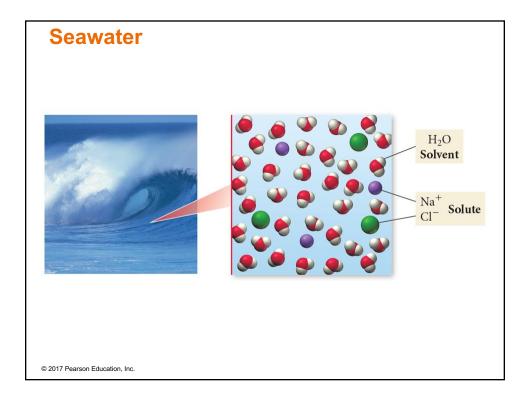


Lecture Presentation

Chapter 13 Solutions

Thirsty Seawater

- Drinking seawater can cause dehydration.
- Seawater
 - is a homogeneous mixture of salts with water.
 - contains higher concentrations of salts than the salt content of your cells.
- As seawater passes through your body, it pulls water out of your cells, due mainly to nature's tendency toward spontaneous mixing.
- This reduces your cells' water level and usually results in diarrhea as this extra liquid flows out with the seawater.



Solutions

- The majority component of a solution is called the **solvent**.
- The minority component is called the **solute**.
- Solutions form in part because of intermolecular forces.
 - The particles of the solute interact with the particles of the solvent through intermolecular forces.

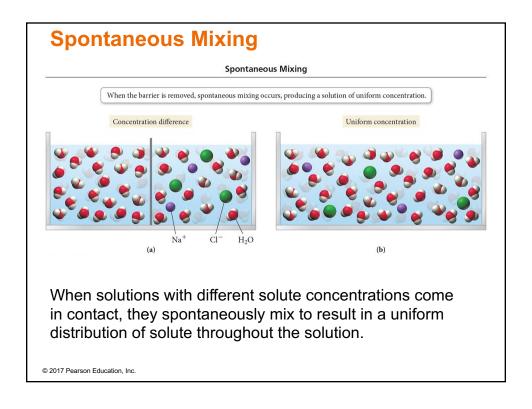
Seawater

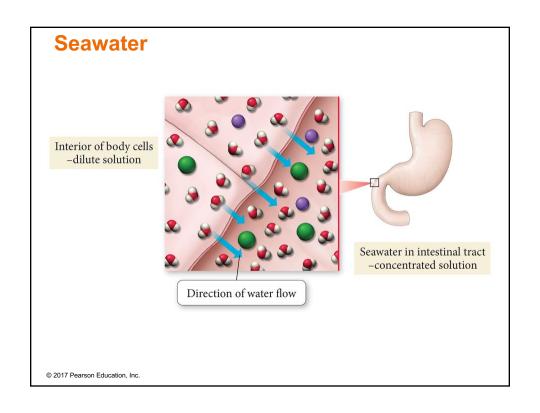
- Drinking seawater will dehydrate you and give you diarrhea.
- The cell wall acts as a barrier to the solute moving, so the only way for the seawater and the cell solution to have uniform mixing is for water to flow out of the cells of your intestine and into your digestive tract.

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Homogeneous Mixtures

- A mixture of two or more substances
- Composition may vary from one sample to another
- Appears to be one substance, though really contains multiple materials
- Most homogeneous materials we encounter are actually solutions.
 - For example, air and seawater
- · Nature has a tendency toward spontaneous mixing.
 - Generally, uniform mixing is more energetically favorable.





Common Types of Solutions

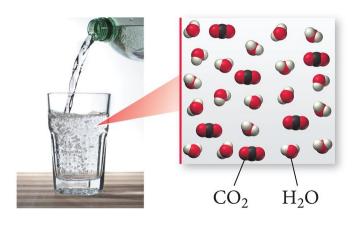
 A solution may be composed of a solid and a liquid or any other combination.

Solution Phase	Solute Phase	Solvent Phase	Example
Gaseous solution	Gas	Gas	Air (mainly oxygen and nitrogen)
Liquid solution	Gas	Liquid	Club soda (CO ₂ and water)
	Liquid	Liquid	Vodka (ethanol and water)
	Solid	Liquid	Seawater (salt and water)
Solid solution	Solid	Solid	Brass (copper and zinc) and other alloys

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Common Types of Solutions

• In aqueous solutions, water is the solvent.



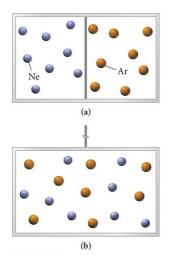
Solubility

- When one substance (solute) dissolves in another (solvent) it is said to be soluble.
 - Salt is soluble in water.
 - Bromine is soluble in methylene chloride.
- When one substance does not dissolve in another it is said to be insoluble.
 - Oil is insoluble in water.
- The solubility of one substance in another depends on
 - 1. nature's tendency toward mixing, and
 - 2. the types of intermolecular attractive forces.

