Chapter 11 Outline – Properties of Solutions

Solution Composition
- Because a mixture, unlike a chemical compound, has a variable composition, the relative amounts of substances in a solution must be specified.
- Some ways to calculate the composition of a solution are shown below. They include: molarity(M), molality(m), Mass percent (sometimes called weight percent), and mole fraction (symbolized by the Greek letter chi, X)

$$Molarity(M) = \frac{moles\ of\ solute}{liters\ of\ solution}$$

$$Mole\ fraction\ of\ component\ A = X_A = \frac{N_A}{N_A + N_B}$$

$$Molality(m) = \frac{moles\ of\ solute}{kilograms\ of\ solvent}$$

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

- **Example:** 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.
  - **Molarity:**
    - Moles C_2H_5OH = 1.00 g C_2H_5OH ÷ 46.07 g/mol C_2H_5OH = 2.17 x 10^{-2} mol C_2H_5OH
    - Volume = 101 mL ÷ 1000 ml/L = 0.101 L
    - Molarity = 2.17 x 10^{-2} mol ÷ 0.101
    - **Molarity = 0.215 M**
  - **Mass Percent:**
    - Mass Percent = (1.00 g C_2H_5OH) ÷ (100.0 g H_2O + 1.00 g C_2H_5OH) x 100%
    - Mass Percent = (1.00 g C_2H_5OH) ÷ (101.0 g solution) x 100%
    - **Mass Percent = 0.990% C_2H_5OH**
  - **Mole Fraction:**
    - Mole Fraction of C_2H_5OH = (moles C_2H_5OH) ÷ (moles C_2H_5OH + moles H_2O)
    - Moles H_2O = 100.0 g H_2O ÷ 18.0 grams/mol = 5.56 mol
    - Moles C_2H_5OH = 1.00 g C_2H_5OH ÷ 46.07 g/mol C_2H_5OH = 2.17 x 10^{-2} mol C_2H_5OH
    - Mole Fraction of C_2H_5OH = 2.17 x 10^{-2} ÷ (2.17 x 10^{-2} + 5.56)
    - Mole Fraction of C_2H_5OH = 2.17 x 10^{-2} ÷ 5.58
    - **Mole Fraction of C_2H_5OH = 0.00389**
  - **Molality:**
    - Molality of C_2H_5OH = (moles C_2H_5OH) ÷ (kilogram of H_2O)
    - Molality of C_2H_5OH = 2.17 x 10^{-2} mol ÷ 0.1000 kg
    - **Molality of C_2H_5OH = 0.217 m**
- **You try:** A solution is prepared by mixing 25.0 g ethanol (C_2H_5OH) with 100.0 g water to give a final volume of 120 mL. Calculate the molarity, mass percent, mole fraction and molality of ethanol in this solution.

- Another concentration measure sometimes encountered is normality (N). Normality is defined as the number of equivalents per liter of solution. For an acid-base reaction, the equivalent is the mass of the acid or base that can furnish or accept exactly 1 mole of protons (H^+). See the table below:

TABLE 11.2 The Molar Mass, Equivalent Mass, and Relationship of Molarity and Normality for Several Acids and Bases
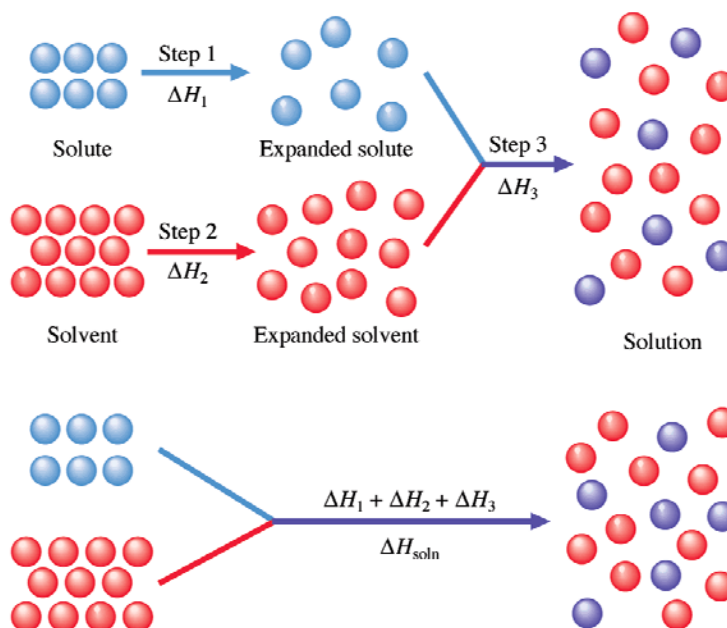
Acid or Base	Molar Mass	Equivalent Mass	Relationship of Molarity and Normality
HCl	36.5	36.5	$1\ M = 1\ N$
H_2SO_4	98	$\dfrac{98}{2} = 49$	$1\ M = 2\ N$
NaOH	40	40	$1\ M = 1\ N$
$Ca(OH)_2$	74	$\dfrac{74}{2} = 37$	$1\ M = 2\ N$

