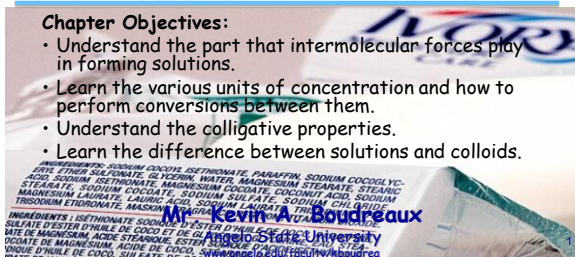


## 11 Properties of Solutions

### Chapter Objectives:

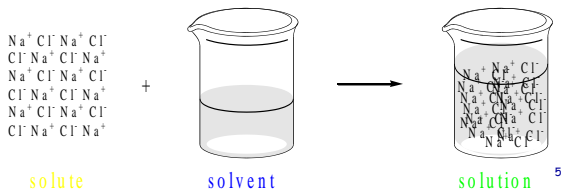
- Understand the part that intermolecular forces play in forming solutions.
- Learn the various units of concentration and how to perform conversions between them.
- Understand the colligative properties.
- Learn the difference between solutions and colloids.



## Solutions

### Solutes and Solvents

- A solution consists of a *solute* and a *solvent*:
  - solute** — the substance which is being dissolved.
  - solvent** — the substance (usually a liquid) that dissolves the solute (usually, the solvent is the most abundant component in the mixture).
- Aqueous solution** are solutions in which the solvent is water.



### Classification of Mixtures

- So far, we've dealt primarily with pure substances, but **mixtures** of substances are far more common.
  - Heterogeneous mixtures** are those in which the mixing is not uniform and which therefore have regions of different compositions — i.e., there are observable boundaries between the components (e.g., ice-water, salad dressing, milk, dust in air).
  - Homogeneous mixtures** are those in which the mixing *is* uniform and which therefore have a constant composition throughout; there are no observable boundaries because the substances are intermingled on the molecular level (e.g., salt water, sugar water, air).
- The composition of a mixture is *variable*, and it retains the properties of some of its components.

### Types of Homogeneous Mixtures

- Homogeneous mixtures can be classified according to the size of their constituent particles:
  - Solutions** contain particles with diameters in the range of 0.1 to 2 nm (the typical size of ions or small molecules). Solutions are transparent, and do not separate on standing. (ex.: salt water, sugar water, gasoline, air)
  - Colloids** contain particles with diameters in range of 2 to 500 nm. They are often opaque or murky, but also do not separate on standing. (ex.: milk, fog, soap in water)
  - Suspensions** are mixtures having even larger particles; these are not truly homogeneous, because the particles separate on standing and are visible with microscopes. (ex.: blood, aerosol sprays)

### Kinds of Solutions

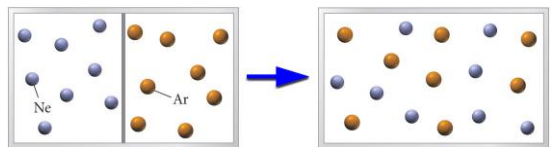
- Solutions are most commonly solids or liquids dissolved in another liquid, but other kinds of solutions are possible:
- Gaseous solutions:** All gases are infinitely soluble in one another (e.g., the atmosphere). Small amounts of nonpolar gases can dissolve in water due to dipole-induced dipole attractions.
  - At 25°C and 1 atm pressure, only 3.2 mL of O<sub>2</sub> dissolves per 100 mL of water, but this small solubility is essential to life in aquatic environments.
  - The solubility of oxygen and carbon dioxide in water is enhanced by some chemical processes.
- Solid solutions:** Gases, liquids, or other solids can be dispersed in solids. Waxes and metal **alloys** are types of solid-solid solutions.

## Kinds of Solutions

Solution Phase	Solute	Solvent	Examples
<b>Gaseous solution</b>	Gas	Gas	Air (O <sub>2</sub> , N <sub>2</sub> , Ar, CO <sub>2</sub> , H <sub>2</sub> O, and other gases), natural gas
<b>Liquid solutions</b>	Gas	Liquid	Carbonated water (CO <sub>2</sub> in water)
	Liquid	Liquid	Gasoline (mixture of hydrocarbons), vodka (ethanol and water)
	Solid	Liquid	Seawater (NaCl and other salts in water)
<b>Solid solutions</b>	Gas	Solid	H <sub>2</sub> in palladium metal
	Liquid	Solid	Dental amalgam (mercury in silver)
	Solid	Solid	Metal alloys such as sterling silver (Ag and Cu), brass (Cu and Zn) and bronze (Cu and Sn); waxes

## Entropy and the Formation of Solutions

- If two gases are separated by a barrier, the gases mix to form a solution when the barrier is removed.
  - Solutions of gases arise because of the natural tendency of a system to become more disordered over time. **Entropy** is a measure of the disorder or energy randomization in a system.
  - The pervasive tendency for all kinds of energy to spread out whenever it is not restrained from doing so is the reason that two ideal gases mix.



## Units of Concentration

### Units of Concentration

- The **concentration** of a solution is the amount of solute dissolved in a certain amount of solution (or solvent).
  - a **dilute solution** contains small quantities of solute relative to the amount of solvent.
  - a **concentrated solution** contains large quantities of solute relative to the amount of solvent.
- There are several common units which are used for expressing concentration:

### Molarity (M)

- Molarity (molar concentration), M (mol/L):**

$$\text{Molarity} = M = \frac{\text{moles of solute}}{\text{Liters of solution}} = \text{mol L}^{-1}$$

- A solution of desired molarity is made by dissolving the required number of moles of solute **to** the desired volume (remember it's moles per liter of **solution**, **NOT** per liter of **solvent**).
  - To prepare a 1.000 M solution of NaCl in water, you would dissolve 1.000 mol of NaCl in enough water to make 1 L of solution.
- Molarity is temperature-dependent, since volume and density are affected by the temperature.
- Solution volumes are not necessarily additive.

