Chemical Kinetics II

Reading: Moore chapter 13, sections 13.4-13.8
Questions for Review and Thought: 45, 54, 56, 60, 62, 63, 65, 67, 69, 71, 75, 80.

Key Concepts and skills:

- definitions of molecularity, elementary step, reaction mechanism, intermediate, transition state, rate-determining step. Review how to derive rate laws given a mechanism in which the first step is rate-determining, the second (or subsequent) step is rate-determining, or if all steps proceed at comparable rates (use the steady-state approximation).
- Review the calculation of Activation energies and rate constants from the Arrhenius law.
- Review the types of catalysts and their effects on the kinetics & thermodynamics of chemical reactions

Lecture Topics:

I. Reaction Mechanisms

1. Chemical reactions occur by a series of simple steps, each of which is called an **elementary step**.
2. The sequence of elementary steps is called the **reaction mechanism**
3. The sum of all of the elementary steps that comprise the mechanism is equal to the overall balanced chemical equation for the reaction

II. Elementary steps

The **molecularity** of an elementary step is the number of reactant particles (molecules, atoms, ions, etc.) that combine to form the products of an elementary step.

Examples

Unimolecular
$CH_3CH_2I(g) \rightarrow CH_2CH_2(g) + HI(g)$
Rate = k $[CH_3CH_2I]$

$O_2(g) \rightarrow 2O(g)$
Rate = $k[O_2]$

Bimolecular
$O(g) + O_3(g) \rightarrow 2\,O_2(g)$
Rate=$k[O][O_3]$

$CH_3Br(aq) + I^-(aq) \rightarrow CH_3I(aq) + Br^-(aq)$
Rate = k $[CH_3Br]\,[I^-]$

Termolecular (rare)
$2NO + O_2 \rightarrow 2NO_2$
Rate = k $[NO]^2[O_2]$

Most Reaction mechanisms involve a sequence of unimolecular or bimolecular reactions!

Reaction Mechanisms, continued

•Many reactions have a single slow step, although a reaction may have more than one slow step.
•The rate of an overall reaction is determined by the rate of the slowest step, also known as the **rate-determining step**
•The rate law for the overall reaction is NOT influenced by elementary steps that occur AFTER the rate-determining step, but is influenced by steps preceding the rate-determining step

__Case #1__ The slow step is the first step. The rate law can easily be written by inspecting the species involved in the first step.
Note: **intermediates** should never show up in the rate law! The concentration of intermediates usually remain low throughout the reaction and their concentration cannot be varied or manipulated at will.
Note: If the proposed mechanism fits the experimentally observed rate law, **this does not constitute a proof of the accuracy of the mechanism.** Detection of a proposed intermediate species may lend strong support to a given mechanism, however.

__Case#2__ The rate-determining step occurs after one or more fast equilibrium steps. This case is usually signaled by reaction order greater than 2, by fractional reaction orders, or negative reaction orders.
__**For the equilibrium step**__: assume that the forward and reverse reactions are occurring at the same rate; express the concentration of the intermediate in terms of the concentrations of starting materials and/or products, and substitute into the rate law derived from the slow step.
Thus,
Overall: $2A + B \rightarrow 2D$
1st: $A + A \Leftrightarrow C$ fast rate forward=rate reverse $=k_1[A]^2=k_{-1}[C]$
2nd $C + B \rightarrow 2D$ slow rate $= k_2[C][B]$
since $[C] = k_1[A]^2/k_{-1}$, the overall rate expression is rate $= k_2k_1[A]^2[B]/k_{-1}$
or simply, rate $= k_{obs}[A]^2[B]$

__Case #3__ All steps in the mechanism proceed at a comparable speed; no single step is rate determining. Use the **steady state approximation,** in which you assume that the __change__ in concentration of a reactive intermediate is zero.
Thus,
Overall: $2A \rightarrow 2C + D$
1st $A \Leftrightarrow B + C$ assume $d[B]/dt = 0$
2nd $A + B \rightarrow C + D$
Thus, rate of formation of [B] = rate of consumption of [B]
And $k_1[A] = k_{-1}[B][C] + k_2[A][B]$; rearranging, $[B] = k_1[A]/(k_{-1}[C] + k_2[A])$
For simplicity, we express the rate of formation of D:
Rate $= d[D]/dt = k_2[A][B]$; substituting for [B] leaves :
rate $= k_2k_1[A]^2/ (k_{-1}[C]+ k_2[A])$

note that, at low [A], the reaction is second order in A
at high [A], the reaction is first order in A
at low [C] the reaction is zero order in C
at high [C], the reaction is –1 order in C,
Thus, you can experimentally test if this mechanism is a valid one!

