Lecture 7: Reaction kinetics
24-11-2009

• Lecture plan:
  – reaction rates and methods to determine them
  – reaction mechanism in terms of the elementary reaction steps
  – basic reaction types
  – potential energy surface of a reaction
  – complex reaction
    • enzymatically catalyzed reactions
    • photochemical reactions
    • chemical oscillations
  – problems
Rates of chemical reactions

\[ A + 2B \longrightarrow 3C + D \]

Instantaneous rate of consumption of a reactant:
\[-d[R]/dt\]

Instantaneous rate of formation of a product:
\[d[P]/dt\]

From stoichiometry
\[
\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}
\]

Rate of the reaction:
\[ \nu = \frac{1}{v_i} \frac{dn_i}{dt} = \frac{d\xi}{dt} \]

In case of heterogeneous reaction the rate will be defined as mol/m²s
Reaction order

Reaction rate is generally dependent on temperature, pressure, concentration of species, the phases where reaction occurs etc. However, an empirical relation called a rate law exists stating that:

\[ v = k[A]^{\alpha}[B]^{\beta} \ldots \]

- algebraic dependence on the reagent concentration raised to some power
- reaction order with respect to species A: \( \alpha \)
- overall reaction order: \( \alpha + \beta \ldots \)

rate constant, depends only on T and not on the concentration

The power is generally **not equal** to the stoichiometric coefficients, has to be determined from the experiment

Order of a reaction:

- \( v = k \) \( \rightarrow \) Zero order. \([M \cdot s^{-1}]\)

- \( v = k[A][B] \) \( \rightarrow \) First order in A, first order in B, overall second order. \([M^{-1} \cdot s^{-1}]\)

- \( v = k[A]^{1/2}[B] \) \( \rightarrow \) Halforder in A, first order in B, overall tree-halves order.
Measuring the rates of chemical reactions

- Experimental measuring progress of the reaction
  - Monitoring pressure in the reaction involving gases
    \[
    2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)
    \]
    
    \[
    n(1 - \alpha) \quad 2\alpha n \quad \frac{1}{2} \alpha n
    \]
    
    \[
    p = (1 + \frac{3}{2}\alpha)p_0
    \]
  - Absorption at particular wavelength (e.g. Br$_2$ below)
    \[
    H_2(g) + Br_2(g) \rightarrow 2HBr(g)
    \]
  - Conductance of the ionic solution
    \[
    (CH_3)_3CCl(aq) + H_2O(aq) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)
    \]
Measuring the Rates of chemical reactions

- Flow method
- Flash photolysis (down to 10 fs = 10^{-14} s range)
- Chemical quench flow
- Freeze quench method

- Stopped-flow method (down to 1 ms range)
Measuring the rates of chemical reactions

- Determination of the rate law

Usual technique is the **isolation method**, where all the components except one are present in large amounts (therefore their concentration is constant)

\[ v = k[A][B_0] = k'[A] \]

It usually accompanied by the **method of initial rates**, when several initial concentration of A measured (again assuming that the concentrations are constant)

\[ v_0 = k'[A_0]^a \quad \log v_0 = \log k' + a \log[A_0] \]
Measuring the rates of chemical reactions

- Example: \[2I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)\]
### Integrated rate laws

- **First order reaction.**
  - Let’s find concentration of reagent A after time \( t \)

\[
\frac{d[A]}{dt} = -k[A] \quad \Rightarrow \quad \int_{A_0}^{A} \frac{d[A]}{[A]} = -k \int_0^t dt
\]

\[
\Rightarrow \quad \ln \left( \frac{[A]}{[A_0]} \right) = -kt \quad \Rightarrow \quad [A] = [A_0] e^{-kt}
\]

- **Half-life** – time required for concentration to drop by \( \frac{1}{2} \).

\[
k t_{1/2} = - \ln \left( \frac{1}{2} \frac{[A_0]}{[A_0]} \right) = \ln 2 \quad t_{1/2} = \frac{\ln 2}{k}
\]

