13.1 The Solution Process

- A solution is a homogeneous mixture of solute and solvent.
- Solutions may be gases, liquids, or solids.
- Each substance present is a component of the solution.
  - The solvent is the component present in the largest amount.
  - The other components are the solutes.
- In the process of making solutions with condensed phases, intermolecular forces become rearranged.
- Consider NaCl (solute) dissolving in water (solvent).
  - Water molecules orient themselves on the NaCl crystals.
  - H-bonds between the water molecules have to be broken.
  - NaCl dissociates into Na⁺ and Cl⁻.
  - Ion-dipole forces form between the Na⁺ and the negative end of the water dipole.
  - Similar ion-dipole interactions form between the Cl⁻ and the positive end of the water dipole.
  - Such an interaction between solvent and solute is called solvation.
    - If water is the solvent, the interaction is called hydration.

Energy Changes and Solution Formation

- There are three steps involving energy in the formation of a solution.
  - Separation of solute molecules ($\Delta H_1$),
  - Separation of solvent molecules ($\Delta H_2$), and
  - Formation of the solute-solvent interactions ($\Delta H_3$).
- We define the enthalpy change in the solution process as:
  $$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
- $\Delta H_{\text{soln}}$ can either be positive or negative depending on the intermolecular forces.
  - To determine whether $\Delta H_{\text{soln}}$ is positive or negative, we consider the strengths of all solute-solute, solvent-solvent, and solute-solvent interactions.
  - Breaking attractive intermolecular forces is always endothermic.
    - $\Delta H_1$ and $\Delta H_2$ are both positive.
  - Forming attractive intermolecular forces is always exothermic.
    - $\Delta H_3$ is always negative.
- It is possible to have either $\Delta H_3 > (\Delta H_1 + \Delta H_2)$ or $\Delta H_3 < (\Delta H_1 + \Delta H_2)$
  - Examples:
    - MgSO₄ added to water has $\Delta H_{\text{soln}} = -91.2 \text{ kJ/mol}$
    - NH₄NO₃ added to water has $\Delta H_{\text{soln}} = +26.4 \text{ kJ/mol}$
      [MgSO₄ is often used in instant heat packs and NH₄NO₃ is often used in instant cold packs!]
  - How can we predict if a solution will form?
    - In general, solutions form if the $\Delta H_{\text{soln}}$ is negative.
    - If $\Delta H_{\text{soln}}$ is too endothermic, a solution will not form.
    - “Rule of Thumb”: polar solvents dissolve polar solutes.
      - Nonpolar solvents dissolve nonpolar solutes.
      - “Like dissolves like”
    - Consider the process of mixing NaCl in gasoline.
      - Only weak interactions are possible because gasoline is nonpolar.
      - These interactions do not compensate for the energy required for separation of ions from one another.
      - Result: NaCl does not dissolve to any great extent in gasoline.
    - Consider the process of mixing water in octane (C₈H₁₈)
      - Water has strong H-bonds.
      - The energy required to break these H-bonds is not compensated for by interaction between water and octane.
      - Result: Water and octane do not mix.
Solution Formation, Spontaneity, and Disorder

- A spontaneous process occurs without outside intervention.
- When the energy of the system decreases (e.g. dropping a book and allowing it to fall to a lower potential energy), the process is spontaneous.
- Some spontaneous processes do not involve the movement of the system to a lower energy state (e.g., an endothermic reaction).
- In most cases, solution formation is favored by the increase in disorder that accompanies mixing.
  - Example: a mixture of CCl₄ and C₆H₁₄ is less ordered than the two separate liquids.
  - Therefore, they spontaneously mix even though ΔH_{soln} is very close to zero.
  - A solution will form unless the solute-solute or solvent-solvent interactions are too strong relative to solute-solvent interactions.

