Unit 10 includes the following OpenStax sections

- 11.1 The Dissolution Process
- 11.2 Electrolytes
- 11.3 Solubility
- 11.4 Colligative Properties

Figure 11.1

Coral reefs, such as this one at the Palmyra Atoll National Wildlife Refuge, are vital to the ecosystem of earth’s oceans but are threatened by climate change and dissolved pollution. Marine life depends on the specific chemical composition of the complex mixture we know as seawater. (credit: modification of work by “USFWS – Pacific Region”/Wikimedia Commons)

Learning Objectives

- 11.1 The Dissolution Process
  - Describe the basic properties of solutions and how they form
  - Predict whether a given mixture will yield a solution based on molecular properties of its components
  - Explain why some solutions either produce or absorb heat when they form

Review of Solutions

- Solutions are homogenous mixtures made up of two or more substances.
  - **Solute:** substance being dissolved

  - **Solvent:** substance that is doing the dissolving
    - Typically, present in largest amount

Review of Solutions

- Solutions can exist in all 3 physical states.
  - **Solid solution:** metal alloys (two or more metals)
  - **Gas solution:** Ex: air—made up of nitrogen, oxygen, and other gases
  - **Liquid solution:** This is what we will be primarily discussing in this Chapter. Mostly solutions where water is the solvent (aqueous solutions).

The Dissolution Process

- Consider the dissolving of different solutes in water.

- Sucrose, $C_{12}H_{22}O_{11}(s)$

- Aluminum sulfate, $Al_2(SO_4)_3(s)$

Traits of Solutions

1) Homogenous

2) The physical state of the solution is typically the same as the solvent.

   - But the properties of the solution and pure solvent can be quite different (11.4).

3) The dissolved solute will not settle out or separate from the solution, even if it is heavier than the solvent.

4) The components of a solution are dispersed and consist of a mixture of separate molecules, atoms, and/or ions.

Figure 11.2

When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Review Intermolecular Forces (IMFs)

- Recall intermolecular forces (IMFs).

The Formation of Solutions

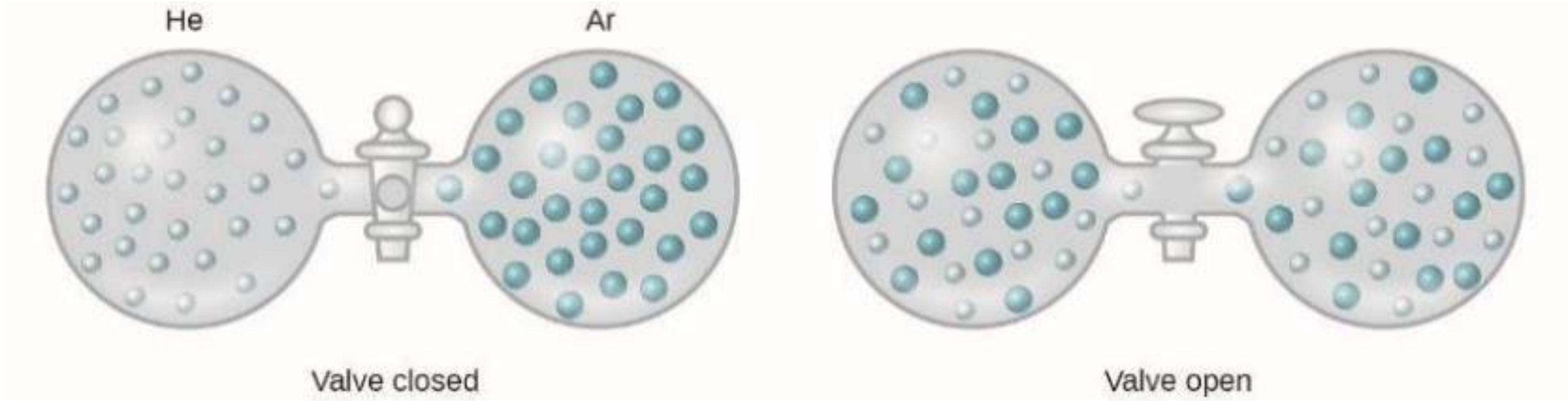
- Three types of intermolecular attractive forces influence whether substances will form a solution.

1) solute-solute

2) solvent-solvent

3) solute-solvent

Figure 11.3

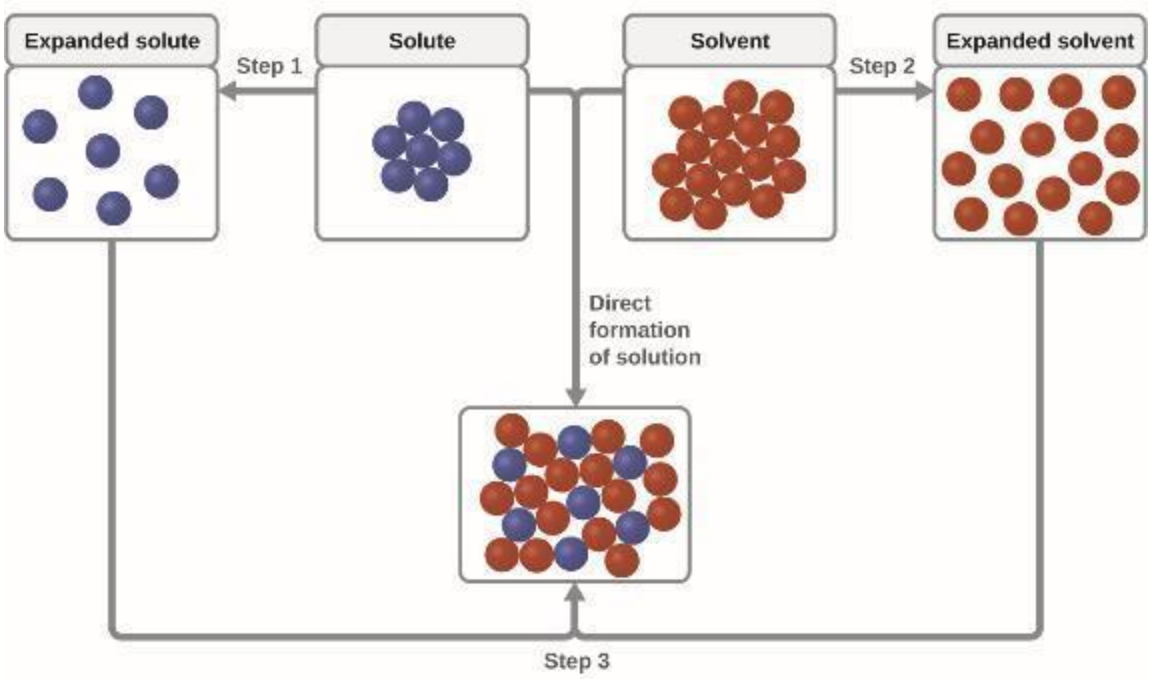


Samples of helium and argon spontaneously mix to give a solution.

The Formation of Solutions

- We can think of solution formation as a step-wise process.
- Step 1: Solute-solute IMFs must be overcome. *Energy is consumed.*
- Step 2: Solvent-solvent IMFs must be overcome. *Energy is consumed*.
- Step 3: Solvation-solute-solvent attractive forces are established. *Energy is released*.

Figure 11.4



This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

The Formation of Solutions

- The relative magnitudes of the energy changes for these three steps determine whether the solution formation process is **exothermic**, **endothermic**, or **does not occur at all**.

1) If,

$$|\Delta H_1 + \Delta H_2| < |\Delta H_3|$$

2) If,

$$|\Delta H_1 + \Delta H_2| > |\Delta H_3|$$

3) If,

$$|\Delta H_1 + \Delta H_2| >> |\Delta H_3|$$

Figure 11.5

An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

Solvent-Solvent Interactions

- *The Golden Rule of Solubility is "Like Dissolves Like"*
- If two substances have very similar IMFs then they are likely to be soluble in one another.
- Step 3 will be highly exothermic.
- **Nonpolar** solvents dissolve nonpolar solutes.
- **Polar** solvents dissolve polar solutes and many ionic solutes.

Learning Objectives

- 11.2 Electrolytes
  - Define and give examples of electrolytes
  - Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
  - Relate electrolyte strength to solute-solvent attractive forces

Electrolytes

- **Electrolytes:** Substances that dissolve in water and undergo a physical or chemical change to produce ions.

