oxidizing or reducing agent that can accept or provide 1 mole of electrons

Interactive Example 11.2 - Calculating Various Methods of Solution Composition from the Molarity

- The electrolyte in automobile lead storage batteries is a 3.75 *M* sulfuric acid solution that has a density of 1.230 g/mL
  - Calculate the mass percent, molality, and normality of the sulfuric acid

Interactive Example 11.2 - Solution

- What is the density of the solution in grams per liter?

$$1.230\frac{\text{g}}{\text{mL}} \times \frac{1000\text{ mL}}{1\text{ L}} = 1.230 \times 10^3\text{ g/L}$$

- What mass of H_2SO_4 is present in 1.00 L of solution?
    - We know 1 liter of this solution contains 1230 g of the mixture of sulfuric acid and water

Interactive Example 11.2 - Solution (Continued 1)

- Since the solution is 3.75 *M*, we know that 3.75 moles of H_2SO_4 is present per liter of solution
- The number of grams of H_2SO_4 present is

$$3.75 \text{ mol} \times \frac{98.0 \text{ g } H_2SO_4}{1 \text{ mol}} = 368 \text{ g } H_2SO_4$$

Interactive Example 11.2 - Solution (Continued 2)

- How much water is present in 1.00 L of solution?
  - The amount of water present in 1 liter of solution is obtained from the difference

$$1230 \text{ g solution} - 368 \text{ g } H_2SO_4 = 862 \text{ g } H_2O$$

- What is the mass percent?
  - Since we now know the masses of the solute and solvent, we can calculate the mass percent

Interactive Example 11.2 - Solution (Continued 3)

$$\text{Mass percent } H_2SO_4 = \frac{\text{mass of } H_2SO_4}{\text{mass of solution}} \times 100\%$$

$$= \frac{368 \text{ g}}{1230 \text{ g}} \times 100\% = 29.9\% \; H_2SO_4$$

- What is the molality?
  - From the moles of solute and the mass of solvent, we can calculate the molality

Interactive Example 11.2 - Solution (Continued 4)

$$\text{Molality of } H_2SO_4 = \frac{\text{moles } H_2SO_4}{\text{kilogram of } H_2O}$$

$$= \frac{3.75 \text{ mol } H_2SO_4}{862 \text{ g } H_2O \times \dfrac{1 \text{ kg } H_2O}{1000 \text{ g } H_2O}} = 4.35\ m$$

Interactive Example 11.2 - Solution (Continued 5)

- What is the normality?
  - Since each sulfuric acid molecule can furnish two protons, 1 mole of H_2SO_4 represents 2 equivalents
  - Thus, a solution with 3.75 moles of H_2SO_4 per liter contains $2 \times 3.75 = 7.50$ equivalents per liter
    - The normality is 7.50 *N*

Steps Involved in the Formation of a Liquid Solution

1. Expand the solute
   - Separate the solute into its individual components
2. Expand the solvent
   - Overcome intermolecular forces in the solvent to make room for the solute
3. Allow the solute and solvent to interact to form the solution

Steps Involved in the Formation of a Liquid Solution (Continued)

- Steps 1 and 2 are endothermic
  - Forces must be overcome to expand the solute and solvent
- Step 3 is often exothermic

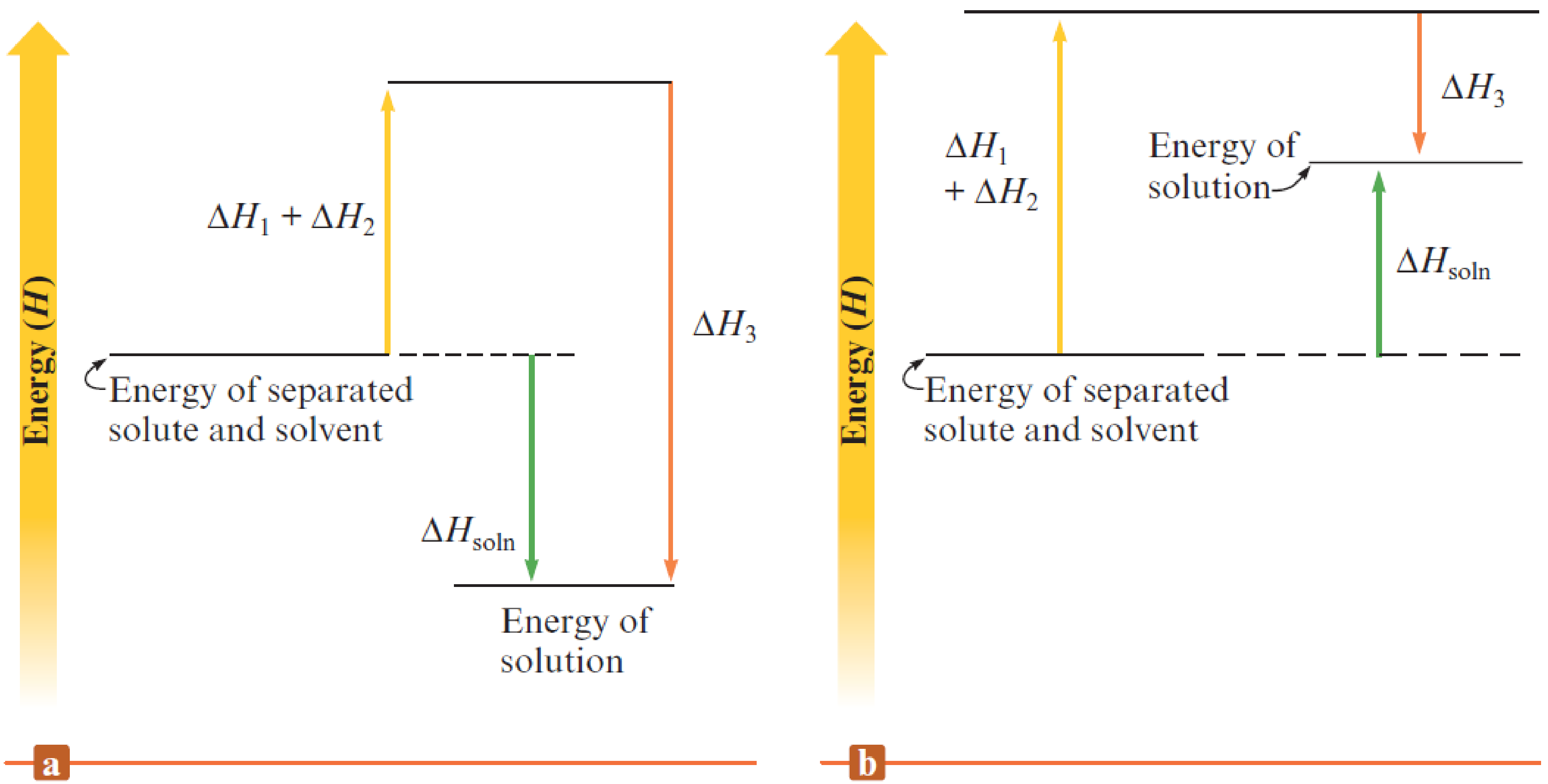
Enthalpy (Heat) of Solution (ΔH_{soln})

- Enthalpy change associated with the formation of the solution is the sum of the ΔH values for the steps:

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

  - ΔH_{soln} can have a positive sign when energy is absorbed or a negative sign when energy is released

Figure 11.2 - The Heat of Solution



Factors That Favor a Process

- Increase in probability of the mixed state when the solute and solvent are placed together
- Processes that require large amounts of energy tend not to occur
- Like dissolves like

Table 11.3 - The Energy Terms for Various Types of Solutes and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

Critical Thinking

- You and a friend are studying for a chemistry exam
  - What if your friend tells you, "Since exothermic processes are favored and the sign of the enthalpy change tells us whether or not a process is endothermic or exothermic, the sign of ΔH_{soln} tells us whether or not a solution will form"?
    - How would you explain to your friend that this conclusion is not correct? What part, if any, of what your friend says is correct?

Interactive Example 11.3 - Differentiating Solvent Properties

- Decide whether liquid hexane (C_6H_{14}) or liquid methanol (CH_3OH) is the more appropriate solvent for the substances grease ($C_{20}H_{42}$) and potassium iodide (KI)

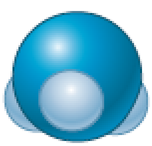
Interactive Example 11.3 - Solution

- Hexane is a nonpolar solvent because it contains C—H bonds
  - Hexane will work best for the nonpolar solute grease
- Methanol has an O—H group that makes it significantly polar
  - Will serve as the better solvent for the ionic solid KI

Exercise

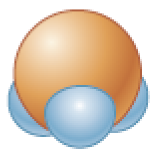
- For each of the following pairs, predict which substance would be more soluble in water

a.