- **Time constant** – time required for concentration to drop by \( \frac{1}{e} \):

\[
\tau = \frac{1}{k}
\]
Integrated rate laws

• Second-order reactions

\[ \frac{d[A]}{dt} = -k[A]^2 \quad \Rightarrow \quad \int_{A_0}^A \frac{d[A]}{[A]^2} = -k \int_0^t dt \quad \Rightarrow \]

\[ \frac{1}{[A]} - \frac{1}{[A_0]} = kt \quad \Rightarrow \quad [A] = \frac{[A_0]}{1 + kt[A_0]} \]

– **Half-life** – depends on initial concentration

\[ \frac{1}{2}[A_0] = \frac{[A_0]}{1 + kt_{1/2}[A_0]} \quad t_{1/2} = \frac{1}{k[A_0]} \]

The concentration of the reagent drops faster in the 1st order reaction than in the 2nd order reaction.
Reaction approaching equilibrium

- Generally, most kinetics measurements are made far from equilibrium where reverse reactions are not important. **Close to equilibrium** the amount of products is significant and reverse reaction should be considered.

\[
A \rightarrow B \quad \nu = k[A]
\]

\[
B \rightarrow A \quad \nu = k'[B]
\]

\[
\frac{dA}{dt} = -k[A] + k'[B] \quad [A] + [B] = [A]_0
\]

\[
\frac{dA}{dt} = -k[A] + k'([A]_0 - [A])
\]

\[
[A] = \frac{k' + ke^{-(k+k')t}}{k + k'}[A]_0
\]

\[
[A]_{eq} = \frac{k'}{k + k'}[A]_0, \quad [B]_{eq} = \frac{k}{k + k'}[A]_0, \quad K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'}
\]

Generally:

\[
K = \frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \ldots
\]
The temperature dependence of reaction rate

- The rate constants of most reactions increase with temperature.
- Experimentally for many reactions, the rate constant $k$ follows the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

- $A$ – pre-exponential (frequency) factor,
- $E_a$ – activation energy

High activation energy means that rate constants depend strongly on the temperature, zero would mean reaction independent on temperature.
The temperature dependence of reaction rate

- Stages of reaction:
  - Reagents
  - Activation complex
  - Product

Activation energy is the minimum kinetic energy reactants must have to form the products.
Pre-exponential is rate of collisions
Arrhenius equation gives the rate of successful collisions.

\[ k = Ae^{-E_a / RT} \]

Fraction of collision with required energy

reaction coordinate: e.g. changes of interactomic distances or angles
Elementary reactions

- Most reactions occur in a sequence of steps called **elementary reactions**.
- Molecularity of an elementary reaction is the number of molecules coming together to react (e.g. **uni-molecular**, **bimolecular**)

Uni-molecular: first order in the reactant

\[
A \rightarrow P \quad \frac{d[A]}{dt} = -k[A]
\]

Bimolecular: first order in the reactant

\[
A + B \rightarrow P \quad \frac{d[A]}{dt} = -k[A][B]
\]

Proportional to collision rate

\[
H + Br_2 \rightarrow HBr + Br
\]
Consecutive elementary reactions

\[ A \xrightarrow{k_a} I \xrightarrow{k_b} P \]

\[ \frac{d[A]}{dt} = -k_a[A] \]
\[ \frac{d[I]}{dt} = k_a[A] - k_b[I] \]
\[ \frac{d[P]}{dt} = k_b[I] \]

Solution for A should be in a form:

\[ [A] = [A]_0 e^{-k_a t} \]

\[ \frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \]

\[ [I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0 \]

\[ [A] + [I] + [P] = [A]_0 \]

\[ [P] = \left(1 + \frac{k_a e^{-k_a t} - k_b e^{-k_b t}}{k_b - k_a}\right) [A]_0 \]
Consecutive elementary reactions

- The (quasi) steady-state approximation

\[
\frac{d[I]}{dt} = 0
\]

Then

\[
\frac{d[I]}{dt} = k_a[A] - k_b[I] = 0
\]

and

\[
\frac{d[P]}{dt} = k_b[I] \approx k_a[A]
\]

\[
[P] \approx (1 - e^{-k_at})[A]_0
\]
Consecutive elementary reactions

- Pre-equilibria

\[ A + B \xrightleftharpoons[k'_a, k_a']{} I \xrightarrow{k_b} P \]

This condition arises when \( k'_a \gg k_b \).