### Molality (m)

- Molal concentration, or molality, m (mol/kg):**

$$\text{Molality} = m = \frac{\text{moles of solute}}{\text{kilograms of solvent}} = \text{mol kg}^{-1}$$

- To prepare a 1.000 m solution of NaCl in water, you would dissolve 1.000 mol of NaCl in 1 kg of water.
- Since molality is temperature-independent, this unit is often used when describing the physical properties of a solution (especially colligative properties [more later!]).
- Molality is additive, unlike molarity.
- Molarity and molality are similar for dilute aqueous solutions.

*Mole Fraction (X) and Mole Percent*

- **Mole fraction, X:**

$$X = \frac{\text{moles of solute}}{\text{moles of solution}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\text{Mole percent (mol\%)} = X \times 100\%$$

- Mole fractions are independent of temperature, and are useful in dealing with gas concentrations.



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*Mass Percent (mass %)*

- **Mass percent, mass % (w/w):**

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

- **Parts per million, ppm:**

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

- **Parts per billion, ppb:**

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9$$

- temperature independent, but it's more difficult to measure liquids by mass.
- The density of a solution must be known to convert mass %, ppm, and ppb to molarity.

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*Volume Percent (vol %)*

- **Volume percent, % (v/v):**

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

- Volume percent is used most often for mixtures of liquids or mixtures of gases (e.g., rubbing alcohol is 70% isopropyl alcohol in water by volume).

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*Normality (N)*

- **Normality, N (mol/L)** is defined as the number of *equivalents* per liter of solution.

- For an acid-base reaction, an equivalent is the mass of acid or base that can furnish or accept one mole of protons ( $\text{H}^+$  ions).
  - Since HCl is monoprotic, molarity = normality.
  - Since  $\text{H}_2\text{SO}_4$  is diprotic, the equivalent mass of  $\text{H}_2\text{SO}_4$  is half the molar mass; a 1M solution would have a normality of 2N. (Similarly, for  $\text{Ca}(\text{OH})_2$ , a 1M solution would be 2 N.)
- For redox reactions, an equivalent is the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons.

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*Examples: Concentration Units*

1. What is the molarity of a solution prepared by dissolving 25.0 g of NaCl in enough water to make 250. mL of solution?

Answer: 1.71 M NaCl

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*Examples: Concentration Units*

2. Assume that you have a 5.75 mass % solution of LiCl in water. What mass of solution (in grams) contains 1.60 g of LiCl?

Answer: 27.8 g solution

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**Examples: Concentration Units**

3. Calculate the ppm of calcium in a 8.20 g pill that contains 5.5 mg Ca.

Answer: 671 ppm Ca

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**Examples: Concentration Units**

4. What is the molality of a solution made by dissolving 1.45 g of table sugar (sucrose,  $C_{12}H_{22}O_{11}$ , MM 342.3 g/mol) in 30.0 mL of water? The density of water is 1.00 g/mL.

Answer: 0.141 m sucrose

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**Examples: Concentration Units**

5. What is the mass % of glucose in a solution prepared by dissolving 10.0 g of glucose in 100.0 g of water?

Answer: 9.09% glucose

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**Examples: Concentration Units**

6. A sample of rubbing alcohol contains 142 g isopropanol ( $C_3H_7OH$ , MM 60.09 g/mol) and 58.0 g water. What are the mole fractions of alcohol and water?

Answer: 0.423  $C_3H_7OH$ , 0.577  $H_2O$

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**Examples: Concentration Units**

7. Hydrogen peroxide is a powerful oxidizing agent that is used in rocket fuels and hair bleach. An aqueous solution of  $H_2O_2$  is 30.0% by mass and has a density of 1.11 g/mL. Calculate its molality, mole fraction of  $H_2O_2$ , and molarity.

Answer: 12.6 m, X = 0.185, 9.79 M

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**Examples: Concentration Units**

8. A solution is prepared by dissolving 17.2 g of ethylene glycol ( $C_2H_6O_2$ ) in 0.500 kg of water. The final volume of the solution is 515 mL. For this solution, calculate the concentration of the solution in units of molarity, molality, percent by mass, mole fraction, and mole percent.

Answer: 0.538 M, 0.554 m, 3.33%, 0.00990, 0.990%

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### Examples: Concentration Units

9. Ethylene glycol,  $C_2H_4(OH)_2$  (MM 62.07 g/mol), is a colorless liquid used as automobile antifreeze. If the density at 20 °C of a 4.028 *m* solution of ethylene glycol in water is 1.0241 g/mL, what is the molarity of the solution?

Answer: 3.299 M

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### Examples: Concentration Units

10. A 0.750 *M* solution of  $H_2SO_4$  (MM 98.1 g/mol) in water has a density of 1.046 g/mL at 20 °C. What is the concentration of this solution in units of mole fraction, mass percent, and molality?

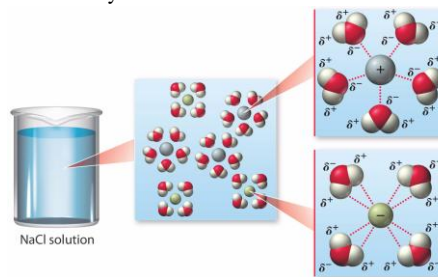
Answer: 0.0137, 7.04%, 0.772 *m*

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## The Energetics of Solution Formation

### An Ionic Compound Dissolving in Water

- In water, the ions in a sodium chloride crystal are solvated (hydrated) by the water molecules, with each cation and anion in solution surrounded and stabilized by an ordered shell of solvent molecules.

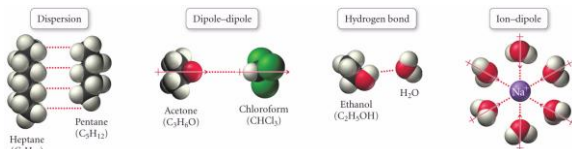


MOV: Dissolution of NaCl in Water

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### Intermolecular Forces in Solutions

- With mixtures of liquids, or mixtures of solids and liquids, we must also consider whether the relative strengths of the intermolecular forces between the solute and solvent particles *promote* the formation of a solution, or *prevent* it.
- Intermolecular Forces** (in order of decreasing strength):
  - ion-dipole forces** — solvent molecules cluster around ions in hydration shells, disrupting the bonding in the crystal lattice.



