Physical Chemistry

Lecture 7

Special steps; chain reactions; surface and enzyme kinetics

Photochemical and sensitized steps

- Light is sometimes used to activate processes
  - ϕ ≡ quantum yield
- Some added materials produce reactive species by reaction

$$Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot$$

$$v = \phi\, I_a$$

$$Na + Cl_2 \rightarrow NaCl + Cl\cdot$$

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

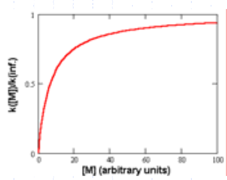
$$A + M \xrightarrow{k_1} M + A^*$$

$$A^* + M \xrightarrow{k_2} M + A$$

$$A^* \xrightarrow{k_3} Products$$

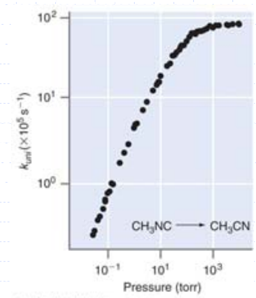
$$\frac{dProducts}{dt} = k_{eff}[A]$$

$$k_{eff} = \frac{k_1 k_3 [M]}{k_3 + k_2 [M]}$$



Variations and refinements of Lindemann's mechanism

- Hinshelwood
  - Explicit energy dependence of the rate constant
- Rice and Ramsperger, and independently Kassel 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



(From Engel and Reid, Thermodynamics)

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

$$Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot$$

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:

$$Br\cdot \; + \; H_2 \; \rightarrow \; HBr \; + \; H\cdot$$

$$H\cdot \; + \; Cl_2 \; \rightarrow \; HCl \; + \; Cl\cdot$$

Termination steps

- Steps that remove reactive species
- Stable-product formation

$$2\,C_2H_5\cdot \; \rightarrow \; C_4H_{10}$$

- Wall deactivation

$$R\cdot \; + \; wall \; \rightarrow \; stable\ wall\ complex$$

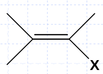
- Stable-radical formation; scavenging

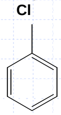
$$R\cdot \; + \; NO \; \rightarrow \; RNO$$

Vinyl polymers

- "Simple" chain reaction

$$n\,(monomer) \; \rightarrow \; polymer$$
$$n \quad M \; \rightarrow \; M_n$$



Sidechain, X	Polymer
H	Poly(ethylene)
CH_3	Poly(propylene)
Cl	Poly(vinyl chloride)
	Poly(styrene)

Vinyl polymerization

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

$$In \; \rightarrow \; R\cdot$$
$$R\cdot \; + \; M \; \rightarrow \; RM\cdot$$
$$\vdots$$
$$RM_n\cdot \; + \; M \; \rightarrow \; RM_{n+1}\cdot$$
$$RM_x\cdot \; + \; RM_y\cdot \; \rightarrow RM_{x+y}R$$

Mathematics of vinyl polymerization

- Approximation at steady state
  - Rate of initiation is equal to rate of termination
- Radical-combination termination

$$v_p \; = \; k_p \sqrt{\frac{k_i f}{k_t}} [M][In]^{1/2}$$

- Other possible termination steps
  - Disproportionation
  - Chain transfer

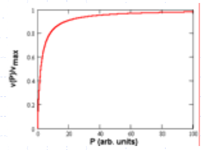
Reactions at surfaces

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

$$A(gas) \xrightarrow{k_{ads}} A(adsorbed)$$
$$A(adsorbed) \xrightarrow{k_{des}} A(gas)$$
$$A(adsorbed) \xrightarrow{k_{react}} P(adsorbed)$$
$$P(adsorbed) \xrightarrow{k_{P,des}} P(gas)$$

Langmuir isotherms

- Assume equilibrium between gas-phase A and adsorbed A
  - Langmuir isotherm gives relation between gas and surface concentrations



$$[A_{adsorbed}] = [A_{sat}]\frac{bP_A}{1+bP_a}$$

  - Generalize for multiple materials adsorbed, as in a chemical reaction

$$[A_{ads}] = S_0\frac{b_A P_A}{1+\sum_j b_j P_j}$$

Langmuir-Hinshelwood kinetics

- Second-order surface-mediated reaction
- 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

$$Rate-determining\ Step$$

$$A_{ads} + B_{ads} \rightarrow Product$$

$$v = k_{react}[A_{ads}][B_{ads}]$$

$$= k_{react} S_0^2 \frac{b_A b_B P_A P_B}{(1+\sum_j b_j P_j)^2}$$

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

$$Rate-determining\ Step$$

$$A_{gas} + B_{ads} \rightarrow Product$$

$$v = k_{react} P_A [B_{ads}]$$

$$= k_{react} S_0 \frac{b_B P_A P_B}{1+\sum_j b_j P_j}$$

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

$$E + S \xrightarrow{k_1} E \sim S$$

$$E \sim S \xrightarrow{k_{-1}} E + S$$

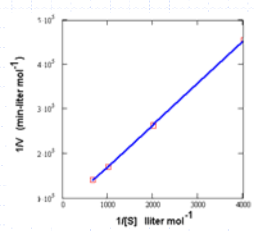
$$E \sim S \xrightarrow{k_2} P + E$$

- 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 α-chymotrypsin
- J. Chem. Ed., 50, 149 (1973).
- Lineweaver-Birk 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