Then

\[ K = \frac{[I]}{[A][B]} = \frac{k_a}{k'_a} \]

and

\[ \frac{d[P]}{d t} = k_b [I] = k_b K [A][B] \]

Second order form with composite rate constant
Unimolecular reactions

• As the molecule acquires the energy as a result of collision why the reaction is still a first order?

• Lindemann-Hinshelwood mechanism

\[
A + A \xrightarrow{k_a} A^* + A \quad \frac{d[A^*]}{dt} = k_a[A]^2
\]

\[
A + A^* \xrightarrow{k'_a} A + A \quad \frac{d[A^*]}{dt} = -k'_a[A^*][A]
\]

\[
A^* \xrightarrow{k_b} P \quad \frac{d[A^*]}{dt} = -k_b[A^*]
\]

If the last step is rate-limiting the overall reaction will have first order kinetics
If the rate of deactivation is much higher than unimolecular decay then:

\[
\frac{dP}{dt} = \frac{k_b k_a [A]^2}{k_b + k'_a [A]} \approx \frac{k_b k_a [A]}{k'_a}
\]

The Lindemann-Hinshelwood mechanism can be tested by reducing the pressure (slowing down the activation step) so the reaction will switch to the second order.
The activation energy of the composite reaction

Let’s consider Lindemann-Hinshelwood mechanism and apply Arrhenius-like temperature dependence to each rate constant

\[
k = \frac{k_a k_b}{k'_a} = \frac{\left( A_a e^{-E_a(a)/RT} \right) \left( A_b e^{-E_a(b)/RT} \right)}{\left( A'_a e^{-E'_a(a)/RT} \right)} = \frac{A_a A_b}{A'_a} e^{-\{E_a(a) + E_a(a) - E'_a(a)\}/RT}
\]

Overall activation energy can be positive or negative

\[E_a(a) + E_a(b) > E'_a(a)\]
\[E_a(a) + E_a(b) < E'_a(a)\]
The kinetics of complex reactions

- Chain reactions
- Polymerization reactions
- Enzyme catalyzed reactions
- Oscillating reaction and chaos
Chain Reactions

- **Chain reaction**: reaction where an intermediate produced in one step can generate another intermediate in the next step. These intermediates are called chain carriers.

- Example: Hydrogen-Bromine reaction

\[
H_2(g) + Br_2(g) \rightarrow 2HBr(g)
\]

\[
v = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}
\]

**Initiation**: \( Br_2 + M \rightarrow Br \cdot + Br \cdot + M \)

**Propagation**: \( Br \cdot + H_2 \rightarrow HBr + H \cdot \)

**Propagation**: \( H \cdot + Br_2 \rightarrow HBr + Br \cdot \)

**Retardation**: \( H \cdot + HBr \rightarrow H_2 + Br \cdot \)

**Termination**: \( Br \cdot + Br \cdot + M \rightarrow Br_2 + M \)

Collision with \( Br_2 \) or \( H_2 \).
Chain Reactions

Initiation: \[ Br_2 + M \rightarrow Br \cdot + Br \cdot + M \] \[ v = k_i[Br_2][M] \]

Propagation: \[ Br \cdot + H_2 \rightarrow HBr + H \cdot \] \[ v = k_p[Br \cdot][H_2] \]

Propagation: \[ H \cdot + Br_2 \rightarrow HBr + Br \cdot \] \[ v = k_p[H \cdot][Br_2] \]