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Nature's Tendency Toward Mixing: Entropy

- Many physical systems tend toward lower potential energy.
- But, formation of a solution does not necessarily lower the potential energy of the system.
- When two ideal gases are put into the same container, they spontaneously mix, even though the difference in attractive forces is negligible.
- The gases mix because the energy of the system is lowered through the release of entropy.



Mixing and the Solution Process Entropy

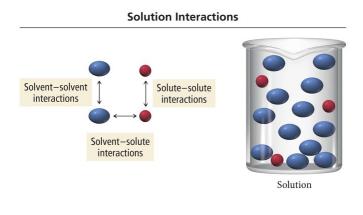
- **Entropy** is the measure of energy dispersal in a system.
- Energy has a spontaneous drive to spread out over as large a volume as it is allowed.
- By each gas expanding to fill the container, the gases' energy is dispersed over a larger volume.

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Solutions: Effect of Intermolecular Forces

 Energy changes in the formation of most solutions also involve differences in attractive forces between the particles.



7

Relative Interactions and Solution Formation

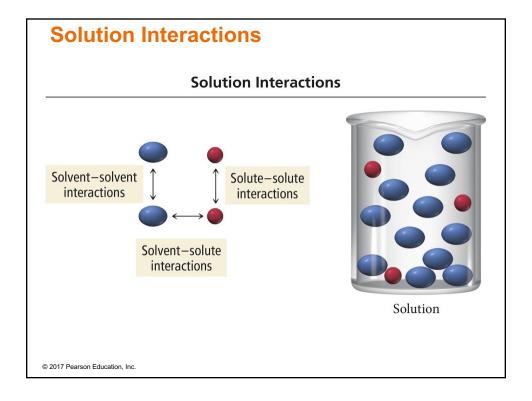
TABLE 13.2 Relative Interactions and Solution Formation			
Solvent–solute interactions	>	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	=	Solvent–solvent and solute–solute interactions	Solution forms
Solvent-solute interactions	<	Solvent–solvent and solute–solute interactions	Solution may or may not form, depending on relative disparity

 When the solute-to-solvent attractions are weaker than the sum of the solute-to-solute and solventto-solvent attractions, the solution will form only if the energy difference is small enough to be overcome by the increase in entropy from mixing.

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Solutions: Effect of Intermolecular Forces

- For the solvent and solute to mix you must overcome
 - 1. all of the solute-solute attractive forces, or
 - 2. some of the solvent–solvent attractive forces.
 - · Both processes are endothermic.
- At least some of the energy to do this comes from making new solute–solvent attractions, which is exothermic.



Solubility

- The maximum amount of solute that can be dissolved in a given amount of solvent is called the solubility.
- There is usually a limit to the solubility of one substance in another.
 - Gases are always soluble in each other.
 - Two liquids that are mutually soluble are said to be miscible.
 - · Alcohol and water are miscible.
 - · Oil and water are immiscible.
- The solubility of one substance in another varies with temperature and pressure.

Will It Dissolve?

- Chemist's rule of thumb: like dissolves like.
- A chemical will dissolve in a solvent if it has a similar structure to the solvent.
- Polar molecules and ionic compounds will be more soluble in polar solvents.
- Nonpolar molecules will be more soluble in nonpolar solvents.

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Heat of Solution

- When some compounds, such as NaOH, dissolve in water, a lot of heat is released.
 - The container gets hot.
- When other compounds, such as NH₄NO₃, dissolve in water, heat is absorbed from the surroundings.
 - The container gets cold.
- Why is this?

Energetics of Solution Formation: The Enthalpy of Solution

To make a solution you must

- 1. overcome all attractions among the solute particles; therefore, ΔH_{solute} is **endothermic**.
- 2. overcome some attractions among solvent molecules; therefore, $\Delta H_{\text{solvent}}$ is **endothermic**.
- 3. form new attractions among solute particles and solvent molecules; therefore, ΔH_{mix} is **exothermic**.
- The overall ΔH for making a solution depends on the relative sizes of the ΔH for these three processes.

