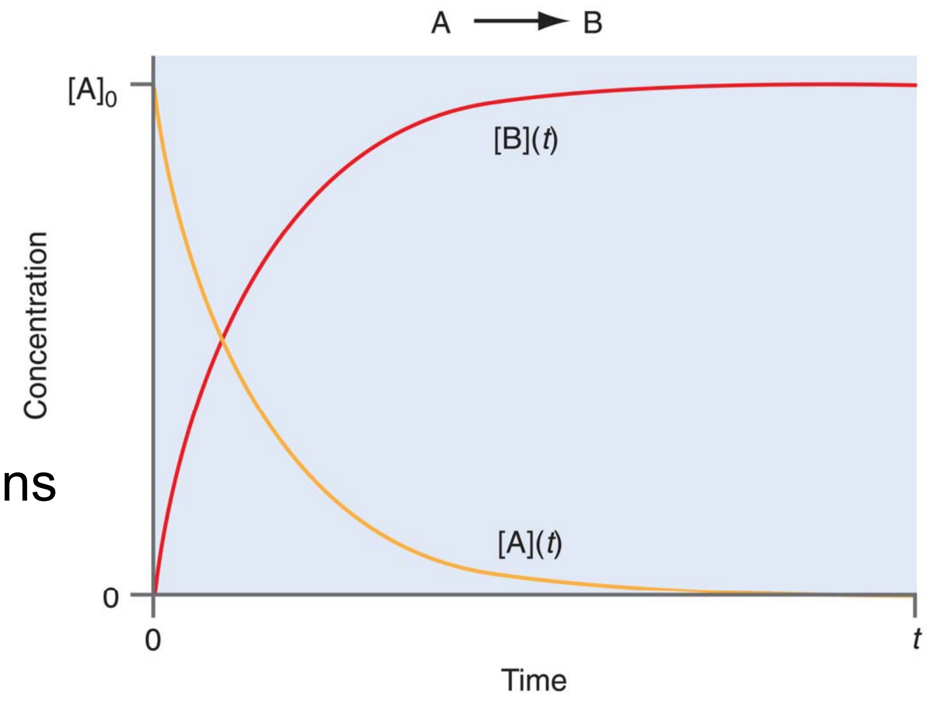
Lecture 7: Reaction kinetics

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:

$$d[P]/dt$$

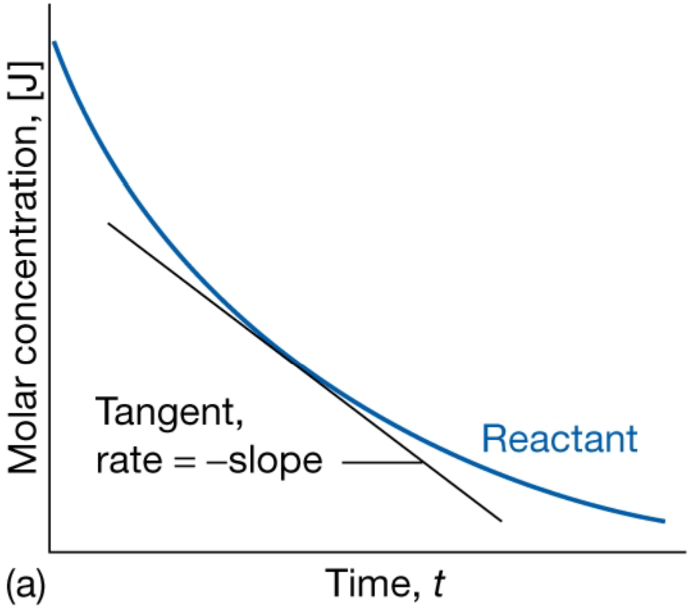
From stoichiometry

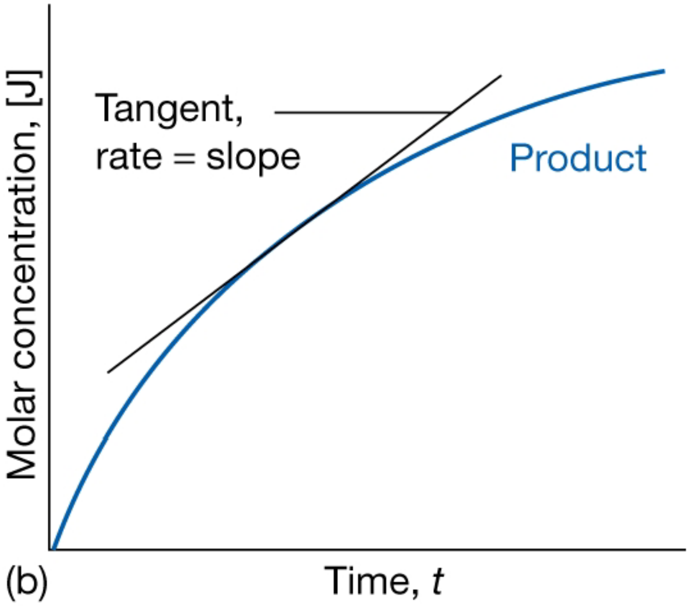
$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

Rate of the reaction:

$$v = \frac{1}{\nu_i}\frac{dn_i}{dt} = \frac{d\xi}{dt}$$

In case of heterogeneous reaction the rate will be defined as mol/m^{2}s





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:

$$v = k[A]^a[B]^b\ldots$$

algebraic dependence on the reagent concentration raised to some power

reaction order with respect to species A: α

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

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Order of a reaction:

$v = k \longrightarrow$ Zero order. $\left[M \cdot s^{-1}\right]$

$v = k[A][B] \longrightarrow$ First order in A, first order in B, overall second order. $\left[M^{-1} \cdot s^{-1}\right]$

$v = k[A]^{1/2}[B] \longrightarrow$ 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

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$n(1-\alpha) \qquad\qquad 2\alpha n \qquad\qquad \frac{1}{2}\alpha n$$

$$p = (1 + \frac{3}{2}\alpha)p_0$$

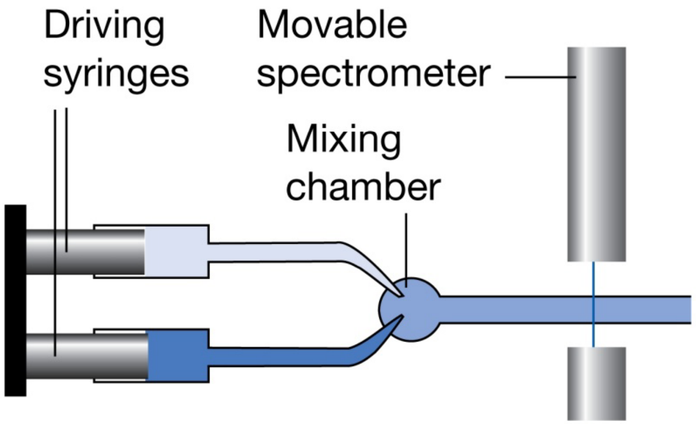
  - Absorption at particular wavelength (e.g. Br_2 below)

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

  - Conductance of the ionic solution

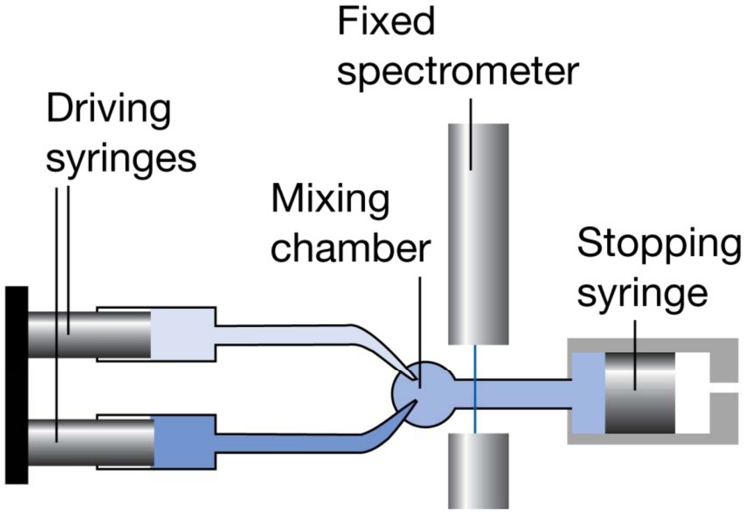
$$(CH_3)_3CCl(aq) + H_2O(aq) \longrightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)$$

Measuring the Rates of chemical reactions



concentration as
function of position

- Flow method



concentration as
function of time

- Stopped-flow method
(down to 1 ms range)

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

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)