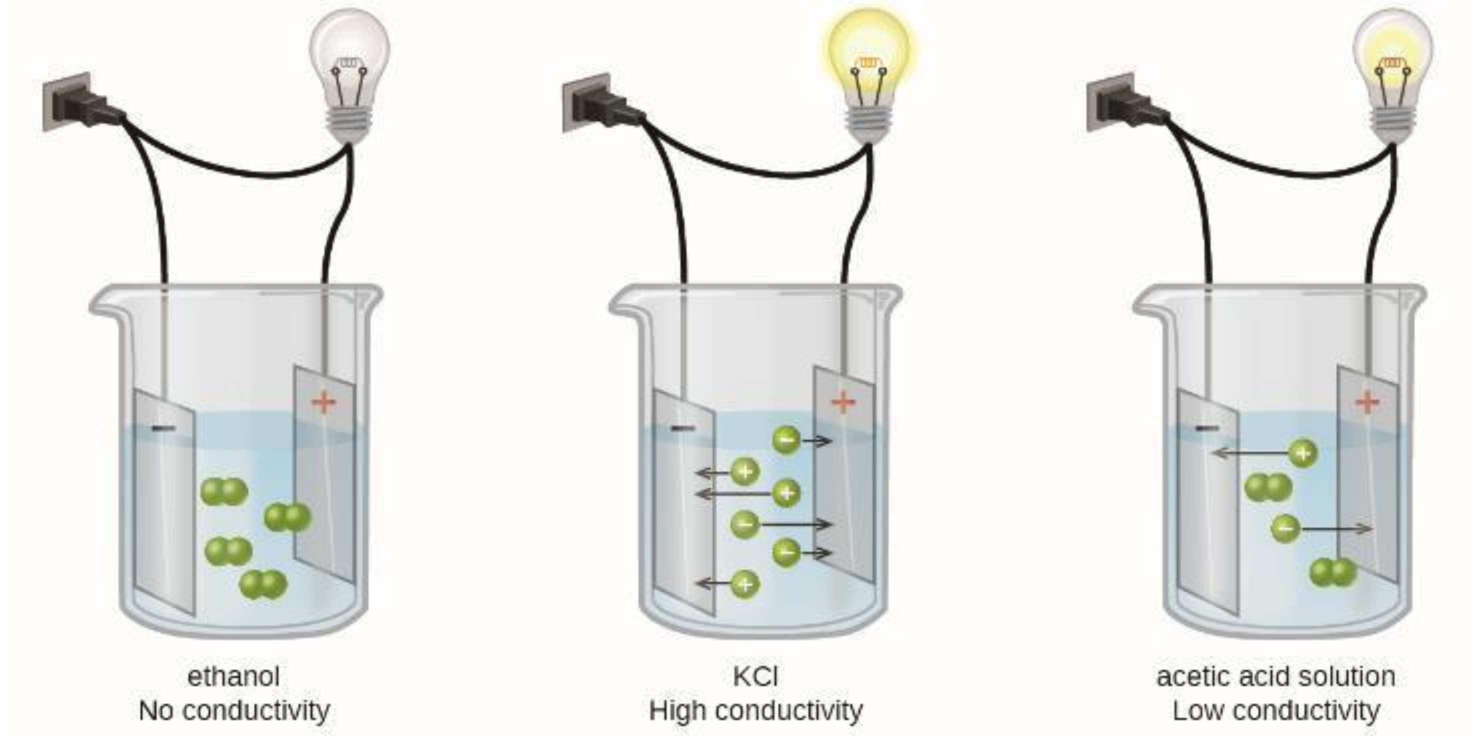
- **Nonelectrolytes:** Substances that do not produce ions when dissolved in water.

Strong vs. Weak Electrolytes

- **Strong electrolytes:** Essentially 100% of the dissolved substance generates ions.

- **Weak electrolytes:** Only a relatively small fraction of the dissolved substance generates ions.

Figure 11.6

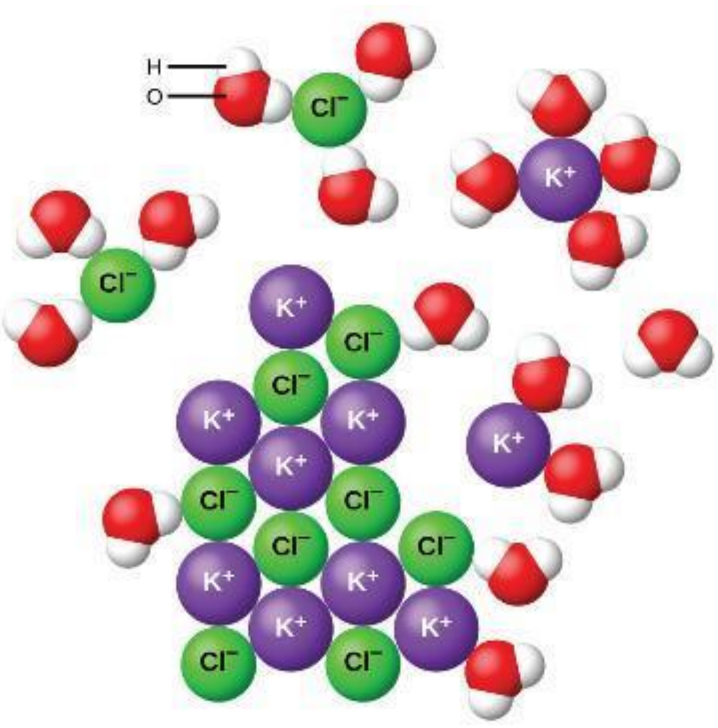


Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

- Water and other polar molecules are attracted to ions.
- The electrostatic attraction between an ion and a molecule with a dipole (polar molecule) is called an **ion-dipole attraction**.
- Water molecules surround and solvate the separated ions.
- This physical process is known as **dissociation**.

Figure 11.7



As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

Solubility of Ionic Compounds

- Competing forces influence the extent of solubility of an ionic compound.

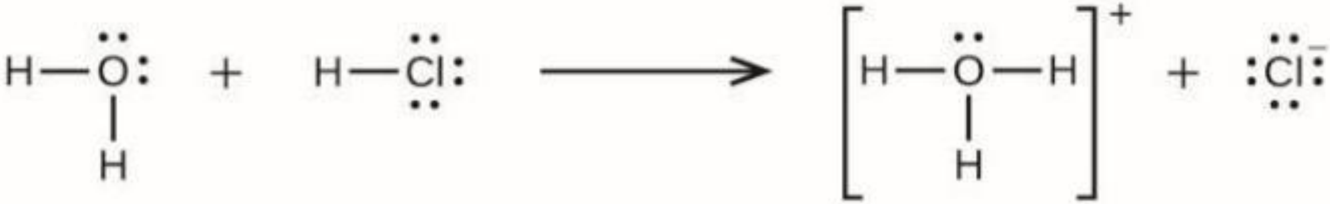
1) Ion-dipole attraction: *If this is the dominate force then the compound it "pulled" into solution and has very high water solubility.*

2) The force of attraction between oppositely charged ions: *If this is the dominate force then the compound tends to remain un-dissolved and in the solid state, and have very low water solubility.*

Covalent Electrolytes

- Some covalent compounds are electrolytes because they chemically react with water to produce ions.

- Example: HCl



Learning Objectives

- 11.3 Solubility
  - Describe the effects of temperature and pressure on solubility
  - State Henry’s law and use it in calculations involving the solubility of a gas in a liquid
  - Explain the degrees of solubility possible for liquid-liquid solutions

Solubility

- Even most highly water soluble compounds have a limit to how much you can dissolve.

- **Solubility:** The maximum concentration of a solute that can be achieved in a particular solvent under given conditions.

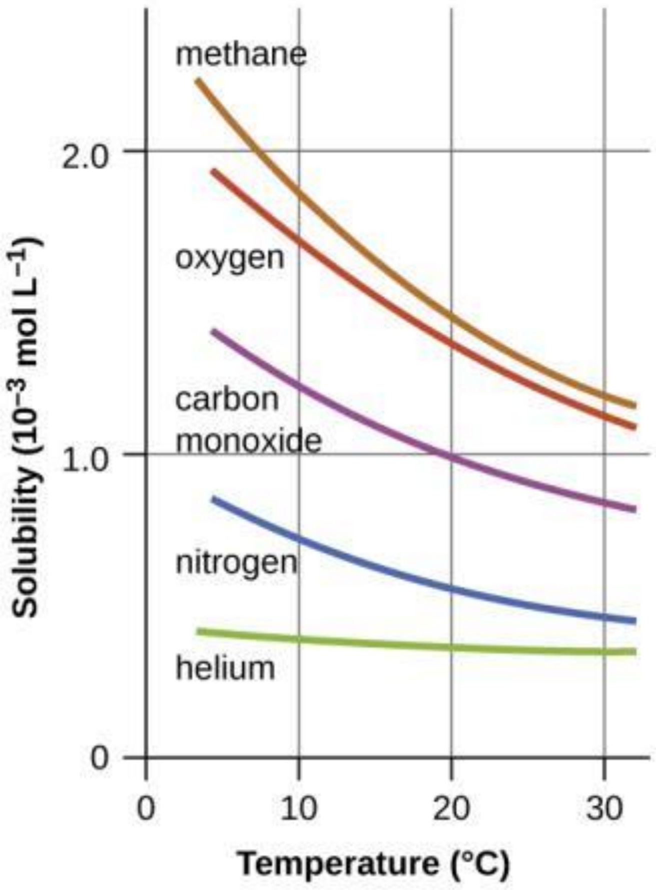
Solubility Terms

- When a solute’s concentration *equals* its solubility the solution is called **saturated**.
- When a solute’s concentration is *less than* its solubility the solution is called **unsaturated**.
- When a solute’s concentration is *greater than* its solubility the solution is called **supersaturated**.

Principles of Solubility

- The extent to which a solute dissolves in a solvent depends on several factors:
    - The nature of the solvent and solute molecules and the interactions between them.
    - The temperature at which the solution is formed.
    - When dealing with a gaseous solute, the pressure is also important.

Figure 11.8



The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

Pressure and Gas Solubility

- Pressure has a major effect on the solubility of a gas in a liquid.

- Gas solubility (C_g) and partial pressure (P_g) are directly proportional.

- **Henry's Law:** Solubility of a Gas

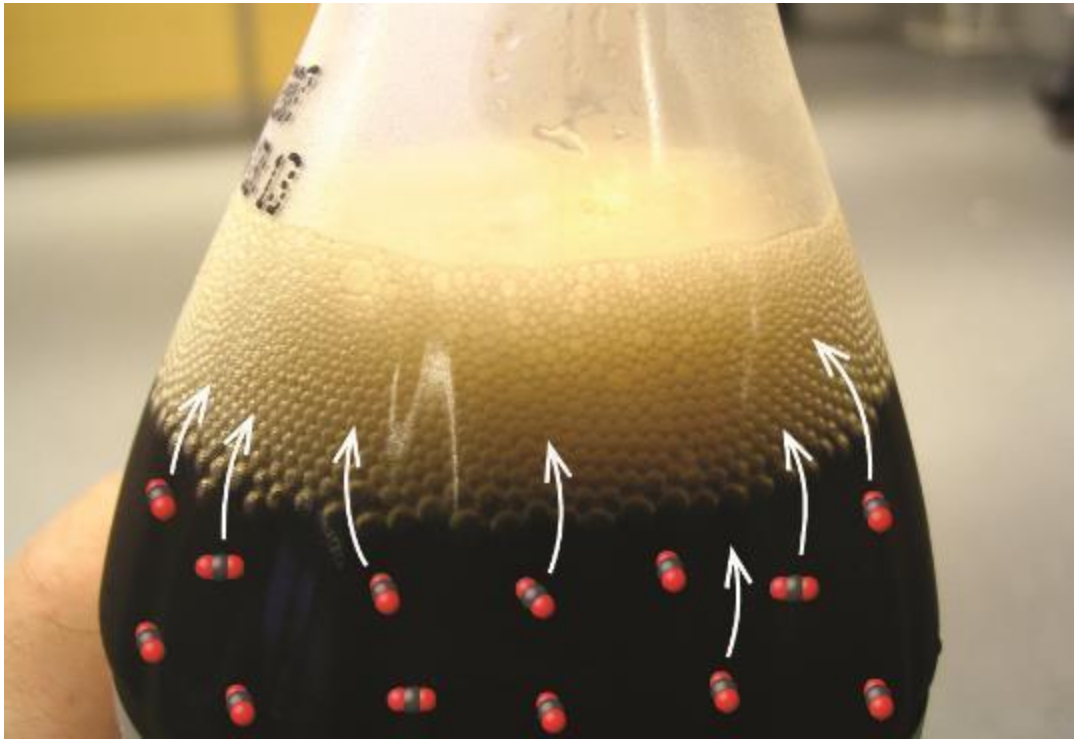
$$C_g = kP_g$$

- *k* = constant of that particular gas-liquid system and temperature.