NH_3

or



PH_3

NH_3

b.

CH_3C—OH
||
O

or

CH_3—C—OCH_3
||
O

CH_3COOH

Structure Effects

- Vitamins can be used to study the relationship among molecular structure, polarity, and solubility
  - Fat-soluble vitamins (A, D, E, and K) are nonpolar
    - Considered to be hydrophobic (water-fearing)
    - Can build up in the fatty tissues of the body
  - Water-soluble vitamins (B and C) are polar
    - Considered to be hydrophilic (water-loving)
    - Must be consumed regularly as they are excreted

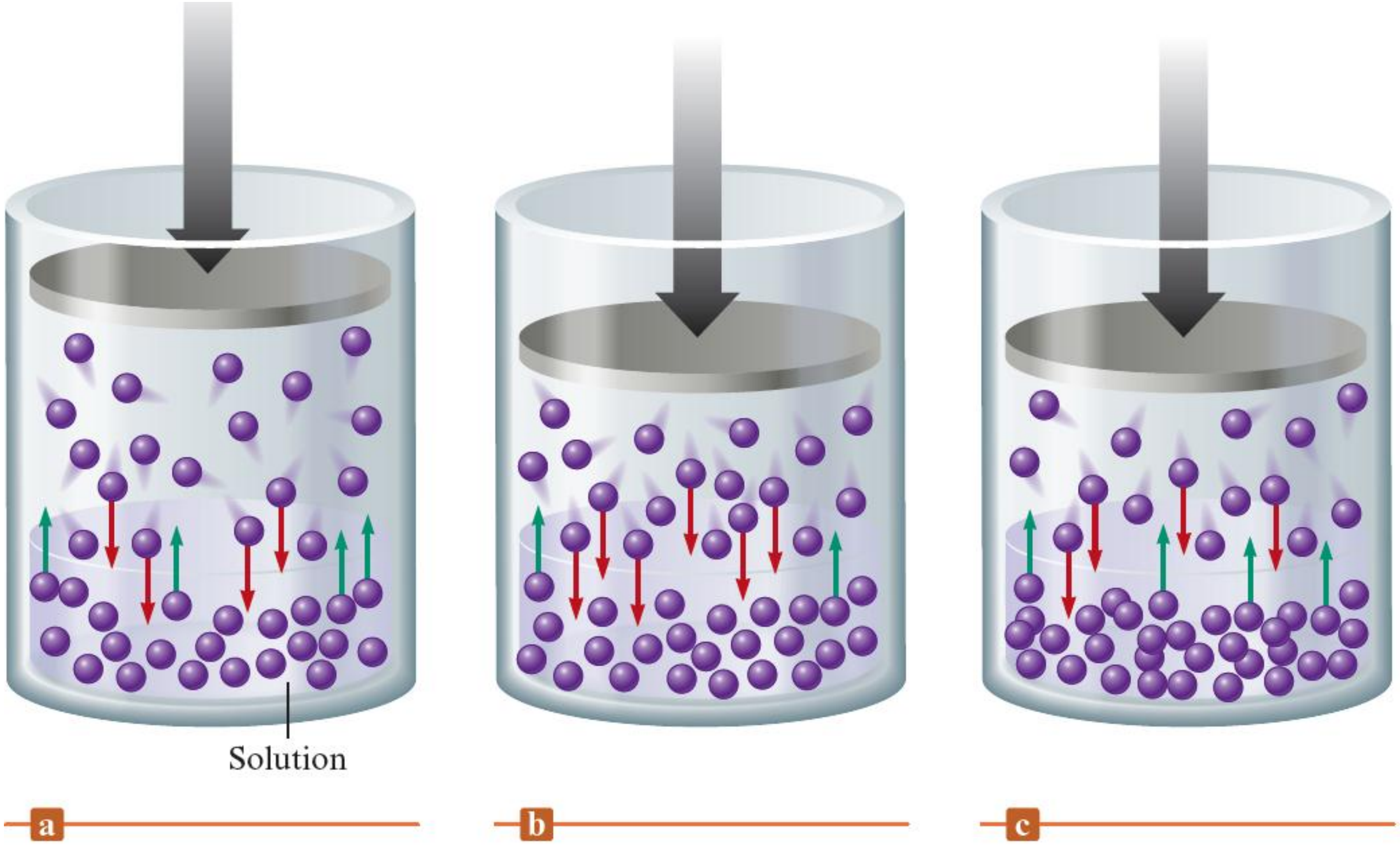
Pressure Effects

- Pressure increases the solubility of a gas
  - **Henry's law**: Amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution

$$C = kP$$

    - *C* - Concentration of the dissolved gas
    - *k* - Constant
    - *P* - Partial pressure of the gaseous solute above the solution

Figure 11.5 - Schematic Diagram That Depicts the Increase in Gas Solubility with Pressure



Interactive Example 11.4 - Calculations Using Henry's Law

- A certain soft drink is bottled so that a bottle at 25° C contains CO_2 gas at a pressure of 5.0 atm over the liquid
  - Assuming that the partial pressure of CO_2 in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO_2 in the soda both before and after the bottle is opened
    - The Henry's law constant for CO_2 in aqueous solution is 3.1×10^{-2} mol/L · atm at 25° C

Interactive Example 11.4 - Solution

- What is Henry's law for CO_2?
  - $C_{CO_2} = k_{CO_2}P_{CO_2}$
    - Where $k_{CO_2} = 3.1 \times 10^{-2}$ mol/L · atm
- What is the C_{CO_2} in the unopened bottle?
  - In the unopened bottle, $P_{CO_2} = 5.0$ atm

$$C_{CO_2} = k_{CO_2}P_{CO_2}$$
$$= \left(3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm}\right)\left(5.0 \text{ atm}\right) = 0.16 \text{ mol/L}$$

Interactive Example 11.4 - Solution (Continued)

- What is the C_{CO_2} in the opened bottle?
  - In the opened bottle, the CO_2 in the soda eventually reaches equilibrium with the atmospheric CO_2, so P_{CO_2} = 4.0×10^{-4} atm and

$$C_{CO_2} = k_{CO_2} P_{CO_2} = \left(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)\left(4.0 \times 10^{-4} \text{ atm}\right)$$

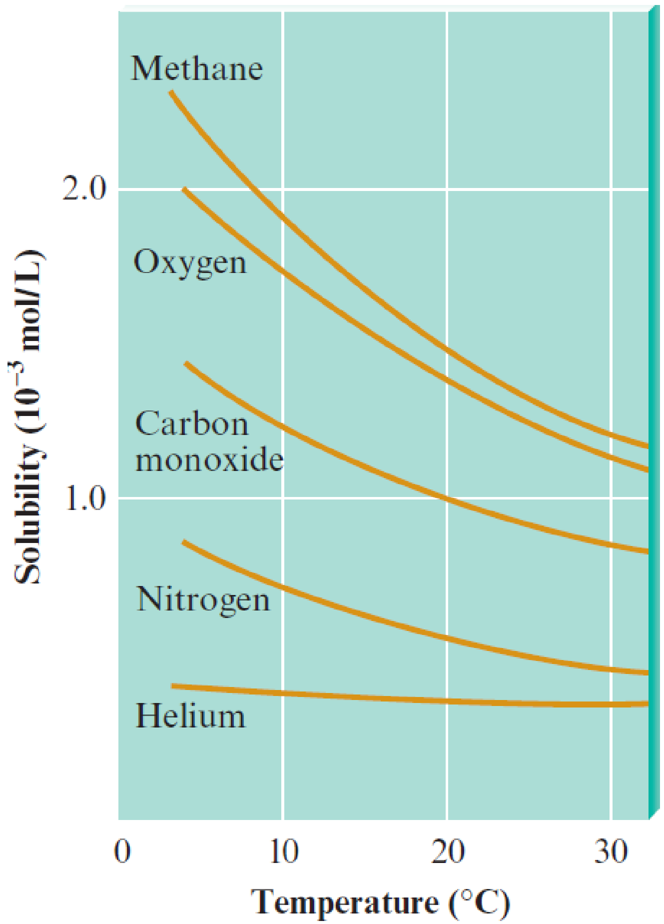
$$= 1.2 \times 10^{-5} \text{ mol/L}$$

  - Note the large change in concentration of CO_2
    - This is why soda goes "flat" after being open for a while

