Physical Chemistry

Lecture 7
Special steps; chain reactions; surface and enzyme kinetics

Photochemical and sensitized steps

- Light is sometimes used to activate processes
  - $\phi = \text{quantum yield}$
- Some added materials produce reactive species by reaction

\[ Na + Cl_2 \rightarrow NaCl + Cl \cdot \]

Unimolecular reactions: Lindemann’s mechanism

- “Simple” reactions are more complex than they seem
- Frederick Lindemann proposed intervention of a mediator to produce a highly reactive intermediate in unimolecular reactions

\[ A + M \rightarrow A'M + A' \]

Variations and refinements of Lindemann’s mechanism

- Hinshelwood
  - Explicit energy dependence of the rate constant
- Rice and Ramsperger, and independently Kasel developed a theory (RRK theory)
  - Explicit account of molecular vibrational state
- Marcus
  - Refined RRK theory in a number of ways
- Modern version is called RRKM theory
  - Predicts functional dependence of unimolecular reaction rates well

Chain reactions

- Many reactions have multiple steps in the mechanism
- Chain reactions, once started, continue
  - Polymerization
  - Some photochemical reactions
- Classes of steps
  - Initiation - produce reactive species
  - Propagation - remove and produce reactive species
  - Termination - remove reactive species

Initiation steps

- Photochemical steps

\[ Cl_2 \rightarrow \text{hv} \rightarrow 2 Cl \cdot \]

- Thermal steps

\[ H_2 \rightarrow 2 H \cdot \]

- Sensitized steps

\[ Na + Cl_2 \rightarrow NaCl + Cl \cdot \]
Propagation steps
- Steps that use and create reactive species
- Examples:

\[ \text{Br} + H_2 \rightarrow HBr + H \cdot \]

\[ H + Cl_2 \rightarrow HCl + Cl \cdot \]

Termination steps
- Steps that remove reactive species
- Stable-product formation
  \[ 2 \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_6 \]
- Wall deactivation
  \[ R \cdot + \text{wall} \rightarrow \text{stable wall complex} \]
- Stable-radical formation; scavenging
  \[ R \cdot + NO \rightarrow RNO \]

Vinyl polymers
- "Simple" chain reaction
  \[ n \text{(monomer)} \rightarrow \text{polymer} \]

- Sidechain, X
  - H, Poly(ethylene)
  - Cl, Poly(propylene)
  - Poly(vinyl chloride)
  - Poly(styrene)

Vinyl polymerization
- Chain reaction
- Generally initiated with some radical
  - Deliberately added
  - Photochemically induced

\[ \begin{align*}
  \text{In} & \rightarrow R \\
  R \cdot + M & \rightarrow RM \\
  \vdots & \\
  RM_{n-1} \cdot + M & \rightarrow RM_n \\
  RM \cdot + RM \cdot & \rightarrow RM_{n+1} \\
  \end{align*} \]

Mathematics of vinyl polymerization
- Approximation at steady state
  - Rate of initiation is equal to rate of termination
- Radical-combination termination
  \[ v_p = k \cdot \left[ \frac{k_f}{k_r} \cdot [M][ln]\right]^{1/2} \]
- Other possible termination steps
  - Disproportionation
  - Chain transfer

Reactions at surfaces
- Very often reaction happens at "special" sites
  - Enzyme action
  - Heterogeneous catalysis
- Simple surface reaction scheme

\[ \begin{align*}
  A \text{(gas)} & \rightarrow A \text{(adsorbed)} \\
  A \text{(adsorbed)} & \rightarrow A \text{(gas)} \\
  A \text{(adsorbed)} & \rightarrow P \text{(adsorbed)} \\
  P \text{(adsorbed)} & \rightarrow P \text{(gas)} \\
  \end{align*} \]
**Langmuir isotherms**
- Assume equilibrium between gas-phase A and adsorbed A
- Langmuir isotherm gives relation between gas and surface concentrations
  \[
  [A_{\text{ads}}] = [A_{\text{sat}}] \frac{b_P}{1 + b_P a} 
  \]
- Generalize for multiple materials adsorbed, as in a chemical reaction
  \[
  [A_{\text{ads}}] = S_0 \frac{b_j P_j}{1 + \sum b_j P_j} 
  \]

**Langmuir-Hinshelwood kinetics**
- Second-order surface-mediated reaction
  \[
  A_{\text{ads}} + B_{\text{ads}} \rightarrow \text{Product}
  \]
- Rate depends on the partial pressures of A and B
  - At low pressure, rate is second-order in the gas pressure
  - At high pressures of both reactants, the rate becomes zero-order in pressure
  \[
  v = \frac{k_{\text{react}} [A_{\text{ads}}] [B_{\text{ads}}]}{1 + \sum b_j P_j^2}
  \]

**Eley-Rideal kinetics**
- Second-order surface-mediated transformation
- One of the reactants comes in from the gas phase (without adsorption)
  - Always first order with respect to A
  - Usually requires a highly reactive gas-phase species such as H atom
  
  \[
  v = k_{\text{react}} [A_{\text{ads}}] [B_{\text{ads}}] 
  \]

**Langmuir-Hinshelwood versus Eley-Rideal kinetics**
- Langmuir-Hinshelwood kinetics
  - Both partners of a second-order reaction at the surface
  - Partners diffuse on surface until meeting to react
- Eley-Rideal kinetics
  - One partner of a second-order reaction held at the surface
  - Second comes directly from the gas phase
  - One or both must be highly reactive

**Michaelis-Menten enzyme catalysis**
- Mechanism is similar to surface catalysis
  - Form complex
  - Complex may fall apart
  - React
  \[
  E + S \xrightarrow{k_+} E \sim S \xrightarrow{k_-} E + S \xrightarrow{k_+} P + E
  \]
  - Velocity is found assuming fast equilibrium of first two steps
  \[
  v = \frac{k_2}{K_M + [S]} [E]_0 [S] 
  \]

**Example of Michaelis-Menten kinetics**
- Hydrolysis of N-glutamyl-L-phenylalanine with \(\alpha\)-chymotrypsin
- Lineweaver-Burk plot
  - Plot 1/v versus 1/[S]
  - Obtain Michaelis-Menten parameters from slope and intercept of plot
Summary

- Complex reactions usually described in terms of elementary steps
- Lindemann’s mechanism
  - Modern version is RRKM theory (Rice, Ramsperger, Kassel, and Marcus)
- Polymerization occurs by a chain reaction
  - Initiation
  - Propagation
  - Termination
- Surface chemistry
  - Adsorption and desorption steps included
  - Langmuir-Hinshelwood versus Eley-Rideal mechanisms
- Enzyme kinetics
  - Formation of complex
  - Michaelis-Menten kinetics