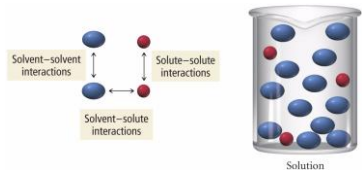
### Intermolecular Forces in Solutions

- Hydrogen bonds** — substances with O—H and N—H bonds are often soluble in water because of H-bonding (unless the molecules are large).
- dipole-dipole forces** — polar solutes interact well with polar solvents through attraction of partial charges.
- ion - induced dipole forces** — responsible for the attraction between  $Fe^{2+}$  and  $O_2$  molecules in the bloodstream.
- dipole - induced dipole forces** — responsible for the solvation of gases (nonpolar) in water (polar).
- London (dispersion) forces** — the principal attractive force in solutions of nonpolar substances (e.g., petroleum).

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## Solution Interactions

- There are three interactions that must be looked at:



### Relative Interactions and Solution Formation

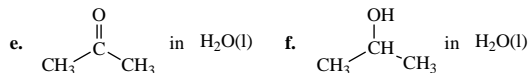
solvent-solute > solvent-solvent and solute-solute	solution forms
solvent-solute = solvent-solvent and solute-solute	solution forms
solvent-solute < solvent-solvent and solute-solute	solution may or may not form, depending on relative disparity

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## Examples: Intermolecular Forces

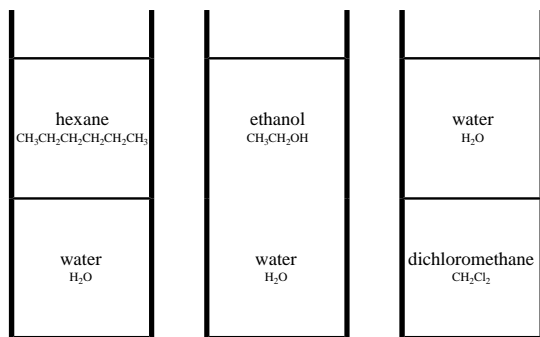
- What is the strongest type of intermolecular force between solute and solvent in each of the following solutions?

- $\text{CH}_3\text{CH}_2\text{CH}_3$  in  $\text{H}_2\text{O}(\text{l})$
- $\text{CsCl}(\text{s})$  in  $\text{H}_2\text{O}(\text{l})$
- $\text{CH}_3\text{CH}_2\text{CH}_3$  in  $\text{CCl}_4$
- $\text{Fe}^{2+}$  and  $\text{O}_2$



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## A Solubility Demonstration



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## The General Solubility Rule

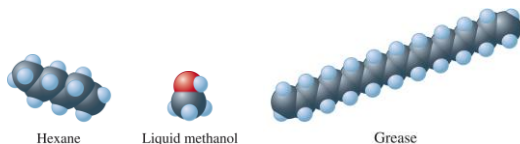
- Water, a polar molecule, dissolves ethanol, which is also polar, but does not dissolve hexane and dichloromethane, which are both nonpolar.
  - Ethanol and water are **miscible** — completely soluble in each other in all proportions.
  - Hexane and water are **immiscible** — they do not mix with each other at all.
  - Hexane and dichloromethane are miscible with each other.
- The general rule in solubility is that

“like dissolves like”

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## Examples: Solubility

- Decide whether liquid hexane ( $\text{C}_6\text{H}_{14}$ ) or liquid methanol ( $\text{CH}_3\text{OH}$ ) is the more appropriate solvent for the substances grease ( $\text{C}_{20}\text{H}_{42}$ ) and potassium iodide (KI).



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## Energetics of Solution Formation

- When a solution forms, the energy change may be exothermic or endothermic, depending on the relative magnitudes of three energy changes:
  - Separating the solute into its constituent particles* ( $\Delta H_{\text{solute}}$ ): energy is required ( $\Delta H > 0$ ) to separate the solute particles from each other; substances with high lattice energies tend to be less soluble.
  - Separating the solvent particles from each other to make room for the solute particles* ( $\Delta H_{\text{solvent}}$ ): energy is required ( $\Delta H > 0$ ) to separate solvent molecules.
  - Mixing the solute particles with the solvent particles* ( $\Delta H_{\text{mix}}$ ): energy is released ( $\Delta H < 0$ ) when solvent molecules cluster around solute particles and solvate them.

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### Energetics of Solution Formation

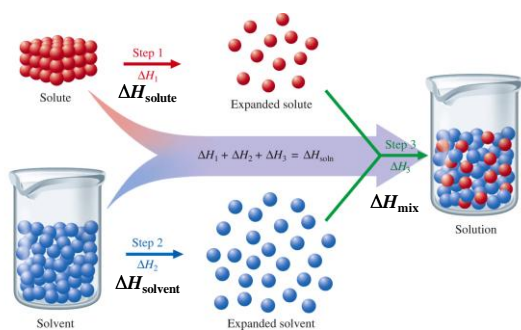


Figure 11.1

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### Energetics of Solution Formation

- The overall enthalpy change for the formation of a solution, called the **enthalpy of solution**,  $\Delta H_{\text{soln}}$  (or *heat of solution*), is the sum of these quantities:

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

- These values may be exothermic or endothermic, depending on the substance involved:

–  $\text{CaCl}_2(\text{s}) \Delta H_{\text{soln}} = -81.3 \text{ kJ/mol}$

–  $\text{NH}_4\text{NO}_3(\text{s}) \Delta H_{\text{soln}} = +25.7 \text{ kJ/mol}$

	$\Delta H_{\text{solute}}$	$\Delta H_{\text{solvent}}$	$\Delta H_{\text{mix}}$	$\Delta H_{\text{soln}}$	Outcome
polar solute, polar solvent	large	large	large, negative	small	solution forms
nonpolar solute, polar solvent	small	large	small	large, positive	no solution forms
nonpolar solute, nonpolar solvent	small	small	small	small	solution forms
polar solute, nonpolar solvent	large	small	small	large, positive	no solution forms

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### Energetics of Solution Formation

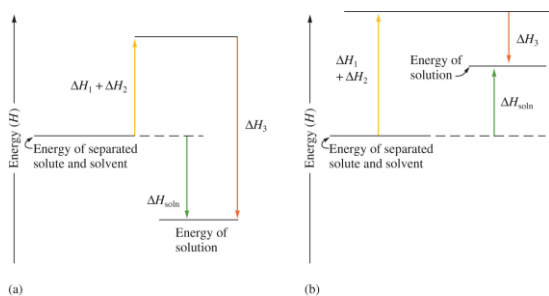


Figure 11.2

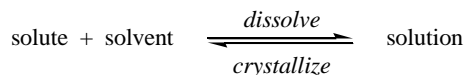
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## Some Factors Affecting Solubility