Retardation: \[ H \cdot + HBr \rightarrow H_2 + Br \cdot \] \[ v = k_r[H \cdot][HBr] \]

Termination: \[ Br \cdot + Br \cdot + M \rightarrow Br_2 + M \] \[ v = k_t[Br \cdot]^2[M] \]

\[
\frac{d[HBr]}{dt} = k_p[Br \cdot][H_2] + k_p[H \cdot][Br_2] - k_r[H \cdot][HBr]
\]

Steady-state approximation:

\[
\frac{d[H \cdot]}{dt} = k_p[Br \cdot][H_2] - k_p[H \cdot][Br_2] - k_r[H \cdot][HBr] = 0
\]

\[
\frac{d[Br \cdot]}{dt} = 2k_i[Br_2][M] - k_p[Br \cdot][H_2] + k_p[H \cdot][Br_2] + k_r[H \cdot][HBr] - 2k_i[Br_2][M] = 0
\]

\[
[Br \cdot] = \left( \frac{k_i}{k_t} \right)^{1/2} [Br_2]^{1/2} \quad [H \cdot] = \frac{k_p\sqrt{k_i/k_t}[H_2][Br_2]^{1/2}}{k_p[Br_2] + k_r[HBr]}
\]

\[
\frac{d[HBr]}{dt} = \frac{2k_p\sqrt{k_i/k_t}[H_2][Br_2]^{1/2}}{[Br_2] + (k_r/k_p')[HBr]}
\]
Explosions

• **Thermal explosion** is caused by a very rapid reaction arising from a rapid increase of reaction rate with temperature.

• **Chain-branching explosion** occurs when number of chain centers grows exponentially.
Explosions

**Example:** reaction of oxygen and hydrogen

\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \]

**Initiation:**

\[ H_2 \rightarrow H \cdot + H \cdot \quad v = \text{const} \]

**Propagation:**

\[ H_2 + \cdot OH \rightarrow H \cdot + H_2O \quad v = k_p[H_2][\cdot OH] \]

**Branching:**

\[ O_2 \cdot + H \cdot \rightarrow \cdot O \cdot + \cdot OH \quad v = k_b[\cdot O_2 \cdot][H \cdot] \]

\[ \cdot O \cdot + H_2 \rightarrow \cdot OH + H \cdot \quad v = k_b'[\cdot O \cdot][H_2] \]

**Termination:**

\[ H \cdot + \text{wall} \rightarrow \frac{1}{2} H_2 \quad v = k_t[H \cdot] \]

\[ H \cdot + O_2 + M \rightarrow HO_2 \cdot + M \quad v = k_t'[H \cdot][O_2][M] \]

**Above 3rd explosion limit**

**Regeneration:**

\[ HO_2 \cdot + H_2 \rightarrow H \cdot + H_2O_2 \]

Three-particle collisions are important

Recombination on the walls is dominant
Polymerization Kinetics

- **Stepwise polymerization:** any two monomers can link together, growth of polymer is not confined to already formed chain. Average mass increasing with time.

- **Chain polymerization:** an activated monomer attacks another monomer to form growing chain. Yield, not the average mass, increasing with time.
Polymerization Kinetics

- **Chain polymerization** occurs by addition of monomers to a growing polymer, as in polymerization of ethene, methyl methacrylate and styrene:

  \[
  -CH_2CHX \cdot + CH_2 = CHX \longrightarrow -CH_2CHXCH_2CHX \cdot
  \]

- Rate of polymerization is proportional to the square root of the initiator concentration:

  \[
  \text{Initiation: } I \longrightarrow R \cdot + R \cdot \quad v = k_i[I]
  \]

  \[
  M + R \cdot \longrightarrow M_1 \quad (\text{fast})
  \]

  \[
  \text{Propagation: } M + M_1 \longrightarrow M_2
  \]

  \[
  M + M_2 \longrightarrow M_3
  \]

  \[
  \vdots
  \]

  \[
  M + M_n \longrightarrow M_{n+1} \quad v = k_p[M][M_\cdot]
  \]