Solution Formation and Chemical Reactions

- Some solutions form by physical processes, and some by chemical processes.
  - Consider:
    Ni (s) + 2 HCl (aq) --> NiCl₂ (aq) + H₂ (g)
  - Note that the chemical form of the substance being dissolved has changed during this process (Ni ---→ NiCl₂).
  - When all the water is removed from the solution, no Ni is found, only NiCl₂ 6 H₂O remains.
  - Therefore, the dissolution of Ni in HCl is a chemical process.
  - By contrast:
    NaCl (s) + H₂O (l) ---→ Na⁺ (aq) + Cl⁻ (aq)
  - When the water is removed from the solution, NaCl is found.
  - Therefore, NaCl dissolution is a physical process.
13.2 Saturated Solutions and Solubility

- As a solid dissolves, a solution forms:
  - Solute + solvent $\rightarrow$ solution
- The opposite process is crystallization.
  - Solution $\rightarrow$ solute + solvent
- If crystallization and dissolution are in equilibrium with undissolved solute present, the solution is saturated.
  - There will be no further increase in the amount of dissolved solute.
- Solubility is the amount of solute required to form a saturated solution.
  - A solution with a concentration of dissolved solute that is less than the solubility is said to be unsaturated.
  - A solution is said to be supersaturated if more solute is dissolved than in a saturated solution.
13.3 Factors Affecting Solubility

- The tendency of one substance to dissolve in another depends on:
  - The nature of the solute.
  - The nature of the solvent.
  - The temperature.
  - The pressure (for gases).

Solute-Solvent Interactions

- Pairs of liquids that mix in any proportions are said to be **miscible**.
  - Example: ethanol and water are miscible liquids.
- In contrast, **immiscible** liquids do not mix significantly.
  - Example: gasoline and water are immiscible.
- Intermolecular forces are an important factor.
  - The stronger the attraction between solute and solvent molecules, the greater the solubility.
    - For example, polar liquids tend to dissolve in polar solvents.
    - Favorable dipole-dipole interactions exist.
- Consider the solubility of alcohols in water.
  - Water and ethanol are miscible because the broken hydrogen bonds in both pure liquids are reestablished in the mixture.
- However, not all alcohols are miscible with water.
  - Why?
    - The number of carbon atoms in a chain affects solubility.
      - The greater the number of carbon atoms in the chain, the more the molecule behaves like a hydrocarbon.
      - Thus, the more C atoms in the alcohol, the lower its solubility in water.
    - Increasing the number of –OH groups within a molecule increases solubility in water.
      - The greater the number of –OH groups along the chain, the more solute-water H-bonding is possible.
- Generalization: “like dissolves like.”
  - Substances with similar intermolecular attractive forces tend to be soluble in one another.
    - The more polar bonds in the molecule, the better it dissolves in a polar solvent.
    - The less polar the molecule, the less likely it is to dissolve in a polar solvent and the more likely it is to dissolve in a nonpolar solvent.
  - Network solids do not dissolve because the strong intermolecular forces in the solid are not reestablished in any solution.

Pressure Effects

- The solubility of a gas in a liquid is a function of the pressure of the gas over the solution.
  - Solubilities of solids and liquids are not greatly affected by pressure.
- With a higher gas pressure, more molecules of gas are close to the surface of the solution and the probability of a gas molecule striking a surface and entering the solution is increased.
  - Therefore, the higher the pressure, the greater the solubility.
- The lower the pressure, the fewer molecules of gas are close to the surface of the solution and the lower the solubility.
  - The solubility of a gas is directly proportional to the partial pressure of the gas above the solution.
  - The lower the pressure, the fewer the number of gas molecules that are close to the surface of the solution and the lower the solubility. This statement is **Henry’s law**.
  - Henry’s law may be expressed mathematically as:
    \[ C_g = kP_g \]
    - Where \( C_g \) is the solubility of the gas, \( P_g \) the partial pressure, and \( k \) is Henry’s law constant.
    - Note: The Henry’s law constant differs for each solute-solvent pair and differs with temperature.
- An application of Henry’s law: preparation of carbonated soda.
  - Carbonated beverages are bottled under \( P_{CO_2} > 1 \) atm.
  - As the bottle is opened \( P_{CO_2} \) decreases and the solubility of \( CO_2 \) decreases.
  - Therefore, bubbles of \( CO_2 \) escape from solution.
Temperature Effects