Temperature Effects (for Aqueous Solutions)

- Solids dissolve rapidly at higher temperatures
  - Amount of solid that can be dissolved may increase or decrease with increasing temperature
  - Solubilities of some substances decrease with increasing temperature
- Predicting temperature dependence of solubility is very difficult

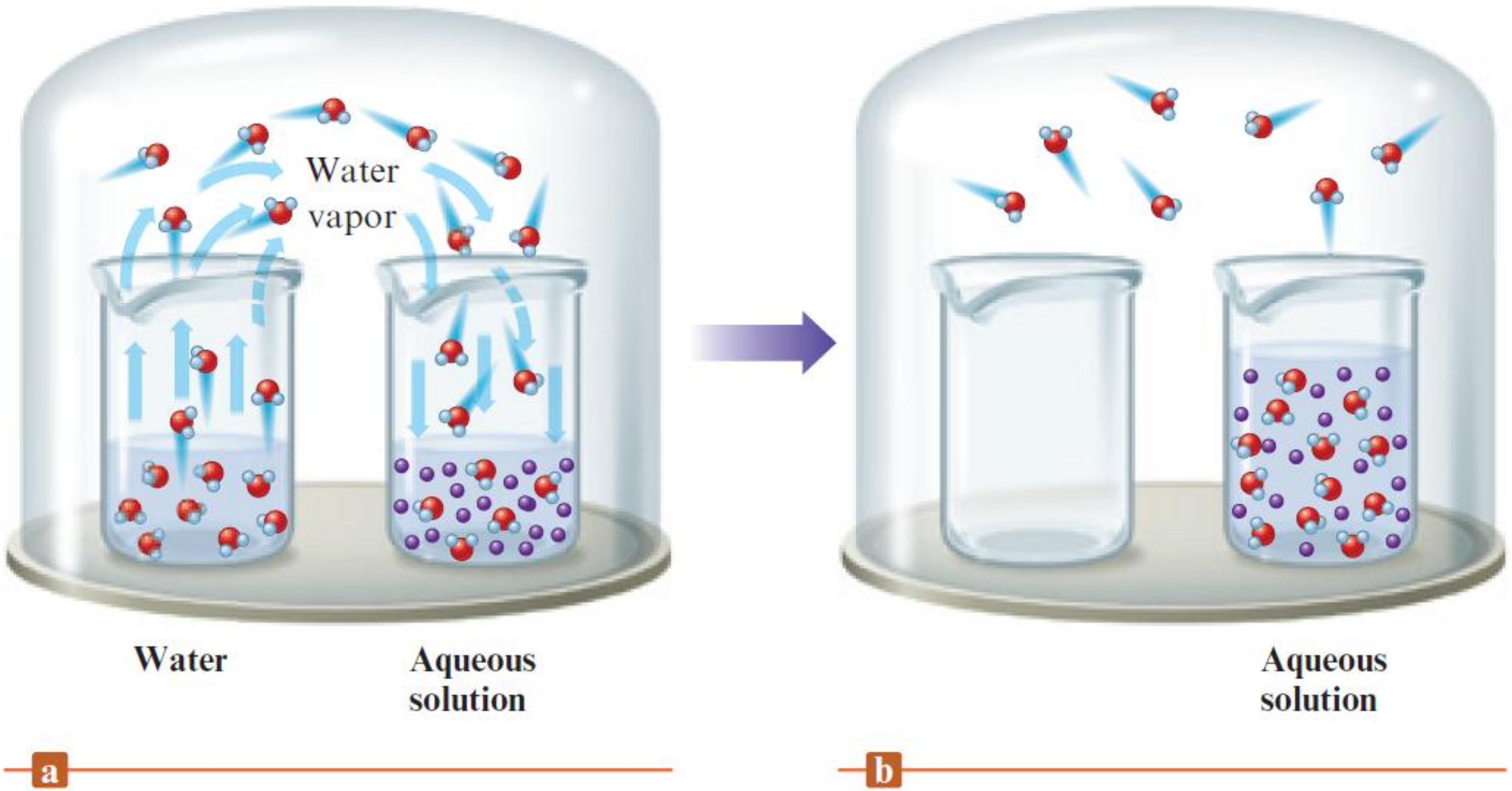
Figure 11.7 - The Solubilities of Several Gases in Water



Temperature Effects (for Aqueous Solutions) (Continued)

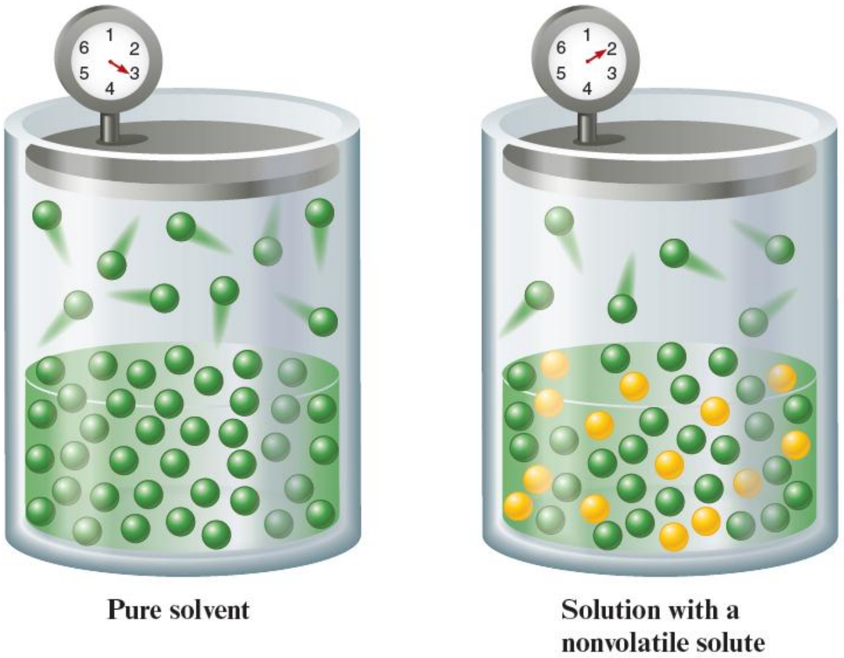
- Solubility of a gas in water decreases with increasing temperature
  - Water used for industrial cooling is returned to its natural source at higher than ambient temperatures
    - Causes **thermal pollution**
    - Warm water tends to float over the colder water, blocking oxygen absorption
  - Leads to the formation of boiler scale

Figure 11.9 - An Aqueous Solution and Pure Water in a Closed Environment



Vapor Pressures of Solutions

- Presence of a nonvolatile solute lowers the vapor pressure of a solvent
  - Inhibits the escape of solvent molecules from the liquid



Raoult's Law

$$P_{\text{soln}} = \chi_{\text{solvent}} P^0_{\text{solvent}}$$

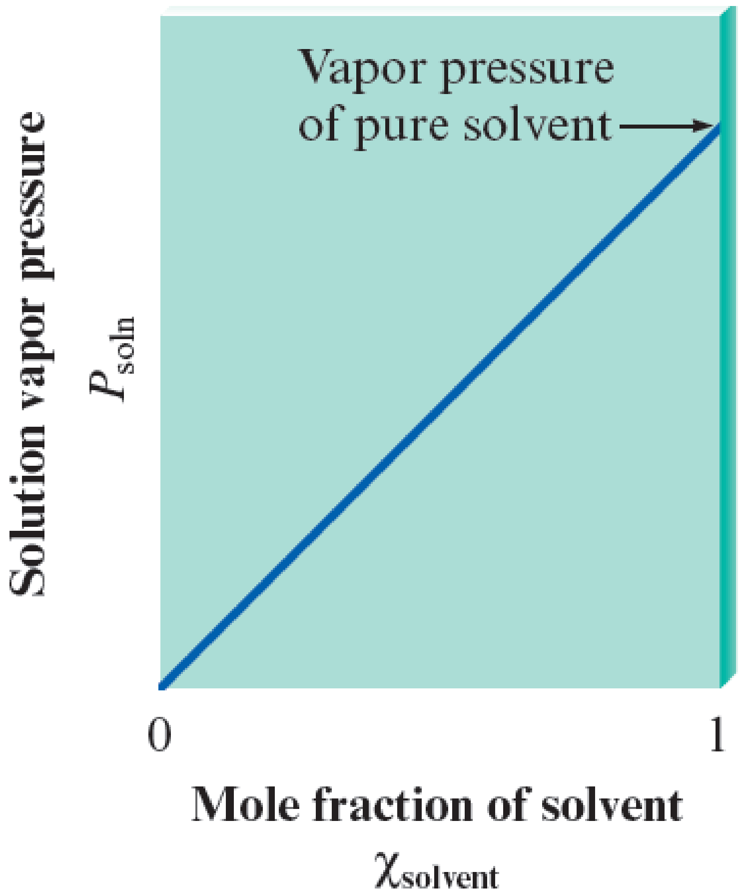
- P_{soln} - Observed vapor pressure of the solution
- $\chi_{solvent}$ - Mole fraction of the solvent
- $P^0_{solvent}$ - Vapor pressure of the pure solvent