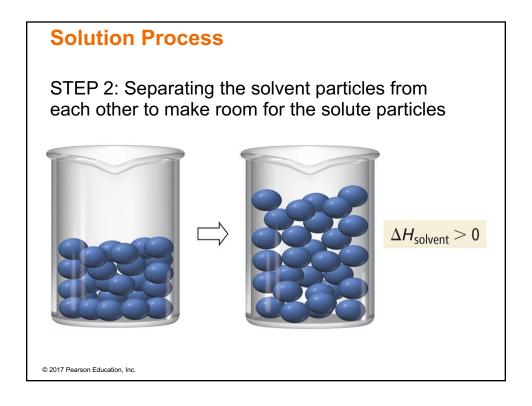
$$\Delta H_{\text{sol'n}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

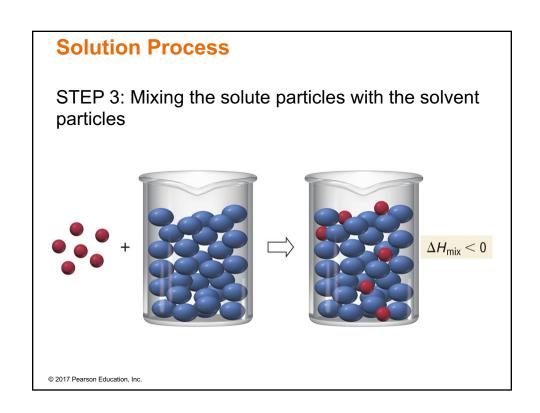
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Solution Process

STEP 1: Separating the solute into its constituent particles

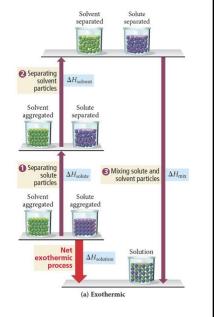






Energetics of Solution Formation

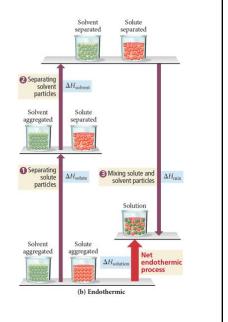
If the total energy cost for breaking attractions between particles in the pure solute and pure solvent is *less than* the energy released in making the new attractions between the solute and solvent, the overall process will be **exothermic**.



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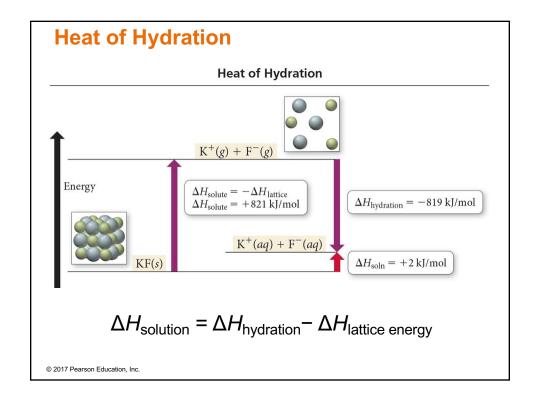
Energetics of Solution Formation

If the total energy cost for breaking attractions between particles in the pure solute and pure solvent is *greater than* the energy released in making the new attractions between the solute and solvent, the overall process will be **endothermic**.



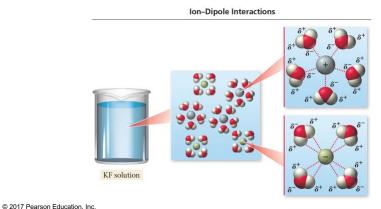
Heats of Hydration

- For aqueous solutions of ionic compounds, the energy added to overcome the attractions between water molecules and the energy released in forming attractions between the water molecules and ions is combined into a term called the heat of hydration.
 - Attractive forces between ions = lattice energy
 - $\Delta H_{\text{solute}} = -\Delta H_{\text{lattice energy}}$
 - Attractive forces in water = H bonds
 - Attractive forces between ion and water = ion-dipole
 - $-\Delta H_{\text{hydration}}$ = heat released when one mole of gaseous ions dissolves in water = $\Delta H_{\text{solvent}}$ + ΔH_{mix}



Ion-Dipole Interactions

- When ions dissolve in water they become hydrated.
 - Each ion is surrounded by water molecules.
- The formation of these ion–dipole attractions causes the heat of hydration to be very exothermic.



Heats of Solution for Ionic Compounds

 For an aqueous solution of an ionic compound, the ΔH_{solution} is the difference between the heat of hydration and the lattice energy.