- Experience tells us that sugar dissolves better in warm water than in cold water.
  - As temperature increases, the solubility of solids generally increases.
  - Sometimes solubility decreases as temperature increases (e.g. Ce₂(SO₄)₃).
- Experience tells us that carbonated beverages go flat as they get warm.
  - Gases are less soluble at higher temperatures.
- An environmental application of this: thermal pollution.
  - Thermal pollution: if lakes get too warm, CO₂ and O₂ become less soluble and are not available for plants or animals.
  - Fish suffocate.
13.4 Ways of Expressing Concentration

- All methods involve quantifying the amount of solute per amount of solvent (or solution).
- Concentration may be expressed qualitatively or quantitatively.
  - The terms dilute and concentrated are qualitative ways to describe concentration.
    - A dilute solution has a relatively small concentration of solute.
    - A concentrated solution has a relatively high concentration of solute.
- Quantitative expressions of concentration require specific information regarding such quantities as masses, moles, or liters of the solute, solvent, or solution.
  - The most commonly used expressions for concentration are:
    - Mass percentage
    - Mole fraction
    - Molarity
    - Molality

Mass percentage, ppm, and ppb
- Mass percentage is one of the simplest ways to express concentration.
  - By definition:
    \[
    \text{Mass \% of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 100
    \]
- Similarly, parts per million (ppm) can be expressed as 1 mg of solute per kilogram of solution.
  - By definition:
    \[
    \text{Parts per million (ppm) of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^6
    \]
    - If the density of the solution is 1 g/mL, then 1 ppm = 1 mg solute per liter of solution.
- We can extend this definition again!
  - Parts per billion (ppb): 1 mg of solute per kilogram of solution.
  - By definition:
    \[
    \text{Parts per billion (ppb) of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^9
    \]
    - If the density of the solution is 1 g/mL, then 1 ppb = 1 mg solute per liter of solution.

Mole Fraction, Molarity, and Molality
- Common expressions of concentration are based on the number of moles of one or more components.
- Recall that mass can be converted to moles using the molar mass.
- Recall:
  \[
  \text{Mole fraction of component, } X = \frac{\text{moles of component}}{\text{total moles of all components}}
  \]
  - Note: Mole fraction has no units.
  - Note: Mole fractions range from 0 to 1.
- Recall:
  \[
  \text{Molarity, } M = \frac{\text{moles of solute}}{\text{liters of solution}}
  \]
  - Note: Molarity will change with a change in temperature (as the solution volume increases or decreases).
- We define:
  \[
  \text{Molality, } m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}
  \]
  - Note: Converting between molarity \( M \) and molality \( m \) requires density.
13.5 Colligative Properties

- **Colligative properties** depend on the number of solute molecules.
- There are four colligative properties to consider:
  - Vapor pressure lowering (Raoult’s law).
  - Boiling point elevation.
  - Freezing point depression.
  - Osmotic pressure.

Lowering the Vapor Pressure

- Nonvolatile solvents reduce the ability of the surface solvent molecules to escape the liquid.
  - Therefore, vapor pressure is lowered.
  - The amount of vapor pressure lowering depends on the amount of solute.
- **Raoult’s law** quantifies the extent to which a nonvolatile solute lowers the vapor pressure of the solvent.
  - If \( P_A \) is the vapor pressure with solute, \( P^o_A \) is the vapor pressure without solvent, and \( X_A \) is the mole fraction of A, then
    \[
    P_A = X_A P^o_A
    \]

- **Ideal solution**: one that obeys Raoult’s law.
  - Real solutions show approximately ideal behavior when:
    - The solute concentration is low.
    - The solute and solvent have similarly sized molecules.
    - The solute and solvent have similar types of intermolecular attractions.
  - Raoult’s law breaks down when the solvent-solvent and solute-solute intermolecular forces are much greater or weaker than solute-solvent intermolecular forces.