- Nonvolatile solute simply dilutes the solvent

Graphical Representation of Raoult's Law

- Can be represented as a linear equation of the form $y = mx + b$
  - $y = P_{soln}$
  - $x = \chi_{solvent}$
  - $m = P^0_{solvent}$
  - $b = 0$
- Slope of the graph is a straight line with a slope equal to $P^0_{solvent}$

Figure 11.11 - Plot of Raoult's Law



Interactive Example 11.5 - Calculating the Vapor Pressure of a Solution

- Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm^3 of water
  - At 25°C, the density of water is 0.9971 g/cm^3 and the vapor pressure is 23.76 torr

Interactive Example 11.5 - Solution

- What is Raoult's law for this case?

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P^0_{\text{H}_2\text{O}}$$

  - To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose and the moles of water present

Interactive Example 11.5 - Solution (Continued 1)

- What are the moles of sucrose?

$$\text{Moles of sucrose} = 158.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} = 0.4616 \text{ mol sucrose}$$

- What are the moles of water?
  - To determine the moles of water present, we first convert volume to mass using the density:

$$643.5 \text{ cm}^3 \text{ H}_2\text{O} \times \frac{0.9971 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} = 641.6 \text{ g H}_2\text{O}$$

Interactive Example 11.5 - Solution (Continued 2)

- The number of moles of water

$$641.6\ \text{g H}_2\text{O} \times \frac{1\ \text{mol H}_2\text{O}}{18.02\ \text{g H}_2\text{O}} = 35.60\ \text{mol H}_2\text{O}$$

- What is the mole fraction of water in the solution?

$$\chi_{\text{H}_2\text{O}} = \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol sucrose}} = \frac{35.60\ \text{mol}}{35.60\ \text{mol} + 0.4616\ \text{mol}}$$

$$= \frac{35.60\ \text{mol}}{36.06\ \text{mol}} = 0.9873$$

Interactive Example 11.5 - Solution (Continued 3)

- The vapor pressure of the solution is:

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P^0_{\text{H}_2\text{O}}$$

$$= (0.9872)(23.76 \text{ torr}) = 23.46 \text{ torr}$$

- The vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution
  - The vapor pressure has been lowered by 0.30 torr

Lowering of the Vapor Pressure

- Helps in counting molecules
  - Provides a means to experimentally determine molar masses
  - Raoult's law helps ascertain the number of moles of solute present in a solution
- Helps characterize solutions
  - Provides valuable information about the nature of the solute after it dissolves

Nonideal Solutions

- Both components are volatile in liquid–liquid solutions
  - Contribute to the total vapor pressure
  - Modified Raoult's law is applied here

$$P_{\text{TOTAL}} = P_{\text{A}} + P_{\text{B}} = \chi_{\text{A}} P_{\text{A}}^{0} + \chi_{\text{B}} P_{\text{B}}^{0}$$

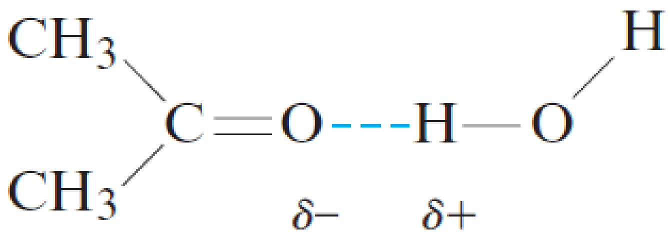
    - P_{TOTAL} - Total vapor pressure of a solution containing A and B
    - χ_{A} and χ_{B} - Mole fractions of A and B

Nonideal Solutions (Continued)

  - P^0_A and P^0_B - Vapor pressures of pure A and pure B
  - P_A and P_B - Partial pressures resulting from molecules of A and of B in the vapor above the solution
- **Ideal solution**: Liquid–liquid solution that obeys Raoult’s law
  - Nearly ideal behavior is observed when solute–solute, solvent–solvent, and solute–solvent interactions are similar

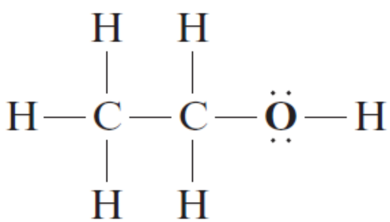
Behavior of Various Types of Solutions

- When ΔH_{soln} is large and negative:
  - Strong interactions exist between the solvent and solute
  - A negative deviation is expected from Raoult's law
    - Both components have low escaping tendency in the solution than in pure liquids
  - Example - Acetone–water solution

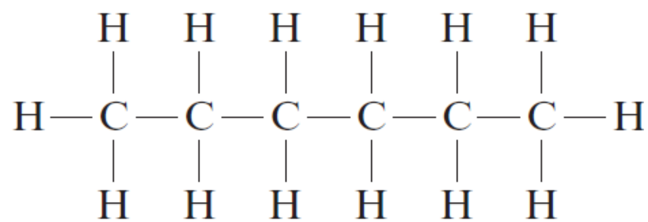


Behavior of Various Types of Solutions (Continued 1)

- When ΔH_{soln} is positive (endothermic), solute–solvent interactions are weaker
  - Molecules in the solution have a higher tendency to escape, and there is positive deviation from Raoult's law
  - Example - Solution of ethanol and hexane



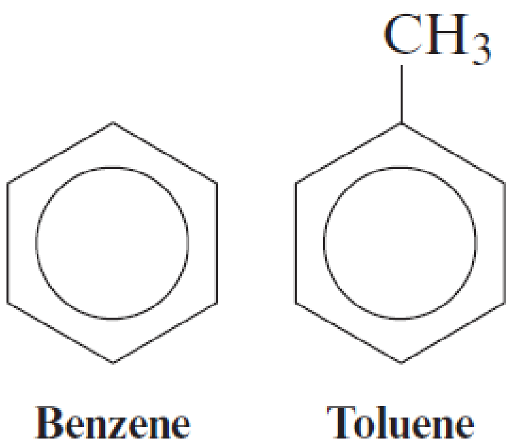
Ethanol



Hexane

Behavior of Various Types of Solutions (Continued 2)

- In a solution of very similar liquids:
  - ΔH_{soln} is close to zero
  - Solution closely obeys Raoult's law
  - Example - Benzene and toluene



Interactive Example 11.7 - Calculating the Vapor Pressure of a Solution Containing Two Liquids

- A solution is prepared by mixing 5.81 g acetone (C_3H_6O, molar mass = 58.1 g/mol) and 11.9 g chloroform ($HCCl_3$, molar mass = 119.4 g/mol)
  - At 35° C, this solution has a total vapor pressure of 260 torr
    - Is this an ideal solution?
    - The vapor pressures of pure acetone and pure chloroform at 35° C are 345 and 293 torr, respectively

Interactive Example 11.7 - Solution

- To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\text{TOTAL}} = \chi_{\text{A}} P_{\text{A}}^{0} + \chi_{\text{C}} P_{\text{C}}^{0}$$

  - A stands for acetone, and C stands for chloroform
    - The calculated value can then be compared with the observed vapor pressure

Interactive Example 11.7 - Solution (Continued 1)

- First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

Interactive Example 11.7 - Solution (Continued 2)