Figure 11.9

(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

Figure 11.10



Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

Figure 11.11

(a) US Navy divers undergo training in a recompression chamber.

(b) Divers receive hyperbaric oxygen therapy.

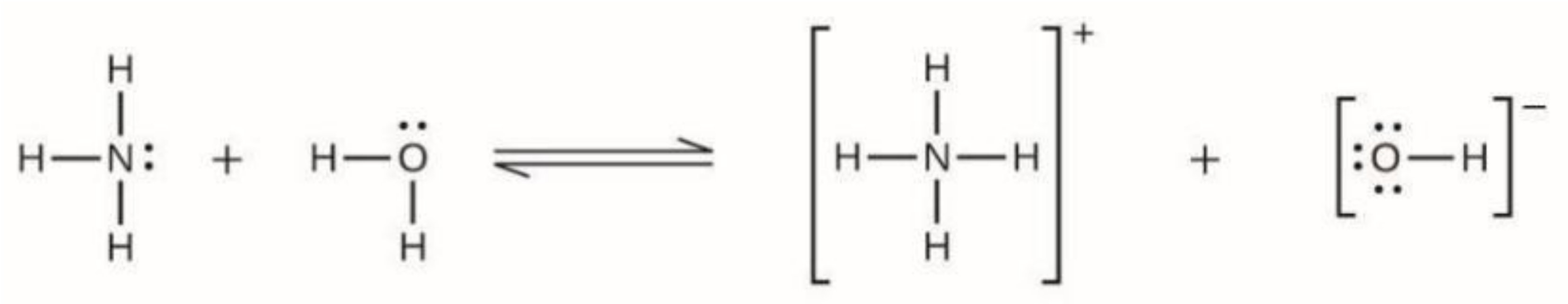


Figure 11.12


(a)

(b)

(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

Solutions of Liquids in Liquids

- Liquids can be dissolved in other liquids.

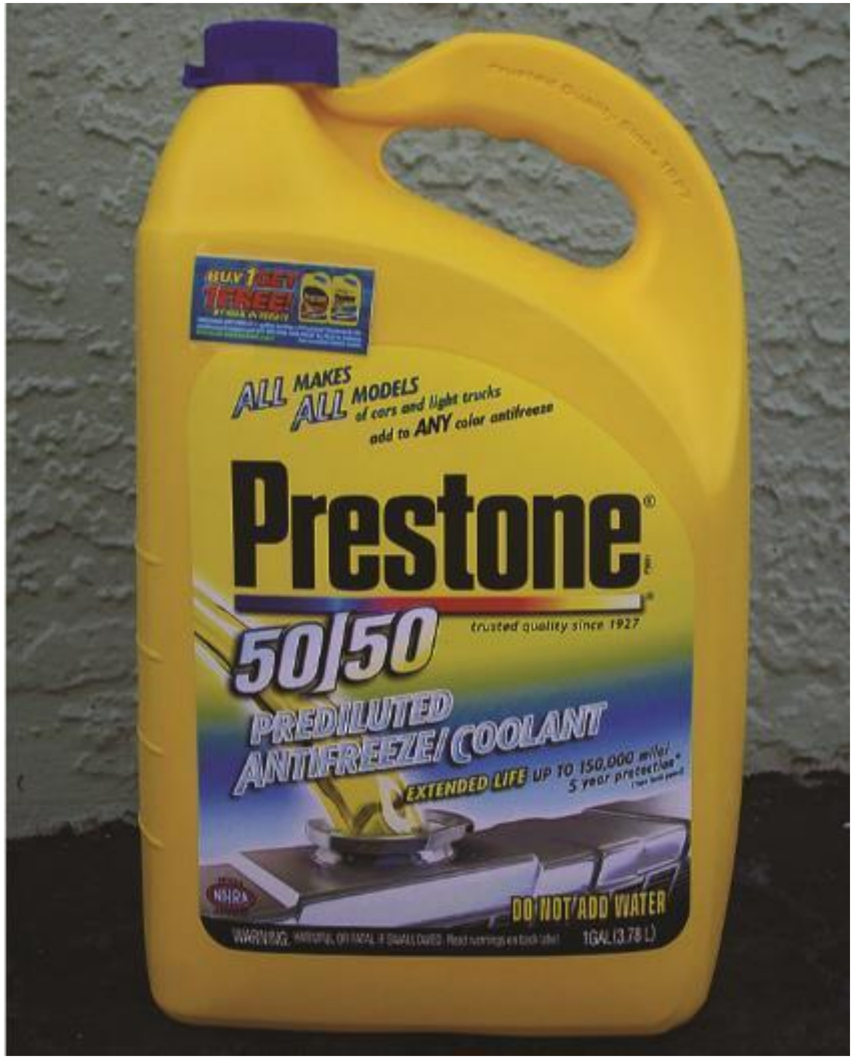
- Both solute and solvent are liquids.

Miscible Liquids

- Two liquids that mix with each other in all proportions are called **miscible**.

- Examples:
  - Ethanol and water
  - Gasoline and oil

Figure 11.13



Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Immiscible Liquids

- Two liquids that do not mix to an appreciable extent are called **immiscible**.

- Example:
  - Non-polar liquids (gasoline, oil, hydrocarbons) and water.

Figure 11.14

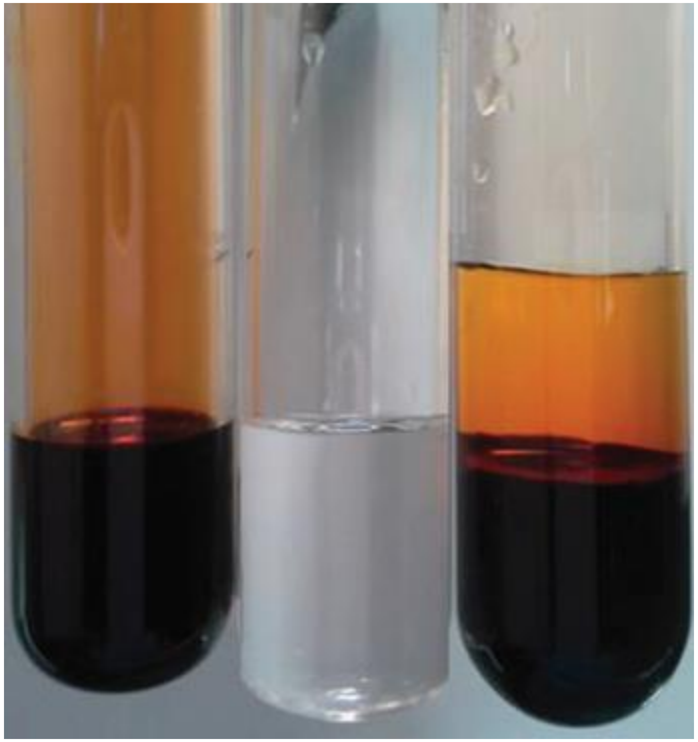
Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Partially Miscible Liquids

- Two liquids that are of moderate mutual solubility are called **partially miscible**.

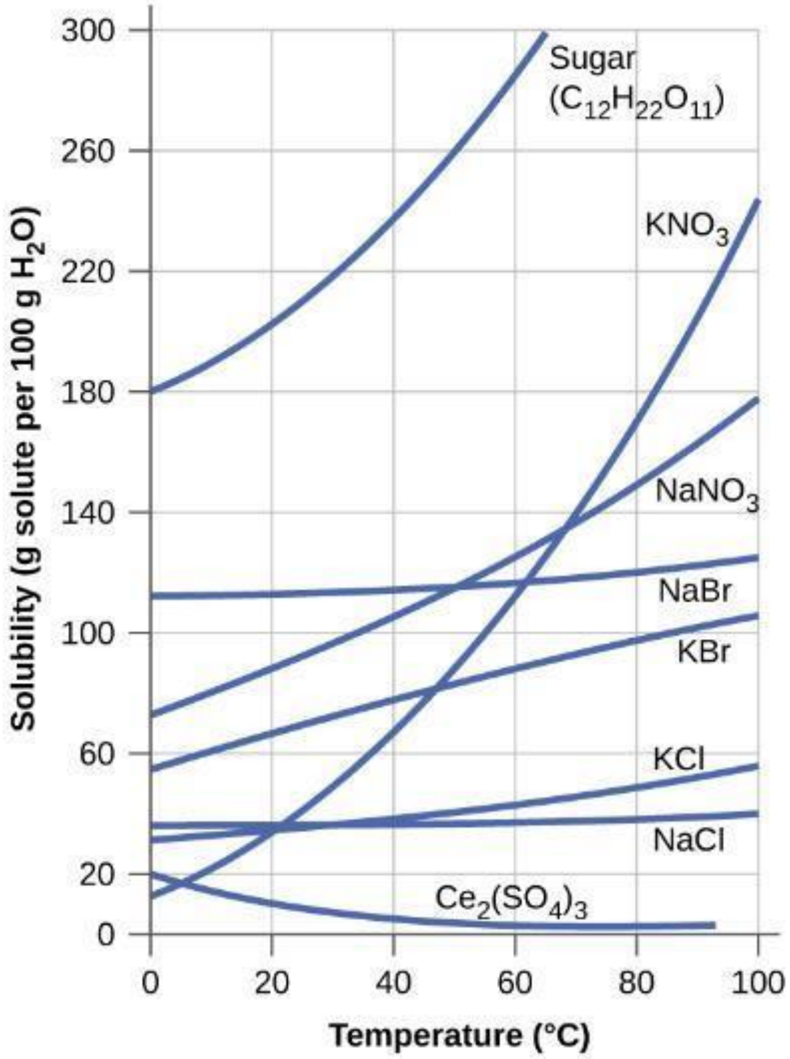
- Example:
  - Bromine and water.