### Solubility and Equilibria

- The **solubility** of a solute is the maximum amount that dissolves in a fixed quantity of a particular solvent at a specified temperature.
  - NaCl: 39.12 g / 100 mL water at 100°C
  - AgCl: 0.0021 g / 100 mL water at 100°C
- Once this maximum has been reached, no more of the solute will dissolve in the solution. A **dynamic equilibrium** has been reached, where the number of ions leaving the crystalline solute to go into the solution equals the number of dissolved ions coming back out of the solution and rejoining the crystal. At this point, the solution is **saturated** in that solute:



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## Solubility and Equilibria

**NaCl(s)**

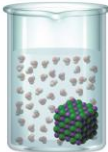
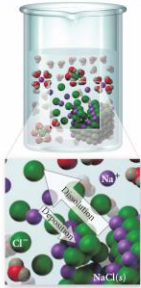
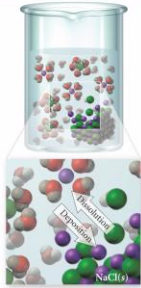
When sodium chloride is first added to water, sodium and chloride ions begin to dissolve into the water.

$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

As the solution becomes more concentrated, some of the sodium and chloride ions can begin to reprecipitate as solid sodium chloride.

$\text{NaCl(s)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

When the rate of dissolution equals the rate of deposition, dynamic equilibrium has been reached.

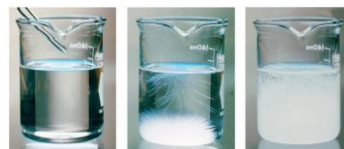




(a) Initial
(b) Dissolving
(c) Dynamic equilibrium

## Saturated and Unsaturated Solutions

- A **saturated solution** contains the maximum amount of dissolved solute, and cannot (usually) dissolve any more of the solute.
- An **unsaturated solution** contains less than the maximum amount of dissolved solute.
- A **supersaturated solution** contains a greater-than-normal amount of a solute; these solutions are unstable, and a slight disturbance causes the “extra” solute to precipitate out.

Sodium acetate is much more soluble in hot water (170.1 g/100 mL at 100°C) than cold water (46.4 g/100 mL at 20°C). If a saturated solution prepared in hot water is cooled slowly, the sodium acetate remains in solution, forming a supersaturated solution. Adding a tiny seed crystal causes the “extra” sodium acetate to precipitate out.



## Effect of Structure on Solubility

- The structure of a molecule affects its polarity, and therefore its solubility in various solvents.
  - Vitamins can be divided into *fat-soluble* (A, D, E, K) and *water-soluble* (B, C)

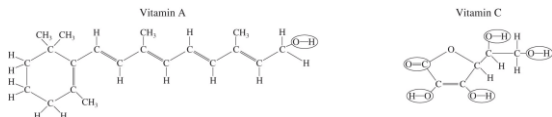


Figure 11.4

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## Effect of Pressure on Solubility

- Pressure has little effect on the solubility of solids and liquids, but has a large effect on gases.
  - At a given pressure, there is an equilibrium between the gas which is dissolved in the solution and the gas in the vapor phase.
  - If the pressure increases, more gas dissolves to reduce the “extra” pressure; the new equilibrium is established with more gas dissolved.

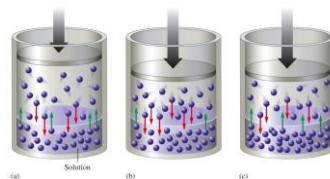


Figure 11.5

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## Effect of Pressure on Solubility

- Henry's law** states that the solubility of a gas ( $S_{\text{gas}}$ , in mol/L) is directly proportional to the partial pressure of the gas ( $P_{\text{gas}}$ , in atm) over the solution. (The *Henry's law constant*,  $k_{\text{H}}$  is a proportionality constant, unique to each gas, at a given temperature, with units of  $\text{mol L}^{-1} \text{atm}^{-1}$ .)

$$S_{\text{gas}} = k_{\text{H}} P_{\text{gas}}$$

- This expression can be rearranged to deal with changing solubility and pressure:

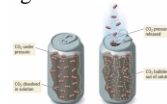
$$\frac{S_1}{P_1} = \frac{S_2}{P_2}$$

Henry's Law Constants at 25°C	
Gas	$k_{\text{H}}$ (M atm <sup>-1</sup> )
O <sub>2</sub>	$1.3 \times 10^{-3}$
N <sub>2</sub>	$6.1 \times 10^{-4}$
CO <sub>2</sub>	$3.4 \times 10^{-2}$
NH <sub>3</sub>	$5.8 \times 10^1$
He	$3.7 \times 10^{-4}$

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## Effect of Pressure on Solubility

- When a can of soda (4 atm) is opened, and exposed to the atmosphere (1 atm), the solubility of the CO<sub>2</sub> decreases, causing bubbles of CO<sub>2</sub> to emerge.



- If a deep sea diver comes up to the surface too quickly, N<sub>2</sub> which has dissolved in his bloodstream at higher pressures comes back out of solution.
  - The N<sub>2</sub> forms bubbles which block capillaries and inhibit blood flow, resulting in a painful, and potentially lethal, condition called the “bends.”
  - Less soluble gases, such as He, are often used in the breathing mixtures to reduce this problem.

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### Examples: Henry's Law

1. A certain soft drink is bottled so that a bottle at 25°C contains CO<sub>2</sub> gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO<sub>2</sub> in the atmosphere is 4.0×10<sup>-4</sup> atm, calculate the equilibrium concentrations of CO<sub>2</sub> in the soda before and after the bottle is opened. The Henry's Law constant for CO<sub>2</sub> is 3.1×10<sup>-2</sup> mol L<sup>-1</sup> atm<sup>-1</sup>.

