Unit 7 – Kinetics and Thermodynamics

17.1 The Flow of Energy – Heat and Work

I. Energy Transformations
- A. Temperature
  1. A measure of the average kinetic energy of the particles in a sample of matter
- B. Heat (or Heat Energy)
  1. The sum total of the kinetic energies of the particles in a sample of matter
     - a. Heat flows spontaneously from matter at higher temperature to matter at lower temperature

II. Exothermic and Endothermic processes
- A. Exothermic processes
  1. Heat is written on the product of the reaction:
  2. the system gives up heat as the surroundings heat up
- B. Endothermic processes
  1. Heat is written on the reactant side of the reaction
  2. The system gains heat as the surroundings cool

III. Units for Measuring Heat Flow
- A. Joules
  1. Heat is usually measured in joules, J

$$1 \quad J = N \cdot m = \frac{kg \cdot m^2}{s^2}$$

     - a. Heat cannot be measured directly, but is measured by temperature changes when heat is transferred
- B. Calories
  1. Heat is sometimes measured in calories
  2. A calorie is the amount of heat that will raise the temperature of one gram of water by one Celsius (or Kelvin) degree
  3. 1 calorie = 4.184 Joules

IV. Heat Capacity and Specific Heat
- A. Specific Heat
  1. The amount of heat required to raise the temperature of one gram of substance by one Celsius degree (1°C) or one Kelvin (1 K)
- B. Calculating Specific Heat
  1. Specific Heat(c_p)
  2. q = heat $\quad m$ = mass $\quad \Delta T$ = change in temperature (in Celsius or Kelvin)

$$c_p = \frac{q}{m \cdot \Delta T} \qquad q = c_p \cdot m \cdot \Delta T$$

17.2 Measuring and Expressing Enthalpy Changes

I. Calorimetry

A. Enthalpy (*H*)

1. Heat content of a substance under constant pressure
2. Enthalpy cannot be measured directly (it is NOT the same as the temperature)

B. Enthalpy Change (ΔH)

1. The amount of heat absorbed or lost by a system during a process at constant temperature

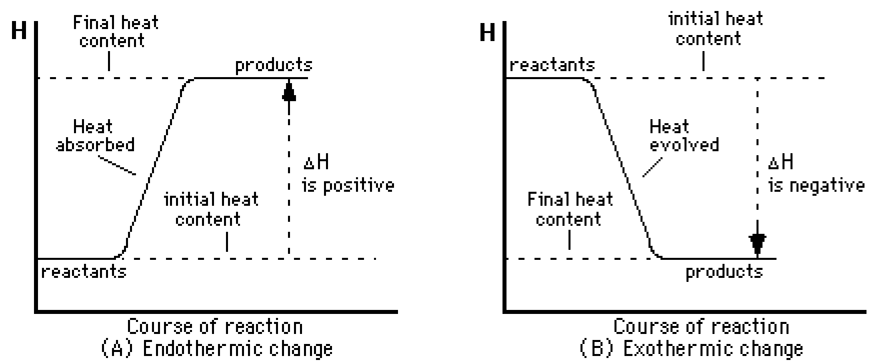
$$\Delta H = H_{products} - H_{reactants}$$

a. ΔH is positive for an endothermic rxn

(1) Heat content of products is greater than the heat content of the reactants

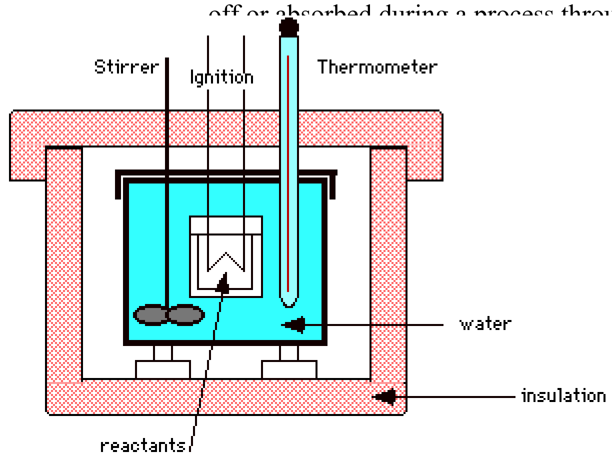
b. ΔH is negative for an exothermic rxn

(1) Heat content of the reactants is greater than the heat content of the products



C. Calorimeters

1. A calorimeter measures the heat given off or absorbed during a process through



II. Thermochemical Equations

A. Writing Thermochemical Equations

1. Fraction coefficients may be used because coefficients represent mole quantities, not atoms or molecules
2. Use appropriate state/phase symbols (*g*) (*l*) (*s*)
3. ΔH is proportional to the number of moles
4. ΔH is usually not influenced significantly by the temperature of the system

