Chapter 12 - Chemical Kinetics

12.1 Reaction Rates
    A. Chemical kinetics
         1. Study of the speed with which reactants are converted to products
    B. Reaction Rate
   1. The change in concentration of a reactant or product per unit of time

$$Rate = \frac{concentration \; of \; A \; at \; time \; t_2 - concentration \; of \; A \; at \; time \; t_1}{t_2 - t_1} = \frac{\Delta[A]}{\Delta t}$$

            a. Rates decrease with time
            b. It is customary to express reaction rates as positive values
            c. Instantaneous rate can be determined by finding the slope of a line
               tangent to a point representing a particular time
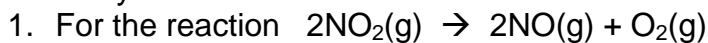   C. Decomposition of NO_2
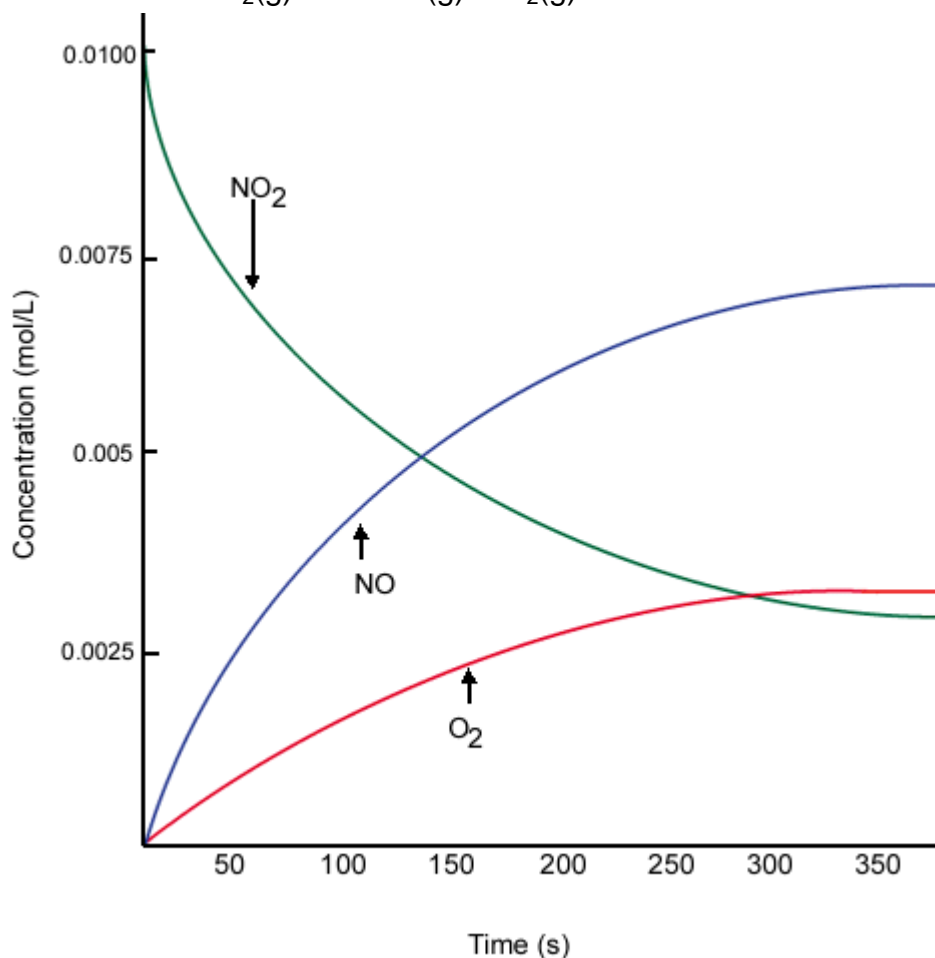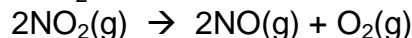
$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Rate of consumption of NO_2 = rate of production of NO = 2(rate of production of O_2)

$$-\frac{\Delta[NO_2]}{\Delta t} \qquad = \qquad \frac{\Delta[NO]}{\Delta t} \qquad = \qquad 2\left(\frac{\Delta[O_2]}{\Delta t}\right)$$

12.2 Rate Laws: An Introduction
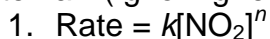   A. Reversibility of reactions
        1. For the reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$
            The reverse reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ may also take place

        2. The reverse reaction effects the rate of change in concentrations
            a. $\Delta[A]$ depends on the difference in the rates of the forward and reverse
                reactions
    B. Rate Law (Ignoring reverse reaction)
        1. Rate = $k[NO_2]^n$
            a. k is a proportionality constant called the rate constant
                n is the order of the reactant (an integer, including zero, or a fraction)
                (1) k and n must be determined experimentally
        2. Concentrations of products do not appear in the rate law
    C. Types of Rate Laws
        1. Differential Rate Law (Rate Law)
            a. Expresses how the rate of a reaction depends upon concentration
                                Rate = $k[NO_2]^n$
        2. Integrated Rate Law
            a. Expresses how the concentration of a species (reactant or product) in
                a reaction depend on time

$$-\frac{\Delta[NO_2]}{\Delta t} \quad = \quad \frac{\Delta[NO]}{\Delta t} \quad = \quad 2\left(\frac{\Delta[O_2]}{\Delta t}\right)$$