**Answer: 0.16 M, 1.2×10<sup>-5</sup> M**

### Effect of Temperature on Solubility

- Solubilities are temperature-dependent.
- The solubility of most molecular and ionic solids increases with temperature, although some are almost unchanged, and some decrease.
  - For a solute with  $\Delta H_{\text{soln}} > 0$ :
    - solute + solvent + heat  $\rightleftharpoons$  saturated solution
    - solubility *increases* with temperature.
  - For a solute with  $\Delta H_{\text{soln}} < 0$ :
    - solute + solvent  $\rightleftharpoons$  saturated solution + heat
    - solubility *decreases* with temperature.

### Effect of Temperature on Solubility

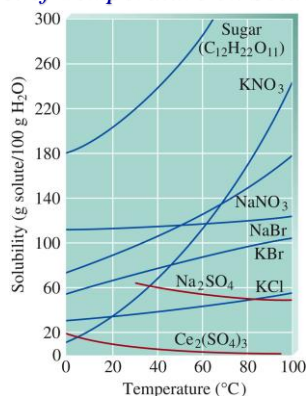


Figure 11.6

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### Effect of Temperature on Solubility

- Gases become less soluble at higher temperatures.
  - Soft drinks become “flat” as they warm up and lose carbon dioxide.
  - Aquatic life is affected by decreasing amounts of dissolved oxygen as a result of thermal pollution.

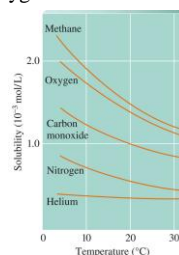


Figure 11.7

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### Molecular Weight and Solubility

- Solubility in water usually decreases as molecular weight increases, since with larger molecular weight, molecules usually become more nonpolar.

Alcohol	Space-Filling Model	Solubility in H <sub>2</sub> O (mol alcohol/100 g H <sub>2</sub> O)	Solubility in Hexane (C <sub>6</sub> H <sub>14</sub> ) (mol alcohol/100 g C <sub>6</sub> H <sub>14</sub> )
Methanol (CH <sub>3</sub> OH)		Miscible	0.12
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Propanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Butanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.11	Miscible
Pentanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.090	Miscible

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### Common Solvents

Common Laboratory Solvents	
Common Polar Solvents	Common Nonpolar Solvents
Water (H <sub>2</sub> O)	Hexane (C <sub>6</sub> H <sub>14</sub> )
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	Diethyl ether (CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> )
Methanol (CH <sub>3</sub> OH)	Toluene (C <sub>7</sub> H <sub>8</sub> )
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	Carbon tetrachloride (CCl <sub>4</sub> )
Acetonitrile (CH <sub>3</sub> CN)	Dichloromethane (CH <sub>2</sub> Cl <sub>2</sub> )

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## Colligative Properties

### Colligative Properties of Solutions

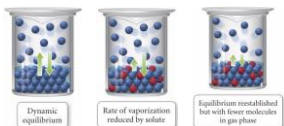
- **Colligative properties** are properties which depend on the *number* of solute particles in the solution, *not* on their chemical identities. These include:
  - vapor pressure lowering
  - boiling point elevation
  - freezing point depression
  - osmosis
- Colligative properties have many practical applications: you are familiar with them, whether you know it or not.

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### Vapor Pressure Lowering — Nonvolatile Solute

- The **vapor pressure** of a liquid is the pressure of the gas above the liquid when the two are in dynamic equilibrium.
- **Vapor Pressure Lowering ( $\Delta P$ )** — when a nonvolatile solute is dissolved in a solvent, the vapor pressure of the resulting solution is always *lower* than that of the pure solvent.
  - The particles of a nonvolatile solute interfere with the ability of solvent particles to vaporize, because they occupy some of the surface area formerly taken up by the solvent. This reduces the rate of evaporation, causing the equilibrium to be reestablished with fewer molecules of solvent in the gas phase.



sim. to Figure 11.10

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### Vapor Pressure Lowering — Nonvolatile Solute

- The vapor pressure of the solution ( $P_{\text{solution}}$ ) is expressed by **Raoult's Law**:
 
$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}$$
- The **vapor pressure lowering** of a solution,  $\Delta P$ , is:
 
$$\Delta P = P_{\text{solvent}} - P_{\text{solution}}$$

$$\Delta P = i X_{\text{solute}} P_{\text{solvent}}$$
 where  $X$  is the mole fraction of the component of interest,  $P_{\text{solvent}}$  is the vapor pressure of the pure solvent, and  $i$  is the *van't Hoff factor* (next slide).
- An **ideal solution** is one that follows Raoult's Law at any concentration; in practice, this law gives good results for dilute solutions.

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### Vapor Pressure Lowering — Nonvolatile Solute

- Since this effect depends on the *total number of solute particles* in the solution, the number of particles that ionic substances dissociate into must be taken into account, through a term called the **van't Hoff factor ( $i$ )**:

$$\text{van't Hoff factor } i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

- **For nonvolatile molecular solutes,  $i = 1$**

• e.g., glycerol, sucrose, etc.

- **For ionic compounds,  $i$  is the number of ions in the compound:**

- NaCl  $i = 2$        $\text{Na}_2\text{SO}_4$   $i = 3$
- $\text{CaCl}_2$   $i = 3$        $\text{Na}_3\text{PO}_4$   $i = 4$

Electrolyte	$i$ (expected)	$i$ (observed)
NaCl	2.0	1.9
MgCl <sub>2</sub>	3.0	2.7
MgSO <sub>4</sub>	2.0	1.5
FeCl <sub>3</sub>	4.0	3.4
HCl	2.0	1.8
Glucose*	1.0	1.0

\*A nonelectrolyte shown for comparison.

### Vapor Pressure Lowering — Volatile Solute

- When we have a mixture of two volatile liquids, A and B, both of which evaporate and contribute to the vapor pressure of the solution, we must combine Raoult's Law with Dalton's Law of partial pressures:

$$P_A = X_A P_A^*$$

$$P_B = X_B P_B^*$$

$$P_{\text{total}} = P_A + P_B = X_A P_A^* + X_B P_B^*$$

where  $P_A^*$  and  $P_B^*$  are the vapor pressures of the pure liquids, and  $X_A$  and  $X_B$  are the mole fractions of those liquids.

- The vapor pressure of the mixture is intermediate between the vapor pressures of the pure liquids.

