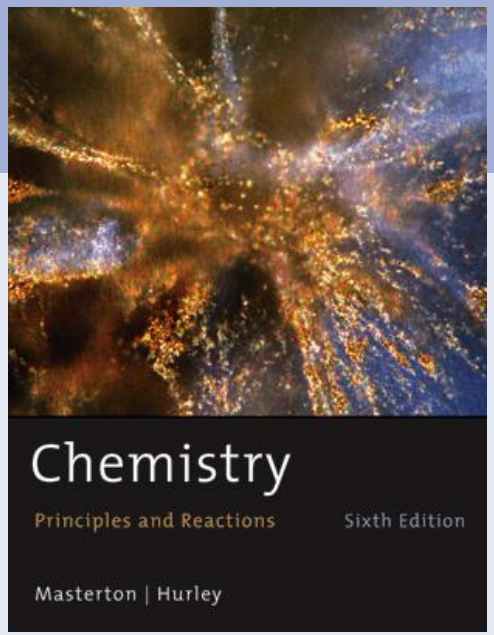

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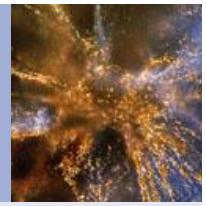
Chapter 10
Solutions

Edward J. Neth • University of Connecticut

Outline

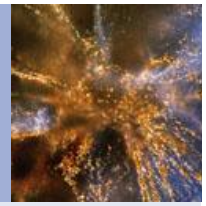


1. Concentration units
2. Principles of solubility
3. Colligative properties of nonelectrolytes
4. Colligative properties of electrolytes

Review

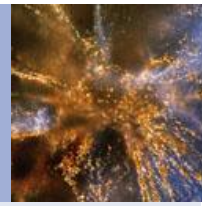
- We have looked briefly at the concept of concentration in terms of the solubility
  - Solubility was given in Chapter 1 as the mass of a solute that will dissolve in 100 g of a solvent
  - Other quantities than mass can be used to express concentrations

Solutions in Everyday Life



- Morning coffee
  - Solutions of solids (sugar, coffee) in liquid (water)
- Gasoline
  - Solution of liquid hydrocarbons
- Soda
  - Solution of sugar, water and carbon dioxide
- Air
  - Solution of oxygen and nitrogen

Physical Aspects of Solutions



- **A solution is a homogeneous mixture of a solute distributed through a solvent.**
- **solute(溶質)**
  - seems to “disappear”
  - “takes on the state” of the solvent
- **Solvent 溶劑**
  - does not appear to change state
- when both solute and solvent have the same state, the **solvent** is the component present in the **highest percentage**

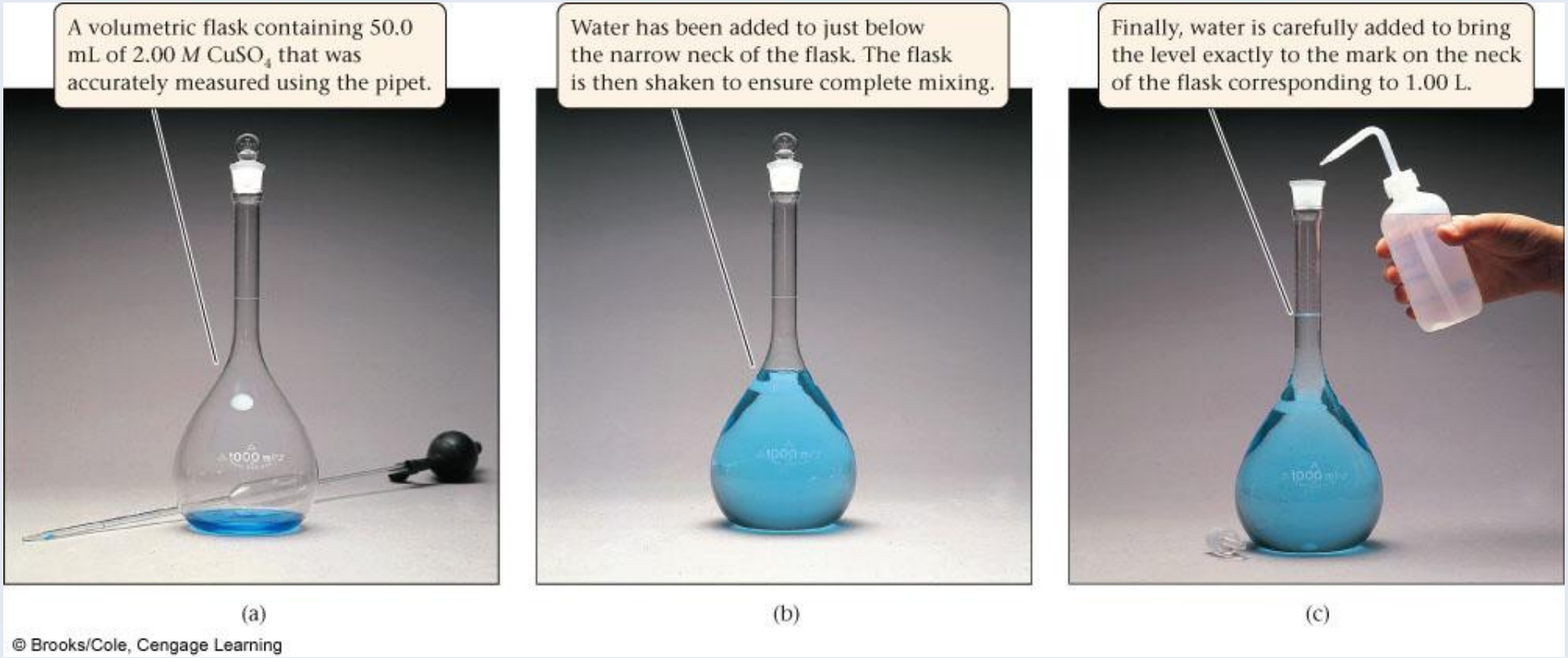
10-1Concentration Units, 1

- Molarity
  - ***Molarity*** is defined as moles of solute per liter of solution
  - ***Molarity = moles of solute/liters of solution***

  Preparation of a solution of specified molarity:
    - Weigh a calculated mass of solute
    - Dissolve in solvent to make a solution of known volume (using a volumetric flask)

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

Figure 10.1



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Example:
Calculate the molarity of a solution made by putting 15.5 g of NaCl into a beaker and adding water to make 1.50 L of NaCl solution.

Information

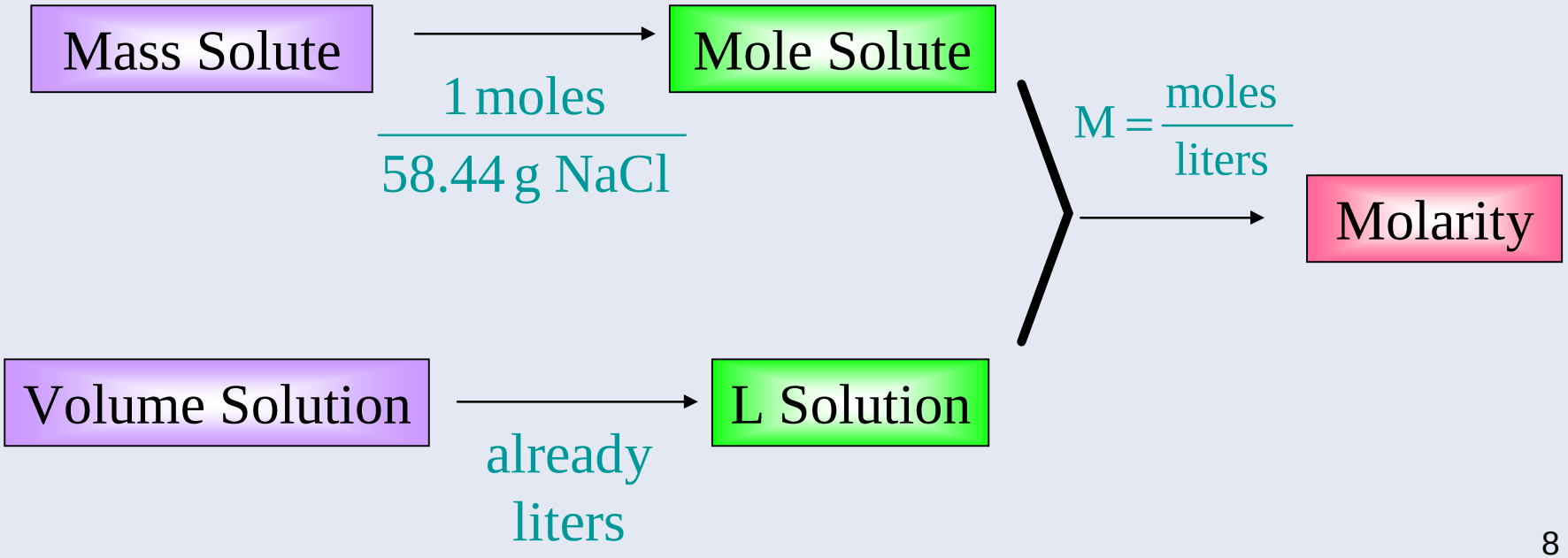
Given: 15.5 g NaCl; 1.50 L sol'n

Find: molarity, M

CF: 58.44 g = 1 mol NaCl;

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

- Design a Solution Map:



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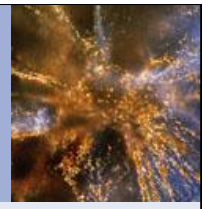

- Apply the Solution Map

$$15.5 \cancel{\text{g}}\ \text{NaCl} \times \frac{1\ \text{mol NaCl}}{58.44 \cancel{\text{g}}} = 0.2652\ \text{mol NaCl}$$

$$\textit{Molarity} = \frac{\textit{moles solute}}{\textit{liters solution}} = \frac{0.2652\ \textit{mol NaCl}}{\textit{1.50 L solution}}$$

$$= 0.177\ \text{M NaCl}$$

Example:
Calculate the molarity of a solution made by putting 15.5 g of NaCl into a beaker and adding water to make 1.50 L of NaCl solution.

Information

Given: 15.5 g NaCl; 1.50 L sol'n

Find: molarity, M

CF: 58.44 g = 1 mol NaCl;

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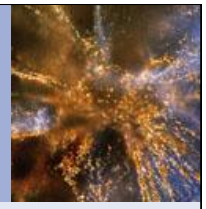
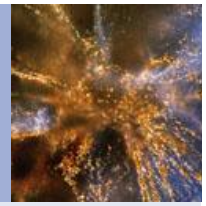


- Check the Solution

molarity of solution = 0.177 M

The units of the answer, M, are correct.
The magnitude of the answer makes sense since the mass of solute is less than the 1 mole and the volume is more than 1 L.

Example 10.1



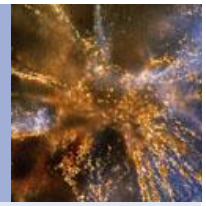
Example 10.1 Copper sulfate is widely used as a dietary supplement for animal feed. A lab technician prepares a "stock" solution of $CuSO_4$ by adding 79.80 g of $CuSO_4$ to enough water to make 500.0 mL of solution. An experiment requires a 0.1000 *M* solution of $CuSO_4$.

(a) What is the molarity of the $CuSO_4$ "stock" solution prepared by the technician?
(b) How would you prepare 1.500 L of 0.1000 *M* solution from the stock solution?

Strategy

(a) Review (from Chapter 4) the discussion on molarity of solutions.
(b) The question is equivalent to: What volume of $CuSO_4$ solution should be diluted to give 1.500 L of 0.1000 *M* $CuSO_4$? To answer this, use Equation 10.1 to calculate V_c, the volume of the more concentrated solution. M_c is the molarity from (a).

Example 10.1, (Cont'd)



SOLUTION

(a) The given data are in the form g/mL. Convert that to M (mol/L) by using the molar mass, 159.6 g/mol, as the conversion factor.

$$\frac{79.80\ \text{g CuSO}_4}{500.0\ \text{mL}} \times \frac{1\ \text{mol}}{159.6\ \text{g CuSO}_4} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 1.000\ M$$

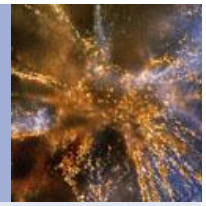
(b) Using Equation 10.1 and solving for V_c, we get

$$V_c = \frac{M_d \times V_d}{M_c} = \frac{0.1000\ M \times 1.500\ \text{L}}{1.000\ M} = 0.1500\ \text{L}$$

Measure out 1.500×10^2 mL of the stock solution and dilute with enough water (about 1.35 L) to form 1.500 L of 0.1000 M solution.

Reality Check The molarity of $CuSO_4$ stock solution (1.000 M) is 10 times what you need (0.1000 M), so it is reasonable to use only one-tenth of the volume you want (1500 mL $\rightarrow$ 1.500 L).

Mole Fraction



- Mole fraction is given the symbol X
  - The mole fraction of A is the number of moles of A divided by the total number of moles

$$X_A = \frac{n_A}{n_{tot}}$$

  - The mole fractions of all components must add to 1

Mole Fraction(*x*)

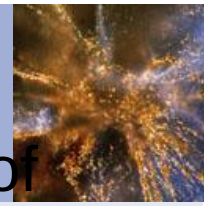
Mole fraction is given the symbol X

The mole fraction of A is the number of moles of A divided by the total number of moles

$$X_A = \frac{\text{Moles A}}{\text{Total moles}} = \frac{n_A}{n_{total}}$$

$$X_A + X_B + \mathbf{L} = 1$$

The mole fractions of all components of a solution (A、B、…)must add to unity



Example 10.2: A water solution contains 20.0% by mass of hydrogen peroxide. What is the mole fraction of H_2O_2?