Figure 11.15



Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

Figure 11.16



This graph shows how the solubility of several solids changes with temperature.

Temperature and Solubility of Solids

- Both ionic and covalent solids can dissolve in liquids.

$$\mathrm{NaC_2H_3O_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}\,(aq) + \mathrm{C_2H_3O_2^-}(aq)$$

- Dissolving a solid in a liquid is usually an endothermic process.
- Added heat favors the formation of products (dissolved ions).
- Thus, the solubility of most solids tends to increase with temperature.

Supersaturated Solutions

- To make a supersaturated solution with a solid solute.
  - Make a saturated solution of the compound at high temperature.
  - Slowly cool to a lower temperature.
  - If cooling is slow and careful, the solid won’t precipitate.
  - At the lower temperature, you will have a solute concentration that is greater than the compound’s solubility.

- Adding a crystal of the solid or agitating the solution results in precipitation of the excess solute. https://www.youtube.com/watch?v=BLq5NibwV5g

Figure 11.17

This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is "clicked." (credit: modification of work by "Velela"/Wikimedia Commons)

Learning Objectives

- 11.4 Colligative Properties
  - Express concentrations of solution components using mole fraction and molality
  - Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
  - Perform calculations using the mathematical equations that describe these various colligative effects
  - Describe the process of distillation and its practical applications
  - Explain the process of osmosis and describe how it is applied industrially and in nature

Colligative Properties

- The properties of a solution differ considerably from those of the pure solvent and pure solute.
- Some solution properties depend on the identity of the solute.
  - Examples: acidity, basicity, density
- Other properties only depend on solute concentration and not its identity.
- Colligative properties depend primarily on the concentration of solute particles, and *not* on the nature or identity of the solute.

Colligative Properties That We Will Discuss

1) Vapor pressure lowering

2) Boiling point elevation

3) Freezing point depression

4) Osmotic pressure

Concentration Units

1) Molarity (M)

2) Mass percent

3) Mole fraction (X)

4) Molarity (m)

Molarity

- **Molarity** is defined as moles of solute per liter of solution. Symbol *M* (capital letter!)

- Limitation: Molarity is temperature dependent. Solution volume changes with temperature.

Concentration by Mass

- Mass percent

Mole Fraction (*X*)

- **Mole fraction** is independent of temperature.
  - The mole fraction of component **A** is the moles of **A** divided by the total number of moles of all solution components.
  - The mole fractions of all components must sum to 1.

Molality (*m*)

- **Molality (*m*):** Moles of solute per kilogram of solvent.

- Lowercase “*m*” is the symbol for molality.

- Molality is also independent of temperature.

Vapor Pressure Lowering

- Adding a nonvolatile solute to a pure solvent lowers the solvent’s vapor pressure.

- **Result:** The Solvent in a solution evaporates more slowly than the pure solvent would.

- Vapor Pressure Lowering (ΔP) is a colligative property.

Vapor Pressure Review

- Think back to Liquid-Vapor Equilibrium (Ch. 10).

- When a liquid is placed in a closed container, vaporization and condensation happen at equal rates.

Liquid ⇌ Gas

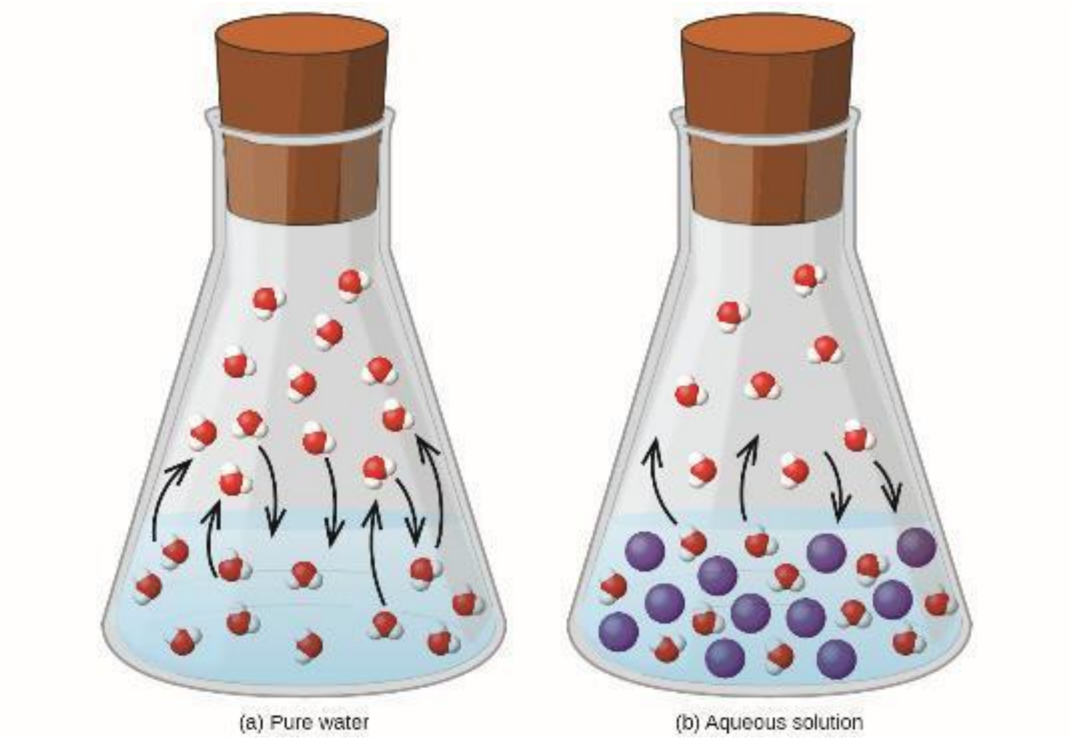
- The vapor pressure of the liquid is the pressure exerted by the gas phase molecules.

Why Does Vapor Pressure Lowering (ΔP) Occur?

$$\text{Liquid} \rightleftharpoons \text{Gas}$$

- To vaporize, solvent molecules must be at the surface of the liquid.
- Solute molecules decrease the surface area available for solvent molecules.
- The rate of solvent vaporization decreases.
- The rate of solvent condensation remains the same.

Figure 11.18


(a) Pure water

(b) Aqueous solution

The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

Why Does Vapor Pressure Lowering (ΔP) Occur?

$$\text{Liquid} \rightleftharpoons \text{Gas}$$

- **Result:** Less solvent molecules in the gas phase.
- The decrease in gas phase molecules results in a lowering of the vapor pressure.

Raoult’s Law

- **Raoult’s law:** The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction.

$$P_{\text{solution}} = X_{\text{solvent}} P^{\text{o}}_{\text{solvent}}$$

- P_{solution} = vapor pressure of the solvent in solution.
- C_{solvent} = mole fraction of the **solvent.**
- P^{*}_{solvent} = vapor pressure of the pure **solvent**.

Boiling Point Elevation and Freezing Point Depression

- A solution *boils* at a *higher* temperature than that of the pure solvent.
  - The difference in boiling point of the solution and pure solvent is called the boiling point elevation (ΔT_b).
- A solution *freezes* at a *lower* temperature than that of the pure solvent.
  - The difference in freezing point of the solution and pure solvent is is called the freezing point depression (ΔT_f).
- **ΔT_b and ΔT_f are both positive quantities.**

Boiling Point Elevation and Freezing Point Depression

- Boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) are both a direct result of vapor pressure lowering.

- Boiling occurs when vapor pressure equals atmospheric pressure.

- Vapor pressure is directly proportional to temperature.

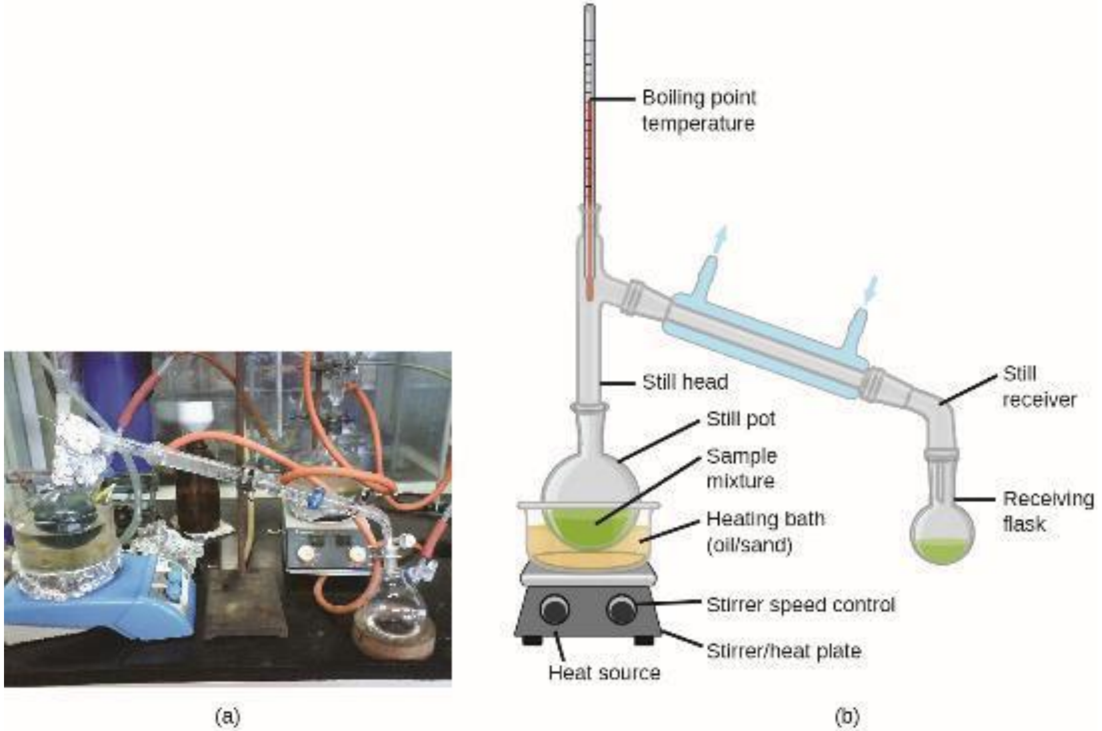
Boiling Point Elevation and Freezing Point Depression

- The presence of a solute lowers the vapor pressure.

