# Chapter 17 - Reaction Energy and Reaction Kinetics

17-1 Thermochemistry
Thermochemistry - The study of the changes in heat energy that accompany chemical reactions and physical changes

I.   Heat and Temperature
    A. Calorimeter
        1. Heat given off or absorbed is determined from the temperature of a known mass of water
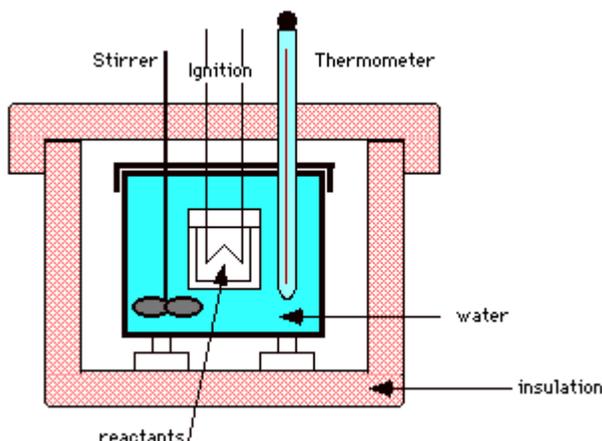
    B. Temperature
        1. A measure of the average kinetic energy of the particles in a sample of matter
    C. Heat (or Heat Energy)
        1. The sum total of the kinetic energies of the particles in a sample of matter
            a. Heat flows spontaneously from matter at higher temperature to matter at lower temperature
        2. Heat is usually measured in joules, J

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

            a. Heat cannot be measured directly, but is measured by temperature changes when heat is transferred

II.   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)

Heat lost or gained with a change
In temperature

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

q = heat m = mass

III. <u>Heat of Reaction</u>
  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. Heat of Reaction
    1. Quantity of heat released or absorbed during a chemical rxn
  C. Thermochemical Equation
    1. An equation that includes the quantity of heat released or absorbed during the reaction as written
$$2H_2(g) \ + \ O_2(g) \ \rightarrow \ 2H_2O(g) \ + \ 483.6 \ kJ$$
  D. 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
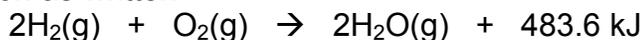
(A) Endothermic change   (B) Exothermic change
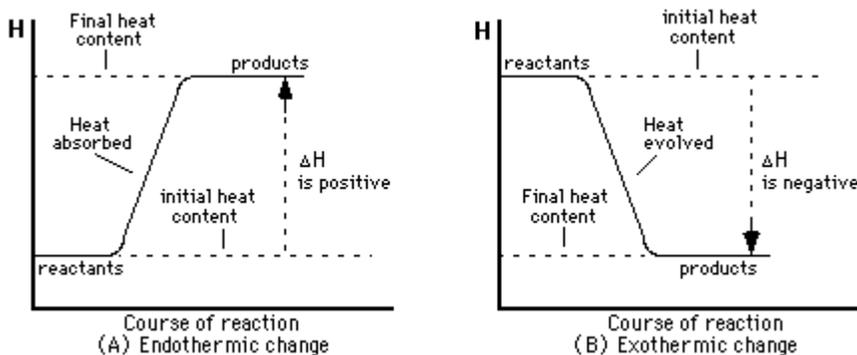
  E. Writing Thermochemical Equations
    1. Fraction coefficients may be used because coefficients represent mole quantities, not atoms or molecules
    2. Use appropriate state/phase symbols (g) (l) (s)
    3. ΔH is proportional to the number of moles
    4. ΔH is usually not influenced significantly by the temperature of the system

IV. <u>Heat of Formation</u>
  A. Molar Heat of Formation ($\triangle H_f$)
    1. The heat of rxn released or absorbed when one mole of a compound is formed from its elements
      a. $\triangle H_f$ of an element in its standard state is zero
      b. Only a few compounds have positive heats of formation
      (See table 20-1 for Heat of Formation data)
    2. Heat of Formation is defined in terms of one mole of <u>product</u>

V.   Stability and Heat of Formation
      A. Stable Compounds
               1. High negative $\triangle H_f^0$
               2. Rxns are usually spontaneous and vigorous
      B. Unstable Compounds
               1. Small positive $\triangle H_f^0$ will decompose slowly at room temperature
               2. Low negative $\triangle H_f^0$ will decompose when heated mildly
      C. Very Unstable Compounds
               1. High positive $\triangle H_f^0$, reacts or decomposes explosively

VI.   The Heat of Combustion
      A. Heat of Combustion
               1. The heat of rxn released by the complete combustion of one mole of a
                   substance
               2. Heat of combustion is defined in terms of one mole of <u>reactant</u>

VII. Calculating Heats of Reaction
      A. Hess's Law
               1. The overall enthalpy change in a reaction is equal to the sum of the
                   enthalpy changes for the individual steps in the process