- The solution contains equal numbers of moles of acetone and chloroform

$$\chi_A = 0.500 \text{ and } \chi_C = 0.500$$

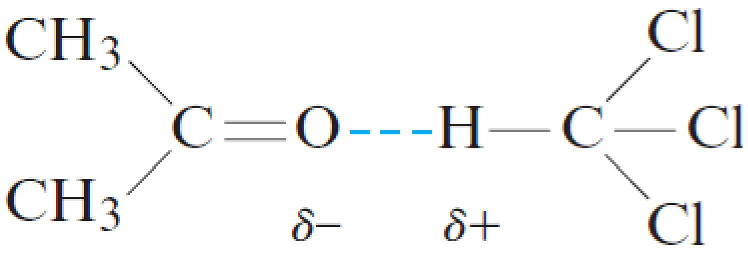
  - The expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$

  - Comparing this value with the observed pressure of 260 torr shows that the solution does not behave ideally

Interactive Example 11.7 - Solution (Continued 3)

- The observed value is lower than that expected
- This negative deviation from Raoult's law can be explained in terms of the hydrogen-bonding interaction which lowers the tendency of these molecules to escape from the solution



Acetone Chloroform

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:

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

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

Figure 11.14 - Phase Diagrams for Pure Water and for an Aqueous Solution Containing a Nonvolatile Solute

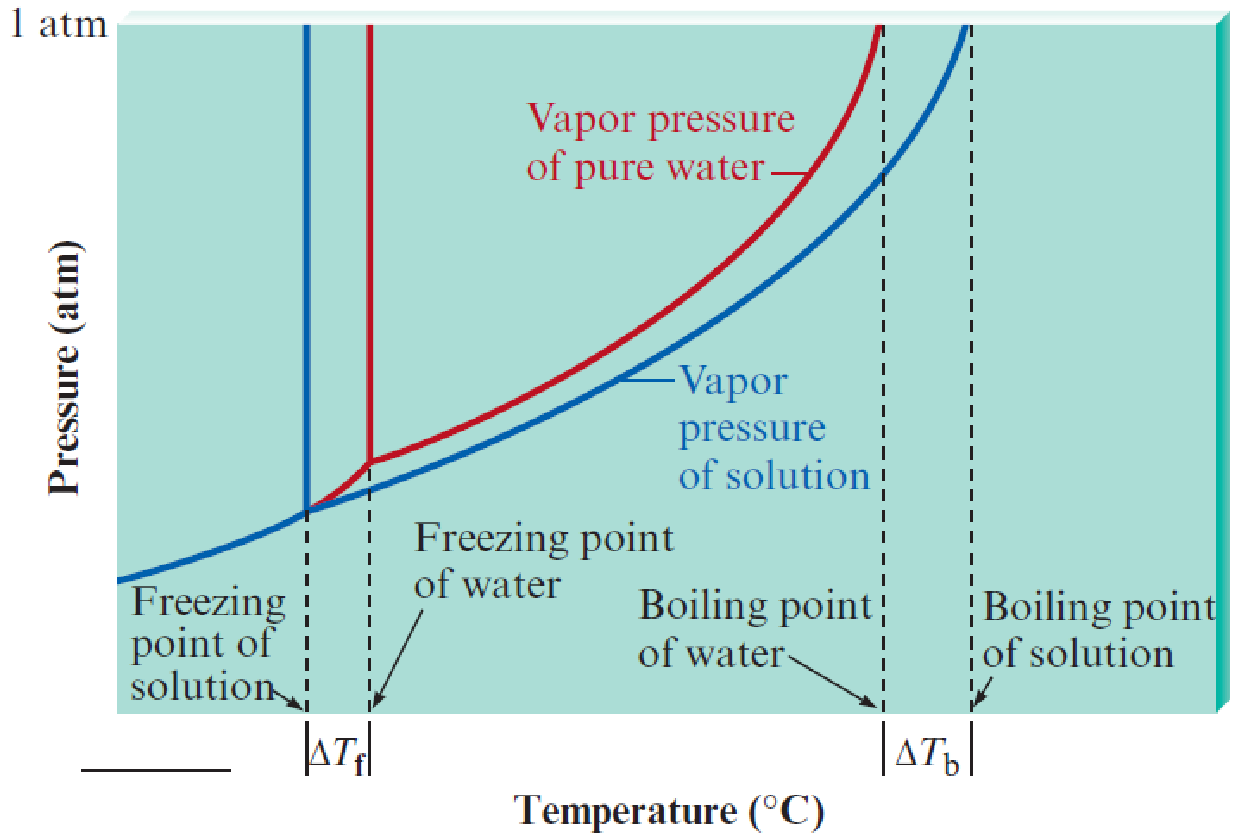


Table 11.5 - Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

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 ΔT = 100.34° C – 100.00° C = 0.34° 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)

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

- 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)

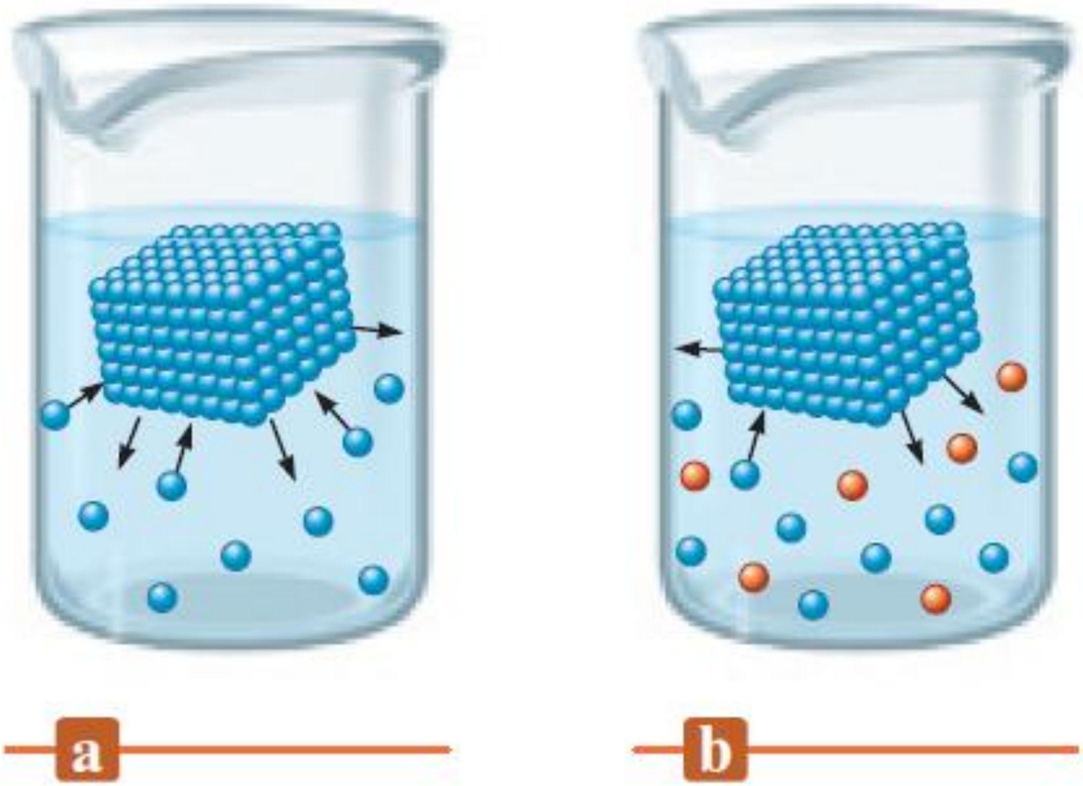
$$n_{\text{glucose}} = (0.67\ \text{mol/kg})(0.1500\ \text{kg}) = 0.10\ \text{mol}$$

- 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 11.15 - Freezing-Point Depression: Model



Ice in equilibrium with liquid water

Ice in equilibrium with liquid water containing a dissolved solute

Equation for Freezing-Point Depression

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

- 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

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

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

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:

$$m_{\text{hormone}} = \frac{\Delta T}{K_f} = \frac{0.240°\text{C}}{5.12°\text{C} \cdot \text{kg/mol}}$$