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

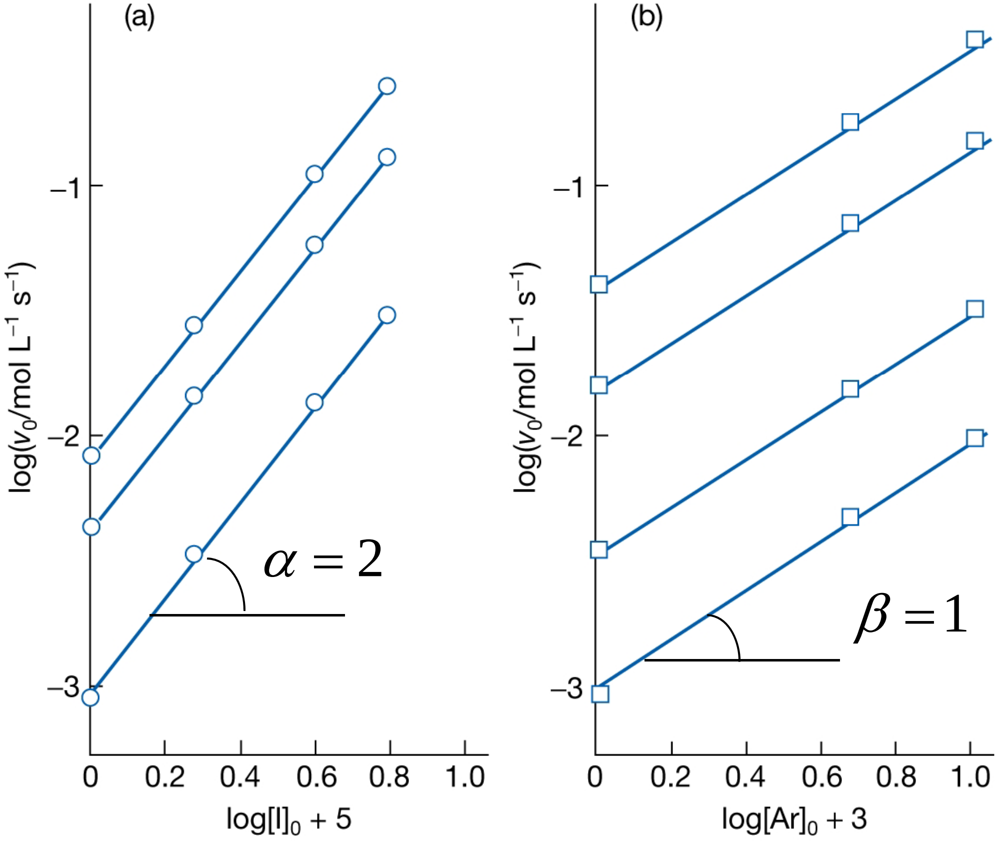
It usually accompanied by the **method of initial rates**, when several initial concentration of A measured (again assuming that the concentrations are constant)