- For oxidation-reduction reactions, the equivalent is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons.
  - MnO_4^- reacting in solution absorbs five electrons to produce Mn^{2+}
  - $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
  - Equivalent mass of KMO_4 = molar mass ÷ 5
  - Equivalent mass of KMO_4 = 158 ÷ 5
  - **Equivalent mass of KMO_4 = 31.6 g**

The Energies of Solution Formation
- The cardinal rule of solubility is ***like dissolves like***.
- The formation of a liquid solution takes place in three distinct steps:
  - 1. Separation of the solute into its individual components (expanding the solute).
  - 2. Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent).
  - 3. Allowing the solute and solvent to interact to form the solution.

- Steps 1 & 2 require energy (endothermic) since forces must be overcome to expand the solute and solvent. Step 3 usually releases energy (exothermic).
- The enthalpy (heat) of solution (ΔH_{soln}) is the sum of the ΔH values for the steps: $\Delta H_1 + \Delta H_2 + \Delta H_3$

- Consider the immiscibility of oil and water. This example is applicable to any interaction between a polar and a non-polar substance.
  - Oil is a mixture of nonpolar molecules that interact through London dispersion forces.
  - ΔH_1 will be small for a typical nonpolar solute, but it will be relatively large for the large oil molecules.
  - ΔH_2 will be large and positive because it takes considerable energy to overcome the hydrogen bonding forces among the water molecules to expand the solvent.
  - ΔH_3 will be small since interactions between the nonpolar solute molecules and the polar water molecules will be negligible.
  - Since a large amount of energy would have to be expended to form an oil-water solution, this process does not occur to any appreciable extent.
- Consider the solubility of an ionic solute, such as sodium chloride in water.
  - ΔH_1 is large and positive because the strong ionic forces in the crystal must be overcome.
  - ΔH_2 is large and positive because hydrogen bonds must be broken in the water.
  - ΔH_3 is large and negative because of the strong interactions between the ions and the water molecules.
  - $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_1 = 786$ kJ/mol
  - $H_2O(l) + Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H_{hyd} = \Delta H_2 + \Delta H_3 = -783$ kJ/mol
  - The enthalpy (heat) of hydration ΔH_{hyd} combines the terms ΔH_2 (for expanding the solvent) and ΔH_3 (for solvent solute interactions)
  - $\Delta H_{soln} = 786$ kJ/mol $- 783$ kJ/mol $= 3$ kJ/mol
  - Since the value is small and positive; the dissolving process requires a small amount of energy.
  - Processes that require large amounts of energy tend not to occur. Since dissolving 1 mole of solid NaCl requires only a small amount of energy, the solution forms.
  - The possible cases for solution formation are shown below.