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

$$\Delta H_{\text{solution}} = -\Delta H_{\text{lattice energy}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

$$\Delta H_{\text{solution}} = \Delta H_{\text{hydration}} - \Delta H_{\text{lattice energy}}$$

$$\Delta H_{\text{solution}} = -\Delta H_{\text{lattice energy}} + \Delta H_{\text{hydration}}$$

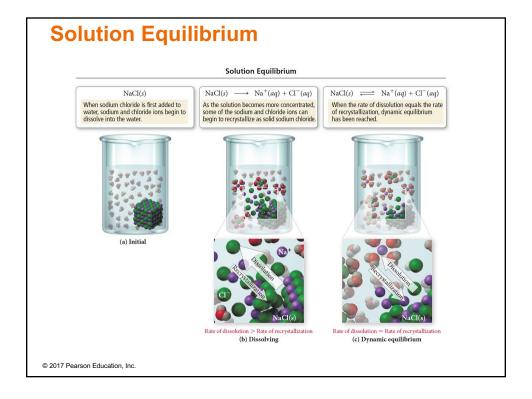
Comparing Heat of Solution to Heat of Hydration

- Because the lattice energy is always exothermic, the size and sign on the $\Delta H_{\text{sol'}\,n}$ tells us something about $\Delta H_{\text{hydration}}$.
- If the heat of solution is large and exothermic, then the amount of energy it costs to separate the ions is less than the energy released from hydrating the ions.
 - $\Delta H_{\text{hydration}} > \Delta H_{\text{solute}}$ when $\Delta H_{\text{sol'n}}$ is (-).
- If the heat of solution is large and endothermic, then the amount of energy it costs to separate the ions is more than the energy released from hydrating the ions.
 - $\Delta H_{\text{hydration}} < \Delta H_{\text{solute}} \text{ when } \Delta H_{\text{sol'} n} \text{ is (+)}.$

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Solution Equilibrium

- The dissolution of a solute in a solvent is an equilibrium process.
- Initially, when there is no dissolved solute, the only process possible is dissolution.
- Shortly after some solute is dissolved, solute particles can start to recombine to reform solute molecules, but when the rate of dissolution >> the rate of deposition, the solute continues to dissolve.
- Eventually, the rate of dissolution = the rate of deposition—the solution is saturated with solute, and no more solute will dissolve.



Solubility Limit

- A solution that has the solute and solvent in dynamic equilibrium is said to be saturated.
 - If you add more solute it will not dissolve.
 - The saturation concentration depends on the temperature and pressure of gases.
- A solution that has less solute than saturation is said to be unsaturated.
 - More solute will dissolve at this temperature.
- A solution that has more solute than saturation is said to be supersaturated.

How Can You Make a Solvent Hold More Solute?

- Solutions can be made saturated at non-room conditions and then can be allowed to come to room conditions slowly.
- For some solutes, instead of coming out of solution when the conditions change, they get stuck between the solvent molecules, and the solution becomes supersaturated.
- Supersaturated solutions are unstable and lose all the solute above saturation when disturbed.
 - For example, shaking a carbonated beverage

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Adding a Crystal of NaC₂H₃O₂ to a Supersaturated Solution

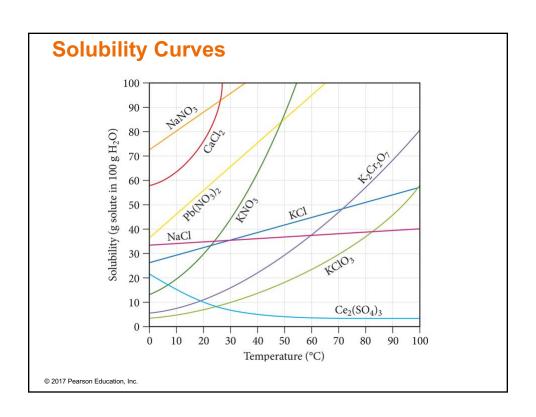






Temperature Dependence of Solubility of Solids in Water

- Solubility is generally given in grams of solute that will dissolve in 100 g of water.
- For *most* solids, the solubility of the solid increases as the temperature increases.
 - When $\Delta H_{\text{solution}}$ is endothermic
- Solubility curves can be used to predict whether a solution with a particular amount of solute dissolved in water is saturated (on the line), unsaturated (below the line), or supersaturated (above the line).



Purification by Recrystallization

- One of the common operations performed by a chemist is removing impurities from a solid compound.
- One method of purification involves dissolving a solid in a hot solvent until the solution is saturated.
- As the solution slowly cools, the solid crystallizes out, leaving impurities behind.



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Temperature Dependence of Solubility of Gases in Water

- Gases generally have lower solubility in water than ionic or polar covalent solids because most are nonpolar molecules.
 - Gases with high solubility usually are actually reacting with water.
- For *all* gases, the solubility of the gas decreases as the temperature increases.
 - The $\Delta H_{\text{solution}}$ is exothermic because you do not need to overcome solute–solute attractions.

