Properties of Solutions

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.

The Effect of Intermolecular Forces

- 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:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- 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 ΔH_{soln} = –91.2 kJ/mol.

    - NH_4NO_3 added to water has ΔH_{soln} = + 26.4 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 (C_8H_{18}).
  - 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.

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.

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 that the Henry's law constant differs for each solute–solvent pair and differs with temperature.

- An application of Henry's law is the 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.

Soda Stream Demo

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

- Consider a *volatile* liquid in a closed container.
  - After a period of time an equilibrium will be established between the liquid and its vapor.
  - The partial pressure exerted by the vapor is 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

$$P_A = X_A P_A^o$$

- An **ideal solution** is 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 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 nature of the solute (electrolyte vs. nonelectrolyte) will impact the colligative molality of the solute.

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**.

$$\Delta T_f = K_f m$$

  - Values of K_f and K_b for most common solvents can be found in Table 13.4.

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.
    - 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.