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

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

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

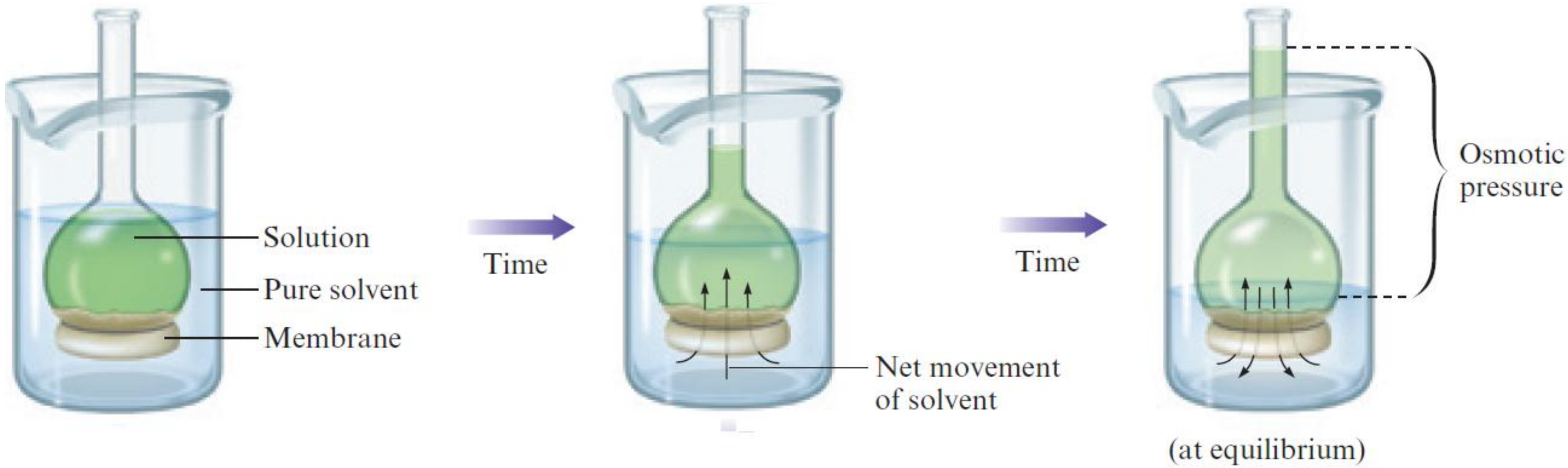
$$x = 776$$

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

Osmosis

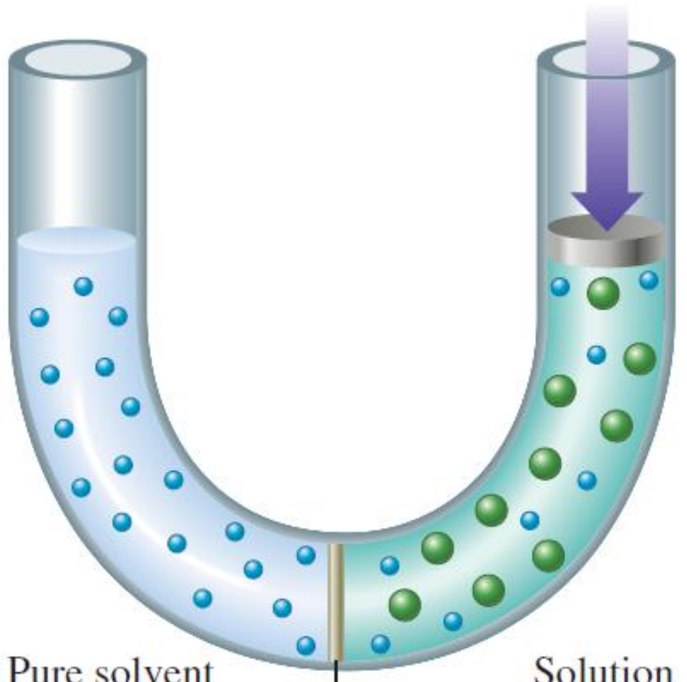
- Flow of solvent into solution through a **semipermeable membrane**
  - **Semipermeable membrane**: Permits solvent but not solute molecules to pass through
- **Osmotic pressure**: Result of increased hydrostatic pressure on the solution than on the pure solvent
  - Caused by the difference in levels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

Figure 11.16 - Process of Osmosis



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

- Characterize solutions
- Determine molar masses
- A small concentration of solute produces a relatively large osmotic pressure

Understanding Osmotic Pressure

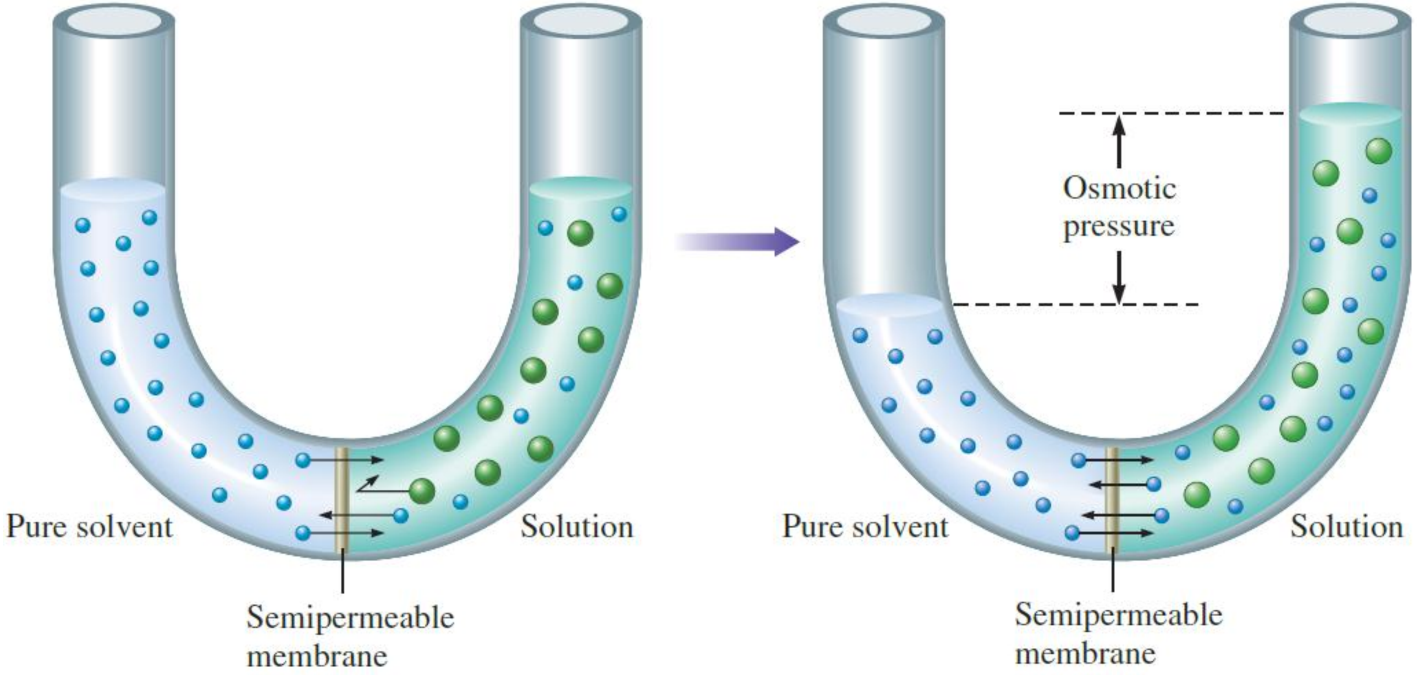
- Equation that represents the dependence of osmotic pressure on solution concentration

$$\Pi = MRT$$

  - 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

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

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)

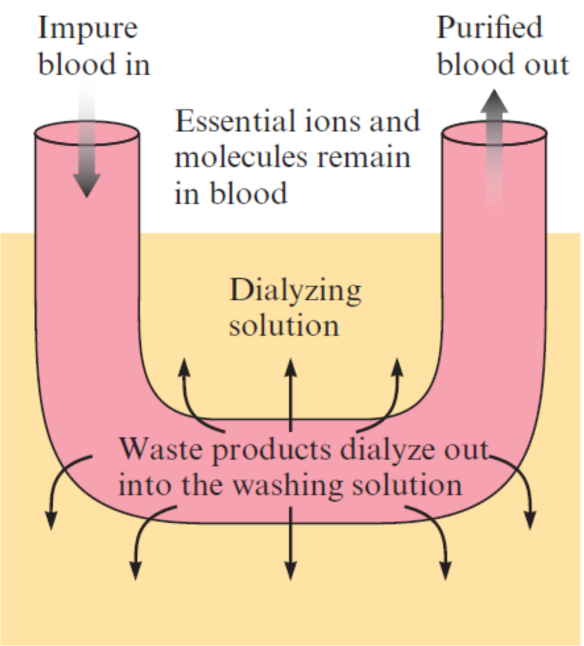
$$\frac{1.00\ \text{g}}{6.01 \times 10^{-5}\ \text{mol}} = \frac{x}{1.00\ \text{mol}}$$