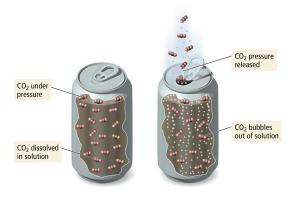
Temperature Dependence of Solubility of Gases in Water



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Pressure Dependence of Solubility of Gases in Water

• The larger the partial pressure of a gas in contact with a liquid, the more soluble the gas is in the liquid.



Henry's Law

The solubility of a gas
 (S_{gas}) is directly
 proportional to its
 partial pressure, (P_{gas}).

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

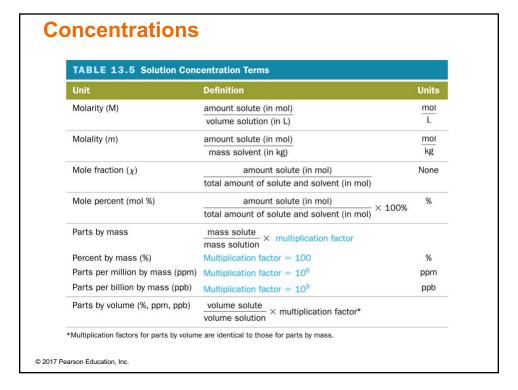
 k_H is called the Henry's law constant. **TABLE 13.4** Henry's Law Constants for Several Gases in Water at 25 °C

Gas	k _H (M/atm)
O ₂	1.3×10^{-3}
N_2	6.1×10^{-4}
CO ₂	3.4×10^{-2}
NH ₃	5.8×10^{1}
Не	3.7×10^{-4}

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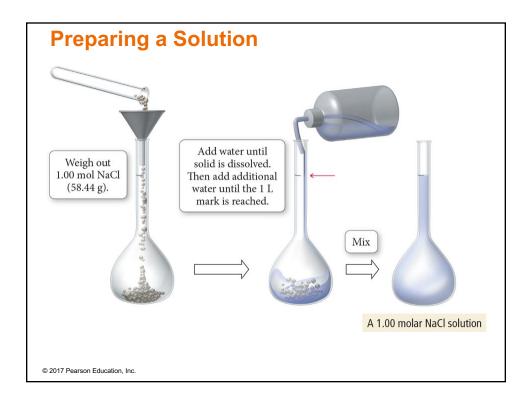
Concentrations

- Solutions have variable composition.
- To describe a solution, you need to describe the components *and* their relative amounts.
- The terms dilute and concentrated can be used as qualitative descriptions of the amount of solute in solution.
- Concentration = amount of solute in a given amount of solution.
 - Occasionally per amount of solvent



Preparing a Solution

- Need to know amount of solution and concentration of solution.
- Calculate the mass of solute needed.
 - Start with an amount of solution.
 - Use concentration as a conversion factor.
 - 5% by mass ⇒ 5 g solute ≡ 100 g solution
 - "Dissolve the grams of solute in enough solvent to total the total amount of solution."



Solution Concentration: Molarity

- Moles of solute per 1 liter of solution
- Describes how many molecules of solute in each liter of solution
- If a sugar solution concentration is 2.0 M,
 - 1 liter of solution contains 2.0 moles of sugar.
 - -2 liters = 4.0 moles sugar.
 - -0.5 liters = 1.0 mole sugar.

Molarity (M) =
$$\frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$$

Solution Concentration: Molality, m

- Moles of solute per 1 kilogram of solvent
 - Defined in terms of amount of solvent, not solution
 - · Like the others
- Does not vary with temperature
 - Because based on masses, not volumes

Molality
$$(m) = \frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$$

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Parts Solute in Parts Solution

- Parts can be measured by mass or volume.
- Parts are generally measured in the same units.
 - By mass in grams, kilograms, lbs., etc.
 - By volume in mL, L, gallons, etc.
 - Mass and volume combined in grams and mL

Parts Solute in Parts Solution

- Percentage = parts of solute in every 100 parts solution
 - If a solution is 0.9% by mass, then there are 0.9 grams of solute in every 100 grams of solution (or 0.9 kg solute in every 100 kg solution).
- Parts per million = parts of solute in every 1 million parts solution
 - If a solution is 36 ppm by volume, then there are 36 mL of solute in 1 million mL of solution.

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PPM

- Grams of solute per 1,000,000 g of solution
- mg of solute per 1 kg of solution
- 1 liter of water = 1 kg of water
 - For aqueous solutions, we often approximate the kg of the solution as the kg or L of water.
 - For dilute solutions, the difference in density between the solution and pure water is usually negligible.