Total concentration of radicals will be determined by the initiation step (rate-determining process)

\[
\left( \frac{d[M \cdot]}{dt} \right)_{\text{production}} = 2fk_i[I]
\]
Termination:  \( \bullet M_n + \bullet M_m \rightarrow M_{n+m} \) (mutual termination)

\( \bullet M_n + \bullet M_m \rightarrow M_n + M_m \) (disproportionation)

\( M + \bullet M_n \rightarrow \bullet M + M_n \) (chain transfer)

Assuming only mutual termination occurs:

\[
\left( \frac{d[M\bullet]}{dt} \right)_{\text{depletion}} = k_i [M\bullet]^2
\]

In a steady-state approximation:

\[
\left( \frac{d[M\bullet]}{dt} \right) = 2f k_i [I] - k_i [M\bullet]^2 = 0 \quad [M\bullet] = \left( \frac{f k_i}{k_i} \right)^{1/2} [I]^{1/2}
\]

The propagation rate is the negative of the monomer consumption rate:

Propagation:  \( M + \bullet M_n \rightarrow \bullet M_{n+1} \)  \( \nu = k_p [M][\bullet M] \)

\[
\nu_p = k_p [M\bullet][M] = k_p \left( \frac{f k_i}{k_i} \right)^{1/2} [I]^{1/2} [M]
\]
Polymerization Kinetics

Kinetic chain length:

\[
\nu = \frac{\text{number of monomer units consumed}}{\text{number of activated centers produced}} = \frac{\text{rate of propagation of the chains}}{\text{rate of production of radicals}}
\]

\[
\nu = \frac{k_p [M \bullet][M]}{2k_t [M \bullet]^2} = \frac{k_p [M]}{2k_t [M \bullet]}
\]

\[
\nu = k_p (fk_t k_i)^{-1/2} [I]^{-1/2}
\]

In chains are terminated by mutual termination, than the average chain length is the length of two chains combining:

\[
\langle n \rangle = 2\nu = 2k_p (fk_t k_i)^{-1/2} [M][I]^{-1/2}
\]

The slower initiation rate the higher the average mass for polymers
Homogeneous Catalysis

- **Catalyst** is a substance that accelerates a reaction but undergoes no net chemical change. Catalyst lowers the activation energy by providing an alternative path.
- **Enzymes** are biological catalysts.
- **Homogeneous catalyst** is a catalyst in the same phase as the reaction mixture.
- **Heterogeneous catalyst** is a catalyst in a different phase.

Example: decomposition of hydrogen peroxide

<table>
<thead>
<tr>
<th></th>
<th>Activation energy</th>
<th>Rate increase at 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-catalyzed:</td>
<td>$E_a=76 \text{ kJ/mol}$</td>
<td>1</td>
</tr>
<tr>
<td>Iodide catalyzed</td>
<td>$E_a=57 \text{ kJ/mol}$</td>
<td>2000</td>
</tr>
<tr>
<td>Enzyme catalase</td>
<td>$E_a=8 \text{ kJ/mol}$</td>
<td>$10^{15}$</td>
</tr>
</tbody>
</table>
Homogeneous Catalysis

\[ 2H_2O_2(aq) \xrightleftharpoons{Br^-}^{Br^-} 2H_2O(l) + H_2(g) \]

**Pre-equilibrium**

\[ H_3O^+ + H_2O_2(aq) \rightarrow H_3O_2^+ + H_2O \]

\[ K = \frac{[H_3O_2^+]}{[H_2O_2][H_3O^+]} \]

\[ H_3O_2^+ + Br^- \rightarrow HOBr + H_2O \]

\[ v = k[H_3O_2^+][Br^-] \quad (fast) \]

\[ HOBr + H_2O_2 \rightarrow H_3O^+ + O_2 + Br^- \]

\[ \frac{d[O_2]}{dt} = kK[H_2O_2][H_3O^+][Br^-] \]
Enzymes

- Enzymes are special proteins or nucleic acids that contain an active site responsible for binding the substrate and processing it into products.
- Enzyme-catalysed reactions can be inhibited by molecules that interfere with the formation of products.