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

- 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

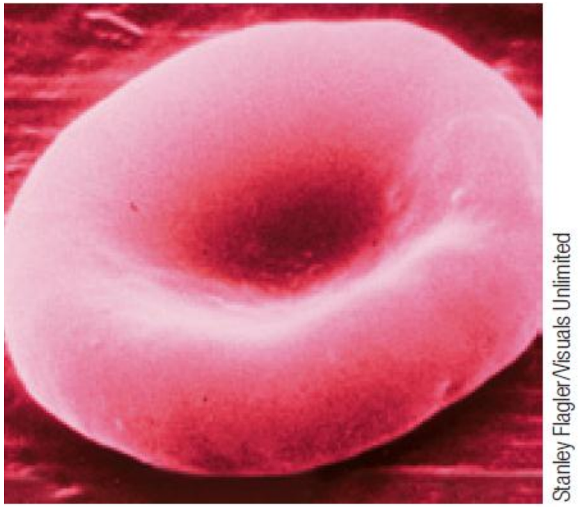


Isotonic, Hypertonic, and Hypotonic Solutions

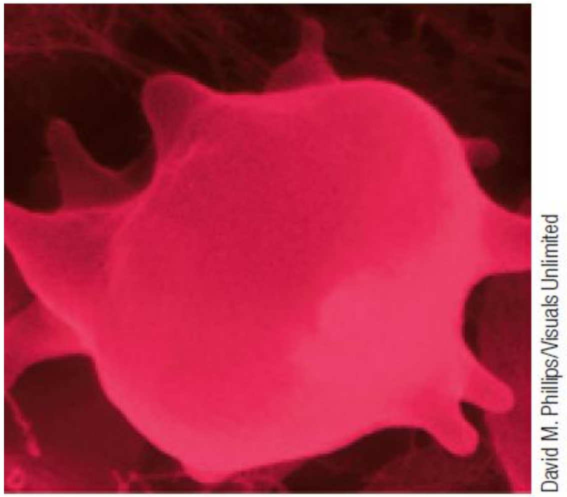
- **Isotonic solutions**: Solutions with identical osmotic pressures
  - Intravenously administered fluids must be isotonic with body fluids
- Hypertonic solutions - Have osmotic pressure higher than that of the cell fluids
- Hypotonic solutions - Have osmotic pressure lower than that of the cell fluids

Red Blood Cells (RBCs) and Osmosis

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



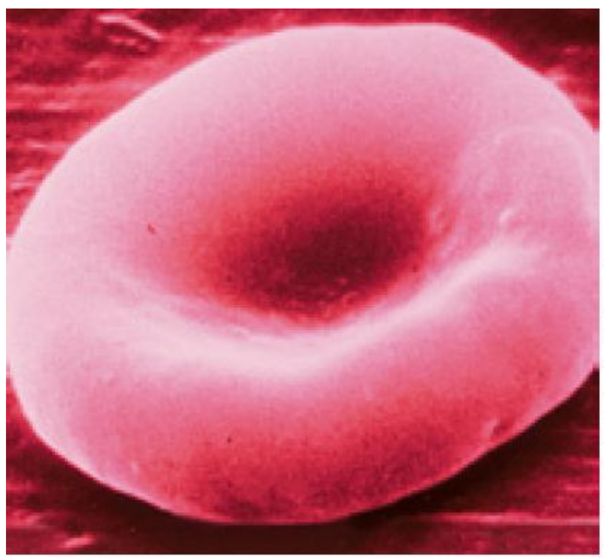
Normal



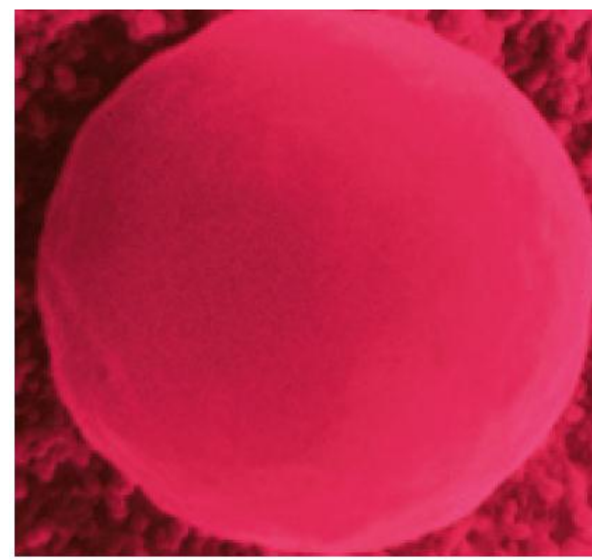
Shriveled

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



Normal



Swollen

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

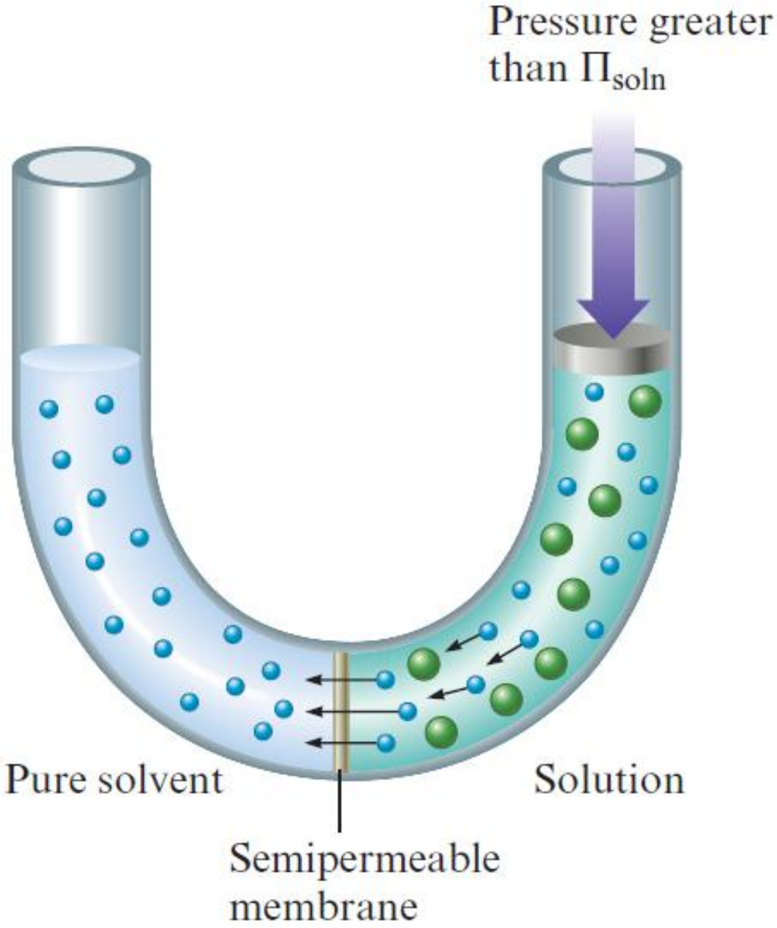
$$\frac{0.315\ M}{2} = 0.1575\ M = 0.158\ M$$