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

Parts per Billion Concentration

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

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Solution Concentrations: Mole Fraction, X_A

- The mole fraction is the fraction of the moles of one component in the total moles of all the components of the solution.
- Total of all the mole fractions in a solution = 1.
- Unitless
- The mole percentage is the percentage of the moles of one component in the total moles of all the components of the solution.
 - = mole fraction \times 100%

Converting Concentration Units

- 1. Write the given concentration as a ratio.
- 2. Separate the numerator and denominator.
 - Separate into the solute part and solution part.
- 3. Convert the solute part into the required unit.
- 4. Convert the solution part into the required unit.
- 5. Use the definitions to calculate the new concentration units.

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Colligative Properties

- Colligative properties are properties whose values depend only on the number of solute particles and not on what they are.
 - Value of the property depends on the concentration of the solution.
- The difference in the value of the property between the solution and the pure substance is generally related to the different attractive forces and solute particles occupying solvent molecules' positions.

Vapor Pressure of Solutions

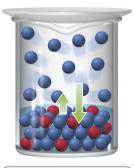
- The vapor pressure of a solvent above a solution is lower than the vapor pressure of the pure solvent.
 - The solute particles replace some of the solvent molecules at the surface.
 - The pure solvent establishes a liquid vapor equilibrium.



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Vapor Pressure of Solutions

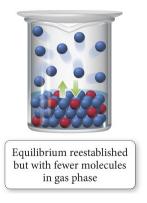
 Addition of a nonvolatile solute reduces the rate of vaporization, decreasing the amount of vapor.



Rate of vaporization reduced by solute

Vapor Pressure of Solutions

 Eventually, equilibrium is reestablished but with a smaller number of vapor molecules; therefore, the vapor pressure will be lower.

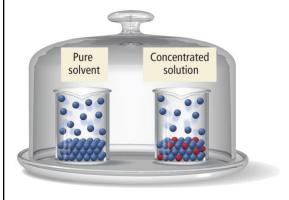


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Thirsty Solutions Revisited

- A concentrated solution will draw solvent molecules toward it due to the natural drive for materials in nature to mix.
- Similarly, a concentrated solution will draw pure solvent vapor into it due to this tendency to mix.
- The result is reduction in vapor pressure.

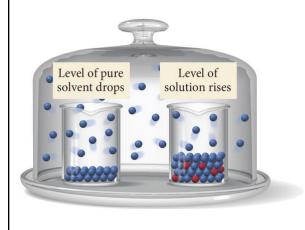
Thirsty Solutions



Beakers with equal liquid levels of pure solvent and a solution are placed in a bell jar. Solvent molecules evaporate from each one and fill the bell jar, establishing an equilibrium with the liquids in the beakers.

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Thirsty Solutions



When equilibrium is established, the liquid level in the solution beaker is higher than the solution level in the pure solvent beaker; the thirsty solution grabs and holds solvent vapor more effectively.

Raoult's Law

 The vapor pressure of a volatile solvent above a solution is equal to its normal vapor pressure, P°, multiplied by its mole fraction in the solution.

$$P_{\text{solvent in solution}} = \chi_{\text{solvent}} \cdot P^{\circ}$$

 Because the mole fraction is always less than 1, the vapor pressure of the solvent in solution will always be less than the vapor pressure of the pure solvent.

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Vapor Pressure Lowering

- The vapor pressure of a solvent in a solution is always lower than the vapor pressure of the pure solvent.
- The vapor pressure of the solution is directly proportional to the amount of the solvent in the solution.
- The difference between the vapor pressure of the pure solvent and the vapor pressure of the solvent in solution is called the vapor pressure lowering.

$$\Delta P = P^{\circ}_{\text{solvent}} - P_{\text{solution}} = \chi_{\text{solute}} \cdot P^{\circ}_{\text{solvent}}$$

Raoult's Law for Volatile Solute

- When both the solvent and the solute can evaporate, both molecules will be found in the vapor phase.
- The total vapor pressure above the solution will be the sum of the vapor pressures of the solute and solvent.
 - For an ideal solution

$$P_{\text{total}} = P_{\text{solute}} + P_{\text{solvent}}$$

 The solvent decreases the solute vapor pressure in the same way the solute decreased the solvent's.

$$P_{\text{solute}} = \chi_{\text{solute}} \cdot P_{\text{solute}}^{\circ}$$
 and $P_{\text{solvent}} = \chi_{\text{solvent}} \cdot P_{\text{solvent}}^{\circ}$