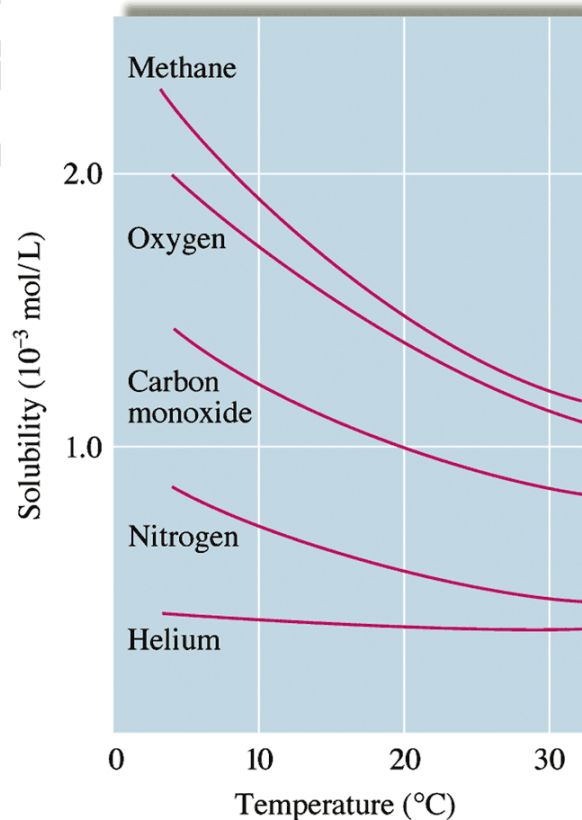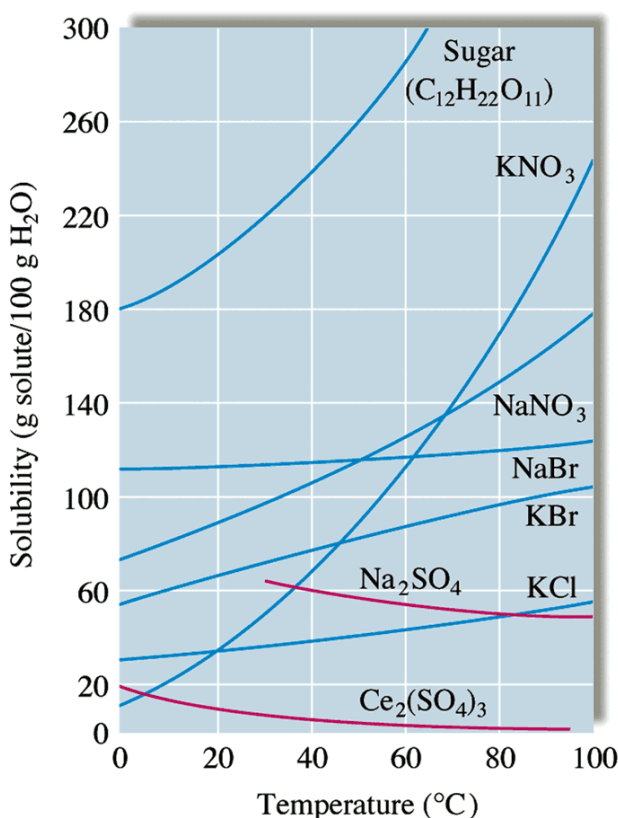**TABLE 11.3 The Energy Terms for Various Types of Solutes and Solvents**

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

Factors Affecting Solubility
- **Structure Effects:**
  - Since it is the molecular structure that determines polarity, there should be a definite connection between structure and solubility.
  - Consider vitamins, which can be divided into two classes: fat-soluble (vitamins A, D, E and K) and water- soluble (vitamins B and C).
  - Nonpolar materials such as vitamin A are called **hydrophobic (water-fearing)** and polar substances such as vitamin C are called **hydrophilic (water-loving).**
- **Pressure Effects:**
  - While pressure has little effect on the solubilities of solids or liquids, it does significantly increase the solubility of a gas.
  - Carbonated beverages are always bottled at high pressures of carbon dioxide to ensure a high concentration of carbon dioxide in the liquid. The fizzing that occurs when you open a can of soda results from the escape of gaseous carbon dioxide because under these conditions the pressure of CO_2 above the solution is now much lower than used in the bottling process.
  - The relationship between gas pressure and the concentration of dissolved gas is given by

Henry's law: $C = kP$; C = concentration of dissolved gas, k is a constant characteristic of a particular solution and P represents the partial pressure of the gaseous solute above the solution.
- o Henry's law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.
- o Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. Henry's law is obeyed by oxygen gas in water, but not by the gas hydrogen chloride (HCl) in water.
- **Temperature Effects (for Aqueous Solutions)**
  - o The **dissolving of a solid occurs more rapidly at higher temperatures**, but the amount of solid that can be dissolved may increase or decrease with increasing temperature.
  - o Although the solubility of most solids in water increases with temperature, the solubilities of some substances (such as sodium sulfate and cerium sulfate) decrease with increasing temperature.
  - o The **solubility of a gas in water typically decreases with increasing temperature**.
  - o This has important environmental implications because of the widespread use of water from lakes and rivers for industrial cooling. After being used, the water is returned to its natural source at a higher than ambient temperature (**thermal pollution** has occurred).
  - o Because it is warmer, this water contains less than the normal concentration of oxygen and is also less dense; it tends to float on the colder water below, thus blocking the normal oxygen absorption. This can be especially important in deep lakes. The warm upper layer can seriously decrease the amount of oxygen available to aquatic life in the deeper layers of the lake.