Sol:

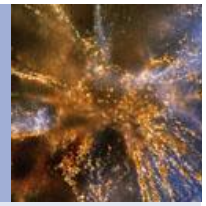
In 100.0g of solution, there are 20.0g of H_2O_2 and 80.0g of H_2O

$$nH_2O_2 = 20.0g \times \frac{1molH_2O_2}{34.02gH_2O_2} = 0.588molH_2O_2$$

$$nH_2O = 80.0g \times \frac{1molH_2O}{18.02gH_2O} = 4.44molH_2O$$

$$X_{H_2O} = \frac{nH_2O}{n_{tot}} = \frac{0.588}{0.588 + 4.44} = 0.117$$

Example 10.2



Example 10.2 Hydrogen peroxide is used by some water treatment systems to remove the disagreeable odor of sulfides in drinking water. It is available commercially in a 20.0% by mass aqueous solution. What is the mole fraction of H_2O_2?

Strategy Start with a fixed mass of solution such as one hundred grams. First calculate the masses of H_2O and H_2O_2, then the number of moles, and finally the mole fraction of H_2O_2.

SOLUTION In 100.0 g of solution, there are 20.0 g of H_2O_2 and 80.0 g of H_2O.

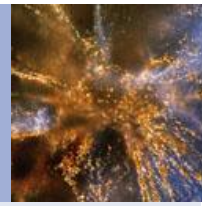
$$n_{H_2O_2} = 20.0\ \text{g} \times \frac{1\ \text{mol}\ H_2O_2}{34.02\ \text{g}\ H_2O_2} = 0.588\ \text{mol}\ H_2O_2$$

$$n_{H_2O} = 80.0\ \text{g} \times \frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} = 4.44\ \text{mol}\ H_2O$$

$$X_{H_2O_2} = \frac{n_{H_2O_2}}{n_{tot}} = \frac{0.588}{0.588 + 4.44} = 0.117$$

Reality Check Notice that the mole fraction of H_2O_2 is considerably less than the "mass fraction" (0.200). That is reasonable because the molar mass of H_2O_2 is larger than that of H_2O.

Mass Percent, Parts Per Million and Parts Per Billion



- Mass percent solute = (mass solute/mass solution) * 100
- Parts per million = (mass solute/mass solution) * 10^6
- Parts per billion = (mass solute/mass solution)*10^9

- The terms parts per million and parts per billion may be used to express the concentration of dilute solutions

- ***Molality*** is the number of moles of solute per kilogram of solvent.The symbol for molality is m

Example:
Calculate the mass percent of a solution containing 27.5 g of ethanol (C_2H_6O) and 175 mL of H_2O (assume the density of H_2O is 1.00 g/mL)

Information

Given: 27.5 g C_2H_6O; 175 mL H_2O

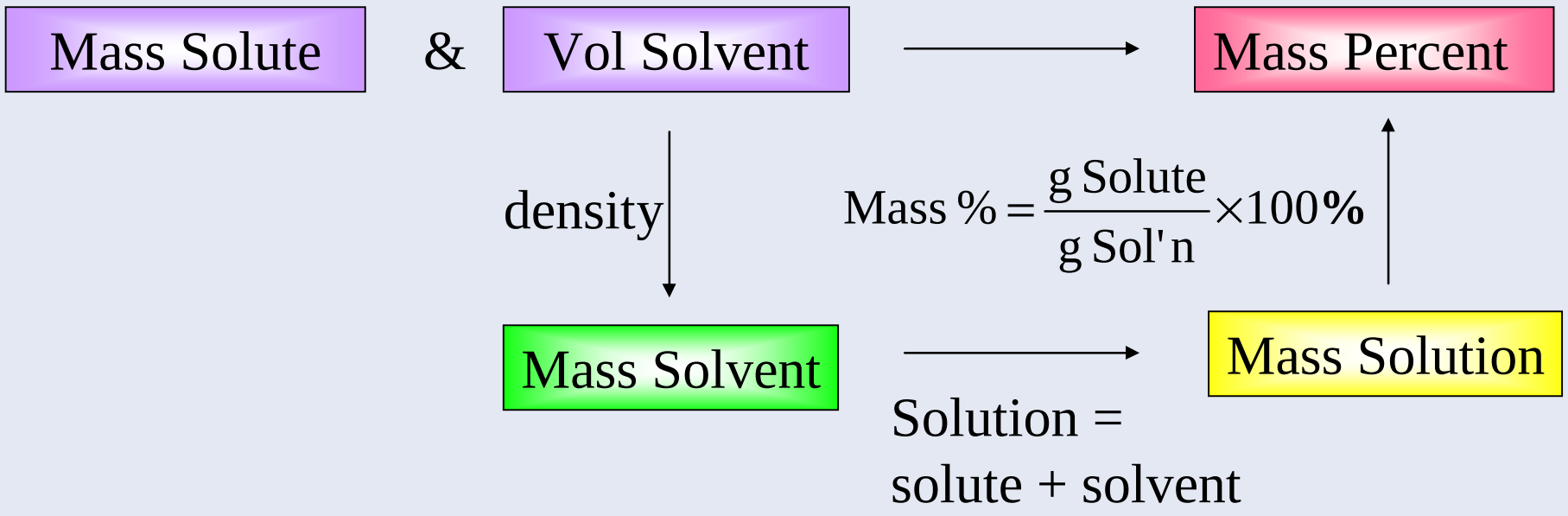
Find: % by mass

Eq'n:

$$\text{Mass \%} = \frac{\text{g Solute}}{\text{g Sol'n}} \times 100\%$$

CF: 1.00 g H_2O = 1 mL H_2O

- Design a Solution Map:



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Information

Given: 27.5 g C_2H_6O; 175 mL H_2O

Find: % by mass

Eq'n: $$\text{Mass \%} = \frac{\text{g Solute}}{\text{g Sol'n}} \times 100\%$$

CF: 1.00 g H_2O = 1 mL H_2O

SM: mass sol & vol solv → mass solv → mass sol'n → mass percent

- Apply the Solution Maps

$$175\,\text{mL}\,H_2O \times \frac{1.00\,\text{g}\,H_2O}{1\,\text{mL}\,H_2O} = 175\,\text{g}\,H_2O$$

$$\begin{aligned}\text{Mass of Solution} &= \text{Mass } C_2H_6O + \text{Mass } H_2O \\ &= 27.5\text{ g } C_2H_6O + 175\text{ g } H_2O \\ &= 202.5\text{ g}\end{aligned}$$

Example:
Calculate the mass percent of a solution containing 27.5 g of ethanol (C_2H_6O) and 175 mL of H_2O (assume the density of H_2O is 1.00 g/mL)

Information

Given: 27.5 g C_2H_6O; 175 mL H_2O

Find: % by mass

Eq'n: $\text{Mass \%} = \frac{\text{g Solute}}{\text{g Sol'n}} \times 100\%$

CF: 1.00 g H_2O = 1 mL H_2O

SM: mass sol & vol solv → mass solv → mass sol'n → mass percent

- Apply the Solution Maps - Equation

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

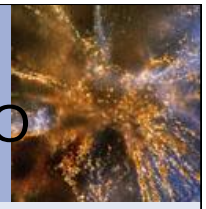
$$\text{Mass Percent} = \frac{27.5\ \text{g}\ C_2H_6O}{202.5\ \text{g sol'n}} \times 100\%$$

$$= 13.5802\%$$

$$= 13.6\%$$

Example:
Calculate the mass percent of a solution containing 27.5 g of ethanol (C_2H_6O) and 175 mL of H_2O (assume the density of H_2O is 1.00 g/mL)

Information



Given: 27.5 g C_2H_6O; 175 mL H_2O

Find: % by mass

Eq'n:

$$\text{Mass \%} = \frac{\text{g Solute}}{\text{g Soln}} \times 100\%$$

CF: 1.00 g H_2O = 1 mL H_2O

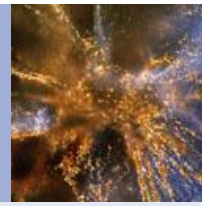
SM: mass sol & vol solv → mass solv → mass sol'n → mass percent

- Check the Solution

Mass Percent = 13.6%

The units of the answer, %, are correct.
The magnitude of the answer makes sense since the mass of solute is less than the mass of solvent.

Example 10.3



Example 10.3

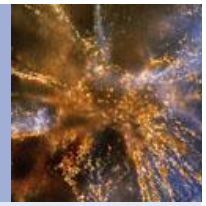
Glucose, $C_6H_{12}O_6$, in water is often used for intravenous feeding. Sometimes sodium ions are added to the solution. A pharmacist prepares a solution by adding 2.0 mg of sodium ions (in the form of NaCl), 6.00 g of glucose, and 112 g of water.

(a) What is the molality of the glucose in solution?
(b) How many ppm of Na^+ does the solution contain?

Strategy

(a) Since molality is equal to the number of moles of solute (glucose) divided by the mass of the solvent (H_2O) in kg, find those two quantities and divide.
(b) To find ppm of Na^+, find the mass of Na^+ and the total mass of solution.

Example 10.3, (Cont'd)



SOLUTION

(a) $n_{\text{glucose}} = 6.00 \text{ g glucose} \times \dfrac{1 \text{ mol glucose}}{180.16 \text{ g glucose}} = 0.0333 \text{ mol glucose}$

$$\text{kg } H_2O = 112 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.112 \text{ kg}$$

$$\text{molality} = \frac{0.0333 \text{ mol glucose}}{0.112 \text{ kg } H_2O} = 0.297 \, m$$

(b) $\text{Mass } Na^+ = 2.0 \text{ mg} \times \dfrac{1 \text{ g}}{1000 \text{ mg}} = 2.0 \times 10^{-3} \text{ g}$

$$\text{total mass of solution} = 2.0 \times 10^{-3} \text{ Na}^+ + 6.00 \text{ g glucose} + 112 \text{ g water} = 118 \text{ g}$$

$$\text{ppm } Na^+ = \frac{2.0 \times 10^{-3} \text{ g } Na^+}{118 \text{ g solution}} \times 10^6 = 17 \text{ ppm}$$

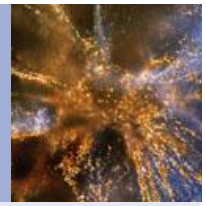
Theoretically, you would also need to calculate the mass of Cl^- ions and add that to the masses of Na^+, glucose, and water. Practically, the mass of Cl^- ions (like the mass of Na^+ ions) is negligible when compared to the mass of the solution.

Conversions Between Concentration Units

- To convert between units, first decide on a fixed amount of solution to start with:

When the original concentration is	Choose
Mass percent	100 g solution
Molarity (M)	1.00 L solution
Molality (m)	1.00 kg solvent
Mole fraction (X)	1.00 mol solution

Example 10.4

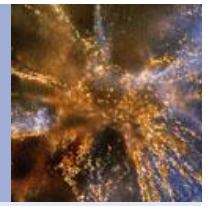


Example 10.4 Graded

Using the information in Figure 10.2, calculate

- * (a) the mass percents of HCl and water in concentrated HCl.
- ** (b) the molality of HCl.
- *** (c) the molarity of HCl.

Example 10.4, (Cont'd)



SOLUTION

(a) The mass percent of HCl (note the caption of Figure 10.2) is 37.7%. That of water must be 100.0 − 37.7 = 62.3%.