17.3 Heat in Changes of State

I. Freezing and Melting

A. Molar Heat of Fusion

1. The amount of heat energy required to melt one mole of solid at its melting point

B. Molar Heat of Solidification

2. The amount of heat energy released when one mole of a liquid freezes to a solid at its freezing point

Problem: The molar heat of fusion of water is 6.009 kJ/mol. How much energy is needed to convert 60 grams of ice at 0°C to liquid water at 0°C?

$$\frac{60\ g\ H_2O}{} \left| \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} \right| \frac{6.009\ kJ}{1\ mol} = 20.00\ kJ$$

II. Vaporization and Condensation

A. Molar Heat of Vaporization

1. The amount of heat energy required to vaporize one mole of a liquid at its boiling point

B. Molar Heat of Condensation

2. The amount of heat energy released when one mole of a vapor condenses to a liquid at its condensation point
3. Strong attractive forces between particles result in high molar heat of vaporization/condensation for water

III. Heat of Solution

A. Definition

1. Heat released or absorbed as a solute associates with the solvent during the formation of a solution

B. Molar Heat of Solution

1. Enthalpy change associated with the dissolving of one mole of a solute

Substance	**Heat of Solution (kJ/mol)**
NaOH	-44.51
NH_4NO_3	+25.69
KNO_3	+34.89
HCl	-74.84

18.1 Rates of Reaction

I. Collision Theory

A. Particles must collide while favorably oriented

B. Particles must collide with enough energy to disrupt the bonds of the molecules

C. Reaction rate

1. The rate of disappearance of reactants
2. The rate of appearance of products

D. Activated Complex

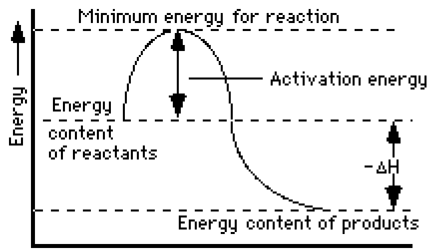
1. A transitional structure resulting from an effective collision that persists while old bonds are breaking and new bonds are forming

E. Activation Energy

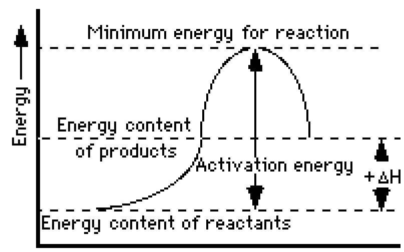
1. The minimum energy required to transform reactants into the activated complex

F. Sources of Activation Energy

1. Flame, spark, high temperature, radiation
2. Once an exothermic rxn is activated (reaches the top) the energy released by the rxn sustains the rxn by activating other molecules



Pathway of an exothermic reaction



Pathway of an endothermic reaction

II. <u>Factors Affecting Reaction Rates</u>

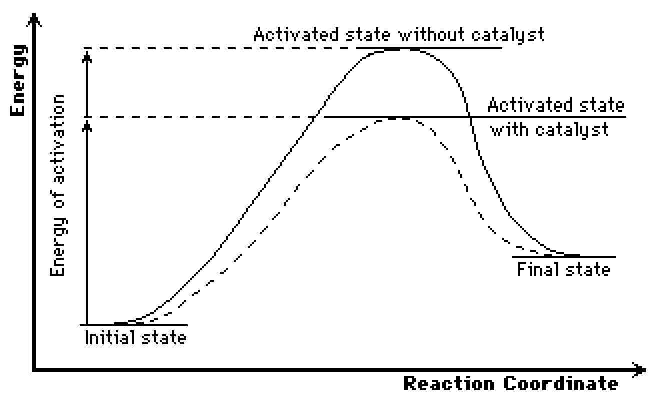
A. Nature of the Reactants
   1. Rate depends on the particular bonds involved

B. Amount of Surface (particle size)
   1. The more surface area of a solid exposed, the faster the rxn

C. Temperature
   1. Rates of rxns are roughly doubled for every 10 °C increase in temperature
      a. increase in collision energy
      b. increase in collision frequency

D. Effect of Concentration
   1. Increasing concentrations of liquid or gaseous solutions <u>usually</u> increases rates of rxns
   2. Actual effect of concentration change must be determined experimentally for each rxn

E. Presence of Catalysts
   1. A catalyst is a substance of substances that increase the rate of a chemical rxn without itself being changed
   2. Catalysts provide an alternate reaction mechanism or pathway with a lower activation energy