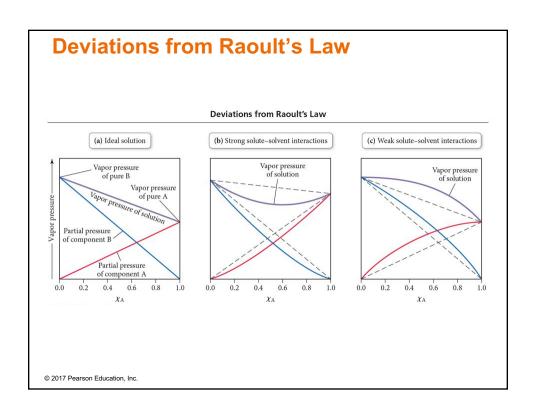
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Ideal versus Nonideal Solutions

- In ideal solutions, the made solute—solvent interactions are equal to the sum of the broken solute—solute and solvent—solvent interactions.
 - Ideal solutions follow Raoult's law.
- Effectively, the solute is diluting the solvent.
- If the solute—solvent interactions are stronger or weaker than the broken interactions, the solution is nonideal.

Vapor Pressure of a Nonideal Solution

- When the solute—solvent interactions are stronger than the solute—solute + solvent—solvent, the total vapor pressure of the solution will be less than predicted by Raoult's law, because the vapor pressures of the solute and solvent are lower than ideal.
- When the solute—solvent interactions are weaker than the solute—solute + solvent—solvent, the total vapor pressure of the solution will be more than predicted by Raoult's law.



Other Colligative Properties Related to Vapor Pressure Lowering

- Vapor pressure lowering occurs at all temperatures.
- This results in the temperature required to boil the solution being higher than the boiling point of the pure solvent.
- This also results in the temperature required to freeze the solution being lower than the freezing point of the pure solvent.

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Freezing Point Depression and Boiling Point Elevation Solution Solution Solution Solution Solution Gas Boiling point of solvent of solvent of solution Temperature © 2017 Pearson Education, Inc.

Freezing Point Depression

- The freezing point of a solution is lower than the freezing point of the pure solvent.
 - Therefore, the melting point of the solid solution is lower.
- The difference between the freezing point of the solution and the freezing point of the pure solvent is directly proportional to the molal concentration of solute particles.

$$(FP_{solvent} - FP_{solution}) = \Delta T_f = m \cdot K_f$$

- The proportionality constant is called the freezing point depression constant, K_f.
 - The value of K_f depends on the solvent.
 - The units of K_f are °C/m.

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K_f and K_b

Solvent	Normal Freezing Point (°C)	K _f (°C/m)	Normal Boiling Point (°C)	K _b (°C/m)
Benzene (C ₆ H ₆)	5.5	5.12	80.1	2.53
Carbon tetrachloride (CCI ₄)	-22.9	29.9	76.7	5.03
Chloroform (CHCl ₃)	-63.5	4.70	61.2	3.63
Ethanol (C ₂ H ₅ OH)	-114.1	1.99	78.3	1.22
Diethyl ether (C ₄ H ₁₀ O)	-116.3	1.79	34.6	2.02
Water (H ₂ O)	0.00	1.86	100.0	0.512

Boiling Point Elevation

- The boiling point of a solution is higher than the boiling point of the pure solvent.
 - For a nonvolatile solute
- The difference between the boiling point of the solution and boiling point of the pure solvent is directly proportional to the molal concentration of solute particles.

$$(BP_{solution} - BP_{solvent}) = \Delta T_b = m \cdot K_b$$

- The proportionality constant is called the boiling point elevation constant, K_b.
 - The value of K_b depends on the solvent.
 - The units of K_b are °C/m.

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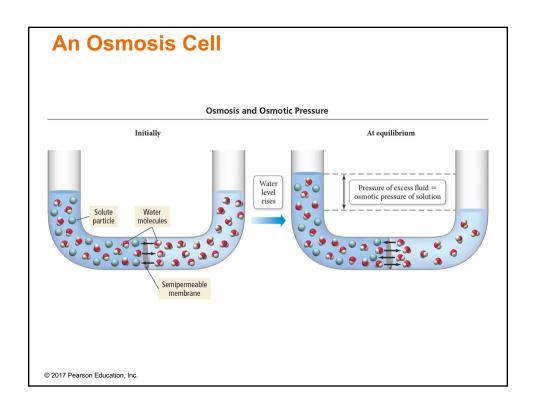
Osmosis

- Osmosis is the flow of solvent from a solution of low concentration into a solution of high concentration.
- The solutions may be separated by a semipermeable membrane.
- A semipermeable membrane allows solvent, but not solute, to flow through it.