(b) Start with 100.0 g of solution, which contains 37.7 g of HCl and 62.3 g of water. Convert to moles of HCl (MM = 36.46 g/mol) and to kilograms of water. Finally, calculate the molality.

$$n_{HCl} = 37.7 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 1.03 \text{ mol HCl}$$

$$\text{kg water} = 62.3 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0623 \text{ kg}$$

$$\text{molality} = \frac{1.03 \text{ mol}}{0.0623 \text{ kg}} = 16.5\ m$$

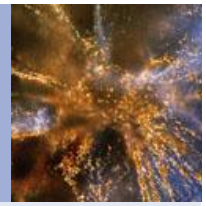
(c) Again, start with 100.0 g of solution. You have already calculated the number of moles of HCl. Find the volume of solution by using the density (1.19 g/mL). Finally, calculate the molarity.

$$n_{HCl} = 1.03 \text{ mol}$$

$$\text{volume of 100.0 g solution} = 100.0 \text{ g} \times \frac{1 \text{ mL}}{1.19 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0840 \text{ L}$$

$$\text{molarity} = \frac{1.03 \text{ mol}}{0.0840 \text{ L}} = 12.3\ M$$

Principles of Solubility

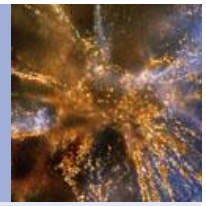


- The extent to which a solute dissolves in a solvent depends on several factors:
  - The nature of solvent and solute particles and the interaction between them
  - The temperature at which the solution forms
  - The pressure, in cases of gaseous solutes
- **saturated** solutions have the maximum amount of solute that will dissolve in that solvent at that temperature
- **unsaturated** solutions can dissolve more solute
- **supersaturated** solutions are holding more solute than they should be able to at that temperature

Solute-Solvent Interactions

- Like dissolves like
  - Polar solutes dissolve in polar solvents
  - Nonpolar solutes dissolve in nonpolar solvents
- Nonpolar substances have poor affinity for water
  - Petroleum
  - Hydrocarbons (pentane, C_5H_{12})
- Polar substances dissolve easily in water
  - Alcohols, CH_3OH
  - Solubility of alcohols decreases as the molar mass of the alcohol increases

Classifying Solvents



Solvent	Class	Structural Feature
Water, H_2O	polar	O-H
Ethyl Alcohol, C_2H_5OH	polar	O-H
Acetone, C_3H_6O	polar	C=O
Benzene, C_6H_6	nonpolar	C-C & C-H
Hexane, C_6H_{14}	nonpolar	C-C & C-H
Diethyl Ether, $C_4H_{10}O$	nonpolar	C-C, C-H & C-O

Solubility and Intermolecular Forces

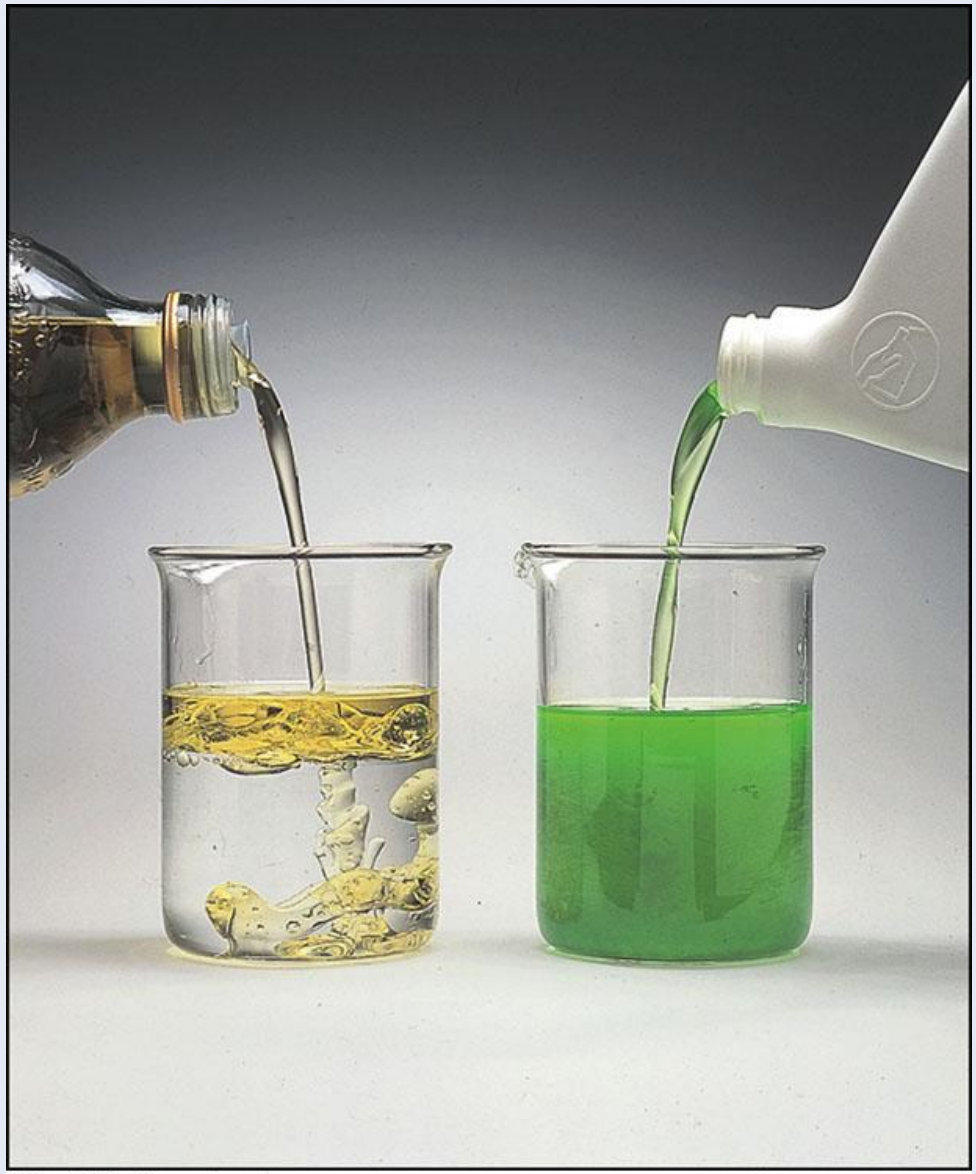


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Table 10.1

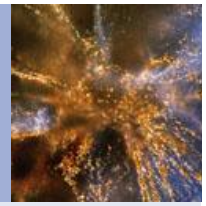

Table 10.1 Solubilities of Alcohols in Water

Substance	Formula	Solubility (g solute/L H_2O)
Methyl alcohol	CH_3OH	Completely soluble
Ethyl alcohol	CH_3CH_2OH	Completely soluble
Propanol	$CH_3CH_2CH_2OH$	Completely soluble
Butanol	$CH_3CH_2CH_2CH_2OH$	74
Pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	27
Hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	6.0
Heptanol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	1.7

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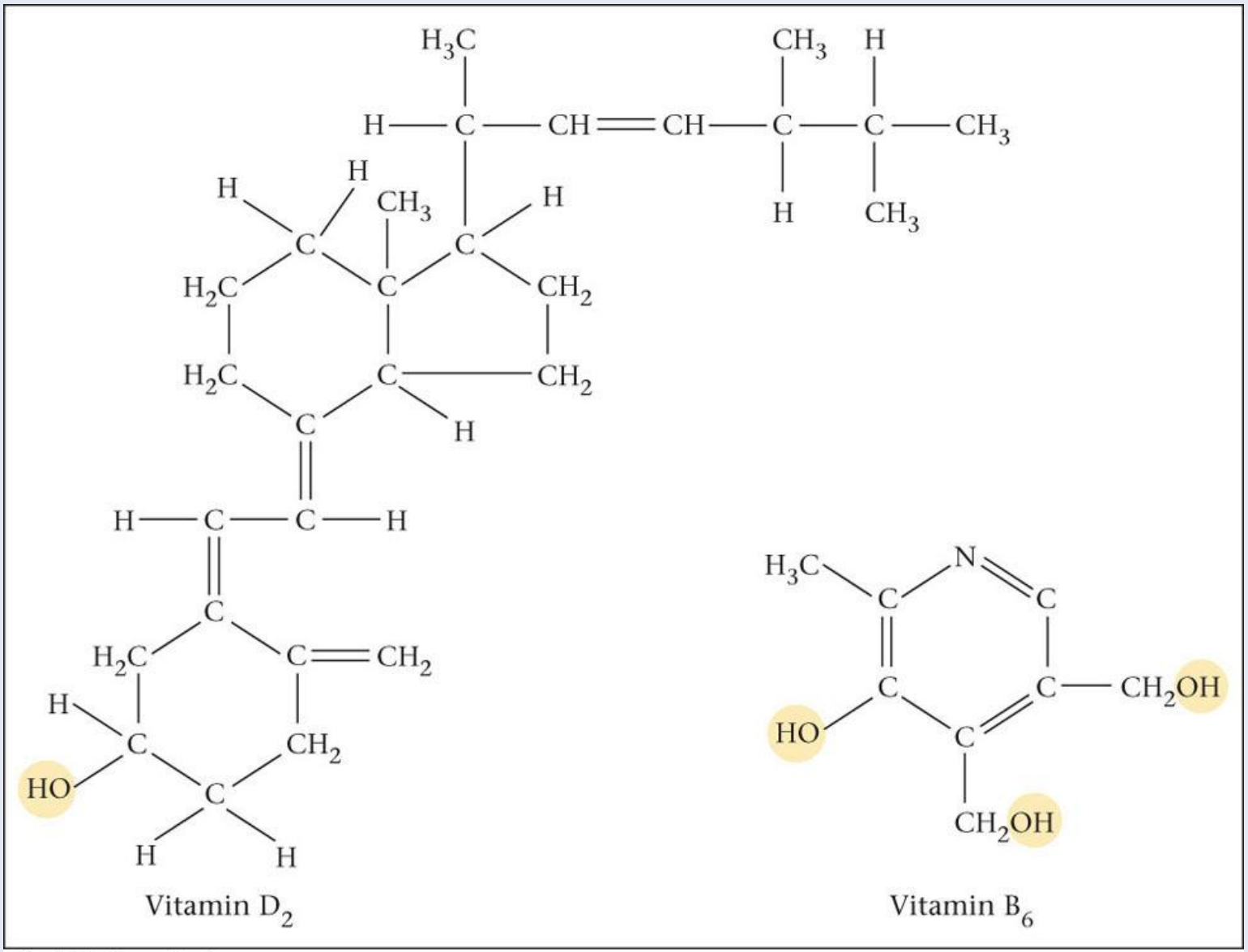
Solubility of Vitamins

- Some vitamins are readily water soluble
  - OH groups can form hydrogen bonds with water
  - Vitamins B and C are water-soluble examples
- Some vitamins are nonpolar and therefore not soluble in water
  - Vitamins A, D, E and K
  - These are soluble in body fats, which are largely nonpolar in character

Figure 10.3 – Fat and Water Soluble Vitamins



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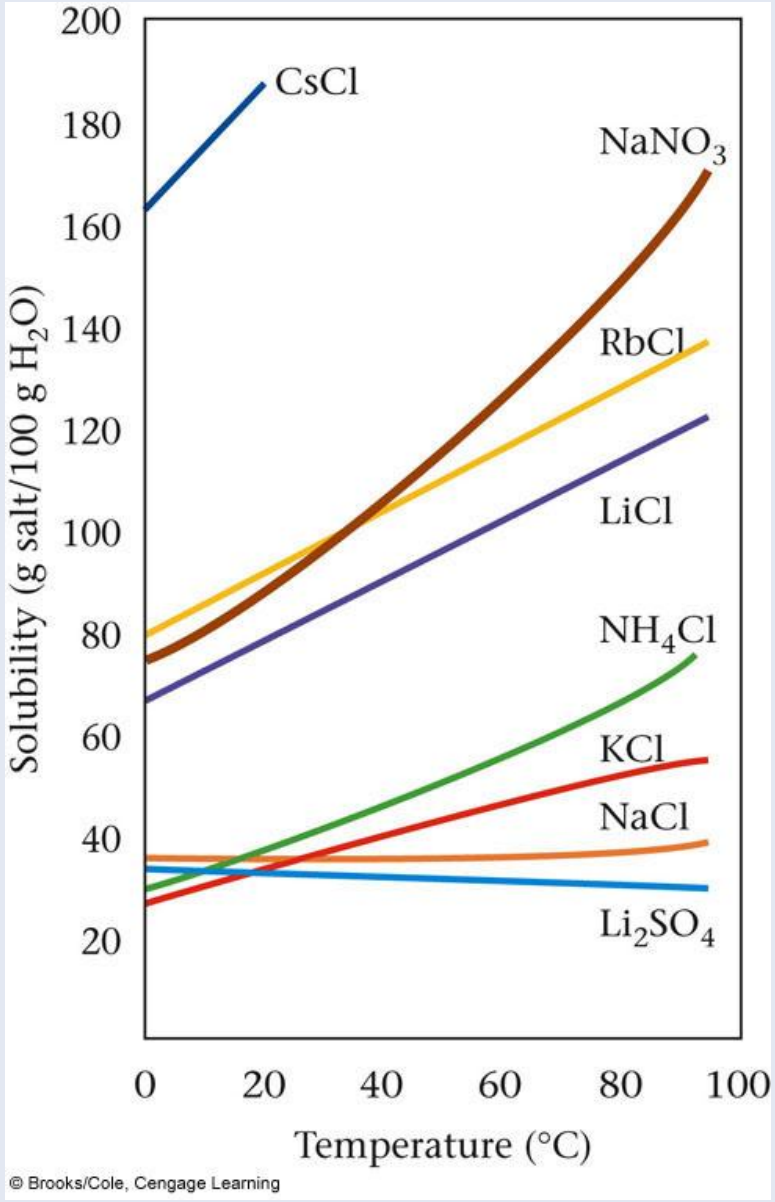
Solubility of Ionic Compounds

- The solubility of ionic compounds in water varies tremendously from one solid to another
- Two forces must be balanced
  - The force of attraction between water molecules and ions: ***the stronger the force, the greater the tendency toward solution***
  - The force of attraction between oppositely charged ions: ***the stronger the force, the more likely the solute will stay in the solid state***

Temperature and Solubility

- When a solute dissolves, equilibrium is established
  - $NaNO_3$ (s) $\rightleftharpoons$ Na^+ (aq) + NO_3^- (aq)
  - O_2 (g) $\rightleftharpoons$ O_2 (aq)
- An ***increase in temperature*** always shifts the equilibrium to ***favor an endothermic process***
  - Dissolving a ***solid in a liquid*** is usually an ***endothermic*** process
  - Solubility tends to ***increase with temperature for most solids***