Principal features of many enzyme-catalysed reactions are:
1. For a given initial concentration of substrate \([S]_0\) the initial rate of product formation is proportional to the enzyme concentration \([E]_0\).
2. For a given \([E]_0\) and low values of \([S]_0\) the rate of the product formation is proportional to \([S]_0\).
3. For a given \([E]_0\) and high values of \([S]_0\) the rate of the product formation becomes independent of \([S]_0\) reaching value of maximum velocity.
Enzymes

- Michaelis-Menten mechanism

\[ E + S \xrightleftharpoons{k_a, k'_a} ES \]

\[ ES \xrightarrow{k_b} P \]

Steady-state approximation

\[ v = k_b[ES] \]

\[ \frac{d[ES]}{dt} = k_a[E][S] - k_a[ES] - k_b[ES] = 0 \]

\[ [ES] = \left( \frac{k_a}{k'_a + k_b} \right)[E][S] \]

As \[ [E]_0 = [E] + [ES] \]

\[ [S] \approx [S]_0 \]

\[ v = k_b[ES] = \frac{k_b[E]_0}{1 + \left( \frac{k'_a + k_b}{k_a} \right) \frac{1}{[S]_0}} \]

\[ v = \frac{v_{\text{max}}}{1 + \frac{K_M}{[S]_0}} \]

\( K_M \) – Michaelis constant
Enzymes

- Experimental analysis of enzyme catalysed reaction

\[ v = \frac{v_{\text{max}}}{1 + \frac{K_M}{[S]_0}} \]

**Lineweaver-Burk plot**

\[ \frac{1}{v} = \frac{1}{v_{\text{max}}} + \left( \frac{K_M}{v_{\text{max}}} \right) \frac{1}{[S]_0} \]

**Eadie-Hofstee plot**

\[ v = -K_M \frac{v}{[S]_0} + v_{\text{max}} \]
Enzymes

- Catalytic efficiency of enzymes

**Turnover number (catalytic constant)** of an enzyme $k_{\text{cat}}$ is the number of catalytic cycles performed by the active site in a unit of time.

$$k_{\text{cat}} = k_b = \frac{v_{\text{max}}}{[E]_0}$$

**Catalytic efficiency** of an enzyme is defined as $k_{\text{cat}}/K_M$.

$$\varepsilon = \frac{k_{\text{cat}}}{K_M} = \frac{k_b k_a}{k_b' + k_b}$$

$$E + S \longleftrightarrow ES \quad k_a, k_a'$$

$$ES \longrightarrow P \quad k_b$$
Enzymes

- **Mechanism of enzyme inhibition**
  Inhibition occurs to the enzyme or to ES complex, or to both:

  $E + S \leftrightarrow ES \quad k_a, k'_a$

  $ES \rightarrow P \quad k_b$

  $EI \leftrightarrow E + I \quad K_I = \frac{[E][I]}{[EI]}$

  $ESI \leftrightarrow ES + I \quad K'_I = \frac{[ES][I]}{[ESI]}$

  $v = \frac{v_{max}}{\alpha' + \frac{\alpha K_M}{[S]_0}} \quad \alpha = 1 + [I]/K_I, \quad \alpha' = 1 + [I]/K'_I,$

  $\frac{1}{v} = \frac{\alpha'}{v_{max}} + \left(\frac{\alpha K_M}{v_{max}}\right) \frac{1}{[S]_0}$

Inhibition modes:
- **competitive inhibition** – binding to the active site of an enzyme – (a)
- **uncompetitive inhibition** – binding to an other site of the enzyme only if the substrate present – (b);
- non-competitive (mixed) inhibition – binding to other site that reduces enzyme ability to bind the substrate
Oscillating reactions

- Belousov-Zhabotinsky reaction

In 1950 Boris Belousov found periodic oscillations in a mixture of bromate, citric acid and ceric ion.
Oscillating reactions

- Concentration of reactants, intermediates and products of certain chemical reactions can vary periodically in space or in time as a result of feedback mechanism in the reaction. Can be sustained indefinitely if condition are kept far from equilibrium.