- A higher temperature is now required for the vapor pressure to equal the atmospheric pressure.

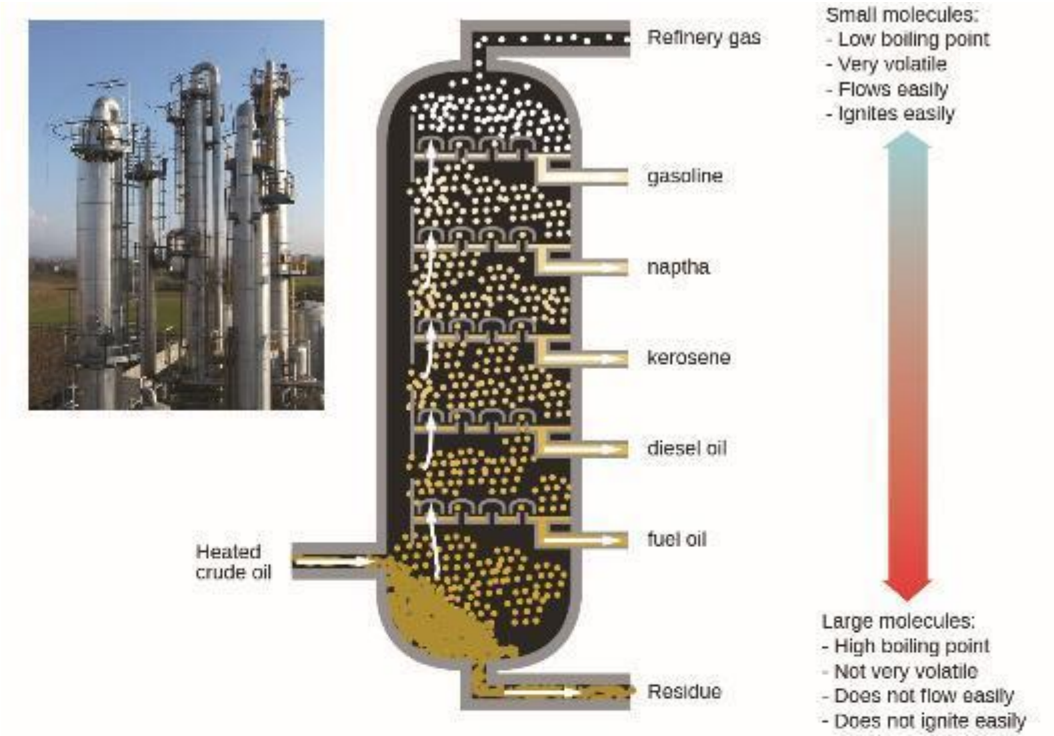
- The boiling point has therefore increased.

Figure 11.19



A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)

Figure 11.20



Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

Boiling Point Elevation and Freezing Point Lowering

- Boiling point elevation (ΔT_b) and freezing point lowering (ΔT_f) are both colligative properties.
  - Depend on the concentration of the solute
  - Concentration expressed in molality (*m*).
  - Example: 1 m sucrose and 1 m ethylene glycol solutions boil at the same temp.

$$\Delta T_b = mk_b \qquad \Delta T_f = mk_f$$

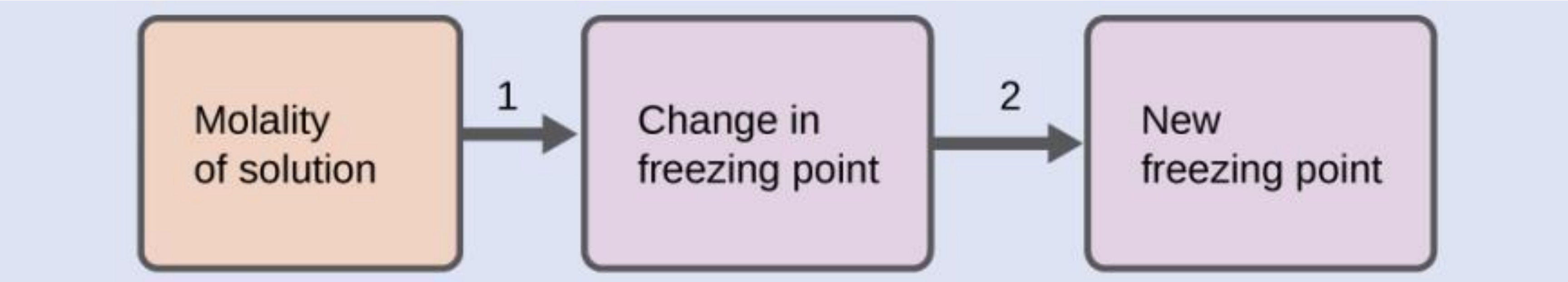
- k_b and k_f are called the boiling point elevation constant and freezing point depression constant, respectively.

Table 11.2 Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	**Boiling Point (°C at 1 atm)**	**Kb (Cm^{-1})**	**Freezing Point (°C at 1 atm)**	**Kt (Cm^{-1})**
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	–63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