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The Vapor Pressure of Solutions
- Liquid solutions have physical properties significantly different from those of the pure solvent.
- Detailed studies of the vapor pressures of solutions containing nonvolatile solutes were carried out by Francois M Raoult (1830-1901). His results are described by the equation known **as Raoult's law:** $P_{soln} = X_{solvent}P^0_{solvent}$ where P_{soln} is the vapor pressure of the solution, $X_{solvent}$ is the mole fraction of the solvent, and $P^0_{solvent}$ is the vapor pressure of the pure solvent.
- Raoult's law states that vapor pressure of a solution is directly proportional to the mole fraction of solvent present.
- **Example: Calculate the Vapor Pressure of a Solution.** Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g of 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.

mass of H_2O = density x volume
mass of H_2O = 0.9971 g/cm^3 x 643.5 cm^3
mass of H_2O = 641.6 g

moles of H_2O = 641.6 g ÷ 18.0 g/mol = 35.64 moles
moles of sucrose = 158.0 g ÷ 342.3 g/mol = 0.4616 moles

mole fraction = 35.64 ÷ (35.64 + 0.4616)
mole fraction = 0.9872

$P_{soln} = X_{solvent}P^0_{solvent}$
P_{soln} = (0.9872)(23.76)
P_{soln} = 23.46 torr

- You try: A solution is prepared by mixing 50.0 g glucose ($C_6H_{12}O_6$) with 600.0 grams of water. What is the vapor pressure of this solution at 25°C? At 25°C the vapor pressure of pure water is 23.76 torr.

- When making vapor pressure calculations of solutions containing ionic compounds it is important to note the number of particles the ionic compound dissociates into when dissolved in solution.
- **Example: Calculate the Vapor Pressure of a Solution Containing Ionic Solute.** Predict the vapor pressure of a solution prepared by mixing 35.0 g solid Na_2SO_4 (molar mass = 142 g/mol) with 175 g water at 25°C. The vapor pressure of pure water is 23.76 torr at 25°C.

moles of H_2O = 175 g ÷ 18.0 g/mol = 9.72 moles
moles of sodium sulfate = 35.0 g ÷ 142 g/mol = 0.246 moles

When sodium sulfate dissociates it forms 2 Na^+ and 1 SO_4^{2-}. $Na_2SO_4 \rightarrow 2\ Na^+ + SO_4^{2-}$
Because of this the number of moles of sodium sulfate in solution should be multiplied by 3.

actual moles of solute in solution: 3 x 0.246 = 0.738

mole fraction = 9.72 ÷ (9.72 + 0.738)
mole fraction = 0.929

$P_{soln} = X_{solvent}P^0_{solvent}$
P_{soln} = (0.929)(23.76)
P_{soln} = 22.1 torr

- You try: Calculate the vapor pressure of a solution by mixing 55.0 grams of Na_3PO_4 with 225 g water at 25°C. The vapor pressure of pure water is 23.76 torr at 25°C.