III. Effect of Temperature on Reaction rate

A **transition state** is a transient configuration of reactant particles at the top of the potential energy surface, intermediate in structure between reactants and products (or intermediates)

1. Temperature affects the distribution of kinetic energies for the reactant molecules
2. As temperature increases, the fraction of molecules with $KE=E_a$ increases
3. Activation energy E_z is the minimum energy needed by molecules to react to form products. Activation energy is **always** positive
4. The frequency of collisions by atoms or molecules increases as the temperature rises.
5. Rates of overall reactions consisting of more than one elementary step can become slower or faster at higher T's.

Arrhenius equation:
$\mathbf{k= Ae^{-Ea/RT}}$
where T is in Kelvin, R is the gas constant, A is a pre-exponential factor with units of k, and k is the reaction rate constant.
Graphically : $\ln k = -Ea/RT + \ln A$ (straight line with slope= E_a and intercept=ln A)
For the same reaction @ two different temperatures:
$\mathbf{\ln(k_1/k_2) = -E_a/R\ (1/T_1 - 1/T_2)}$
Remember, $E_{a,f}$ = E(activated complex)-E(reactants)>0
And $E_{a,r}$ = E (activated complex)-E(products)>0 and $\Delta H_{rxn}= E_{a,f}-E_{a,r}$

IV. Kinetic and Thermodynamic Properties of Catalysts

Catalysts:
1. act by providing an alternate reaction pathway with a lower E_a
2. increase the rate of a reaction by the reaction pathway of lower E_a
3. can be recovered at the end of a reaction
4. does not alter the position of equilibrium of a reaction.
5. for equilibrium reactions, accelerates the forward and reverse reactions to same extent; thus, the position of the equilibrium is not disturbed.
6. does not affect ΔH_{rxn}
7. Can do nothing for a reaction that could not proceed thermodynamically
8. Can show up in the rate law, but not in the overall chemical equation!

Homogenous Catalysis – reactions occur entirely in one phase

Heterogenous Catalysis – reactions occur at the interface between two phases

Problem Set #2

1. Phosgene gas can be produced by the reaction
   $CO(g) + Cl_2\ (g) \rightarrow COCl_2$
   The rate law for the reaction is found to be rate=k $[Cl_2]^{3/2}[CO]$
   A postulated mechanism is:

   Step1 $\quad Cl_2 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} 2Cl$

   Step 2 $\quad Cl + CO \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} COCl$

   Step 3 $\quad COCl + Cl_2 \overset{k_3}{\rightarrow} COCl_2 + Cl$

   (a) if this mechanism is correct, which step is rate-determining?
   (b) Using the response to (a), determine the value of rate constant k in terms of the individual k's (k_1, k_{-1}, k_2,…etc)

2. A key step in the formation of sulfuric acid from dissolved SO_2 in acid precipitation is the oxidation of hydrogen sufilte ion by hydrogen peroxide:

   $HSO_3^-(aq) + H_2O_2\ (aq) \rightarrow HSO_4^-\ (aq) + H_2O\ (l)$

   The mechanism involves the species SO_2OOH^-:

   $HSO_3^-\ (aq) + H_2O_2\ (aq) \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} SO_2OOH^-\ (aq) + H_2O\ (l)$

   $SO_2OOH^-(aq) + H_3O^+(aq) \overset{k_2}{\rightarrow} HSO_4^-\ (aq) + H_3O^+(aq)$

   By making a steady-state approximation for the reactive intermediate concentration, $[SO_2OOH^-(aq)]$, express the rate of formation of HSO_4^- (aq) in terms of the concentrations of HSO_3^- (aq), H_2O_2 (aq), and H_3O^+(aq)

3. The rate constant for a reaction at 40°C is exactly 3.00 times the rate constant at 20°C. Calculate the Arrhenius energy of activation for the reaction assuming a temperature-independent pre-exponential factor A.

4. The reaction
   $A \rightarrow B + C$
   Is second order in A. When $[A]_o$=0.100M, the reaction is 20% complete in 40 minutes
   (a) Calculate the value of the rate constant (in L/min mol)
   (b) Calculate the half-life of the reaction