Chapter 13

Properties of Solutions

- Many reactions do not occur until the solid reactants are dissolved to make a solution.
- A solution is a homogeneous mixture of a solvent and a solute.
- The solvent is the substance present in greater amount.

13.1 The Solution Process

- During dissolution, existing forces are broken and new forces are created.

The Solution Process

- The forces involved in solutions are the bonding and intermolecular forces discussed earlier.

Hydration

- Hydration (solvation) of cations and anions makes new forces.
- $\Delta H_{\text{solvation}}$ is the energy for the process:
  $\text{solute(g)} + \text{solvent(g)} \rightarrow \text{solvated solute particles}$

Heat of Solution

- $\Delta H_{\text{soln}}$ is the energy for the process: $\text{solute + solvent} \rightarrow \text{solution}$
- Can analyze as a three-step process.

Energy Changes and Solution Formation

- 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.

Heat of Solution

- New forces to be made: $\Delta H_{\text{solvation}}$, which increases with increasing charge and decreasing size of an ion
- Old forces to be broken: lattice energy of an ionic solute and intermolecular forces (IMF) of a liquid
- The difference is the heat of solution:
  $\Delta H_{\text{soln}} = \Delta H_{\text{solvation}} - \text{lattice energy} - \text{IMF}$

Endothermic Solution Process

- If the heat of solution has a positive value ($>0$), the solution is less stable than the separated solute and solvent.

Exothermic Solution Process

- If the heat of solution has a negative value ($<0$), the solution is more stable than the separated solute and solvent.

Solution Process

- Processes tend to occur spontaneously if they lead to a lower energy (enthalpy) or to
an increased randomness or disorder (entropy).

- Why does an exothermic solution process occur?
- Why does an endothermic solution process occur?

13.2 Saturated Solutions and Solubility

- Concentration: measure of the relative amounts of substances making up a solution
- Solute: the substance being dissolved; the substance present in lesser amount
- Solvent: the substance doing the dissolving; the substance present in greater amount
- Solubility: the maximum amount of solute in a given amount of solution

**Solubility**

- Saturated solution: an equilibrium situation in which the maximum amount of solute is dissolved in a given amount of solvent
- Unsaturated solution: less than the maximum amount of solute is dissolved
- Supersaturated solution: more than the maximum amount of solute is dissolved; an unstable state that reverts to a saturated solution if the solution is disturbed in some way

13.3 Factors Affecting Solubility

- What causes different solubilities?
- General Rule: “Like dissolves like”
- The definition of “like” involves the nature of the bonding and structure of solute and solvent: ionic or polar covalent vs. non-polar covalent
- The solution process involves making and breaking ionic bonds and/or intermolecular forces (IMF).

**Effect of Molecular Structure on Solubility**

- Non-polar liquids, like C₆H₆ (benzene) and CCl₄, dissolve readily in other non-polar liquids, but not very readily in polar liquids.
- Polar liquids, like HO-CH₂-CH₂-OH (ethylene glycol) and H₂O, dissolve readily in other polar liquids, but not very readily in non-polar liquids.
- Why is this the case? Hint: Analyze the solution process in terms of forces made and broken.

**Solubility of Gases**

- Most gases are only slightly soluble in water. Exceptions are HCl and NH₃.
- Why are these molecules unusually soluble?

**Effect of Pressure on Solubility**

- Strong effect only for gases dissolved in liquids.
- Increase in pressure of the gas above the solution increases the solubility of the gas in the solution.
- Henry’s Law: C = k P
- Why does a soft drink fizz when the container is opened?
- Why are patients with breathing difficulties placed in an oxygen tent?
Chapter 13

Effect of Temperature on Solubility

- Most, but not all, ionic solids are more soluble at higher temperatures.
- Endothermic solution process: added heat at higher temperatures helps overcome the intermolecular forces, so solubility increases with increased temperature.
- Exothermic solution process: added heat overcomes solute-solvent forces, so solubility decreases with increased temperature.
- The solubility of gases in water decreases with increasing temperature. The solubility goes to zero at the boiling point of water.
- Why does the taste of water change if it is boiled?

13.4 Ways of Expressing Concentration

- Qualitative terms relating to solubility
  - insoluble, slightly soluble, soluble, very soluble
  - <0.1 g/100g  >2 g/100 g
- Other comparative terms:
  - dilute, concentrated
  - miscible, immiscible, partially miscible
- Concentration = amount of solute/amount of solvent or solution
- Variety of units
  Most commonly used is M (molarity)

Concentration Units

- Molarity
  M = moles solute/Liter solution = mol/L
  Depends on temperature because liquid volumes change with temperature
- Molality
  m = moles solute/kilograms solvent = mol/kg
  Independent of temperature because masses do not change with temperature
- Difference between molarity and molality

13.5 Colligative Properties

- Colligative properties are those whose value depends only on the concentration of dissolved particles, not on their identity. The particles may be molecules or ions. If they are ions, the important factor is the sum of the concentrations of cations and anions.
- Examples: vapor pressure
  - boiling point
  - melting point
  - osmotic pressure

Vapor Pressure

- \( P_{\text{vap}} \) of a solution < \( P_{\text{vap}} \) of the solvent
- Evidence: solvent evaporates from a less concentrated solution and condenses into a more concentrated solution in a closed container.
• $P_{\text{vap}}$ is lowered because fewer surface positions are occupied by solvent molecules and because intermolecular forces in solutions are usually greater than those in the separated substances.

• The lowering of vapor pressure can also be seen on a phase diagram.

*Freezing Point Depression*

*Boiling Point Elevation*

• Note on phase diagram that the freezing point decreases and the boiling point increases for a solution, as a result of the lowering of the vapor pressure.

• Equations that govern these effects:

\[
\Delta T_f = i K_f m
\]

\[
\Delta T_b = i K_b m
\]

• $\Delta T$ is defined to be always positive

$m = \text{moles solute/kg solvent, independent of } T$

$i = \text{number of particles per formula unit}$

$K$ is determined by the identity of the solvent

*Applications of $\Delta T$*

• antifreeze and “antiboil”

• ice cream makers

• CaCl$_2$ on icy roads and in aqueous slurries in winter

• measure molar masses

• distinguish between electrolytes and non-electrolytes

*Osmosis*

• Solvent molecules move through a semipermeable membrane from a dilute solution to a concentrated solution; solute cannot move through the membrane.

*Osmotic Pressure*

• Equilibrium is reached when the two solutions have identical concentrations, but solvent continues to move in both directions at equal rates. The movement of solvent creates a pressure that opposes additional net movement.

• Osmotic pressure ($\pi$) follows an equation much like the ideal gas law:

\[
\pi V = n R T
\]

or

\[
\pi = M R T
\]

• $R = 0.08206 \text{ L atm/mol K}$

$M = \text{concentration of particles (molecules or ions) in mol/L}$

• Easy to measure small $\pi$, so useful for determining molar masses of large molecules like proteins and polymers.

*Applications of Osmosis*

• Why does lettuce become crispy when soaked in water?

• Why do prunes expand when soaked in water?

• Blood cells were soaked in water, 5% glucose, and 25% glucose. Identify the blood
cell that received each treatment.

13.6 Colloids
- Colloids are suspensions in which the suspended particles are larger than molecules but too small to drop out of the suspension due to gravity.
- Particle size: 10 to 2000 Å.
- There are several types of colloid:
  - 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)