

Chapter 13. Properties of Solutions

Lecture Outline

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.
- Intermolecular forces become rearranged in the process of making solutions with condensed phases.
- 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 (ΔH_1),
 - Separation of solvent molecules (ΔH_2), and
 - Formation of solute-solvent interactions (ΔH_3).
- We define the enthalpy change in the solution process as:
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
- ΔH_{soln} can either be positive or negative depending on the intermolecular forces.
 - To determine whether ΔH_{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.
 - ΔH_1 and ΔH_2 are both positive.
 - Forming attractive intermolecular forces is always exothermic.
 - ΔH_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:
 - MgSO_4 added to water has $\Delta H_{\text{soln}} = -91.2 \text{ kJ/mol}$.
 - NH_4NO_3 added to water has $\Delta H_{\text{soln}} = +26.4 \text{ kJ/mol}$.
 - MgSO_4 is often used in instant heat packs and NH_4NO_3 is often used in instant cold packs.
- How can we predict if a solution will form?
 - In general, solutions form if the ΔH_{soln} is negative.
 - If ΔH_{soln} is too endothermic a solution will not form.
 - “Rule of thumb”: Polar solvents dissolve polar solutes.
 - Nonpolar solvents dissolve nonpolar solutes.
 - Consider the process of mixing NaCl in gasoline.
 - Only weak interactions are possible because gasoline is nonpolar.

- These interactions do not compensate for the separation of ions from one another.
 - Result: NaCl doesn't 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 interactions 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.
- Spontaneous processes tend to be exothermic.
 - However some spontaneous processes do not involve the movement of the system to a lower energy state (e.g., an endothermic reaction).
- The amount of randomness or disorder of the system is given by its **entropy**.
 - In most cases, solution formation is favored by the increase in entropy that accompanies mixing.
 - Example: A mixture of CCl₄ and C₆H₁₄ is less ordered than the two separate liquids.
 - Therefore, they spontaneously mix even though ∞H_{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:

$$\text{Ni}(s) + 2\text{HCl}(aq) \rightarrow \text{NiCl}_2(aq) + \text{H}_2(g)$$
 - 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 NiCl₂·6H₂O remains.
 - Therefore, the dissolution of Ni in HCl is a chemical process.
 - By contrast:

$$\text{NaCl}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq).$$
 - 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 → solution
- The opposite process is **crystallization**.
 - Solution → solute + solvent
- If crystallization and dissolution are in equilibrium with undissolved solute, 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 a 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

- Intermolecular forces are an important factor in determining solubility of a solute in a solvent.
 - 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 (solute-solute, solvent-solvent, and solute-solvent).
- 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.
- Consider the solubility of alcohols in water.
 - Water and ethanol are miscible because the broken hydrogen bonds in both pure liquids are re-established 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 carbons 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 its 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 higher gas pressure, more molecules of gas are close to the surface of the solution and the probability of a gas molecule striking the surface and entering the solution is increased.
 - Therefore, the higher the pressure, the greater the solubility.
- The lower the pressure, the smaller the number molecules of gas close to the surface of the solution resulting in a lower solubility.
 - The solubility of a gas is directly proportional to the partial pressure of the gas above the solution.
 - This statement is called **Henry's law**.
 - Henry's law may be expressed mathematically as:

$$S_g = kP_g$$
 - Where S_g is the solubility of gas, P_g the partial pressure, k = 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 $P_{\text{CO}_2} > 1$ atm.
 - As the bottle is opened, P_{CO_2} decreases and the solubility of CO_2 decreases.

- Therefore, bubbles of CO₂ escape from solution.

Temperature Effects

- Experience tells us that sugar dissolves better in warm water than in cold water.
 - As temperature increases, 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 is 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:

$$\text{Mass \% of component} = \frac{\text{mass of component in soln}}{\text{total mass of solution}} \times 100$$

- Similarly, **parts per million (ppm)** can be expressed as the number of mg of solute per kilogram of solution.
 - By definition:

$$\text{Parts per million (ppm) of component} = \frac{\text{mass of component in soln}}{\text{total mass of solution}} \times 10^6$$

- If the density of the solution is 1g/ml, then 1 ppm = 1 mg solute per liter of solution.
- We can extend this again!
 - **Parts per billion (ppb)** can be expressed as the number of µg of solute per kilogram of solution.
 - By definition:

$$\text{Parts per billion (ppb) of component} = \frac{\text{mass of component in soln}}{\text{total mass of solution}} \times 10^9$$

- If the density of the solution is 1g/ml, then 1 ppb = 1 µg 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 can define **molality** (m), yet another concentration unit:

$$\text{Molality, } m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

- Molality does not vary with temperature.
- Note: converting between molarity (M) and molality (m) requires density.

13.5 Colligative Properties

- Colligative properties depend on number of solute particles.
- 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 solutes (with no measurable vapor pressure) 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_A° is the vapor pressure of the pure solvent, and X_A is the mole fraction of A, then

$$P_A = X_A P_A^\circ$$

- **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 (ΔT_b).
- The **molal boiling-point-elevation constant**, K_b , expresses how much ΔT_b changes with molality, m :

$$\Delta T_b = K_b m$$

- The boiling-point elevation is proportional to the concentration of solute particles.
 - A 1 *m* solution of NaCl is 2 *m* in total solute particles.

Freezing-Point Depression

- 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 (ΔT_f) than the pure solvent.
 - The decrease in freezing point (ΔT_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 are 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 movement of solvent in both directions across a semipermeable membrane.
 - The rate of movement of solvent from the pure solvent to the 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**, π , 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 an 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 π , relative to a more concentrated solution.
 - *Hypertonic* solutions have a higher π , relative to a more dilute solution.
- We can illustrate this with a biological system: red blood cells.
 - Red blood cells are surrounded by semipermeable membranes.
 - If red blood cells are placed in a hypertonic solution (relative to intracellular solution), there is a lower solute concentration in the cell than 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 include:
 - If a cucumber is placed in NaCl solution, it will lose water to 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 concentration 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.

13.6 Colloids

- **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 Å.
- 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 up 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 adsorb 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 hydrophobic tails and hydrophilic heads that remove dirt by stabilizing the colloid in water.
 - Most dirt stains on people and clothing are oil-based.
- Biological application of this principle:
 - The gallbladder excretes a fluid called bile.
 - Bile contains substances (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:
 - Colloid 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 include:
 - Colloid particles move more rapidly when the colloidal dispersion is heated, increasing the number of collisions. The particles stick to each other when they collide.
 - Adding an electrolyte neutralizes the surface charges on the colloid particles.
- A biological application of another approach to 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 have the waste products that are found in the blood.
 - Wastes therefore dialyze out of the blood (move from the blood into the washing solution).
 - The "good" ions remain in the blood.