Boiling-Point Elevation

- A nonvolatile solute lowers the vapor pressure of a solution.
- At the normal boiling point of the pure liquid the solution has a vapor pressure less than 1 atm.
  - Therefore, a higher temperature is required to reach a vapor pressure of 1 atm for the solution (\( \Delta T_b \)).
- The **molal boiling-point-elevation constant**, \( K_b \), expresses how much \( \Delta T_b \) changes with molality, \( m \).
  \[
  \Delta T_b = K_b m
  \]

Freezing-Point Elevation

- When a solution freezes, crystals of almost pure solvent are formed first.
  - Solute molecules are usually not soluble in the solid phase of the solvent.
  - Therefore, the triple point occurs at a lower temperature because of the lower vapor pressure for the solution.
- The melting-point (freezing-point) curve is a vertical line from the triple point.
  - Therefore, the solution freezes at a lower temperature (\( \Delta T_f \)) than the pure solvent.
  - The decrease in freezing point (\( \Delta T_f \)) is directly proportional to molality.
- \( K_f \) is the **molal freezing-point-depression constant**:
  \[
  \Delta T_f = K_f m
  \]
Osmosis

- Semipermeable membranes permit passage of some components of a solution.
  - Often they permit passage of water but not larger molecules or ions.
  - Examples of semipermeable membranes: cell membranes and cellophane.
- **Osmosis** is the net movement of a solvent from an area of low solute concentration to an area of high solute concentration.
- Consider a U-shaped tube with a two liquids separated by a semipermeable membrane.
  - One arm of the tube contains pure solvent.
  - The other arm contains a solution.
  - There is a higher concentration of solvent in the dilute solution.
    - The rate of movement of solvent from the dilute solution to the concentrated solution is faster than the rate of movement in the opposite direction.
  - As solvent moves across the membrane, the fluid levels in the arms become uneven.
    - The vapor pressure of solvent is higher in the arm with pure solvent.
  - Eventually, the pressure difference due to the difference in height of liquid in the arms stops osmosis.
- **Osmotic pressure**, \( \pi \), is the pressure required to prevent osmosis.
  - Osmotic pressure obeys a law similar in form to the ideal-gas law.
    - For \( n \) moles, \( V = \) volume, \( M = \) molarity, \( R = \) the ideal-gas constant, and absolute temperature, \( T \), the osmotic pressure is:

\[
\pi V = nRT
\]

\[
\pi = \left( \frac{n}{V} \right)RT = MRT
\]

- Two solutions are said to be **isotonic** if they have the same osmotic pressure.
  - Hypotonic solutions have a lower \( \pi \), relative to a more concentrated solution.
  - Hypertonic solution have a higher \( \pi \), relative to a more dilute solution.
- We can illustrate this with a biological system: red blood cells.
  - Red blood cells have semipermeable membranes.
    - If red blood cells are placed in a hypertonic solution (relative to their intracellular solution), there is a lower solute concentration in the cell than in the surrounding tissue.
      - Osmosis occurs and water passes through the membrane out of the cell.
      - The cell shrivels up.
      - This process is called **crenation**.
    - If red blood cells are placed in a hypotonic solution, there is a higher solute concentration in the cell than outside the cell.
      - Osmosis occurs and water moves into the cell.
      - The cell bursts (**hemolysis**).
  - To prevent crenation or hemolysis, IV (intravenous) solutions must be isotonic relative to the intracellular fluids of cells.
- Everyday examples of osmosis:
  - If a cucumber is placed in NaCl solution, it will lose water, shrivel up, and become a pickle.
  - A limp carrot placed in water becomes firm because water enters via osmosis.
  - Eating large quantities of salty food causes retention of water and swelling of tissues (edema).
  - Water moves into plants to a great extent through osmosis.
  - Salt may be added to meat (or sugar added to fruit) as a preservative.
    - Salt prevents bacterial infection: a bacterium placed on the salt will lose water through osmosis and die.
  - **Active transport** is the movement of nutrients and waste material through a biological membrane against a concentration gradient.
    - Movement is from an area of low to an area of high concentration.
    - Active transport is not spontaneous.
      - Energy must be expended by the cell to accomplish this.
Determination of Molar Mass
  
  Any of the four colligative properties may be used to determine molar mass.

Colligative Properties of Electrolyte Solutions
  
  Colligative properties of solutions depend on the total concentration of particles in solution.
  
  - Colligative properties are the same for molecules and ions.
  - In a 0.100 m solution of NaCl the total concentration of particles is 0.200 m.
  
  0.100 m NaCl has a Na\(^+\) concentration of 0.100 m and Cl\(^-\) concentration of 0.100 m.