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

Reverse Osmosis

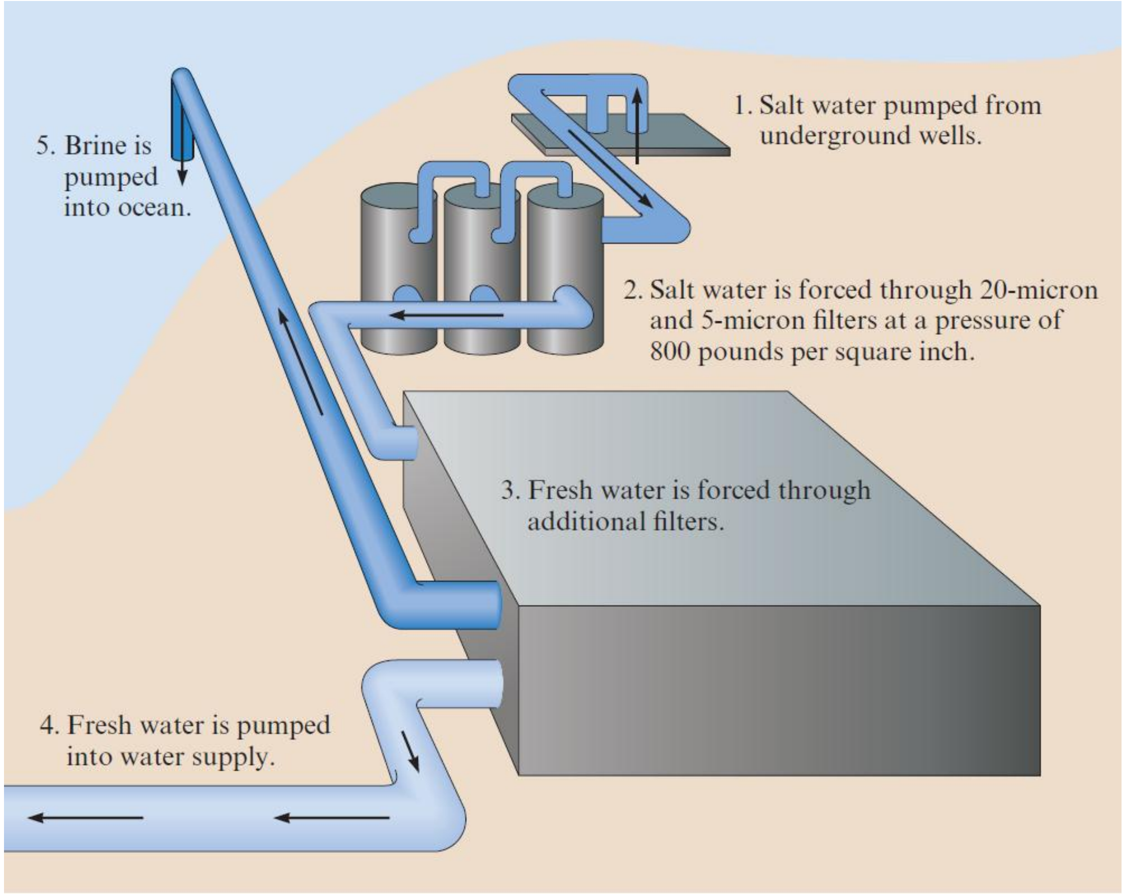
- Results when a solution in contact with a pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure
  - Pressure will cause a net flow of solvent from the solution to the solvent
  - Semipermeable membrane acts as a molecular filter
    - Removes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

Figure 11.20 - Reverse Osmosis



Desalination

- Removal of dissolved salts from a solution



van't Hoff Factor, *i*

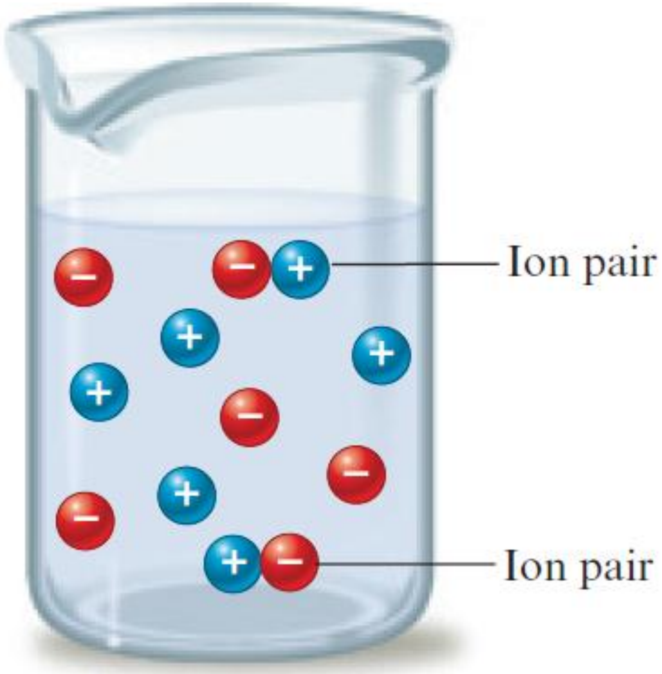
- Provides the relationship between the moles of solute dissolved and the moles of particles in solution

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

  - 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:

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

  - 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:

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

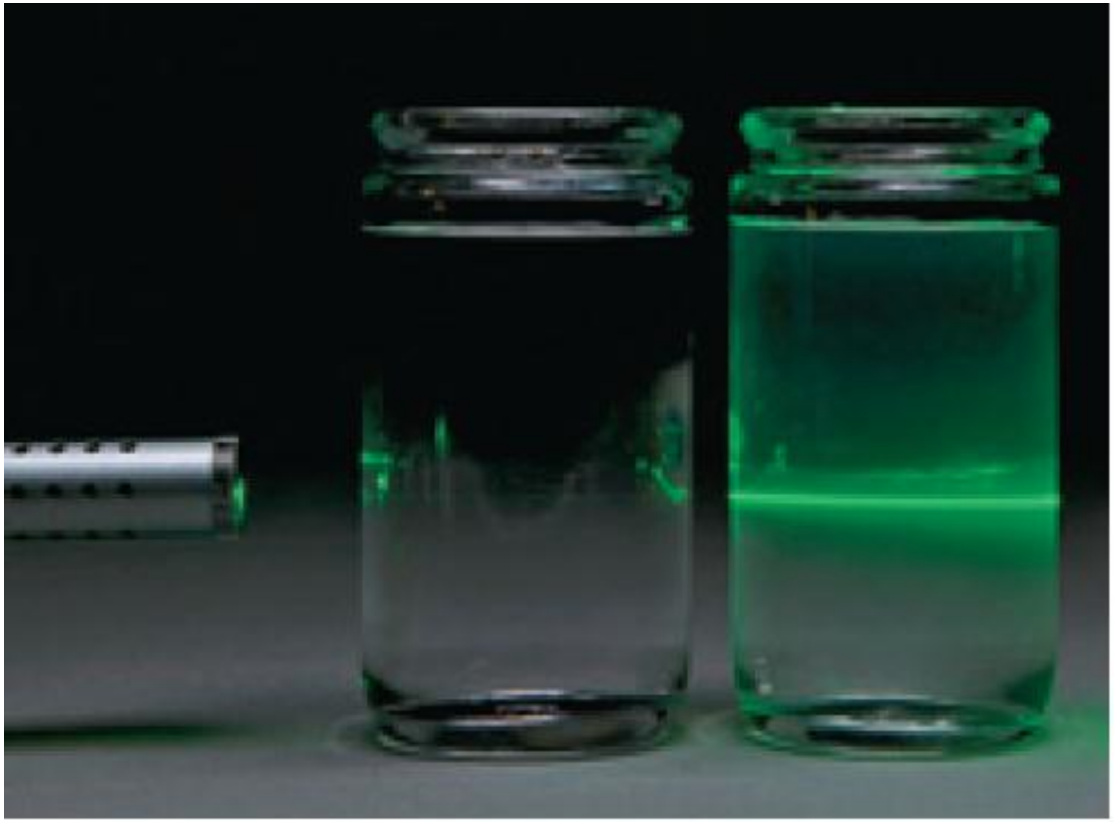
$$i = 4.4$$

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

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 is in a true solution
      - Individual ions and molecules dispersed in the solution are too small to scatter visible light

Figure 11.23 - The Tyndall Effect



Colloidal Dispersion or Colloids

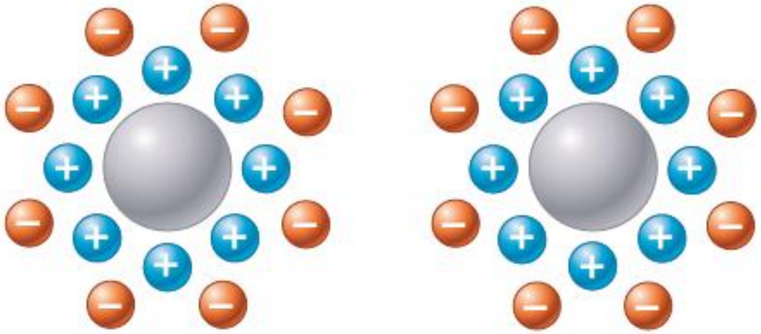
- Suspension of tiny particles in some medium
  - Can be either single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm
- Classified according to the states of the dispersed phase and the dispersing medium

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, soap suds	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 center particle 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 due to high salt content
- Removal of soot from smoke
  - The suspended particles are removed when smoke is passed through an electrostatic precipitator