17-2 Driving Forces of Reactions
      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 $\triangle H$
      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)
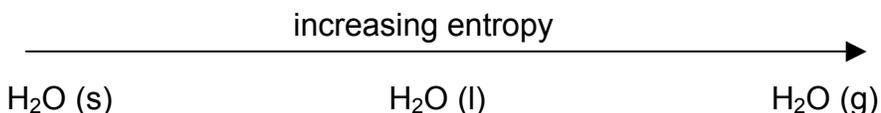
      C. Entropy and Reaction Tendency
               1. There is a tendency for the disorder of the system to increase
      D. Free Energy (G)
               1. Combined enthalpy-entropy function that helps to determine the spontaneity
                   of a reaction
      E. Free Energy Change ($\triangle G$)
               1. A rxn system proceeds spontaneously in the way that lowers its free energy
                   ($-\triangle G$)

$$\triangle G^0 \;=\; \triangle H^0 - T \triangle S^0$$

                   Note: T$\triangle$S means higher temp = higher entropy
                   a. the more negative $\triangle H^0$, the more negative is $\triangle G^0$
                   b. the more positive $\triangle S^0$, the more negative is $\triangle G^0$

2. Predicting spontaneity
   a. $\triangle H^0$ negative, $\triangle S^0$ positive
     (1) rxn is spontaneous
   b. $\triangle H^0$ positive, $\triangle S^0$ negative
     (1) rxn is not spontaneous
   c. $\triangle H^0$ negative, $\triangle S^0$ negative
     (1) do the math
   d. $\triangle H^0$ positive, $\triangle S^0$ positive
   (1) do the math

17-3 The Reaction Process

I.   Reaction Mechanisms
   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

II.   The Two Principals of Collision Theory
   A. Particles must collide while favorably oriented
   B. Particles must collide with enough energy to disrupt the bonds of the molecules

III.   Activation Energy and the Activated Complex
   A. Activated Complex
     1. A transitional structure resulting from an effective collision that persists while old bonds are breaking and new bonds are forming
   B. Activation Energy
     1. The minimum energy required to transform reactants into the activated complex
   C. 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
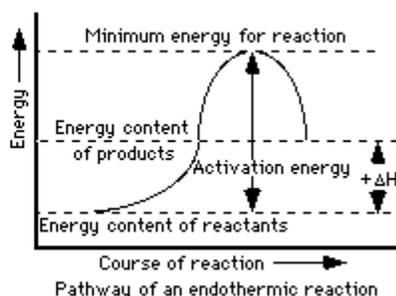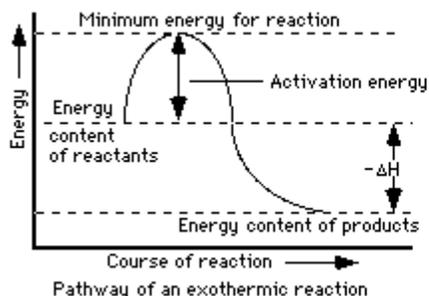
17-4 Reaction Rate
I.   <u>Rate Influencing Factors</u>
    A. Nature of the Reactants
         1. Rate depends on the particular bonds involved
    B. Amount of Surface
         1. The more surface area of a solid exposed, the faster the rxn
    C. Temperature
         1. Rates of rxns are roughly doubled 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
             a. Homogeneous catalyst
                 (1) Catalyst is in the same phase as the reactants
             b. Heterogeneous catalyst
                 (1) Catalyst in different phase from reactants
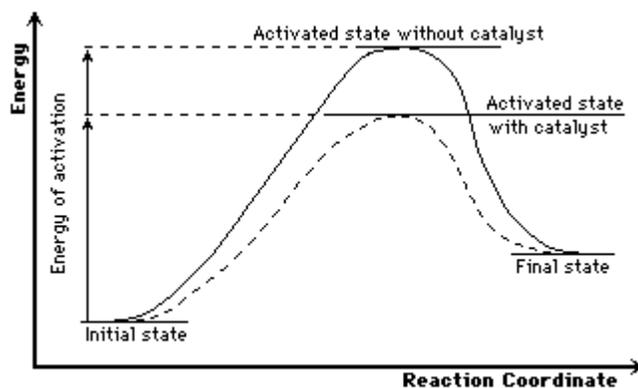
         2. Catalysts provide an alternate reaction mechanism or pathway with a lower activation energy

II.   <u>Rate Laws for Reactions</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. Single Step Reactions
        1. A + B $\rightarrow$ 2C
            a. R = k[A][B]
                (1) exponent = coefficient
        2. 2C $\rightarrow$ A + B
            a. R = $K[C]^2$
    D. Rxns Involving Several Steps
        1. Rate law is that for the slowest step (Rate-determining step)
        2. Rate law cannot be written from the equation for the net rxn
    E. 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