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### Deviations from Raoult's Law

- An **ideal solution** is a liquid-liquid solution that obeys Raoult's law. Nearly ideal behavior is observed when all of the interactions are similar (i.e., when solute and solvent are very similar).
- When a solute and solvent mix exothermically, there are strong interactions between the solute and the solvent (if for instance the solute and solvent hydrogen-bond to each other). In these cases, there are **negative deviations** from Raoult's law because both solute and solvent have a lower tendency to escape the solution (e.g. acetone + water).
- When a solute and solvent mix endothermically, the solute-solvent interactions are weak. In these cases, there are **positive deviations** from Raoult's law because the molecules have a higher tendency to escape the solution (e.g., ethanol + hexane).

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### Deviations from Raoult's Law

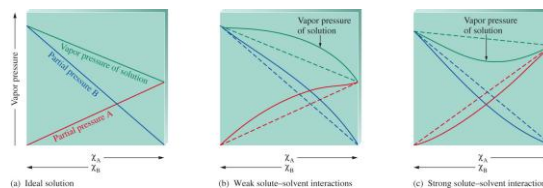


TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Interactive Forces Between Solute (A) and Solvent (B) Particles	$\Delta H_{\text{mix}}$	$\Delta T$ for Solution Formation	Deviation from Raoult's Law	Example
$A \leftrightarrow A, B \leftrightarrow B = A \leftrightarrow B$	Zero	Zero	None (ideal solution)	Benzene-toluene
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative (exothermic)	Positive	Negative	Acetone-water
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive (endothermic)	Negative	Positive	Ethanol-hexane

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### Examples: Vapor Pressure Lowering

- Calculate the vapor pressure lowering,  $\Delta P$ , when 10.0 mL of glycerol,  $C_3H_8O_3$ , is added to 500.0 mL of water at  $50.^\circ\text{C}$ . At this temperature, the vapor pressure of water is 92.5 torr and its density is 0.988 g/mL. The density of glycerol is 1.26 g/mL.

Answer: 0.461 torr

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### Examples: Vapor Pressure Lowering

- What is the vapor pressure of a solution made by mixing 35.0 g of solid  $Na_2SO_4$  (MM 142.05 g/mol) with 175 g of water at  $25^\circ\text{C}$ . (The vapor pressure of pure water at  $25^\circ\text{C}$  is 23.76 torr).

Answer: 22.00 torr

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### Examples: Vapor Pressure Lowering

- Calculate the vapor pressure of each component in a solution consisting of equal numbers of moles of benzene ( $P_{\text{ben}}^\circ$  95.1 torr) and toluene ( $P_{\text{tol}}^\circ$  28.4 torr). [Both are volatile liquids.] What is the mole fraction of each component in the vapor?

Answer:  $X_{\text{ben}} = 0.770$ ,  $X_{\text{tol}} = 0.230$ 

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### Examples: Vapor Pressure Lowering

- A solution contains 3.95 g of carbon disulfide ( $CS_2$ ), and 2.43 g of acetone ( $C_3H_6O$ ). The vapor pressures at  $35^\circ\text{C}$  of pure carbon disulfide and pure acetone are 515 torr and 332 torr, respectively. Assuming ideal behavior, calculate the vapor pressures of each of the components and the total vapor pressure above the solution.

Answer: 433 torr

66

### Boiling Point Elevation

- Since a nonvolatile solute lowers the vapor pressure of the solution, a higher temperature is needed to raise the solution's vapor pressure to make it equal to the external pressure. Thus, a nonvolatile solute **elevates the boiling point** of a solvent:

$$\Delta T_b = K_b \cdot m \cdot i$$

$$T_b(\text{solution}) = T_b(\text{pure solvent}) + \Delta T_b$$

where  $\Delta T_b$  is the change in boiling point,  $m$  is the molality of the solution,  $K_b$  is the *molal boiling point elevation constant* ( $^{\circ}\text{C}/m$ ), and  $i$  is the number of ions an ionic solute dissociates into.

- The effect is usually small: 1.00 mol of glucose or 0.500 mol NaCl would raise the boiling point of 1.00 kg of water to 100.512 $^{\circ}\text{C}$ .

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### Molal Boiling-Point Elevation and Freezing-Point Depression Constants

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

Solvent	Boiling Point ( $^{\circ}\text{C}$ )	$K_b$ ( $^{\circ}\text{C} \cdot \text{kg}/\text{mol}$ )	Freezing Point ( $^{\circ}\text{C}$ )	$K_f$ ( $^{\circ}\text{C} \cdot \text{kg}/\text{mol}$ )
Water ( $\text{H}_2\text{O}$ )	100.0	0.51	0	1.86
Carbon tetrachloride ( $\text{CCl}_4$ )	76.5	5.03	-22.99	30.
Chloroform ( $\text{CHCl}_3$ )	61.2	3.63	-63.5	4.70
Benzene ( $\text{C}_6\text{H}_6$ )	80.1	2.53	-5.5	5.12
Carbon disulfide ( $\text{CS}_2$ )	46.2	2.34	-111.5	3.83
Ethyl ether ( $\text{C}_2\text{H}_5\text{O}$ )	34.5	2.02	-116.2	1.79
Camphor ( $\text{C}_{10}\text{H}_8\text{O}$ )	208.0	5.95	179.8	40.

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### Freezing Point Depression

- Since a nonvolatile solute lowers the vapor pressure of the solution, a lower temperature is needed to freeze the solution. Thus, a nonvolatile solute **lowers (depresses) the freezing point** of a solvent:

$$\Delta T_f = K_f \cdot m \cdot i$$

$$T_f(\text{solution}) = T_f(\text{pure solvent}) - \Delta T_f$$

where  $\Delta T_f$  is the change in freezing point,  $m$  is the molality of the solution, and  $K_f$  is the *molal freezing point depression constant* ( $^{\circ}\text{C}/m$ ).

- The effect is small but important: 1.00 mol of glucose or 0.500 mol NaCl would lower the freezing point of 1.00 kg of water to -1.86 $^{\circ}\text{C}$ .