Figure 10.4



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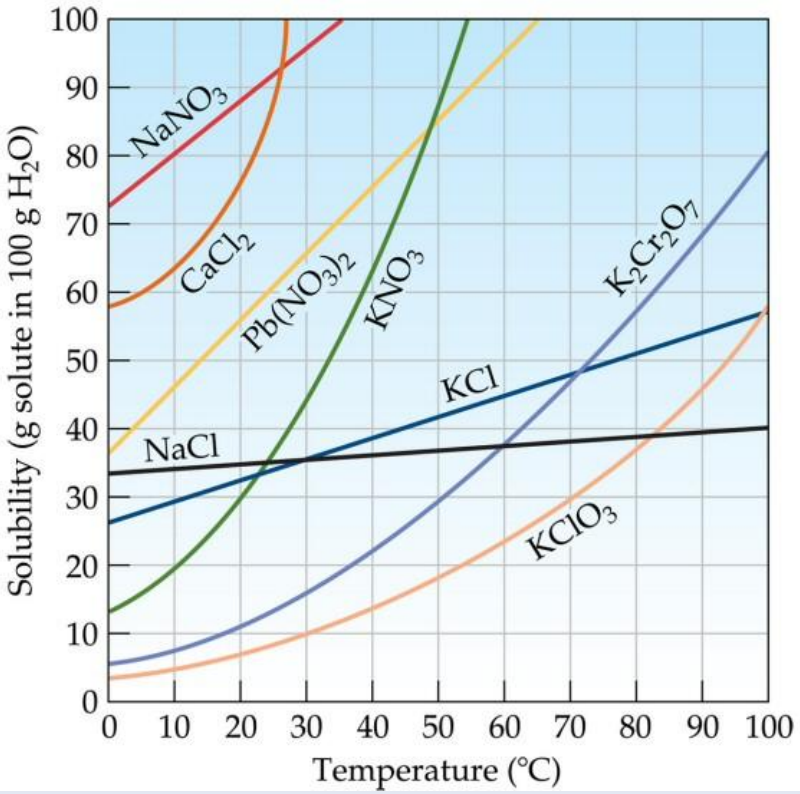
Temperature and the Solubility of a Gas

- For a gas, the dissolution process is ***exothermic***, so the reverse process ***(gas evolving from solution) is endothermic***
- Therefore, for gases, ***solubility decreases with increasing temperature***

2.Effect of Temperature on Solubility

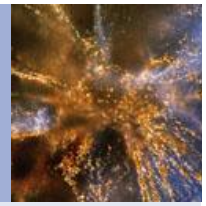
- the solubility of the solute in the solvent depends on the temperature
  - higher temp = higher solubility of solid in liquid
  - lower temp = higher solubility of gas in liquid



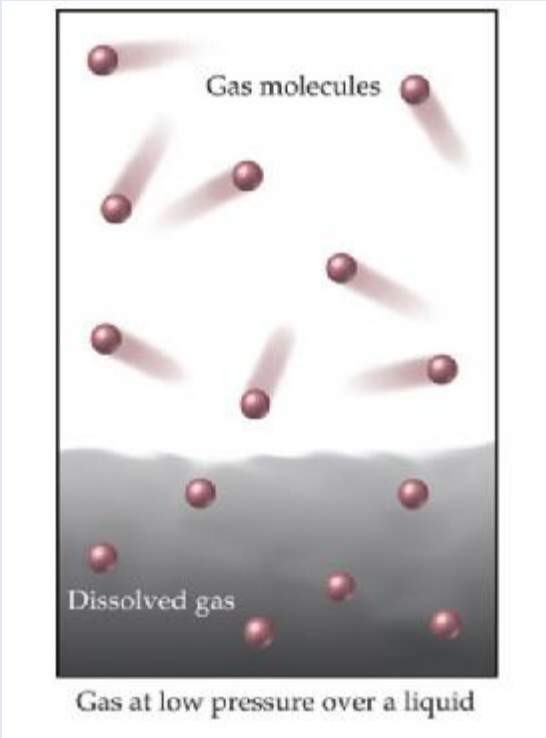
Pressure and the Solubility of a Gas

- Pressure has a major effect on the solubility of a gas in a liquid, but little effect on other systems
- At low to moderate pressure, the concentration of a gas increases with the pressure (***Henry's law***):
  - $C_g = kP_g$, where
    - P_g is the partial pressure of the gas over the solution
    - C_g is the concentration of the gas
    - k is a constant (the Henry's Law constant)

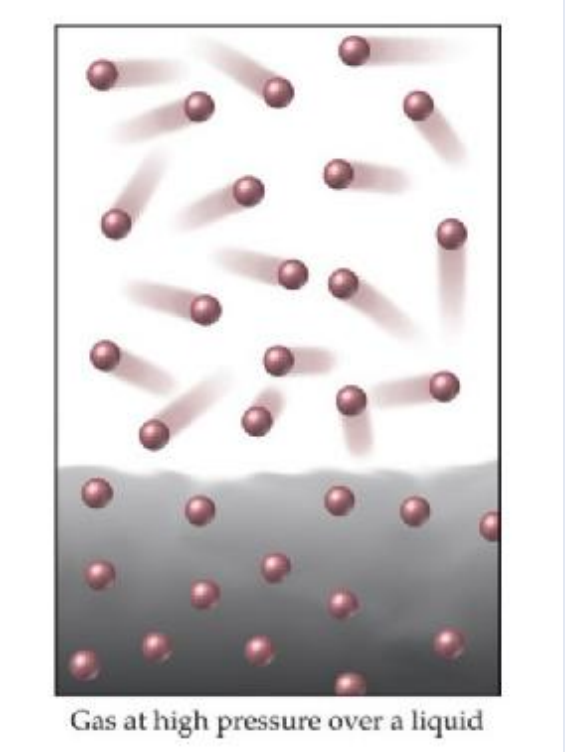
Solubility and Pressure



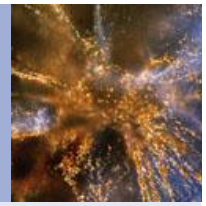
- the solubility of gases in water depends on the pressure of the gas
- higher pressure = higher solubility



Gas at low pressure over a liquid


Gas at high pressure over a liquid

Pressure and the Solubility of a Gas (Cont'd)



- Carbonated beverages
  - Pressure of carbon dioxide is kept high by pressurizing the container
  - Releasing the pressure causes the beverage to go "flat"; carbon dioxide bubbles out of the solution
- Deep-sea diving
  - Increased pressure while diving increases gas solubility in bodily fluids
  - Rising too rapidly to the surface can lead to bubbling of gas forming in the blood and other fluids in the body; this phenomenon is called the ***bends***

Solubility Effects of Pressure

(a) SCUBA divers must pay attention to the solubility of gases in the blood and the fact that solubility increases with pressure.

(b) A hyperbaric chamber. People who have problems breathing can be placed in a hyperbaric chamber where they are exposed to a higher partial pressure of oxygen.

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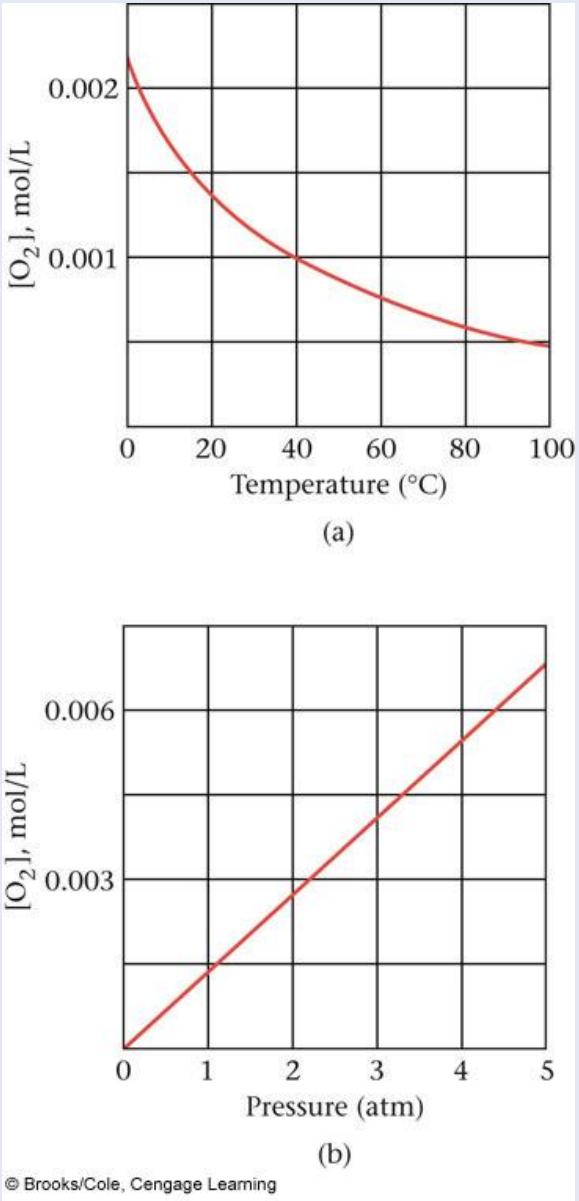
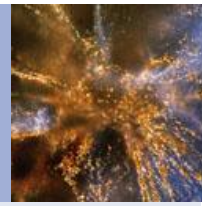
Figure 10.5 – Logarithmic and Linear Relationships



Pressure and Solubility of Gases



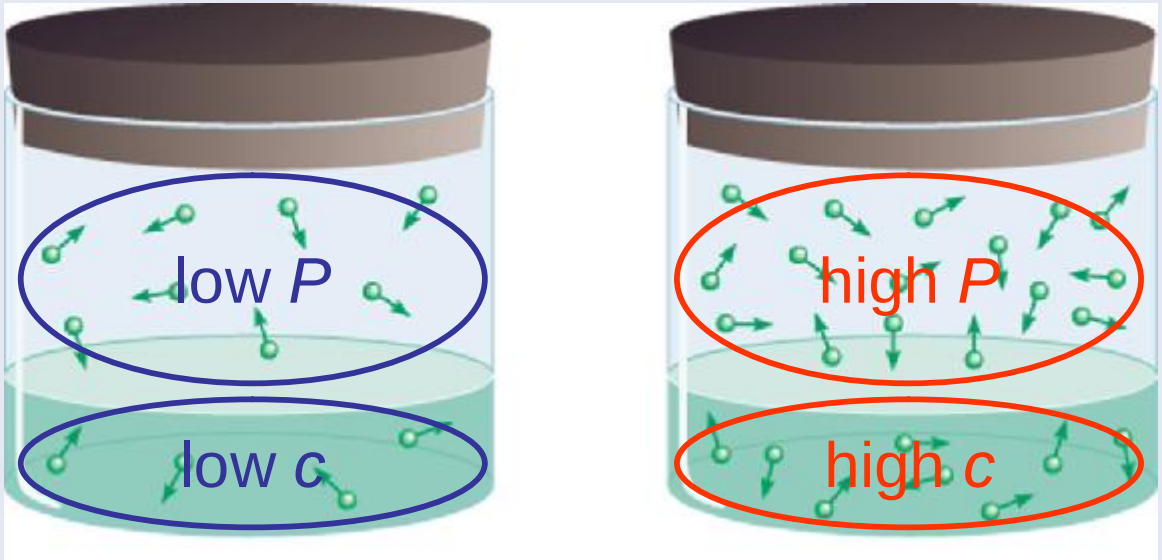
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = kP$$

c is the concentration (*M*) of the dissolved gas

P is the pressure of the gas over the solution

k is a constant (mol/L•atm) that depends only on temperature



Ex10-6: The solubility of pure nitrogen in blood at body temperature, 37.0°C and one atmosphere is 6.2×10^{-4} M, If a diver breathes air **(X_{N2} = 0.78) at a depth where the total pressure is 2.5 atm , Calculate the concentration of nitrogen in his blood.**

$$K = \frac{\text{Concentration of } N_2}{\text{Pressure of } N_2} = \frac{6.2 \times 10^{-4}\ M}{1.00\ atm}$$

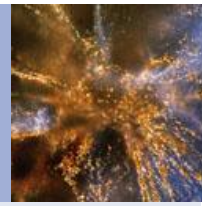
$$P_{N_2} = X_{N_2} \times P_{total} = 0.78 \times 2.5 = 2.0 atm$$

$$[N_2] = KP_{N_2} = 6.2 \times 10^{-4} \frac{M}{atm} \times 2.0 atm = 1.2 \times 10^{-3} M$$

Colligative Properties of Nonelectrolytes

- The properties of a solution may differ considerably from those of the pure solvent
- Some of these properties depend on the concentration of dissolved particles and not on their nature
  - These are ***colligative*** properties
  - Physical description of these properties are limiting laws: ***they are approached as the solution becomes more dilute***
    - Limit to applicability of these laws is 1M

Colligative Properties in Summary



- Vapor Pressure Lowering
- Boiling Point Elevation
- Freezing Point Lowering
- Osmotic Pressure

Vapor Pressure Lowering

- True colligative property: independent of the nature of the solute but dependent on the concentration
- The vapor pressure of a solvent over a solution is always lower than the vapor pressure of a pure solvent
- Raoult’s Law