        3. Choice of rate law depends on what data is easiest to collect

***Why study rate law? Re-read the paragraph at the bottom of page 556.

12.3 Determining the Form of the Rate Law
    A. Determining the value of n (Order of the reactant)
        1. Example

[A]	Rate (mol/L·s)
1.00 M	8.4 x 10^{-3}
0.50 M	2.1 x 10^{-3}

            a. Doubling the concentration of species A quadruples the rate of the
                reaction. Therefore, the reaction is of second order with respect to A
                                Rate = $k[A]^2$
    B. Method of Initial Rates
        1. Initial rate
            a. Instantaneous rate just after $t = 0$
        2. Experimental method
            a. Vary initial concentration of reactant(s)
            b. Determine initial rate for each concentration
            c. Examine relationship between rate and initial concentration

3. Example:

Table 12-4	Intial Rates from Three Experiments for the Reaction: $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$		
Experiment	Initial Concentration Of NH_4^+	Initial Concentration Of NO_2^-	Initial rate (mol/L·s)
1	0.100 M	0.0050 M	1.35 x 10^{-7}
2	0.100 M	0.010 M	2.70 x 10^{-7}
3	0.200 M	0.010 M	5.40 x 10^{-7}

    a. In experiment 1 and 2, the concentration of NH_4^+ is held constant
    b. In experiment 2 and 3, the concentration of NO_2^- is held constant
    c. Basic rate law for the reaction:
$$Rate = k[NH_4^+]^n[NO_2^-]^m$$
4. Calculations
    a. Experiment 1 and 2
        (1) Rate doubles when concentration of NO_2^- doubles
        (2) $m = 1$ (first order)
    b. Experiment 2 and 3
        (1) Rate doubles when concentration of NH_4^+ doubles
        (2) $n = 1$ (first order)
5. Overall reaction order
    a. Overall reaction order is the sum of m and n
        (1) $m + n = 2$ so overall the reaction is second order
$$Rate = k[NH_4^+][NO_2^-]$$
6. Calculate k, the rate constant
    a. Rate is known
    b. Both concentrations are known
    c. Exponents are known
        1.35 x 10^{-7} mol/L·s $= k(0.100\ M)(0.0050\ M)$

$$k = \frac{1.35 \times 10^{-7}\ \text{mol/L·s}}{(0.100\ M)(0.0050\ M)}$$

12.4 The Integrated Rate Law
    A. Integrated First-Order Rate Law (single reactant)
        1. $\ln[A] = -kt + \ln[A]_0$ or $\ln\left(\frac{[A]_0}{[A]}\right) = kt$
            a. $[A]$ is concentration of reactant A at time $= t$
            b. $[A]_0$ is concentration of reactant A at $t = 0$
            c. Equation is linear ($y = mx + b$)
        2. Half-life of a First-Order Reaction
            a. Half life of a reaction is the time required for a reactant to reach half its original concentration

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt \rightarrow [A] = \frac{[A]_0}{2} \rightarrow \ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2} \rightarrow \ln(2) = kt_{1/2} \rightarrow t_{1/2} = \frac{\ln(2)}{k}$$

B. Integrated Second-Order Rate Law (single reactant)

    1. $\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$

        a. Graph of 1/[A] versus t is a straight line with slope k

    2. Half-life of a Second-Order Reaction (derivation on page 567)

        a. $t_{1/2} = \dfrac{1}{k[A]_0}$

        b. For a second-order reaction each successive half-life is double the preceding one

C. Zero Order reactions

    1. Rate is constant; it does not change with changing concentration

    2. Zero order sometimes happens with catalysis

    3. Integrated rate law for zero-order reactions

        a. $[A] = -kt + [A]_0$

    4. Half-life of a zero-order reaction

        a. $t_{1/2} = \dfrac{[A]_0}{2k}$

D. Integrated Rate Laws for Reactions with More than One Reactant

    1. Examine rate with one reactant in very low concentration and the others much higher

$$\text{Rate} = k[A]^n[B]^m[C]^p$$

        a. If [B]> >[A] and [C] > >[A] then [B] and [C] do not change as greatly relative to [A] so…

$$\text{Rate} = k'[A]^n$$

    2. Pseudo-first-order rate law (or zero-order , or second-order)

        a. Simplification yields a rate law of a particular order

12.5 Reaction Mechanisms

A. Reaction Mechanism

    1. A series of elementary steps that must satisfy two requirements

        a. The sum of the elementary steps must give the overall balanced equation for the reaction

        b. The mechanism must agree with the experimentally determined rate law

B. Intermediates

    1. A species that is neither a reactant nor a product, but that is formed and consumed during a chemical reaction

C. Elementary steps

    1. Reactions whose rate law can be written from their molecularity (balanced eqn for the step)

D. Molecularity
  1. The number of species that must collide to produce the reaction indicated by that step
       a. Unimolecular step - a reaction involving one molecule
       b. Bimolecular step - reaction involving the collisions of two species
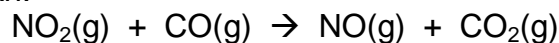   c. Termolecular step - reaction involving the collisions of three species