- k_b and k_f values depend on the identity of the solvent

Example 11.7



Molality of solution

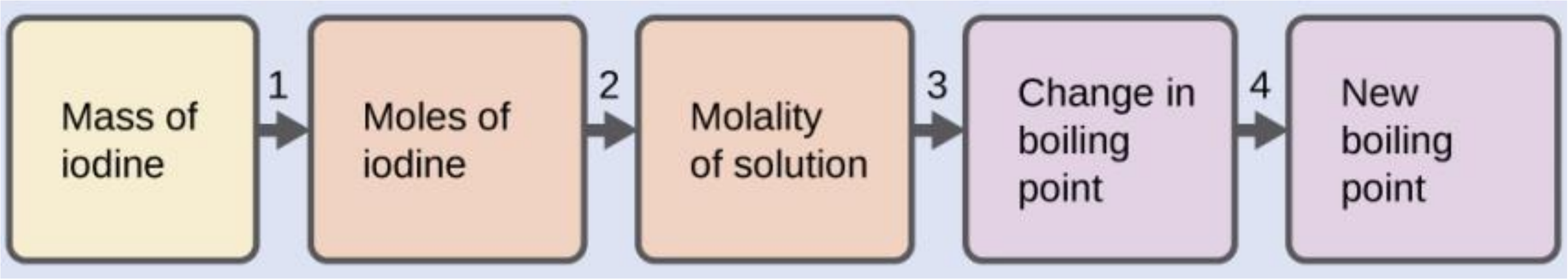
1

Change in freezing point

2

New freezing point

Example 11.8



Mass of iodine

1

Moles of iodine

2

Molality of solution

3

Change in boiling point

4

New boiling point

Figure 11.21

Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

Example 11.9

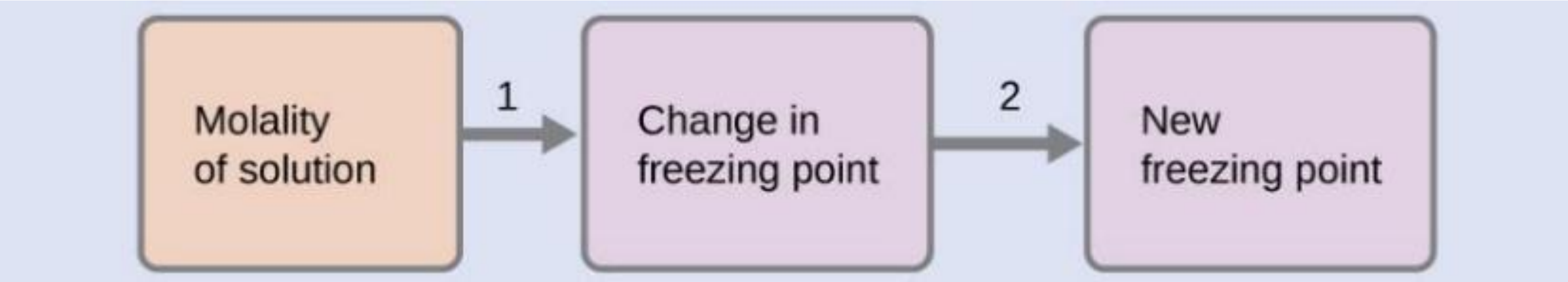
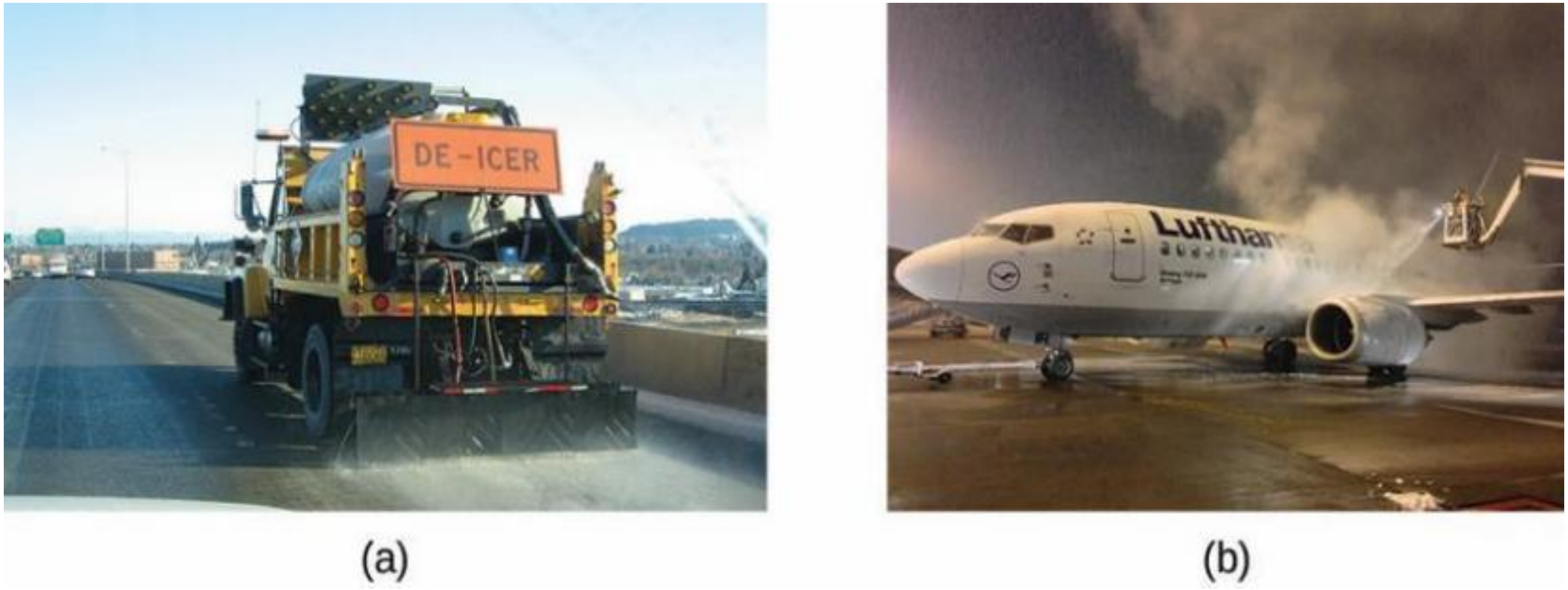
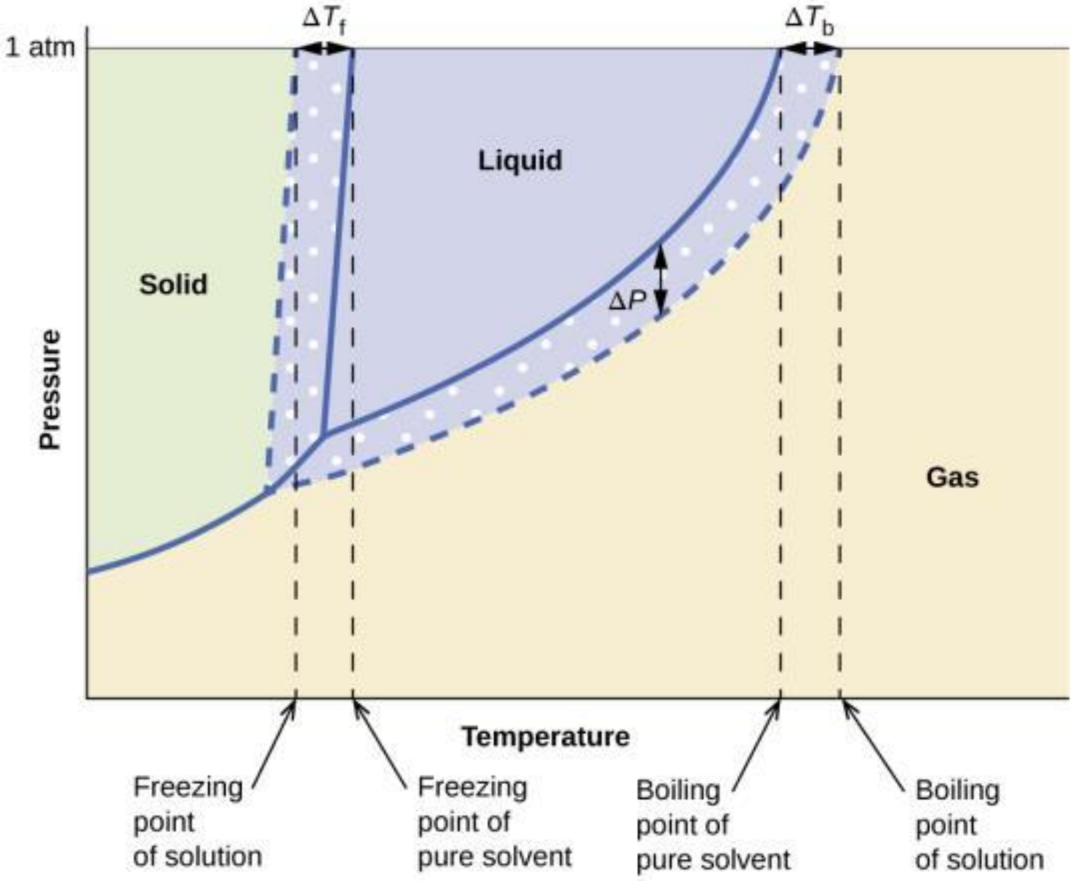

Molality of solution
1
Change in freezing point
2
New freezing point

Figure 11.22



Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

Figure 11.23



These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).

Semipermeable Membranes

- **Semipermeable membranes:** Material that only allows select molecules or ions to pass through of certain size, shape, polarity, charge, or other factor.

- Consider a semipermeable membrane that only allows solvent molecules to permeate and not solute.

- This semipermeable membrane separates a sample of pure solvent from a solution.

Osmosis and Osmotic Pressure of Solutions

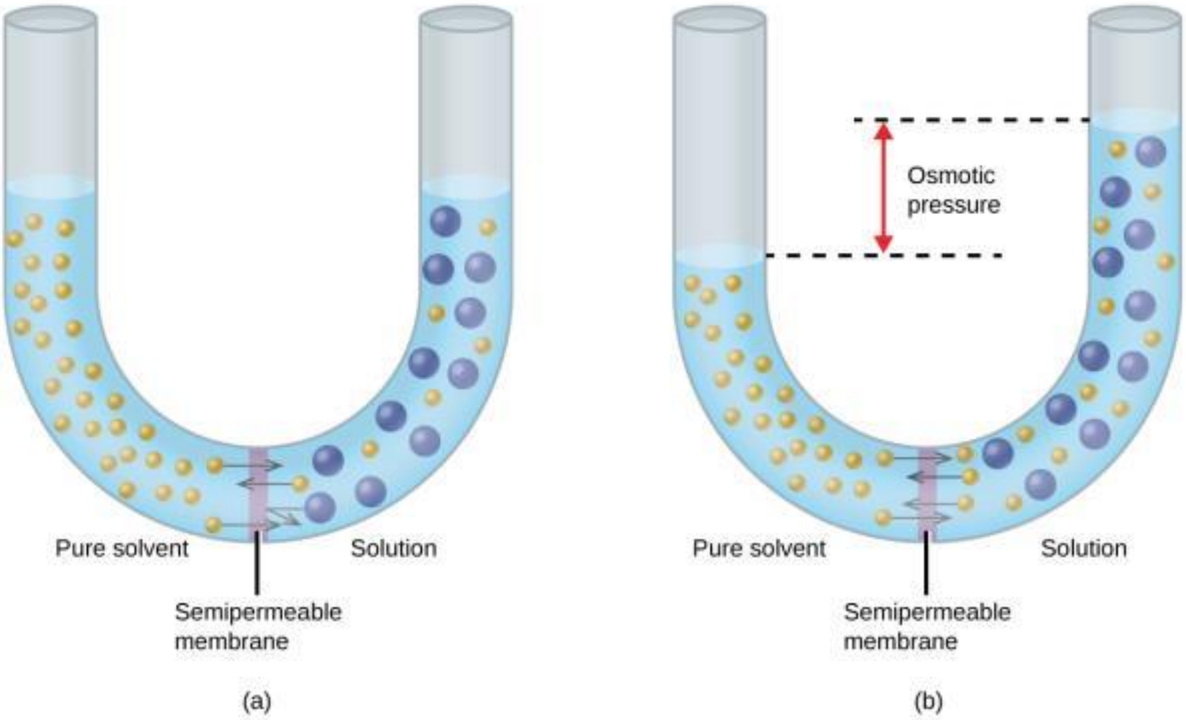
- Solvent molecules diffuse across the membrane in both directions.
- The concentration of solvent is higher in the pure sample.
- This results in solvent molecules diffusing at a faster rate from pure solvent to solution relative to the reverse direction.

Osmosis and Osmotic Pressure of Solutions

- **Result:** A net transfer of solvent molecules from the pure solvent to the solution.

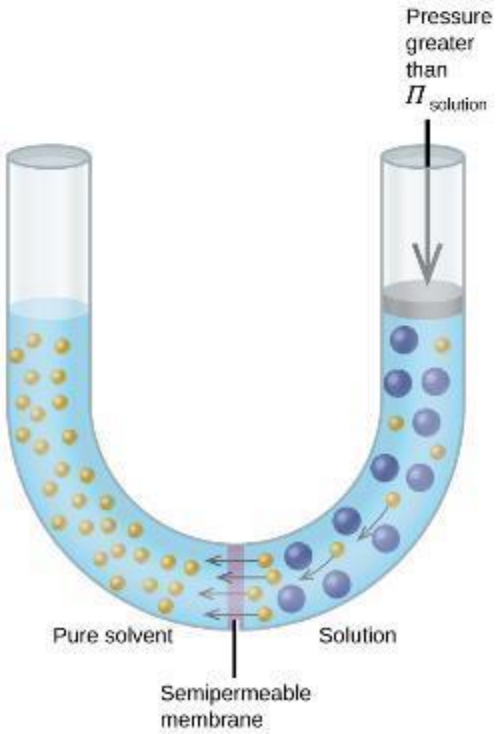
- Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process called **osmosis**.

Figure 11.24



(a) A solution and pure solvent are initially separated by an osmotic membrane. (b) Net transfer of solvent molecules to the solution occurs until its osmotic pressure yields equal rates of transfer in both directions.

Figure 11.25



Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

Osmotic Pressure Is a Colligative Property

- The flow of solvent during osmosis creates a force.