- For liquid-liquid solutions where both components are volatile, a modified form of Raoult's law:
  - $P_{total} = P_A + P_B = X_A P^0_A + X_B P^0_B$ where P_{total} represents the total vapor pressure of a solution containing A and B, X_A and X_B are the mole fractions of A and B, P^0_A and P^0_B are the partial pressures resulting from molecules of A and of B in the vapor pressure above the solution.
- A liquid-liquid solution that obeys Raoult's law is called an ideal solution. Raoult's law is to solutions what the ideal gas law is to gases. As with gases, ideal behavior for solutions is never perfectly achieved but is sometimes closely approached.
- In solutions where the solute and solvent are very much alike, the solute simply acts to dilute the solvent. For example, when benzene and toluene mix, the enthalpy of solution is very close to zero because they are very similar in structure. This solution closely follows Raoult's law.
- If the solvent has a special affinity for the solute, such as if hydrogen bonding occurs, the tendency of the solvent molecules to escape will be lowered more than expected. The observed vapor pressure will be lower than the value predicted by Raoult's law; there will be a negative deviation from Raoult's law. When a solute and a solvent release large quantities of energy in the formation of a solution (**exothermic**, ΔH_{soln} is large and negative), we can assume that strong interactions exist between the solute and the solvent.
- When two solutions mix **endothermically**, it indicates that the solute-solvent interactions are weaker than the interactions among the molecules in the pure liquids. In this case the molecules in the solution have a higher tendency to escape than expected and positive deviations from Raoult's law are observed. For example, when ethanol(polar) and hexane(non-polar) are mixed the reaction is endothermic.
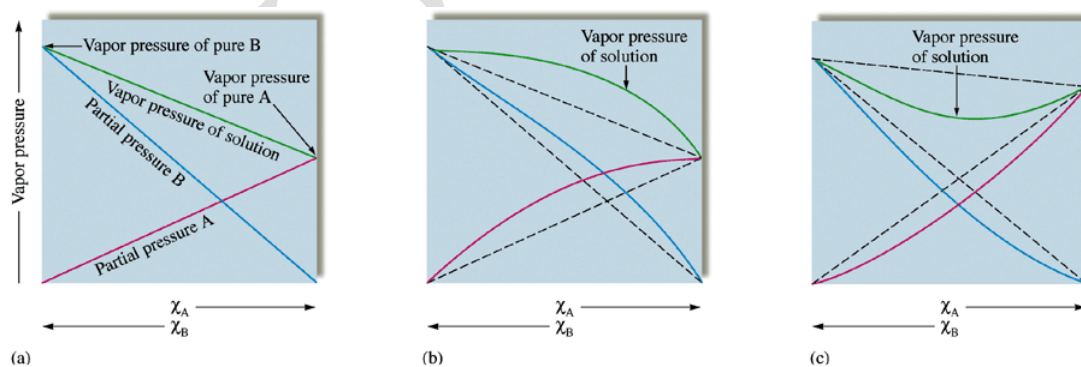
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TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Interactive Forces Between Solute (A) and Solvent (B) Particles	ΔH_{soln}	ΔT for Solution Formation	Deviation from Raoult's Law	Example
A ↔ A, B ↔ B ≡ A ↔ B	Zero	Zero	None (ideal solution)	Benzene–toluene
A ↔ A, B ↔ B < A ↔ B	Negative (exothermic)	Positive	Negative	Acetone–water
A ↔ A, B ↔ B > A ↔ B	Positive (endothermic)	Negative	Positive	Ethanol–hexane

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Boiling-Point Elevation and Freezing Point Depression

- Above you saw how a solute affects the vapor pressure of a liquid. Because changes of state depend on vapor pressure, the presence of a solute also affects the freezing point and boiling point of a solvent.
- Freezing point depression, boiling point elevation and osmotic pressure lowering are called colligative properties.
- The normal boiling point of a liquid occurs at the temperature where the vapor pressure is equal to 1 atmosphere. A **nonvolatile** solute lowers the vapor pressure of a solvent. Therefore it would require a solution to be heated to a higher temperature than the boiling point of the pure solvent to reach a vapor pressure of the atmosphere. Therefore a **nonvolatile** solute elevates the boiling point of the solvent.
- The change in boiling point can be represented by the equation: $\Delta T = K_b m_{solute}$ where ΔT is the boiling-point elevation, K_b is the molal boiling-point elevation constant and m_{solute} is the molality of the solution.

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.

- **Example. Calculate the Molar Mass by Boiling-Point Elevation.** A solution was prepared by dissolving 18.00 grams of glucose in 150.0 g H_2O. 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.