Table 12.7 Examples of Elementary Steps		
Elementary Step	*Molecularity*	*Rate Law*
A → products	Unimolecular	Rate = k[A]
A + A → products (2A → products)	Bimolecular	Rate = k[A]^2
A + B → products	Bimolecular	Rate = k[A][B]
A + A + B → products (2A + B → products)	Termolecular	Rate = k[A]^2[B]
A + B + C → products	Termolecular	Rate = k[A][B][C]

E. Rate-Determining Step
  1. The slowest step in a reaction determines the rate of the reaction
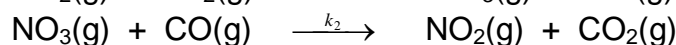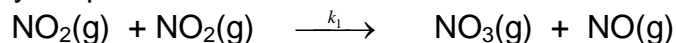F. Example
  1. Overall rxn:
           NO_2(g) + CO(g) → NO(g) + CO_2(g)
  2. Rate law determined experimentally:
           Rate = k[NO_2]^2
  3. Elementary Steps
           NO_2(g) + NO_2(g) $\xrightarrow{k_1}$ NO_3(g) + NO(g)
           NO_3(g) + CO(g) $\xrightarrow{k_2}$ NO_2(g) + CO_2(g)
  4. Which step is rate determining?
       a. IF step 1,   Rate = k[NO_2]^2
            (1) this agrees with experimental results
       b. IF step 2,   Rate = k[NO_3][CO]
            (1) this does not agree with experimental results

12.6 A Model for Chemical Kinetics
  A. Collision Model
     1. Molecules must collide in order to react
        a. They must collide with sufficient energy
        b. They must collide with correct orientation
  B. Activation Energy (E_a)
     1. The energy required to convert atoms or molecules into the activated complex (transition state)
     2. The minimum energy required for an effective collision
  C. The Arrhenius Equation
     1. Form #1: $k = zpe^{-E_a/RT}$
        a. *z* is collision frequency
        b. *p* is the stearic factor representing the fraction of collisions with correct orientation

2. Form #2: $k = Ae^{-E_a/RT}$
   a. z and p are combined to make A, the frequency factor (frequency of effective collisions)
3. Taking the natural log of both sides:
$$\ln(k) = \ln(Ae^{-E_a/RT})$$

$$\ln(k) = \ln(A) + \ln(e^{-E_a/RT})$$

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

   a. Linear equation
      $y = \ln(k)$ slope $= -E_a/R$ $x = 1/T$ intercept $= \ln(A)$

12.7 Catalysis
   A. Catalysts
      1. A substance that speeds up a reaction without being consumed itself
   B. Effects of Catalysis
      1. Catalysts lower activation energy but do not change ΔE for the reaction
      2. Catalysts provide alternate reaction pathways
      3. Catalysis results in a higher percentage of effective collisions
   C. Heterogeneous Catalysis (usually gaseous reactants on a solid surface)
      1. Four steps
         a. Adsorption and activation of the reactants
   (1) Adsorption refers to the collection of one substance on the surface of another substance
         b. Migration of the adsorbed reactants on the surface
         c. Reaction of the adsorbed substances
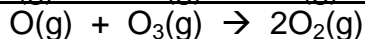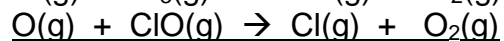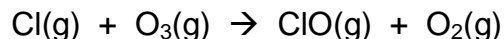   d. Escape, or desorption, of the products
      2. Uses
         a. Conversion of alkenes to alkanes
         b. Conversion of CO and NO in auto exhaust to CO_2 and N_2
   D. Homogeneous Catalysis
      1. Reactants and catalysts are in the same phase
      2. Example - The decomposition of ozone
         a. Freon, $CCl_2F_2(g) \xrightarrow{light} CClF_2(g) + Cl(g)$
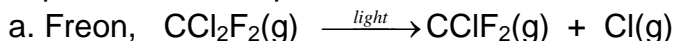
         b. Chlorine catalyzes the decomposition of ozone

            $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$
            $\underline{O(g) + ClO(g) \rightarrow Cl(g) + O_2(g)}$
            $O(g) + O_3(g) \rightarrow 2O_2(g)$

         c. Notice that the Cl(g) is not used up, a qualification for it to be catalytic. This is also why small amounts of chlorofluorocarbons such as freon can do immense damage to the ozone layer