Belousov-Zhabotinski reaction: spatial patterns
Autocatalysis and Oscillations

- Autocatalysis – catalysis of a reaction by the products.

\[ \text{Autocatalysis} \quad A \rightarrow P \quad v = k[A][P] \]

- The Lotka-Volterra mechanism

\[ \begin{align*}
  A + X & \rightarrow X + X \\
  X + Y & \rightarrow Y + Y \\
  Y & \rightarrow B
\end{align*} \]

\[ \begin{align*}
  \frac{d[A]}{dt} &= -k_a[A][X] \\
  \frac{d[X]}{dt} &= -k_b[X][Y] \\
  \frac{d[B]}{dt} &= k_c[Y]
\end{align*} \]

Concentration of A is held constant, product B is not participating in the reaction but is normally removed as well.
Chemical Chaos

• For some reactions the solution can be infinitely sensitive to the initial condition: deterministic chaos
• Certain systems can go to chaos through period doubling
• **E22.10a** The second-order rate constant for the reaction

\[
\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{CH}_3\text{CH}_2\text{OH}(\text{aq})
\]

is 0.11 dm\(^3\) mol\(^{-1}\) s\(^{-1}\). What is the concentration of ester after (a) 10 s, (b) 10 min when ethyl acetate is added to sodium hydroxide so that the initial concentrations are [NaOH] = 0.050 mol dm\(^{-3}\) and [CH\(_3\)COOC\(_2\)H\(_5\)] = 0.100 mol dm\(^{-3}\)?

• **E22.16a** The effective rate constant for a gaseous reaction that has a Lindemann–Hinshelwood mechanism is \(2.50 \times 10^{-4} \text{ s}^{-1}\) at 1.30 kPa and \(2.10 \times 10^{-5} \text{ s}^{-1}\) at 12 Pa. Calculate the rate constant for the activation step in the mechanism.

• **E23.1a** Derive the rate law for the decomposition of ozone in the reaction

\[
2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})
\]

on the basis of the following proposed mechanism:

1. \(\text{O}_3 \leftrightarrow \text{O}_2 + \text{O} \quad k_1, k_1'\)
2. \(\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \quad k_2\)
Assignment VII

- E22.7b The rate constant for the first-order decomposition of a compound A in the reaction \(2A \rightarrow P\) is \(k=1.78 \times 10^{-7} \text{ s}^{-1}\) at 25°C. What is the half-life of A?

What will be the pressure initially 32.1kPa at (a) 10s (b) 10min after initiation of the reaction

- P23.3 The following radical chain mechanism proposed for the initial stages of gas-phase oxidation of silane by nitrous oxide

\[
\begin{align*}
(1) & \quad N_2O \rightarrow N_2 + O \\
(2) & \quad O + SiH_4 \rightarrow SiH_3 + OH \\
(3) & \quad OH + SiH_4 \rightarrow SiH_3 + H_2O \\
(4) & \quad SiH_3 + N_2O \rightarrow SiH_3O + N_2 \\
(5) & \quad SiH_3O + SiH_4 \rightarrow SiH_3OH + SiH_3 \\
(6) & \quad SiH_3 + SiH_3O \rightarrow (H_3Si)_2O \\
\end{align*}
\]

(a) Label each step with its role in the chain

(b) Use steady state approximation to show that (provided \(k_1\) and \(k_6\) are small):

\[
\frac{d[SiH_4]}{dt} = -k[N_2O][SiH_4]^{1/2}
\]