The Mathematics of Raoult's Law

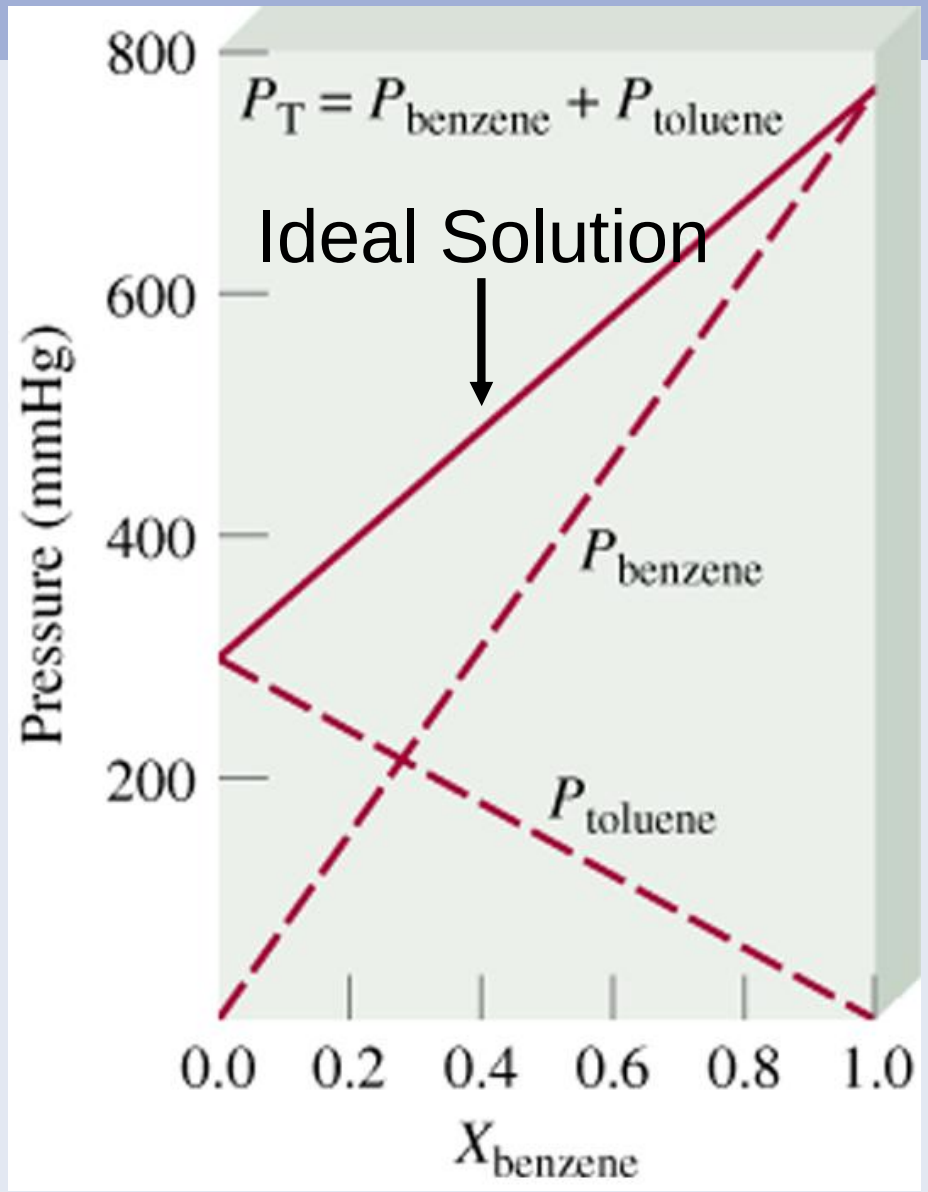
$$P_1 = X_1 P_1^0$$

$$P_1 = (1 - X_2) P_1^0$$

$$P_1^0 - P_1 = X_2 P_1^0$$

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

- P_1 is the vapor pressure of the solvent over the solution
- P°_1 Is the vapor pressure of the pure solvent
- X_1 is the mole fraction of the solute
- X_2 is the mole fraction of the solvent
- ΔP is the vapor pressure lowering



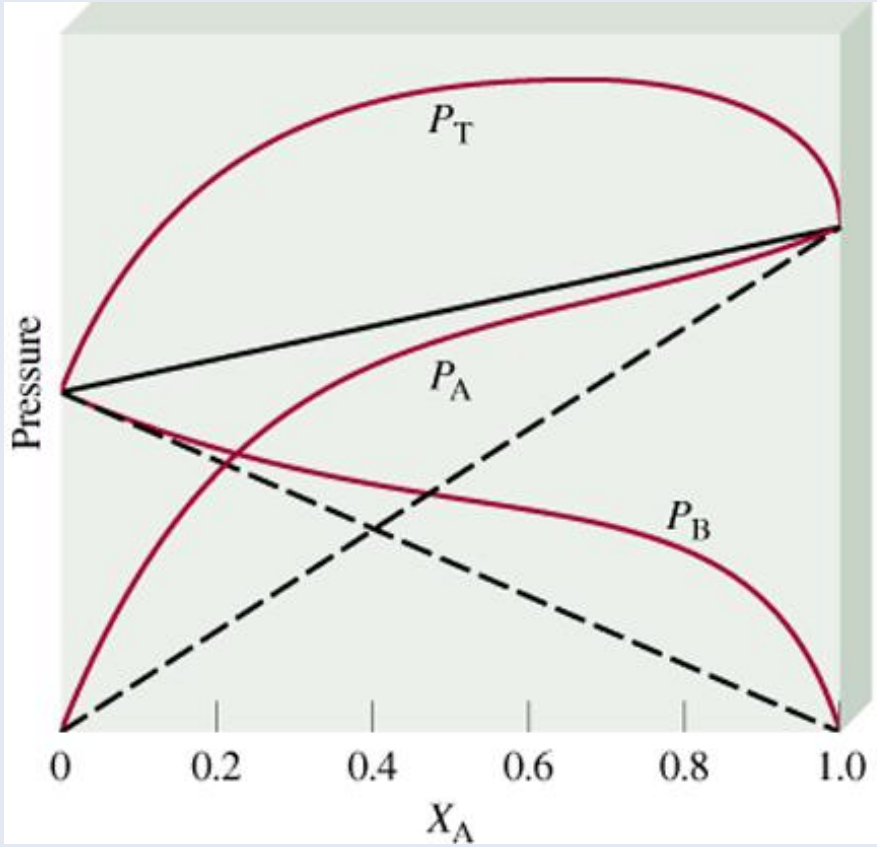
$$P_A = X_A P^0_A$$

$$P_B = X_B P^0_B$$

$$P_T = P_A + P_B$$

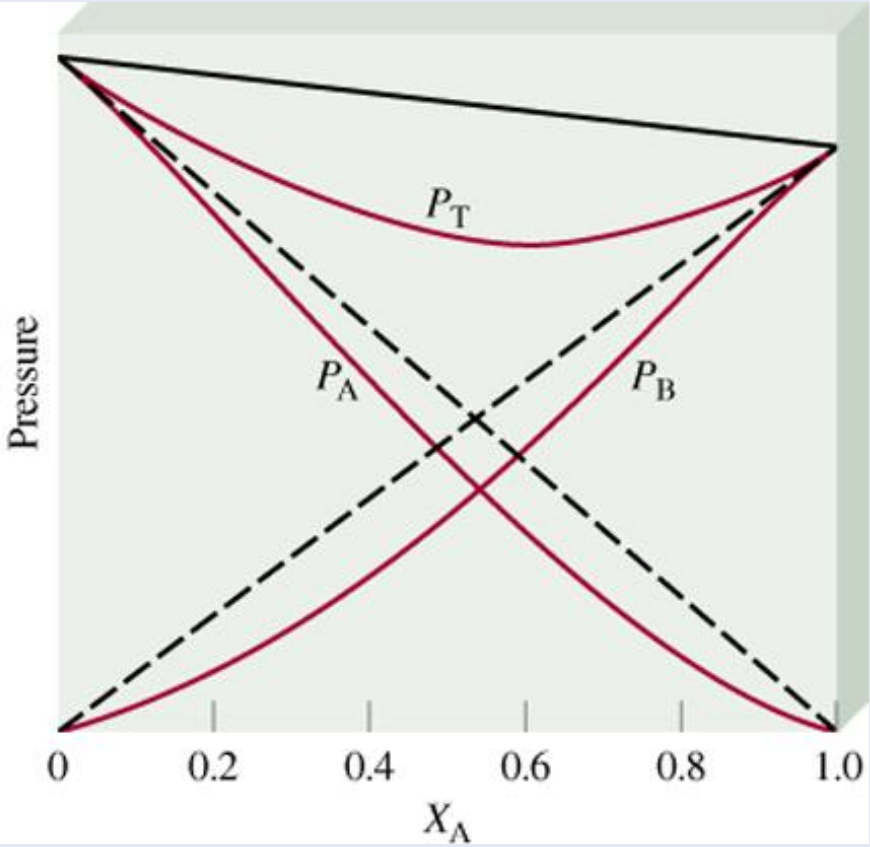
$$P_T = X_A P^0_A + X_B P^0_B$$

P_T is greater than predicted by Raoults's law



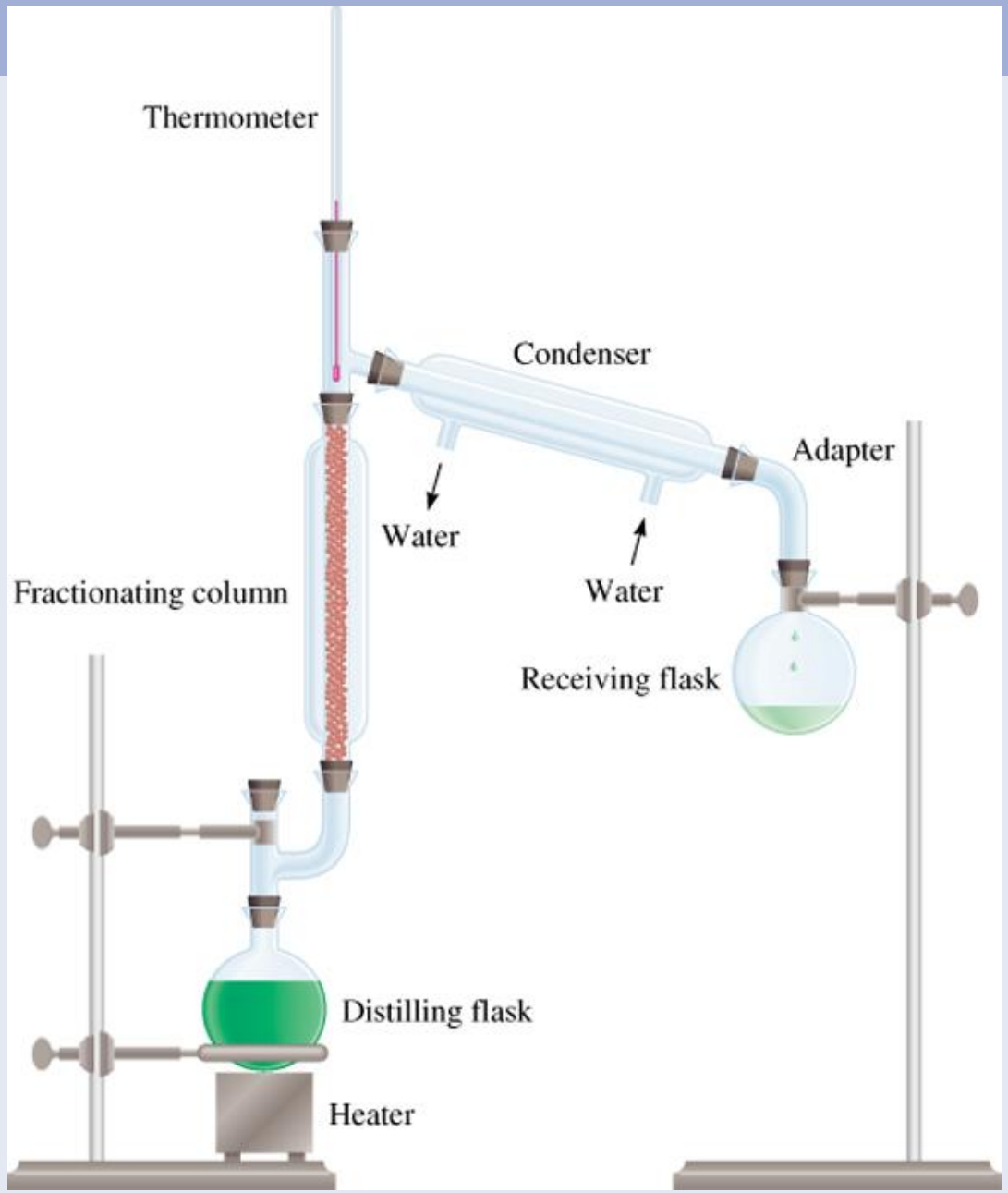
Force A-B < Force A-A & Force B-B

P_T is less than predicted by Raoults's law

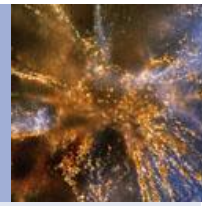


Force A-B > Force A-A & Force B-B

Fractional Distillation Apparatus



Example 10.6



Example 10.6 A solution contains 82.0 g of glucose, $C_6H_{12}O_6$, in 322 g of water. Calculate the vapor pressure lowering at 25°C (vapor pressure of pure water = 23.76 mm Hg).