  - The expected freezing-point depression of 0.100 m NaCl is (0.200 m) \(\times\) (1.86 °C/m) = 0.372 °C.
  - The actual freezing-point depression is less than expected (0.348 °C).

  - Ions in solution form ion-pairs in which oppositely charged ions associate with each other for a short time.

  - This reduces the number (and consequently the concentration) of independent particles in solution.

  - The van’t Hoff factor \((i)\) is a measure of the extent of dissociation of electrolytes in solution.

  - The van’t Hoff factor is determined using the ratio of the actual value of a colligative property to the value calculated for a nonelectrolyte.

  \[
  i = \frac{\Delta T_f (measured)}{\Delta T_f (calculated \ for \ nonelectrolyte)}
  \]
Colloids or colloidal dispersions are suspensions in which the suspended particles are larger than molecules but too small to separate out of the suspension due to gravity.
- Particle size: 10 to 2000 angstrom.

There are several types of colloids.
- Aerosol: gas + liquid or solid (e.g., fog and smoke),
- Foam: liquid + gas (e.g., whipped cream),
- Emulsion: liquid + liquid (e.g., milk),
- Sol: liquid + solid (e.g., paint),
- Solid foam: solid + gas (e.g., marshmallow),
- Solid emulsion: solid + liquid (e.g., butter),
- Solid sol: solid + solid (e.g., ruby glass).

**Tyndall effect**: ability of colloidal particles to scatter light.
- The path of a beam of light projected through a colloidal suspension can be seen through the suspension.

Hydrophilic and Hydrophobic Colloids

- Focus on colloids in water.
  - Water-loving colloids: hydrophilic.
  - Water-hating colloids: hydrophobic.
- In the human body, large biological molecules such as proteins are kept in suspension by association with surrounding water molecules.
  - These macromolecules fold us so that hydrophobic groups are away from the water (inside the folded molecule).
  - Hydrophilic groups are on the surface of these molecules and interact with solvent (water) molecules.
    - Typical hydrophilic groups are polar (containing C-O, O-H, N-H bonds) or charged.
- Hydrophobic colloids need to be stabilized in water.
  - One way to stabilize hydrophobic colloids is to absorb ions on their surface.
    - Adsorption: When something sticks to a surface we say that it is adsorbed.
  - If ions are adsorbed onto the surface of a colloid, the colloid appears hydrophilic and is stabilized in water.
  - Consider a small drop of oil in water.
    - Add a small amount of sodium stearate.
    - Sodium stearate has a long hydrophobic hydrocarbon tail and a small hydrophilic head.
    - The hydrophobic tail can be absorbed into the oil drop, leaving the hydrophilic head on the surface.
    - The hydrophilic heads then interact with the water and the oil drop is stabilized in water.
- A soap acts in a similar fashion.
  - Soaps are molecules with long hydrocarbon tails and hydrophilic heads that remove dirt by stabilizing the colloid in water.
  - Most dirt stains on people and clothing are oil-based.
- Biological applications of this principle:
  - The gallbladder excretes a fluid called bile.
  - Bile contains a substance (bile salts) that form an emulsion with fats in our small intestine.
  - Emulsifying agents help form an emulsion.
    - Emulsification of dietary fats and fat-soluble vitamins is important in their absorption and digestion by the body.
Removal of Colloid Particles

- We often need to separate colloidal particles from the dispersing medium.
- This may be problematic:
  - Colloidal particles are too small to be separated by physical means (e.g., filtration).
  - However, colloid particles often may be coagulated (enlarged) until they can be removed by filtration.
- Methods of coagulation:
  - Heating (colloid particles move and are attracted to one another when they collide);
  - Adding an electrolyte (neutralizes the surface charges on the colloid particles).
- A biological application of another method of separating colloidal particles from the suspending medium is dialysis.
  - In dialysis a semipermeable membrane is used to separate ions from colloidal particles.
  - In kidney dialysis, the blood is allowed to pass through a semipermeable membrane immersed in a washing solution.
  - The washing solution is isotonic in ions that must be retained.
  - The washing solution does not contain the waste products that are found in the blood.
    - Waste dialyze out of the blood (move from the blood into the washing solution).
      - The "good" ions remain in the blood.