- The osmotic pressure (symbol π) is the pressure just sufficient to prevent osmosis from occurring.

- Conc. is expressed in **molarity (*M*)**, not molality (*m*)!

- *R* = Gas Law Constant = 0.08206 L · atm/mol · *K*
- *T* = Temperature in *K*

Reverse Osmosis

- Applying a pressure to the solution greater than the osmotic pressure results in **reverse osmosis**.

- Solvent molecules are pushed from the solution to the pure solvent.

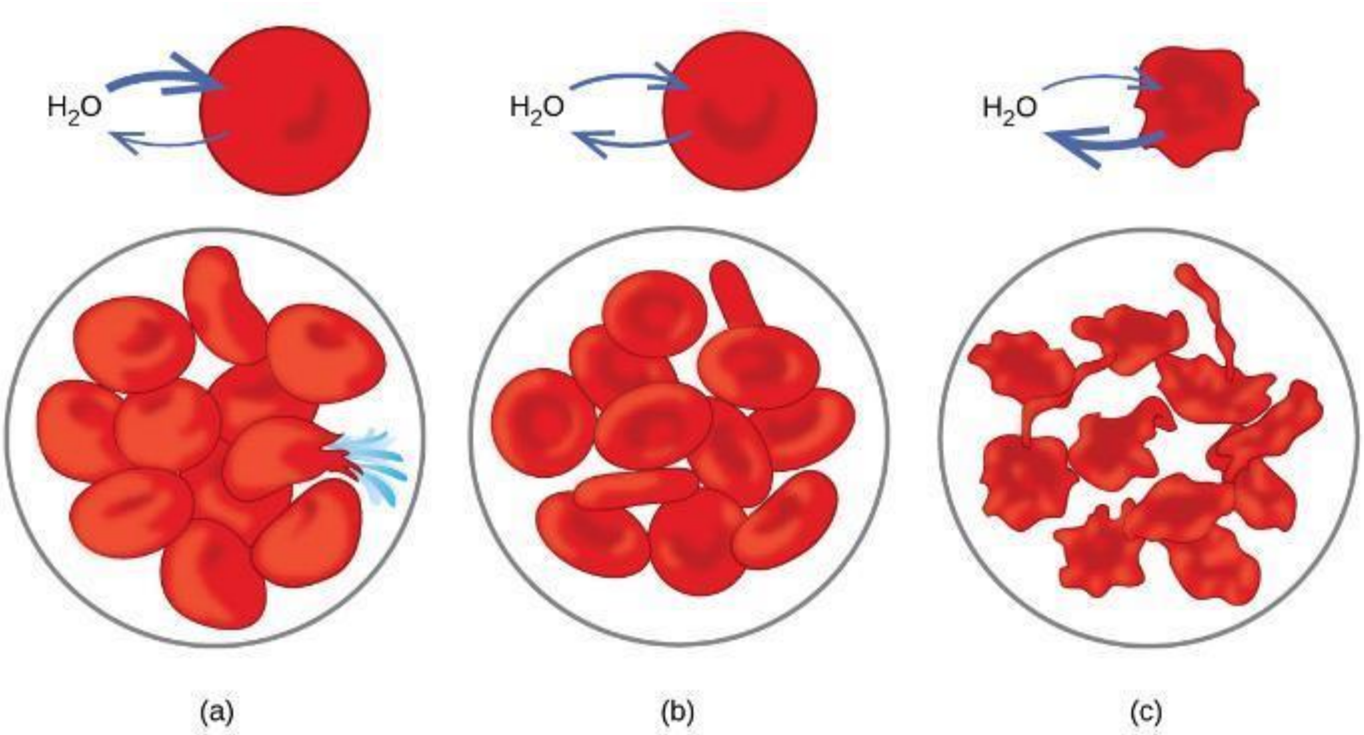
Figure 11.26

(a)

(b)

Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

Figure 11.27



Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

Determination of Molar Mass from Colligative Properties

- Colligative properties can be used to determine the molar mass of an unknown solute.
  - Freezing point lowering (ΔT_f) and osmotic pressure (Π) are most commonly used.

$$\Delta T_f = mk_f$$

$$\pi = MRT$$

Determination of Molar Mass from Colligative Properties

- Typical Procedure:

1) Add a known mass of the solute to either
    - A known mass of the solvent
    - Or to create a solution of known volume

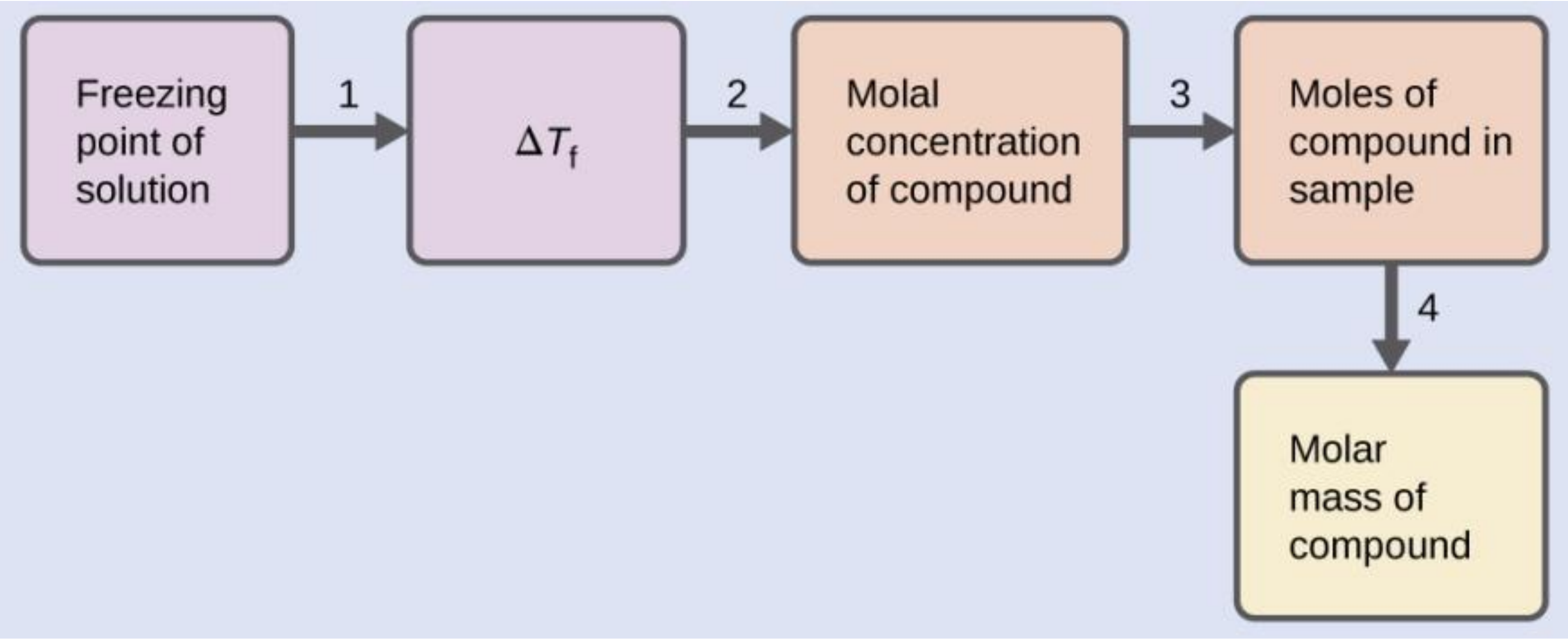
2) Measure the colligative property (ΔT_f or Π).
3) Calculate the concentration (*m* or *M*) of the solute.

$$m = \frac{\Delta T_f}{k_f} \qquad m = \frac{\pi}{RT}$$

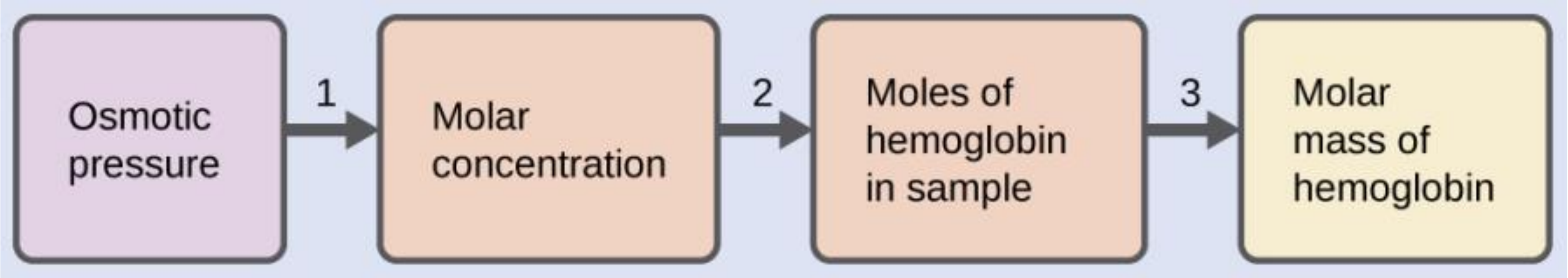
4) Determine the number of moles of solute present from the concentration.
5) Calculate the molar mass (*MM*).

$$MM = \text{g/mole}$$

Example 11.11



Example 11.12


Osmotic pressure
1
Molar concentration
2
Moles of hemoglobin in sample
3
Molar mass of hemoglobin

Colligative Properties of Electrolytes

- Colligative properties are directly proportional to the concentration of solute particles. It doesn‘t matter what those particles are.
- At a given concentration, electrolytes have a greater effect on colligative properties than non-electrolytes.
- Dissolving 1 mole of a glucose, $C_6H_{12}O_6$ (non-electrolyte), results in 1 mole of solute particles.
- Dissolving 1 mole of NaCl (electrolyte) results in 2 moles of solute particles.

The van’t Hoff Factor (*i*)

- *The* **van’t Hoff factor, (*i*)**, is the ratio of solute particles in solution to the number of formula units dissolved.

- For NaCl, *i (predicted)* = 2
- For $C_6H_{12}O_6$, *i (predicted)* = 1

- What is the predicted *i* for $CaCl_2$?

- What is the predicted *i* for Na_3PO_4?