Strategy First (1), calculate the number of moles of glucose (MM = 180.16 g/mol) and water (MM = 18.02 g/mol). That information allows you to find (2) the mole fraction of glucose. Finally (3), use Raoult's law to find the vapor pressure lowering.

SOLUTION

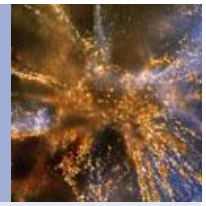
(1) $$n_{\text{glucose}} = 82.0 \text{ g glucose} \times \frac{1 \text{ mol glucose}}{180.16 \text{ g glucose}} = 0.455 \text{ mol glucose}$$

$$n_{\text{water}} = 322 \text{ g water} \times \frac{1 \text{ mol water}}{18.02 \text{ g water}} = 17.9 \text{ mol water}$$

(2) $$X_{\text{glucose}} = \frac{0.455}{0.455 + 17.9} = 0.0248$$

(3) $$\Delta P = X_{\text{glucose}} \times P^{\circ}_{H_2O} = 0.0248 \times 23.76 \text{ mm Hg} = 0.589 \text{ mm Hg}$$

Reality Check You expect the vapor pressure lowering to be small (0.589 mm Hg) because the mole fraction of solute is small (0.0248).



Ex10.6: A solution contains 82.0g of glucose ($C_6H_{12}O_6$),in 322g of water. Calculate the vapor pressure lowering at 在25°C (vapor pressure of pure water=23.76 mmHg**)**

$$n_{糖} = 82\ g \times \frac{1\,mol\ 糖}{180.16g\ 糖} = 0.455mol$$

$$n_{水} = 322g \times \frac{1\,mol\ 水}{18.02g\ 水} = 17.9mol$$

$$X_{糖} = \frac{0.455}{0.455 + 17.9} = 0.0248$$

$$\Delta P = X_{糖} \times P^{0}_{H_2O} = 0.0248 \times 23.76 = 0.589\,mmHg$$

Boiling Point Elevation

- When a solution of a nonvolatile solute is heated, it does not boil until the temperature exceeds the boiling point of the pure solvent
  - The difference in temperature is called the boiling point elevation

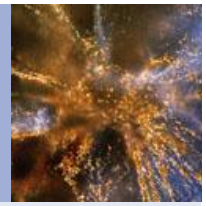
$$\Delta T_b = T_b - T_b^0$$

Freezing Point Lowering

- When a solution of a nonvolatile solute is cooled, it does not freeze until a temperature below the freezing point of the pure solvent is reached
  - The difference in temperature is called the freezing point lowering

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

Boiling and Freezing Point Alteration



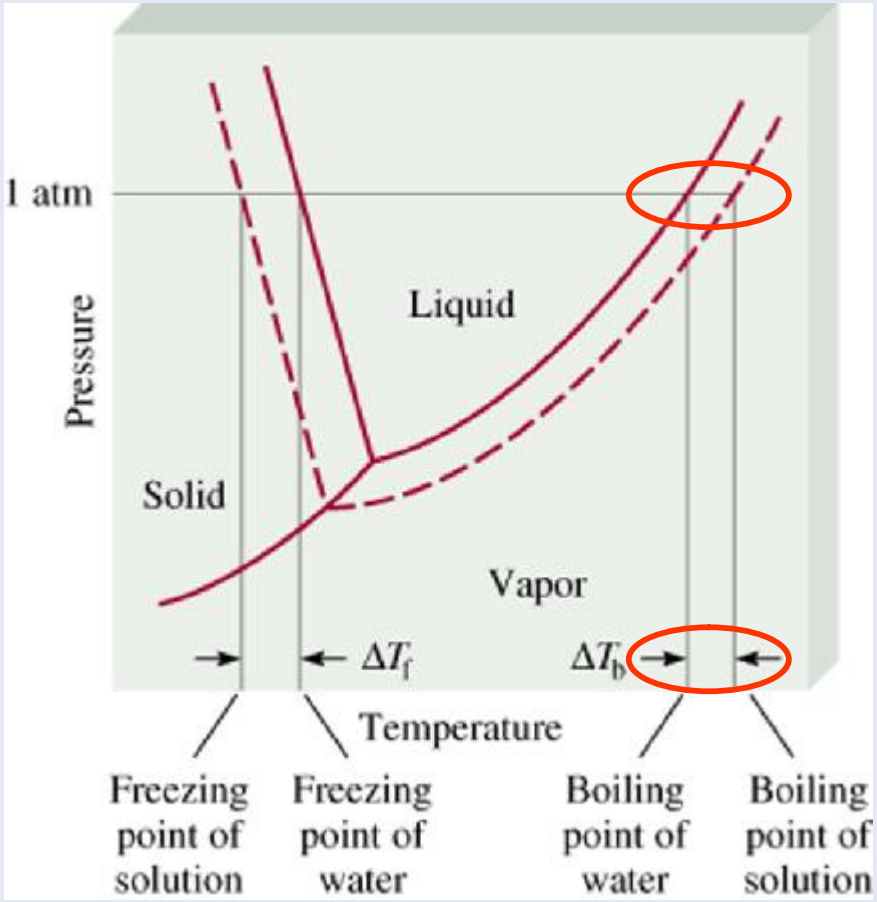
- Boiling point elevation and freezing point lowering are both colligative properties
  - Depend on the concentration of the solute in molality
  - Both follow the same dependence:

$$\Delta T_f = mK_f$$

$$\Delta T_b = mK_b$$

  - K_f is the freezing point lowering constant
  - K_b is the boiling point elevation constant

Boiling-Point Elevation



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

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

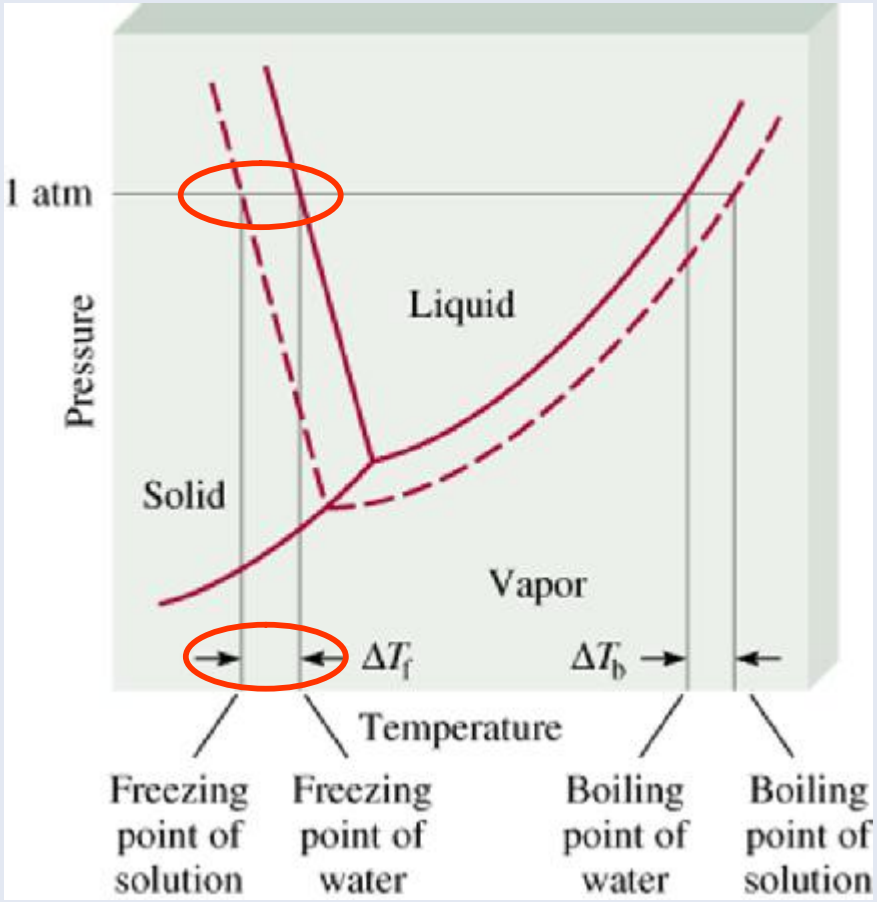
$$T_b > T_b^0 \qquad \Delta T_b > 0$$

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

m is the molality of the solution

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

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

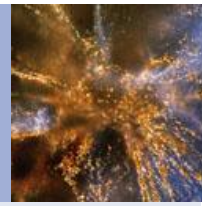
$T_f^0 > T_f \qquad \Delta T_f > 0$

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

m is the molality of the solution

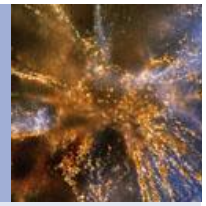
K_f is the molal freezing-point depression constant ($^0C/m$)

Freezing & Boiling Point Constants



Solvent	K_f °C kg solvent / mol solute	FP °C	K_b °C kg solvent / mol solute	BP °C
water, H_2O	1.86	0.00	0.512	100.0
benzene, C_6H_6	5.12	5.53	2.53	80.1
cyclohexane,C_6H_{12}	20.0	6.47	2.79	80.7
naphthalene, $C_{10}H_8$	6.9	80.2	5.65	218
ethanol, C_2H_5OH	1.99	-115	1.22	78.4
t-butanol, $(CH_3)_3COH$	8.3	25.6		82.4
carbon tetrachloride,CCl_4	29.8	-22.3	5.02	76.8
methanol, CH_3OH		-97.8	0.80	64.7
acetic acid, $HC_2H_3O_2$	3.9	16.7	3.07	118

FPL and BPE Constants for Water

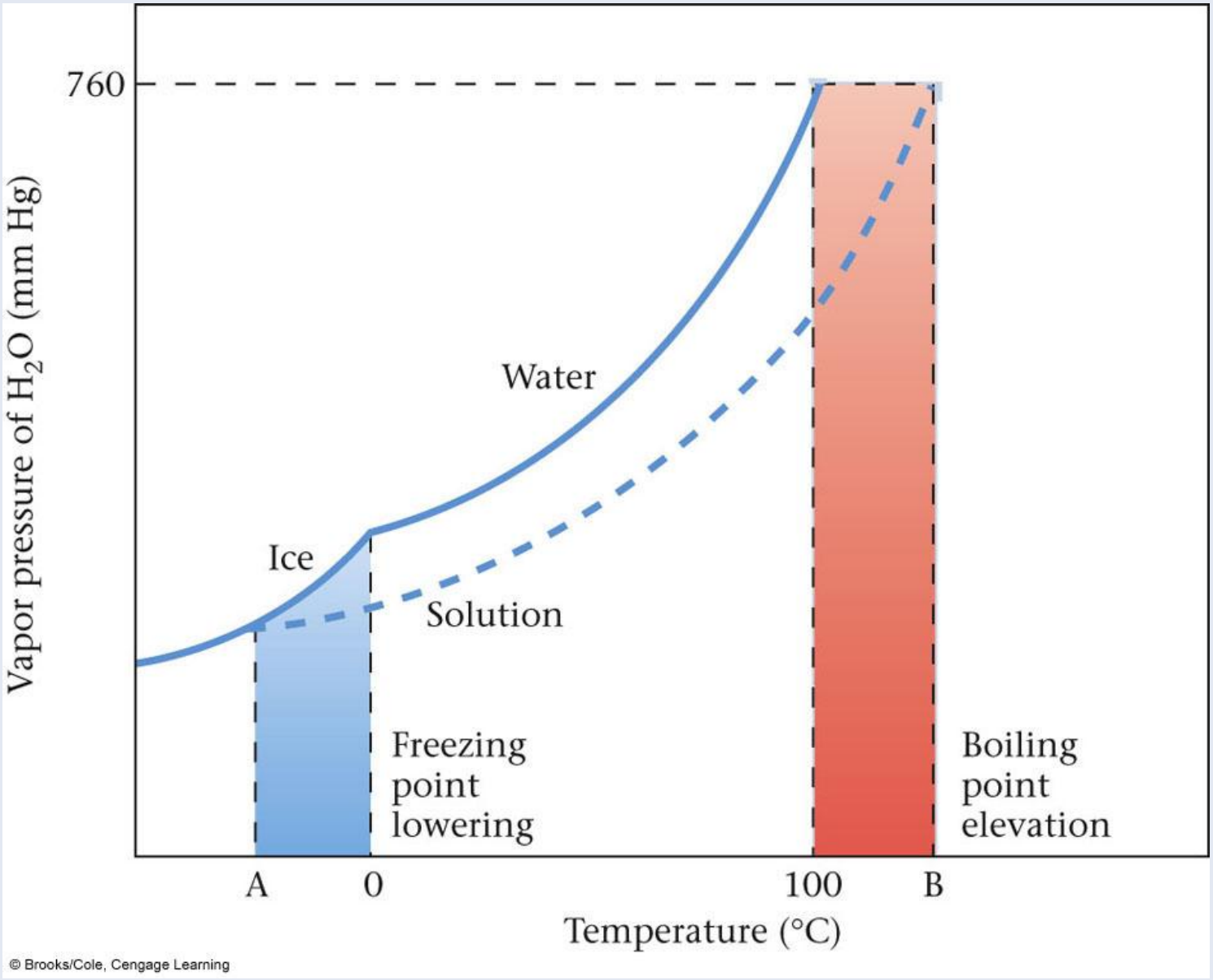


- For water,

$$K_f = 0.52 \frac{^{o}C}{m}$$

$$K_b = 1.86 \frac{^{o}C}{m}$$

Figure 10.8 – Raoult's Law Diagram



Ex10.7: An antifreeze solution is prepared containing 50.0 cm^3 of ethylene glycol,乙二醇 $C_2H_6O_2$(d=1.12g/cm^3) in 50.0gof water.Calculate the freezing point of this 50-50 mixture.