$\Delta T = K_b m_{solute}$
$\Delta T = 100.34°C − 100.00°C$
$\Delta T = 0.34°C$

K_b for H_2O: 0.51 °C * kg/mol

$\Delta T = K_b m_{solute}$
$0.34 = 0.51 \ x$
$x = 0.67 \ m$

$m = 0.67$ mol/kg
molality = moles solute ÷ kilogram solvent
moles solute = molality x kilogram solvent
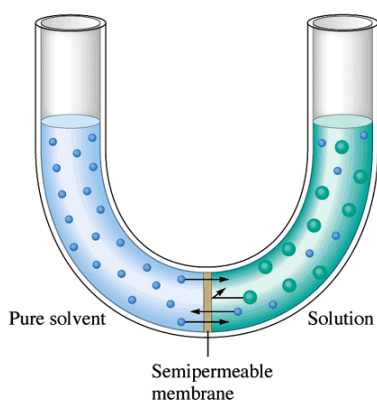moles solute = 0.67 m x 0.1500 kg
moles solute = 0.10 mol

molar mass = gram ÷ mol
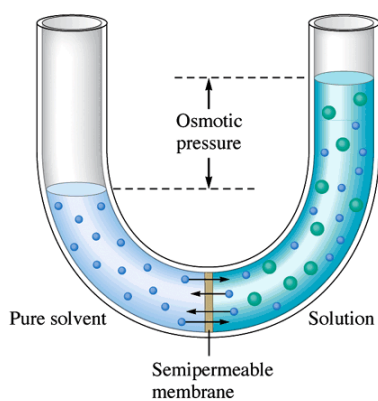molar mass = 18.00 ÷ 0.10
molar mass = 180 g/mol

- You try: It is a little different, but uses the same equation. Calculate what mass of glycerin($C_3H_8O_3$), a nonelectrolyte, must be dissolved in 200.0 grams of water to give a solution with a boiling-point of 101.5°C?

- When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent.
- If a substance is dissolved in water, it will not freeze at 0°C because the water has a lower vapor pressure than that of pure ice. Because a solute lowers the freezing point of water, compounds such as sodium chloride and calcium chloride are often spread on streets and sidewalks to prevent ice from forming in freezing weather. Of course if the outside temperature is lower than the freezing point of the resulting salt solution, ice forms anyway.
- The change in freezing point can be represented by the equation: $\Delta T = K_f m_{solute}$ where ΔT is the freezing-point depression, K_f is the molal freezing-point depression constant and m_{solute} is the molality of the solution.
- Since there is little difference between the boiling-point elevation and freezing-point depression equations, I am not going to do an example.
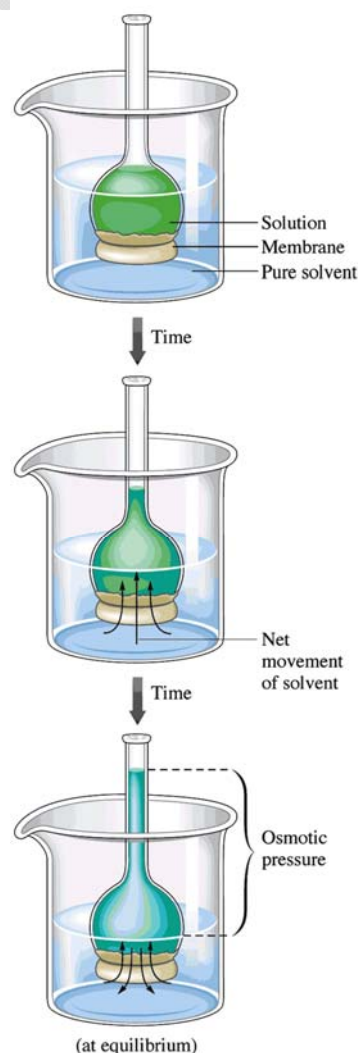
Osmotic Pressure
- Consider the diagram to the right. A solution and pure solvent are separated by a semipermeable membrane, which allows solvent but not solute molecules to pass through.
- The flow of solvent into the solution through a semipermeable membrane is called osmosis.
- Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. The excess pressure is called the osmotic pressure.
- The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution.
- As the solution levels rise in the tube, the resulting pressure exerts an extra "push" on the solvent molecules in the solution, forcing them back through the membrane. Eventually enough pressure develops so that the solvent transfer becomes equal in both directions.
- Osmotic pressure can be used to characterize solutions and determine molar masses, but osmotic pressure is particularly useful because a small concentration of solute produces a relatively large osmotic pressure
- $\Pi = MRT$, where Π is the osmotic pressure in atmospheres, M is the molarity of the solution, R is the gas law constant, and T is the Kelvin temperature.