Table 11.3 Predicated and Measured van't Hoff Factors for Several 0.050 m Aqueous Solutions

Formula unit	**Classification**	**Dissolution products**	***i*, (predicted)**	***i*, (measured)**
$C_{12}H_{22}O_{11}$ (glucose)	Nonelectrolyte	$C_{12}H_{22}O_{11}$	1	1.0
NaCl	Strong electrolyte	Na^+, Cl^-	2	1.9
HCl	Strong electrolyte (acid)	H_3O^+, Cl^-	2	1.9
$MgSO_4$	Strong electrolyte	Mg^{2+}, $SO_4{}^{2-}$	2	1.3
$MgCl_2$	Strong electrolyte	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Strong electrolyte	Fe^{3+}, $3Cl^-$	4	3.4

- For strong electrolytes, the experimentally measured van't Hoff factors are lower than that predicted.

- This implies incomplete dissociation.

Why Incomplete Dissociation?

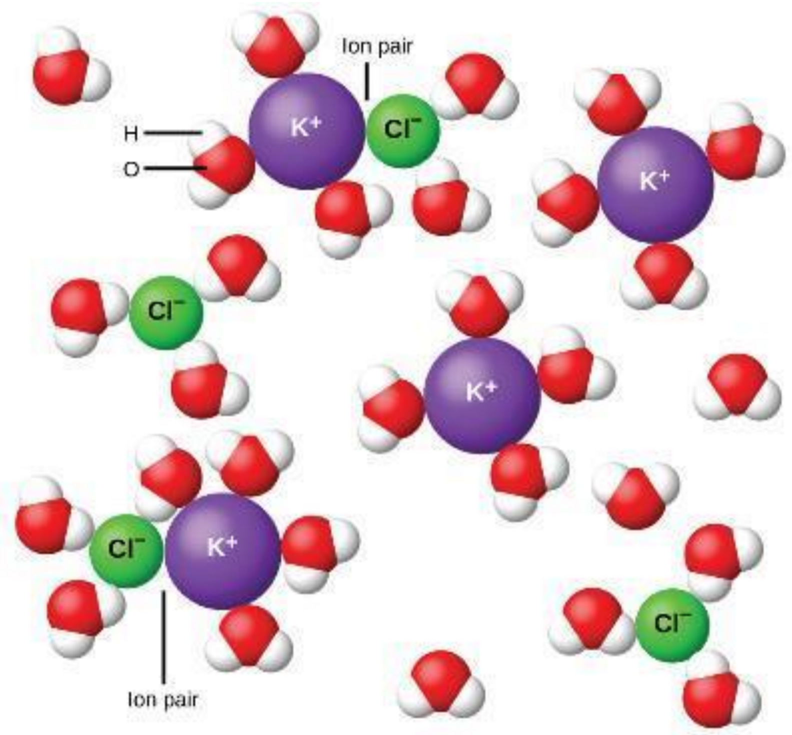
- Cation-anion attraction prevents some of the ions from behaving as completely independent particles.

- Some “ion pairs” are formed.

- The “effective concentration” known as **activity** is less than the predicted concentration of ions in solution.

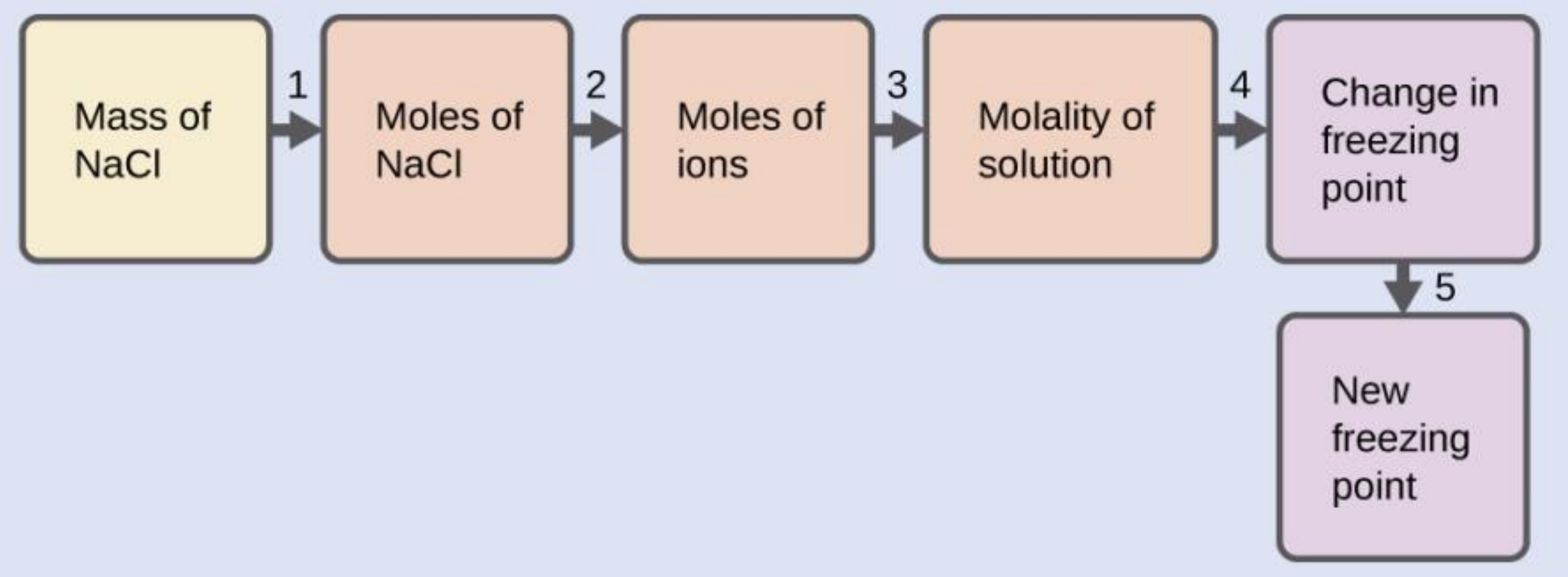
- This is less of an issue in dilute solutions.

Figure 11.28



Dissociation of ionic compounds in water is not always complete due to the formation of ion pairs.

Example 11.13



Mass of NaCl

1

Moles of NaCl

2

Moles of ions

3

Molality of solution

4

Change in freezing point

5

New freezing point

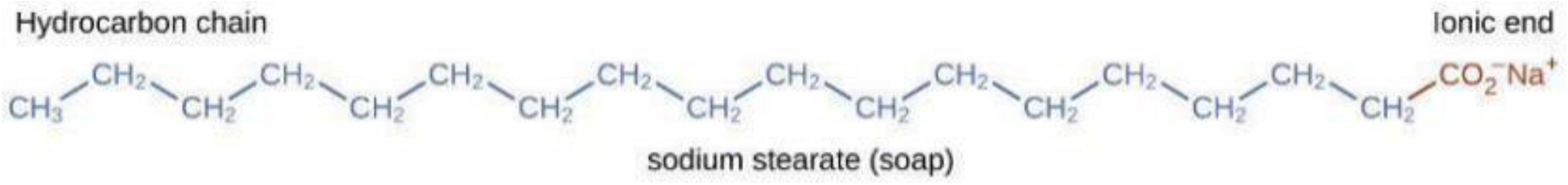
Adjusted Colligative Property Equations for Electrolyte Solutions

$$\Delta T_b = imk_b$$

$$\Delta T_f = imk_f$$

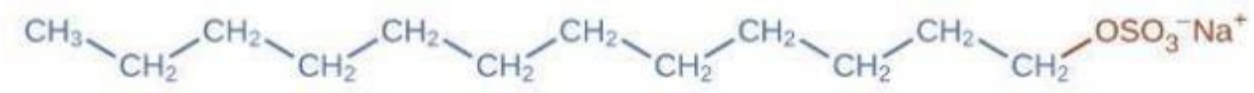
$$\pi = iMRT$$

Figure 11.31



Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

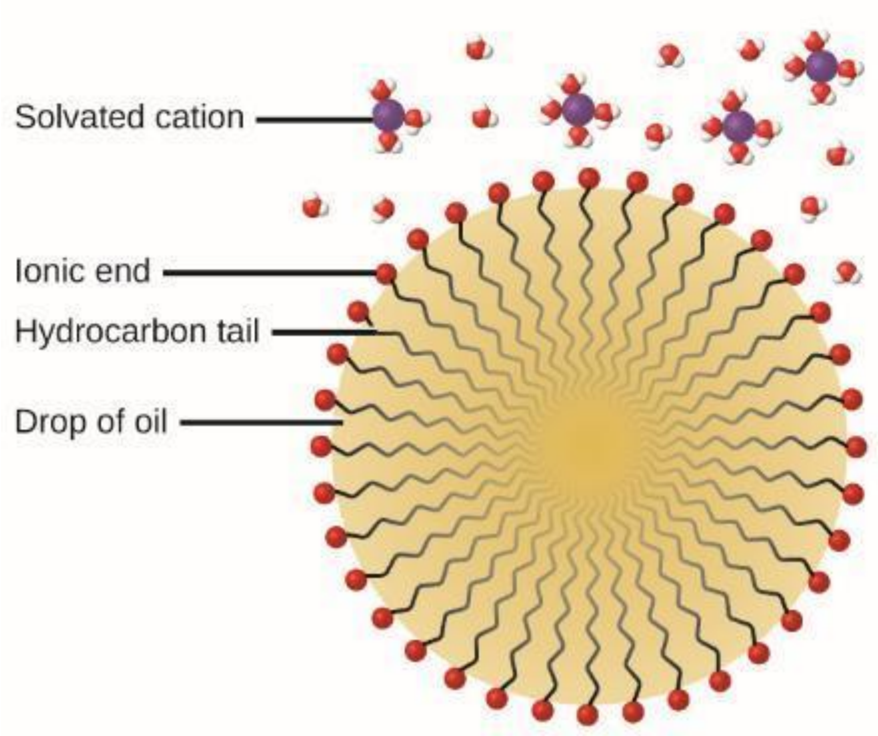
Figure 11.32



sodium lauryl sulfate (detergent)

Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

Figure 11.33



This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.