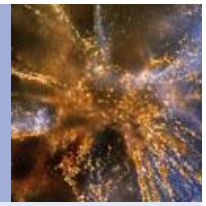
$$n_{C_2H_6O_2} = 50.0\,cm^3 \times \frac{1.12\,g}{1\,cm^3} \times \frac{1\,mol}{62.07\,g} = 0.902\,mol$$

$$m = \frac{mol\ of\ C_2H_6O_2}{Kg\ of\ water} = \frac{0.902\,mol}{0.0500\,Kg} = 18.0\,m$$

$$\Delta T_f = K_f \times m = \frac{1.86\ ^0C}{1\,m} \times 18.0\,m = 33.5\ ^0C$$

溶液應低於純水33.5°C結冰，故凝固點為-33.5°C

Example 10.7



Example 10.7 An antifreeze solution is prepared containing 50.0 cm^3 of ethylene glycol, $C_2H_6O_2$ (d = 1.12 g/cm^3), in 50.0 g of water. Calculate the freezing point of this 50-50 mixture.

Strategy First (1) calculate the number of moles of $C_2H_6O_2$ (MM = 62.07 g/mol). Then (2) apply the defining equation to calculate the molality. Finally (3), use the equation $\Delta T_f = (1.86°C/m) \times$ molality to find the freezing point lowering.

SOLUTION

$$(1)\ n_{C_2H_6O_2} = 50.0\ cm^3 \times \frac{1.12\ g}{1\ cm^3} \times \frac{1\ mol}{62.04\ g} = 0.903\ mol$$

$$(2)\ \text{molality} = \frac{\text{mol of } C_2H_6O_2}{\text{kg of water}} = \frac{0.903\ mol}{0.0500\ kg} = 18.1\ m$$

$$(3)\ \Delta T_f = k_f\,(\text{molality}) = 1.86°C/m \times 18.1\ m = 33.7°C$$

The freezing point of the solution is 33.7°C below that of pure water (0°C). Hence the solution should freeze at −33.7°C.

Reality Check Actually, the freezing point is somewhat lower, about −37°C (−35°F), which reminds us that the equation used, $\Delta T_f = k_f m$, is a limiting law, strictly valid only in very dilute solution.

Molal Constants

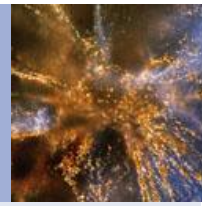


Table 10.2 Molal Freezing Point and Boiling Point Constants

Solvent	fp (°C)	k_f (°C/*m*)	bp (°C)	k_b (°C/*m*)
Water	0.00	1.86	100.00	0.52
Acetic acid	16.66	3.90	117.90	2.53
Benzene	5.50	5.10	80.10	2.53
Cyclohexane	6.50	20.2	80.72	2.75
Camphor	178.40	40.0	207.42	5.61
p-Dichlorobenzene	53.1	7.1	174.1	6.2
Naphthalene	80.29	6.94	217.96	5.80

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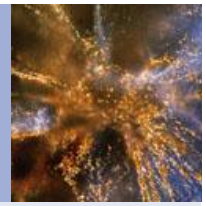
Automotive Applications

- The coolant/antifreeze in an automobile is a direct application of the boiling point elevation and freezing point lowering
- Ethylene glycol, $HO(CH_2)_2OH$
  - High boiling point, 197 ° C
  - Virtually nonvolatile at 100 ° C

Osmosis and Semi-Permeable Membranes

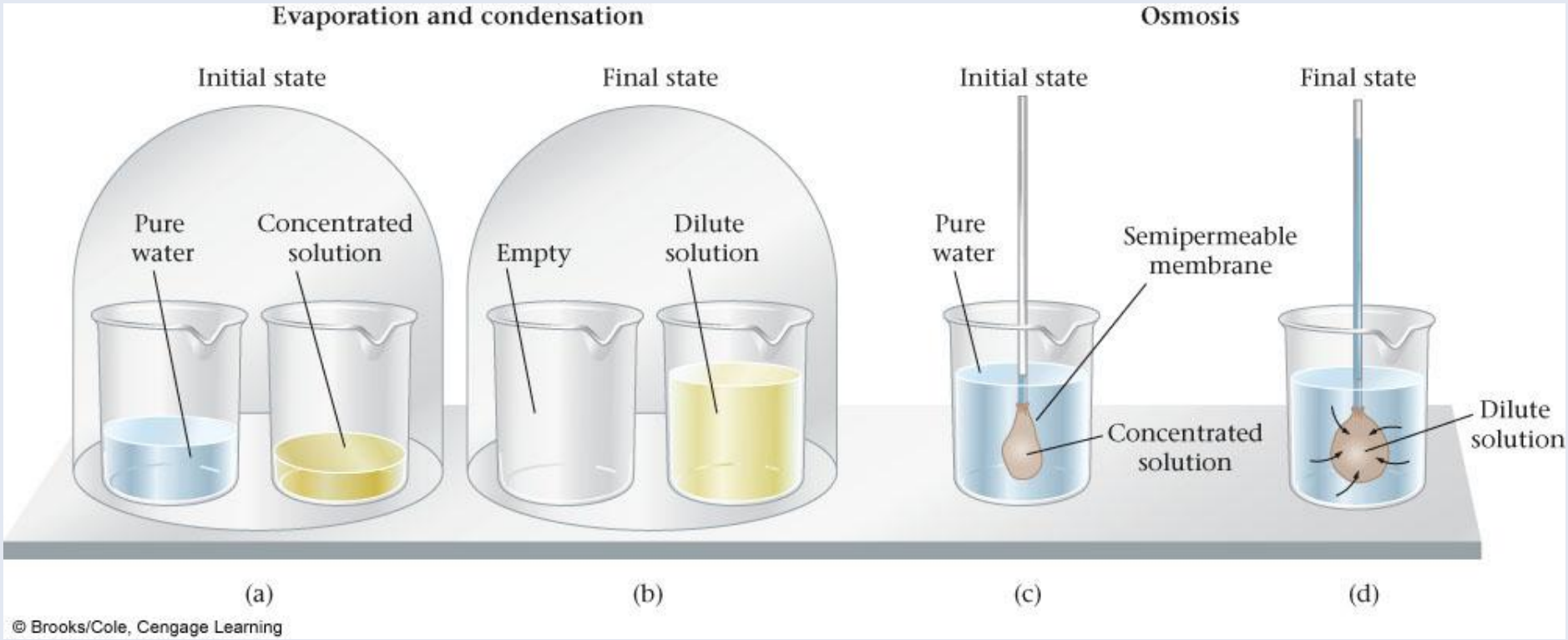
- Consider the concentration of solvent in a solution
  - Concentration is lower than it is for the pure solvent
  - Solvent will flow from an area of high concentration to an area of low concentration
- Next consider a semi-permeable membrane
  - Allows water (and small molecules) to pass, but not larger molecules
  - Water will flow from high concentration to low
  - Process is called ***osmosis***

Osmosis and Evaporation and Condensation



- The difference in concentration of solvent between a beaker of pure water and one of a solution will cause the liquid level in the solution to rise, while the level in the beaker containing water will fall
  - Vapor pressure is higher over pure water
  - Water is transferred to the beaker containing the solution

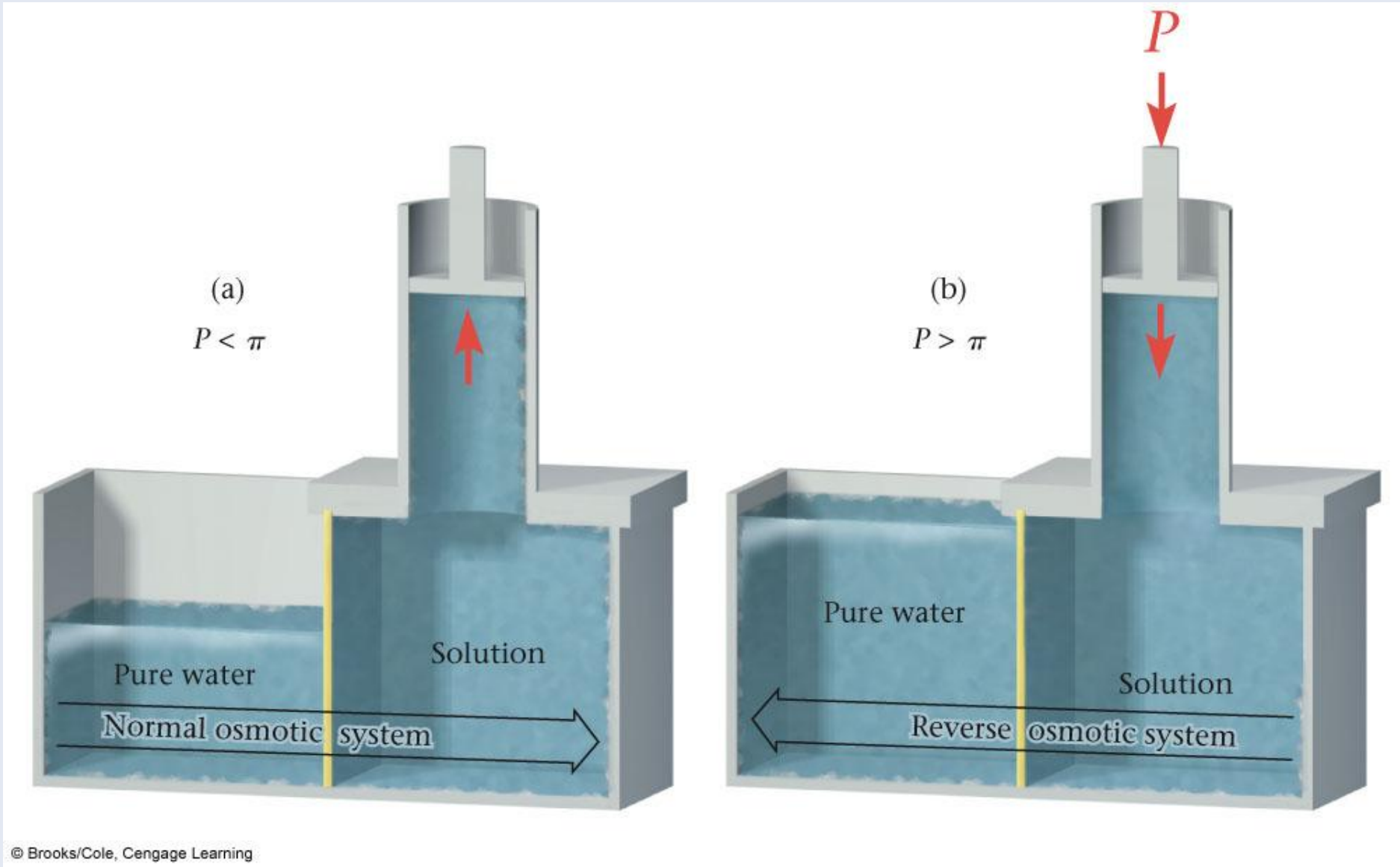
Figure 10.9 – Osmosis and Osmotic Pressure



Osmotic Pressure

- The ***osmotic pressure*** (symbol π) is the pressure required to ***prevent osmosis from occurring***
  - The ***flow of solvent causes the pressure***
  - ***Applying a pressure greater than*** π will cause the water to flow in the other direction; this is ***reverse osmosis***
  - Reverse osmosis can be used to prepare fresh water from seawater

Figure 10.10



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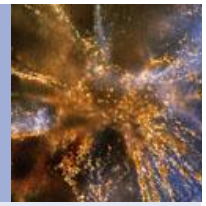
Notes on Osmotic Pressure

- Osmotic pressure is a colligative property
  - Unlike the vapor pressure lowering, π depends on molarity
  - The osmotic pressure equation is similar to the ideal gas law:

$$p = \frac{nRT}{V} = MRT$$

  - Where R = 0.0821 L-atm/mol-K and T is the temperature in K

Example 10.8



Example 10.8 Calculate the osmotic pressure at 15°C of a solution prepared by dissolving 50.0 g of sugar, $C_{12}H_{22}O_{11}$, in enough water to form one liter of solution.

Strategy Determine the molarity of the solution (MM $C_{12}H_{22}O_{11}$ = 342.3 g/mol). Then substitute into Equation 10.5 to obtain the osmotic pressure.

SOLUTION

$$\text{Molarity } (M) = \frac{50.0 \text{ g}/(342.3 \text{ g/mol})}{1.000 \text{ L}} = 0.146 \text{ mol/L}$$

$$\pi = 0.146 \frac{\text{mol}}{\text{L}} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 288 \text{ K} = 3.45 \text{ atm}$$

Reality Check This is a quite reasonable answer; as shown earlier, a 0.10 *M* solution at 25°C has an osmotic pressure of 2.4 atm.