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### Phase Diagram for a Pure Solvent and a Solution

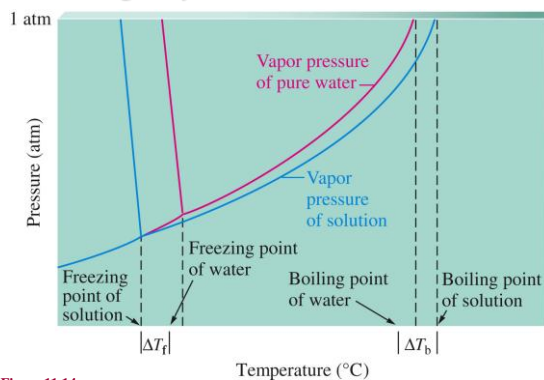


Figure 11.14

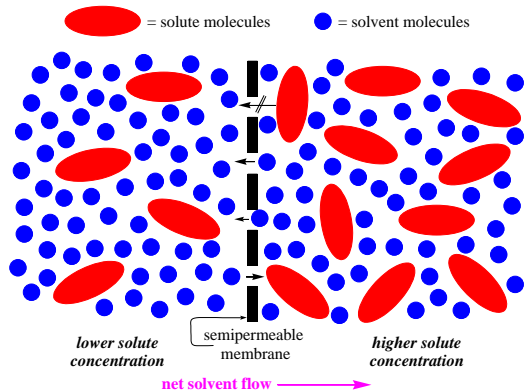
70

### Osmosis and Osmotic Pressure

- Semipermeable membranes**, such as those which enclose living cells, are those which allow water and small molecules to pass through, but not large solute molecules or ions.
- When a solution and a pure solvent (or two solutions of different concentration) are separated by a semipermeable membrane, solvent molecules can pass through in a process called **osmosis**.
  - Although solvent flow occurs in both directions, in osmosis the net solvent flow is from the *less concentrated* solution into the *more concentrated* solution.

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### Osmosis and Osmotic Pressure



72

### Osmosis and Osmotic Pressure

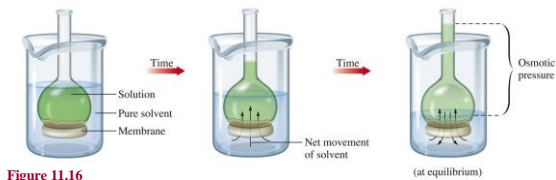


Figure 11.16

MOV:  
Osmosis  
and  
Osmotic  
Pressure

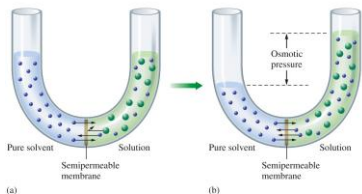


Figure 11.18

### Osmosis and Osmotic Pressure

- **Osmotic pressure** ( $\Pi$ ) — the pressure that must be applied in order to *prevent* osmotic flow through a membrane.

$$\Pi = i \frac{n_{\text{solute}}}{V_{\text{soln}}} RT = iMRT$$

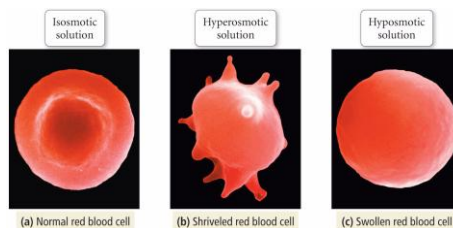
- **Reverse osmosis (RO)** occurs when a pressure greater than the osmotic pressure is applied to a solution, causing the solvent to flow into a region of lesser (or zero) concentration; this is commonly used in water purification and desalination plants.
- **Dialysis** occurs when a semipermeable membrane allows solvent molecules and small solute particles (such as  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) through. The kidneys regulate the volume of water in the body by changing the concentration of  $\text{Na}^+$ .

### Osmosis and Cells

- Cells are essentially solutions surrounded by a semipermeable membrane (the cell wall). (Figure)
- If a cell is placed in a solution, one of three things can happen:

Concentration of Solution	Cell Behavior
At cell concentration (an <b>isotonic</b> or <b>isosmotic</b> solution)	Cell maintains normal shape.
Lower than cell concentration (a <b>hypotonic</b> or <b>hyposmotic</b> solution)	Cell absorbs more water, and bursts.
Higher than cell concentration (a <b>hypertonic</b> or <b>hyperosmotic</b> solution)	Cell shrivels and dies.

### Osmosis and Cells



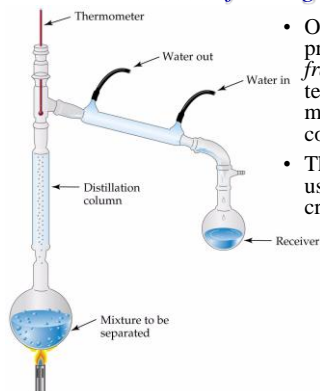
### Some Uses of Colligative Properties

- Ethylene glycol is used in antifreeze and airplane de-icers to lower the freezing point of water.
- Salt and calcium chloride are used to de-ice roads; salt is also used in making homemade ice cream.
- A cucumber shrivels into a pickle in salt water, because the water leaves the cucumber by osmosis.
- Osmosis is also responsible in part for the rise of sap in tall trees and water in flowers.
- The high salt concentration of sea water would literally dehydrate the body if you try to drink it.
- Freezing-point depression and osmotic pressure can be used to determine the molar masses of molecules that are difficult to determine by other means.

### Some Uses of Colligative Properties

- For centuries, salt, sugar, and other spices were often (and, in fact, still are) used as preservatives.
  - Adding salt to foods kills bacterial cells by dehydrating them, allowing the food to last longer before spoiling. (This was particularly important in the days before refrigeration.)
  - The same principle is exploited in canning and other forms of preserves.
  - This was also important on long ocean voyages, to preserve vitamin C-containing fruits and vegetables.
  - Roman soldiers used to be paid in salt (*L. sal*), from which we get the word “salary.”

## Some Uses of Colligative Properties



- One application of vapor-pressure lowering is *fractional distillation*, a technique for separating a mixture of liquids into its components.
- This technique is also used in the refining of crude oil into gasoline.

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## Examples: Colligative Properties

5. You add 1.00 kg of the antifreeze ethylene glycol ( $C_2H_6O_2$ ) to your car radiator, which contains 4450 g of water. What are the boiling and freezing points of the solution? For water,  $K_f = 1.86 \text{ }^\circ\text{C/m}$ ,  $K_b = 0.512 \text{ }^\circ\text{C/m}$ ,  $T_f = 0.00 \text{ }^\circ\text{C}$ , and  $T_b = 100.00 \text{ }^\circ\text{C}$ .