Osmotic Pressure

- The amount of pressure needed to keep osmotic flow from taking place is called the osmotic pressure.
- The osmotic pressure, Π, is directly proportional to the molarity of the solute particles.
 - $-R = 0.08206 (atm \cdot L)/(mol \cdot K)$

 $\Pi = MRT$

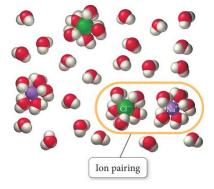


Van't Hoff Factor

- Ionic compounds produce multiple solute particles for each formula unit.
- The theoretical van't Hoff factor, i, is the ratio of moles of solute particles to moles of formula units dissolved.
- The measured van't Hoff factor is generally less than the theoretical due to ion pairing in solution.
 - Therefore, the measured van't Hoff factors often cause the ΔT to be smaller than one might expect.

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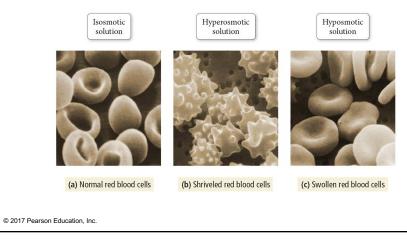
Colligative Properties of Strong Electrolyte Solutions



Solute	i Expected	i Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO ₄	2	1.3
MgCl ₂	3	2.7
K ₂ SO ₄	3	2.6
FeCl ₃	4	3.4

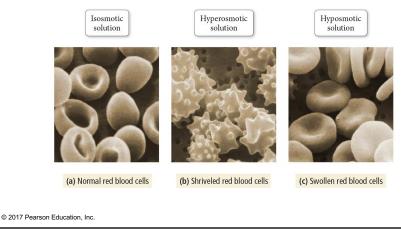
Colligative Properties and Medical Solutions

An isosmotic solution has the same osmotic pressure as the solution inside the cell; as a result, there is no net flow of water into or out of the cell.



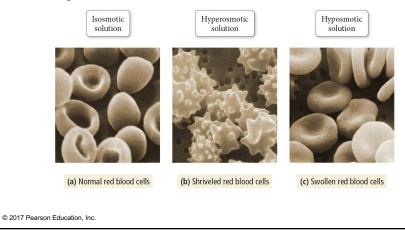
Colligative Properties and Medical Solutions

A hyperosmotic solution has a higher osmotic pressure than the solution inside the cell; as a result there is a net flow of water out of the cell, causing it to shrivel.



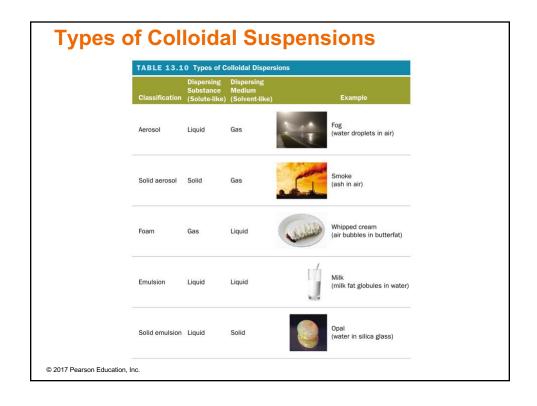
Colligative Properties and Medical Solutions

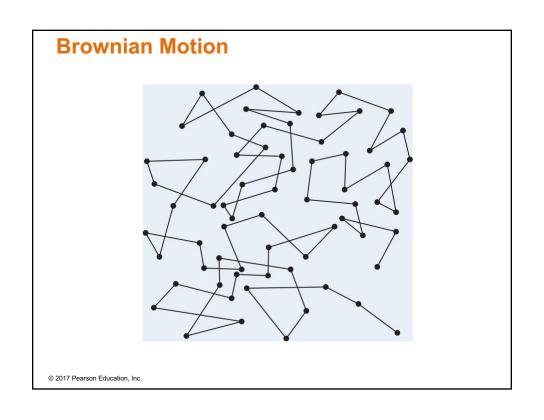
A hyposmotic solution has a lower osmotic pressure than the solution inside the cell; as a result, there is a net flow of water into the cell, causing it to swell.



Mixtures

- Solutions = homogeneous
- Suspensions = heterogeneous, separate on standing
- Colloids = heterogeneous, do not separate on standing
 - Particles can coagulate.
 - Cannot pass through semipermeable membrane
 - Hydrophilic
 - Stabilized by attraction for solvent (water)
 - Hydrophobic
 - · Stabilized by charged surface repulsions
- Show the Tyndall effect and Brownian motion.





Soaps

- Soap is a fatty acid salt that forms a colloid because of its unique structure.
- One end of the molecule is ionic, the "head," and the other end is very nonpolar, the "tail."
 - Hydrophilic head and hydrophobic tail
- This unique structure allows soaps to help oily substances be attracted to water.
 - Micelle formation
 - Emulsification