18.2 Reversible Reactions and Equilibrium

I. <u>Reversible Reactions</u>

A. Reversible Reactions
   1. A chemical reaction in which the products can react to re-form the reactants

B. Chemical Equilibrium
   1. When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged

$$2HgO(s) \leftrightarrows 2Hg(l) + O_2(g)$$

   2. Arrows going both directions indicates equilibrium in a chemical equation

II. Factors Affecting Equilibrium: Le Chatelier's Principle

A. Le Chatelier's Principle

1. When a closed system <u>at equilibrium</u> is disturbed by application of a stress, it attains a new equilibrium position that minimizes the stress

B. Equilibrium and System Stresses – Predicting the direction of shift

1. Pressure

a. An increase in pressure will cause the reaction to shift in the direction that results in fewer collisions – toward the side of the reaction with the least number of moles of gas molecules

$$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$$
$$\longrightarrow$$

An increase in pressure causes the equilibrium position to shift to the right, where there are only two moles of gas. The left side has four moles of gas

b. Decreases in pressure cause the reaction to shift in the direction that increases collisions; toward the side with more moles of gas

$$N_2O_4(g) \leftrightarrows 2NO_2(g)$$
$$\longrightarrow$$

A decrease in pressure causes the equilibrium position to shift to the right, because there are more moles of gas (2 moles) than on the left (1 mole)

c. Pressure has no effect on equilibrium if there are no gas phase reactants or products

2. Temperature

a. Increasing temperature causes the reaction to shift in a way so as to use up the added energy (away from the side that has energy)

Endothermic reaction

$$X + Y + \text{Energy} \leftrightarrows Z$$
$$\longrightarrow$$

Exothermic reaction

$$A + B \leftrightarrows C + D + \text{Energy}$$
$$\longleftarrow$$

b. Decreasing temperature causes the reaction to shift in a way so as to replace the missing energy (toward the side that has energy)

3. Concentration

a. Increasing the concentration of a reactant or product causes the reaction to shift in such a way as to try to use up the added substance (away from that substance)

Result of increasing [X] or [Y]

$$X + Y + \text{Energy} \leftrightarrows Z$$
$$\longrightarrow$$

The reaction shifts away from [X] and [Y] and produces more [Z]

b. Decreasing the concentration of a reactant or product causes the reaction to shift in such a way as to try to replace the missing substance (toward that substance)

Result of decreasing [X] or [Y]

$$X + Y + \text{Energy} \leftrightarrows Z$$
$$\longleftarrow$$

The reaction shifts toward [X] and [Y] and produces more [X] and [Y]

18.4 Entropy and Free Energy

A. Enthalpy and Reaction Tendency
  1. Tendency for processes to occur that lead to the lowest possible energy state
  2. Most spontaneous reactions have a negative value for ΔH

B. Entropy (S)
  1. Entropy is a measure of the degree of randomness of the particles, such as molecules in a system

increasing entropy →

H_2O (s) H_2O (l) H_2O (g)

C. Entropy and Reaction Tendency
  1. There is a tendency for the disorder of the system to increase

D. Free Energy (G)
  1. Combined enthalpy-entropy function that helps to determine the spontaneity of a reaction

E. Free Energy Change (ΔG)
  1. A rxn system proceeds spontaneously in the way that lowers its free energy ($-\Delta G$)

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

Note: $T\Delta S$ means higher temp = higher entropy

  a. the more negative ΔH^0, the more negative is ΔG^0
  b. the more positive ΔS^0, the more negative is ΔG^0

  2. Predicting spontaneity
    a. ΔH^0 negative, ΔS^0 positive
      (1) rxn is spontaneous
    b. ΔH^0 positive, ΔS^0 negative
      (1) rxn is not spontaneous
    c. ΔH^0 negative, ΔS^0 negative
      (1) do the math
    d. ΔH^0 positive, ΔS^0 positive
      (1) do the math

18.5 The Progress of Chemical Reactions

I. <u>Rate Laws</u>

A. Rate Law
  1. An equation that relates reaction rate and concentrations of reactants

B. Determining Effect of Concentration
  1. Vary concentration of one reactant
  2. Keep other concentrations and temperature constant

C. General Form of the Rate Law
  1. $R = k[A]^n[B]^m$
    a. R = rate of the rxn
    b. [A] and [B] represent molar concentrations of reactants
    c. *n* and *m* are exponents determined experimentally

II. <u>Reaction Mechanisms</u>

A. Reaction Mechanism
  1. The step-by-step sequence of reactions by which the overall chemical change occurs
  2. Reactions proceed by a series of simple steps called the reaction pathway

B. Intermediates
  1. Species that appear in some steps but not in the net equation

C. Homogeneous Reaction
  1. A reaction whose reactants and products exist in the same phase