Solution
Membrane
Pure solvent

Time

Net movement of solvent

Time

Osmotic pressure

(at equilibrium)

Osmotic pressure

Pure solvent   Solution
Semipermeable membrane
(a)

Pure solvent   Solution
Semipermeable membrane
(b)

- Example: Determining the Molar Mass From Osmotic Pressure. To determine the molar mass of a certain protein, 1.00 x 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°C. Calculate the molar mass of the protein.

  T = 25°C + 273 = 298 K
  Π = 1.12 torr ÷ 760 = 1.47 x 10^{-3} atm

  Π = MRT
  1.47 x 10^{-3} atm = M (0.08206 L*atm/mol K)(298 K)
  M = 6.01 x 10^{-5} mol/L

  Molarity = moles of solute / Liters of solution
  1.00 mL ÷ 1000 = 0.00100 liters
  moles of solute = Molarity x Liters of solution
  moles of solute = 6.01 x 10^{-5} x 0.00100
  moles of solute = 6.01 x 10^{-8} moles

  molar mass = grams / mole
  molar mass = 1.00 x 10^{-3} g / 6.01 x 10^{-8} mol
  molar mass = 1.66 x 10^{4} g/mol

- In osmosis, a semipermeable membrane prevents transfer of all solute particles. In dialysis, which occurs at the walls of most plant and animal cells, the membrane allows transfer of both solvent molecules and small solute molecules and ions.
- One of the most common uses of dialysis is the use of artificial kidney machines to purify the blood.
- Solutions that have identical osmotic pressures are said to be **isotonic** solutions. Fluids administered intravenously must be isotonic with body fluids.

Reverse Osmosis
- If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure, **reverse osmosis** occurs. The pressure will cause a net flow of solvent from solution to the solvent. In reverse osmosis, the semipermeable membrane acts as a "molecular filter" to remove solute particles.
- Reverse osmosis can be used to desalinate (remove dissolved salts) from seawater.

Colligative Properties of Electrolyte Solutions
- The relationship between the moles of solute dissolved and the moles of particles in solutions usually expressed using the **van't Hoff factor, i.**
- The expected value for i can be calculated for a salt by noting the number of ions per formula unit. For example, for NaCl, i is 2, for K_2SO_4, i is 3 and for $Fe_3(PO_4)_2$, i is 5. These calculated values assume that when a salt dissolves, it completely dissociates into its component ions, which then move around independently. This assumption is not always true. For example, the freezing point depression observed for 0.10 m NaCl is 1.87 times that for a 0.10 m glucose rather than twice as great (since i is 2). The best

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

explanation is that ion pairing occurs in solution. At any given instant a small percentage of the sodium and chloride ions are paired and thus count as a single particle.
- Ion pairing occurs to some extent in all electrolyte solutions.
- The colligative properties of electrolyte solutions are described by including the van't Hoff factor in the appropriate equation.

- The change in freezing point and boiling point can be calculated using the modified equation: $\Delta T = i m K$, where K represents the freezing-point depression or boiling-point elevation constant for the solution. For osmotic pressure of electrolyte solutions, the equation is: $\Pi = i MRT$
- You try: Calculate the freezing point and boiling point of a solution that contains 125 grams of $CaCl_2$ dissolved in 500 grams of water. Refer to the table on page 7 for the freezing-point depression and boiling-point elevation constants.

- Try another: Calculate the mass of $MgSO_4$ that needs to be added to 750.0 mL of solution to produce an osmotic pressure of 7.70 atm at 25°C. Assume the volume change is negligible.

Colloids
- Mud can be suspended in water by vigorous stirring. When stirring stops, most of the particles rapidly settle out, but even after several days some of the smallest particles remain suspended. Although undetected in normal lighting, their presence can be demonstrated by shining a beam of intense light though the suspension. The beam is visible from the side because the light is scattered by the suspended particles.
- In a true solution, on the other hand, the beam is invisible from the side because the individual ions and molecules dispersed in solution are too small to scatter visible light.
- The scattering of light by particles is called the Tyndall effect and is often used to distinguish between a suspension and a true solution.
- A suspension of tiny particles in some medium is called a **colloidal dispersion**, or a **colloid**.

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