Examples of Osmotic Behavior

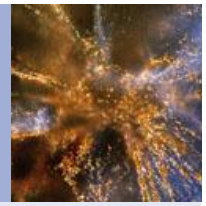
- If a cucumber is placed in a concentrated brine solution, it shrinks and becomes a pickle, with a wrinkled skin
  - Concentration of water is higher inside the cucumber
  - Skin of cucumber acts as a semipermeable membrane
- Conversely, if a dried fruit such as a prune (known now as a dried plum) is placed in water, it swells due to the flow of water into the fruit

Osmolarity

- Solutions of the same osmotic pressure are said to be osmolar; i.e., they have equal osmolarity
  - Important to medical applications
  - Consider a red blood cell
    - If the concentration of ions is larger inside the cell, water will flow in, causing the cell to burst (hemolysis)
    - If the concentration of ions is larger outside the cell, water will flow out, causing the cell to shrivel (crenation)
    - Solutions such as intravenous fluid are prepared to be osmolar with the blood plasma to prevent hemolysis or crenation from occurring

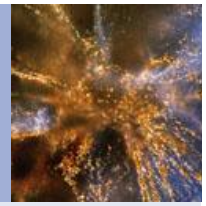
Figure 10.11

Determination of Molar Masses from Colligative Properties



- Colligative properties such as freezing point depression can be used to determine molar masses
  - The freezing point depression is measured, and the freezing point depression constant, K_f is known.
  - If the mass of solvent is known, the number of moles of solute may be calculated from the molality
  - Combining the mass of the solute with the number of moles gives the molar mass

Example 10.9



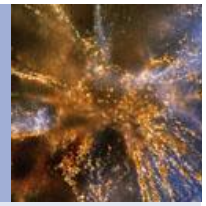
Example 10.9 A laboratory experiment on colligative properties directs students to determine the molar mass of an unknown solid. Each student receives 1.00 g of solute, 225 mL of solvent and information that may be pertinent to the unknown.

(a) Student A determines the freezing point of her solution to be 6.18°C. She is told that her solvent is cyclohexane, which has density 0.779 g/mL, freezing point 6.50°C and $k_f = 20.2°C/m$.

(b) Student B determines the osmotic pressure of his solution to be 0.846 atm at 25°C. He is told that his solvent is water ($d = 1.00$ g/mL) and that the density of the solution is also 1.00 g/mL.

Strategy To arrive at the molar mass, you must determine the concentration of the solution.

Example 10.9, (Cont'd)



SOLUTION

(a) First, calculate the freezing point lowering, ΔT_f.

$$\Delta T_f = T_f^\circ - T_f = 6.50°C - 6.18°C = 0.32°C$$

Then obtain the molality by using the following equation:

$$\Delta T_f = m \times k_f$$

$$\text{molality} = \frac{0.32°C}{20.2°C/m} = 0.016\ m$$

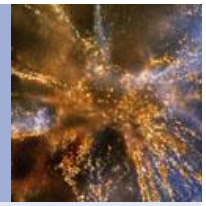
To determine the number of moles of solute from the definition of molality, m = (moles solute)/(kg solvent), first find the mass of solvent using its density:

$$m_{\text{solvent}} = 225\ \text{mL} \times \frac{0.779\ \text{g}}{\text{mL}} = 175\ \text{g} = 0.175\ \text{kg}$$

Then the number of moles of solute is

$$n_{\text{solute}} = \text{molality} \times \text{mass of solvent} = \frac{0.016\ \text{moles solute}}{\text{kg solvent}} \times 0.175\ \text{kg solvent} = 2.8 \times 10^{-3}$$

Example 10.9, (Cont'd)



Finally, the definition of molar mass (MM = m/n) gives

$$\text{MM of solute} = \frac{1.00\ \text{g}}{2.8 \times 10^{-3}\ \text{mol}} = 3.6 \times 10^{2}\ \text{g/mol}$$

(b) The concentration unit in this case is molarity (M). We use the formula for osmotic pressure, $\pi = MRT$.

$$M = \frac{0.846\ \text{atm}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\ \text{K})} = 0.0346\ \text{mol/L}$$

You then need the volume of the solution to get the moles of solute.

$$\text{mass of solution} = 1.00\ \text{g solute} + 225\ \text{g } H_2O = 226\ \text{g}$$

$$\text{volume of solution} = 226\ \text{g} \times \frac{1\ \text{mL}}{1.00\ \text{g}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.226\ \text{L}$$

Again using the definition for the concentration unit M = (mol solute)/(L of solution), we arrive at the number of moles solute:

$$n_{\text{solute}} = \frac{0.0346\ \text{mol solute}}{1\ \text{L solution}} \times 0.226\ \text{L solution} = 7.81 \times 10^{-3}\ \text{moles solute}$$

The molar mass is therefore

$$\text{MM} = \frac{m}{n} = \frac{1.00\ \text{g}}{7.81 \times 10^{-3}\ \text{mol}} = 128\ \text{g/mol}$$

Considerations for Molar Mass Determination

- The solute must be soluble in the solvent
- The K_f for the solvent should be as large as possible
  - Camphor
  - Paradichlorobenzene
- Osmotic pressure can also be used to determine molar mass
  - Osmotic pressure is a much larger effect than the freezing point depression

Colligative Properties of Electrolytes

- Recall that colligative properties depend on the concentration of dissolved particles
  - Since an electrolyte will produce more than one mole of ions per mole of compound dissolved, the colligative effect should be larger than that of a nonelectrolyte of the same concentration
  - 1 mol NaCl produces 1 mol Na^+ and 1 mol Cl^-

Comparing Solutes

	Glucose	NaCl	$CaCl_2$
ΔP	0.42 mmHg	0.77 mmHg	1.3 mmHg

- Note that ΔP increases as the number of moles of ions per mole of compound increases

Deliquescence

- For many electrolytes, ΔP is so large that the solid will pick up moisture from the air and dissolves
- When the relative humidity exceeds 30%, calcium chloride can actually dissolve in the water it picks up
- This phenomenon is known as ***deliquescence***

BPE, FPL and Osmotic Pressure of Electrolytes

- All colligative properties are affected by the presence of an electrolyte:
  - The freezing point is lowered more than for an equivalent nonelectrolyte solution
  - The boiling point is elevated beyond that for an equivalent nonelectrolyte solution
  - The osmotic pressure is higher for an electrolyte than for an equivalent-molarity electrolyte

The van't Hoff *i*-factor: Limiting

- As a limiting case, the ***van't Hoff i-factor*** is the number of moles of particles per mole of solute
  - For NaCl, i=2
  - For $CaCl_2$, i=3

$$\Delta T_f = imK_f$$

$$\Delta T_b = imK_b$$

$$p = iMRT$$

Colligative Properties of Electrolyte Solutions

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

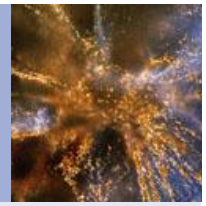
Freezing-Point Depression $\Delta T_f = i\,K_f\,m$

Osmotic Pressure (p) $p = iMRT$

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 10.10



Example 10.10 Estimate the freezing points of 0.20 *m* solutions of

(a) KNO_3 (b) $Cr(NO_3)_3$

Assume that *i* is the number of moles of ions formed per mole of electrolyte.

Strategy Find *i* and apply Equation 10.6.

SOLUTION

(a) One mole of KNO_3 forms two moles of ions:

$$KNO_3(s) \longrightarrow K^+(aq) + NO_3^-(aq)$$

Hence *i* should be 2, and we have

$$\Delta T_f = (2)\ (1.86°C)\ (0.20) = 0.74°C; \qquad T_f = -0.74°C$$

(b) For $Cr(NO_3)_3$, $i = 4$:

$$Cr(NO_3)_3(s) \longrightarrow Cr^{3+}(aq) + 3NO_3^-(aq)$$

$$\Delta T_f = (4)(1.86°C)(0.20) = 1.5°C; \qquad T_f = -1.5°C$$

Freezing Point Lowering of Solutions

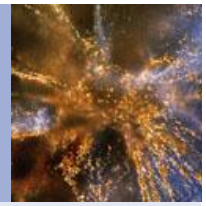


Table 10.3 Freezing Point Lowerings of Solutions

	ΔT_f Observed (°C)		i (Calc from ΔT_f)	
Molality	NaCl	$MgSO_4$	NaCl	$MgSO_4$
0.00500	0.0182	0.0160	1.96	1.72
0.0100	0.0360	0.0285	1.94	1.53
0.0200	0.0714	0.0534	1.92	1.44
0.0500	0.176	0.121	1.89	1.30
0.100	0.348	0.225	1.87	1.21
0.200	0.685	0.418	1.84	1.12
0.500	1.68	0.995	1.81	1.07

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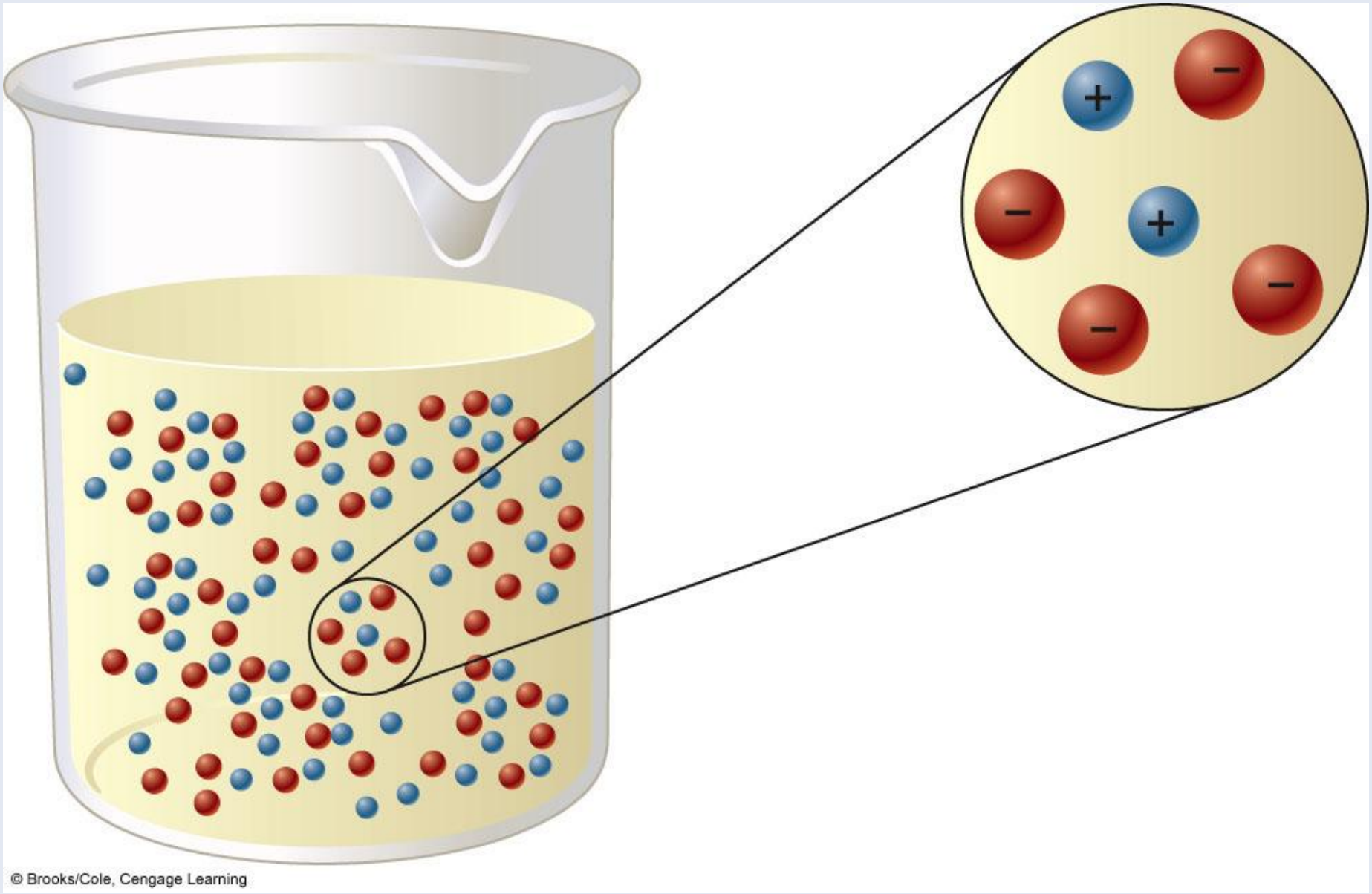
Observed Freezing Points

- The observed freezing point is not as low as calculated using the limiting case for *i*
  - Ions in solution are surrounded by ions of opposite charge, resulting in an ionic atmosphere that prohibits ions for acting completely independently as they are reported to be using the limiting value for *i*
  - Oppositely-charged species can form an ion pair, which effectively reduces the number of particles in solution

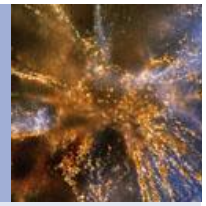
Figure 10.12



Key Concepts

1. Perform dilution calculations
2. Calculate concentrations in M, m, X, percent, ppm and ppb
3. Convert from one set of concentration units to another
4. Apply Henry's law to relate gas solubility to partial pressure
5. Apply Raoult's Law to calculate vapor pressure lowering
6. Relate freezing point, boiling point and osmotic pressure to solute concentrations

Key Concepts, (Cont'd)



7. Use colligative properties to determine the molar mass of a solute
8. Use colligative properties to determine the extent of ionization