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.
- $\Delta H_{solvation}$ is the energy for the process:
  solute(g) + solvent(g) → solvated solute particles

Heat of Solution

- ΔH_{soln} is the energy for the process: solute + solvent → solution
- Can analyze as a three-step process.

Energy Changes and Solution Formation

- We define the enthalpy change in the solution process as
  $$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3.$$
- ΔH_{soln} can either be positive or negative depending on the intermolecular forces.

Heat of Solution

- New forces to be made: $\Delta H_{solvation}$, 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:
  $\Delta H_{soln} = \Delta H_{solvation}$ - lattice energy – 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 C_6H_6 (benzene) and CCl_4, dissolve readily in other non-polar liquids, but not very readily in polar liquids.
- Polar liquids, like $HO\text{-}CH_2\text{-}CH_2\text{-}OH$ (ethylene glycol) and H_2O, 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 NH_3.
- 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?

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 <u>particles</u>, 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_{vap} of a solution < P_{vap} of the solvent
- Evidence: solvent evaporates from a less concentrated solution and condenses into a more concentrated solution in a closed container.

- P_{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:
  $\Delta T_f = i\ K_f\ m$
  $\Delta T_b = i\ K_b\ m$
- ΔT is defined to be always positive
  m = moles solute/kg solvent, independent of T
  i = number of particles per formula unit
  K is determined by the identity of the solvent

Applications of ΔT

- 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 (π) follows an equation much like the ideal gas law:
  $\pi V = n R T$
  or
  $\pi = M R T$
- R = 0.08206 L atm/mol K
  M = concentration of <u>particles</u> (molecules or ions) in mol/L
- Easy to measure small π, 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)