Answer: BP = 101.85°C, FP = -6.73°C

80

## Examples: Colligative Properties

6. What is the freezing point and boiling point of a solution prepared by dissolving 7.40 g of  $MgCl_2$  in 110. g of water? Assume complete dissociation of the  $MgCl_2$ . For water,  $K_f = 1.86 \text{ }^\circ\text{C/m}$ ,  $K_b = 0.512 \text{ }^\circ\text{C/m}$ ,  $T_f = 0.00 \text{ }^\circ\text{C}$ , and  $T_b = 100.00 \text{ }^\circ\text{C}$ .

Answer: -3.94°C, 101.08°C

81

## Examples: Colligative Properties

7. Assuming complete dissociation, what is the molality of an aqueous solution of KBr whose freezing point is  $-2.95 \text{ }^\circ\text{C}$ ? For water,  $K_f = 1.86 \text{ }^\circ\text{C/m}$ ,  $K_b = 0.512 \text{ }^\circ\text{C/m}$ ,  $T_f = 0.00 \text{ }^\circ\text{C}$ , and  $T_b = 100.00 \text{ }^\circ\text{C}$ .

Answer: 0.793 m

82

## Examples: Colligative Properties

8. How much ethylene glycol ( $C_2H_6O_2$ ), in grams, must be added to 1.00 kg of water to produce a solution that boils at  $105.0 \text{ }^\circ\text{C}$ ? For water,  $K_f = 1.86 \text{ }^\circ\text{C/m}$ ,  $K_b = 0.512 \text{ }^\circ\text{C/m}$ ,  $T_f = 0.00 \text{ }^\circ\text{C}$ , and  $T_b = 100.00 \text{ }^\circ\text{C}$ .

Answer: 606 g  $C_2H_6O_2$ 

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## Examples: Colligative Properties

9. Which of the following solutions will have the highest boiling point?

- 0.50 M  $C_{12}H_{22}O_{11}$  (sucrose)
- 0.25 M NaCl
- 0.25 M  $MgCl_2$
- 0.4 M  $C_2H_6O_2$  (ethylene glycol)
- 0.20 M  $Na_2SO_4$
- 0.25 M  $Na_3PO_4$

84

## Examples: Colligative Properties

10. A cell with an internal solute concentration of  $0.400\text{ M}$  is placed in a glucose solution with concentration of  $0.200\text{ M}$ . What will happen to the cell?
- The cell will absorb water, swell up, and burst.
  - The cell will shrivel up and die.
  - The cell will remain the same.
  - The cell will call for help on its portable phone.

85

## Examples: Colligative Properties

11. The total concentration of dissolved particles inside red blood cells is approximately  $0.30\text{ M}$ , and the membrane surrounding the cells is semipermeable. What would the osmotic pressure (in atm) inside the cells become if they were removed from blood plasma and placed in pure water at  $298\text{ K}$ ?

Answer: 7.3 atm

86

## Examples: Colligative Properties

12. What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood ( $\Pi = 7.70\text{ atm}$  at  $25^\circ\text{C}$ ).

Answer: 7.3 atm

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## Examples: Colligative Properties

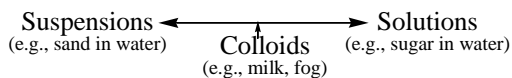
13. A physician studying a variety of hemoglobin associated with a fatal disease dissolved  $21.5\text{ mg}$  of the protein in water at  $5.0^\circ\text{C}$  to make  $1.50\text{ mL}$  of solution and measures an osmotic pressure of  $3.61\text{ torr}$ . What is the molar mass of this hemoglobin variety?

Answer:  $6.89 \times 10^4\text{ g/mol}$

88

## Colloids

### The Structure and Properties of Colloids



- Between the extremes of suspensions and solutions, we have **colloidal suspensions**, or **colloids**, in which a *dispersed* (solute-like) substance is distributed throughout a *dispersing* (solvent-like) substance.
- Colloidal particles are larger than simple molecules, but small enough to remain suspended, without settling out (sizes between  $1$  and  $1000\text{ nm}$ ).
- Colloidal particles have large surface areas, giving rise to a large total adhesive force.
- Colloids have many practical uses, such as in foods, soaps and detergents, paints, etc.

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90



## Colloid Coagulation

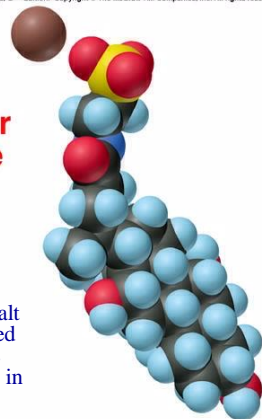
- The destruction of a colloid, called **coagulation**, can be accomplished either by heating or by adding an electrolyte.
  - Heating increases the velocities of the colloidal particles, causing them to collide with enough energy that the ion barriers are penetrated and the particles can aggregate. The particles eventually grow to a size where the particles settle out.
  - Adding an electrolyte neutralizes the adsorbed ion layers. (This process is responsible for the deposition of suspended clays when river water reaches the ocean, creating delta regions.)

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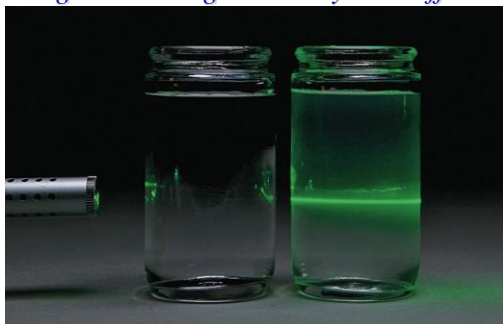
Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

## "Soaps" in Your Small Intestine

Sodium taurocholate, a bile salt secreted by the liver and stored in the gall bladder, emulsifies fats, allowing them to remain in solution for further digestion.



## Light Scattering and the Tyndall Effect



**Figure 11.23.** When a beam of light passes through a solution (left), it is barely visible; when it passes through a colloid (right), the beam is scattered and broadened by the colloidal particles (the **Tyndall effect**). 99

# The End