$$v_0 = k'[A_0]^a \qquad \log v_0 = \log k' + a \log[A_0]$$

Measuring the rates of chemical reactions

- Example $2I(g)+Ar(g)\longrightarrow I_2(g)+Ar(g)$

A B



Integrated rate laws

- First order reaction.
  - Let's find concentration of reagent A after time t

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

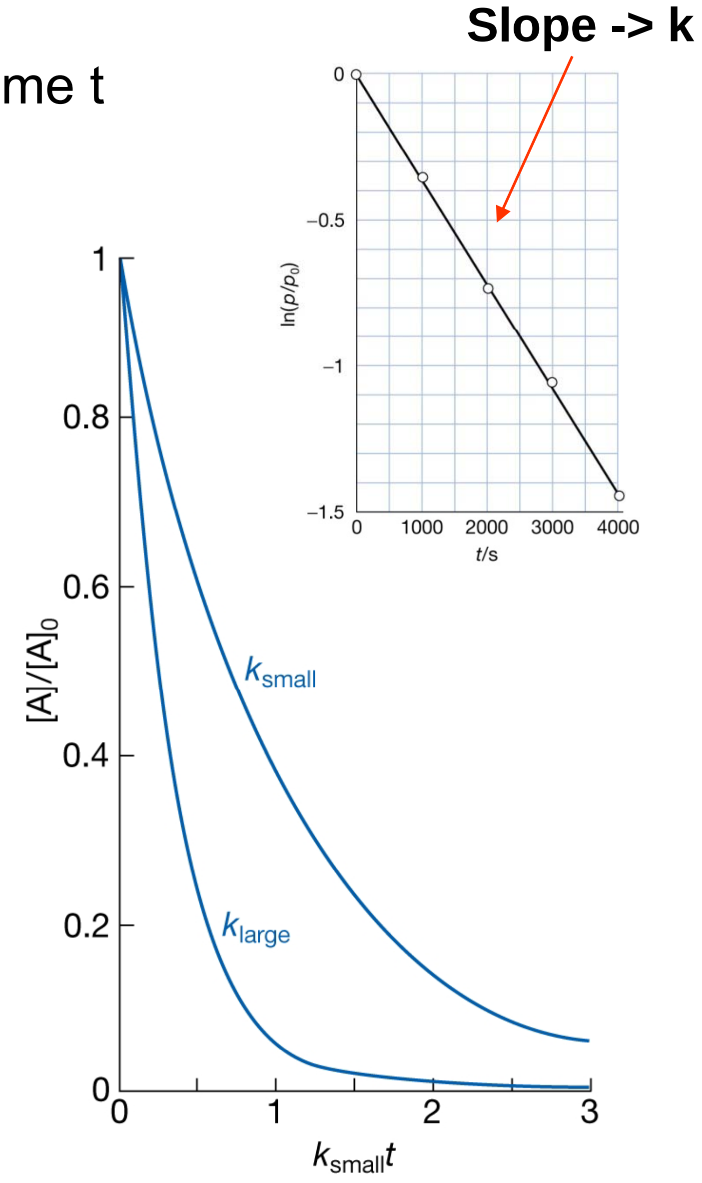
$$\Rightarrow \quad \ln\left(\frac{[A]}{[A_0]}\right) = -kt \quad \Rightarrow \quad [A] = [A_0]e^{-kt}$$

  - **Half-life** – time required for concentration to drop by ½.

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

  - **Time constant** – time required for concentration to drop by 1/e:

$$\tau = \frac{1}{k}$$


Slope -> k

Integrated rate laws

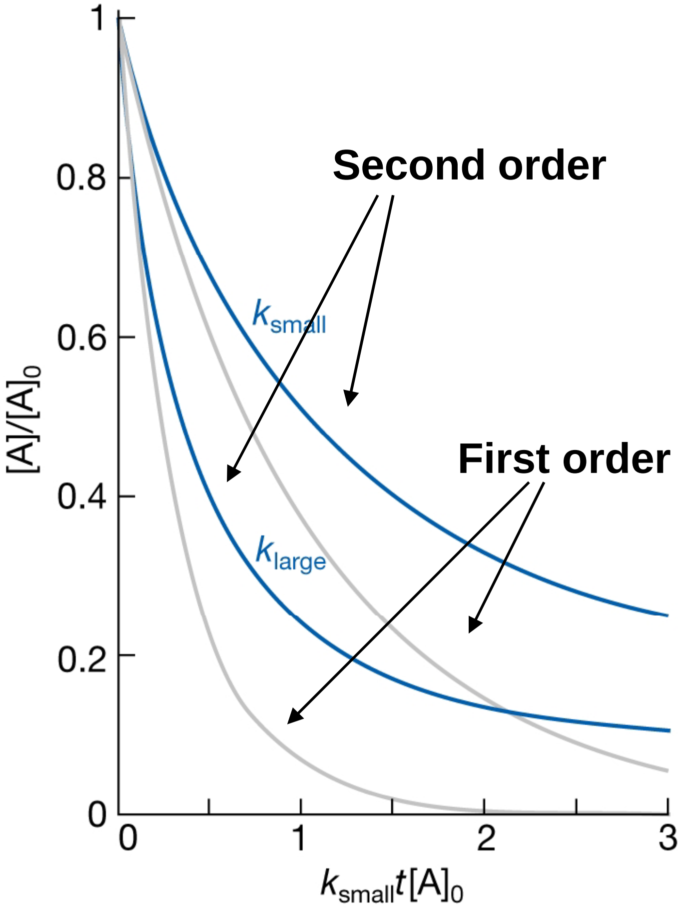
- Second-order reactions

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

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

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

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



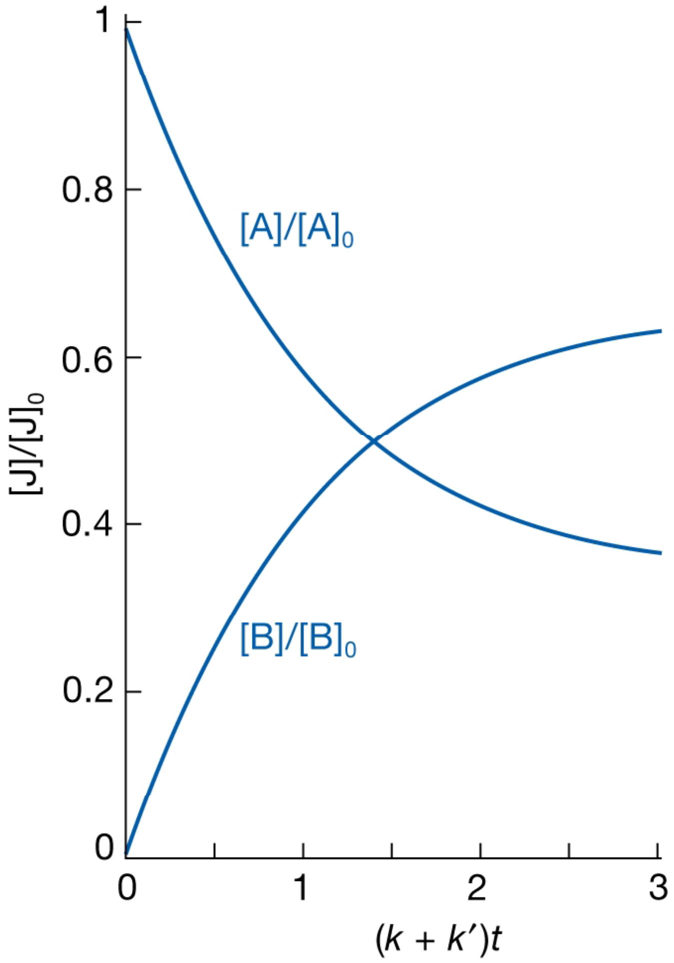
The concentration of the reagent drops faster in the 1st order reaction than in the 2nd order reaction

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**.

$$A \longrightarrow B \qquad v = k[A]$$

$$B \longrightarrow A \qquad v = k'[B]$$



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

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

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

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

Generally:

$$K = \frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \ldots$$

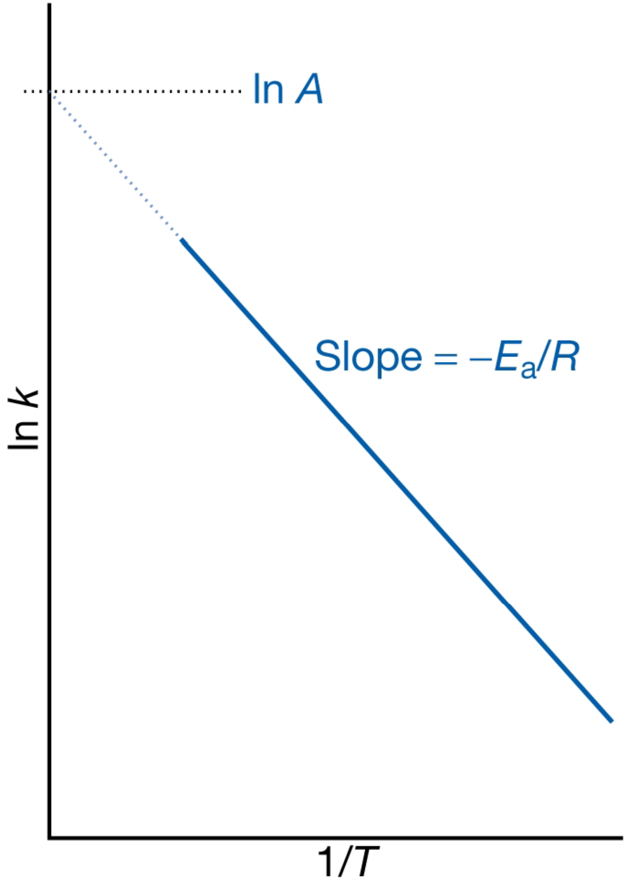
The temperature dependence of reaction rate

- The rate constants of most reaction increase with the temperature.
- Experimentally for many reactions k follows 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



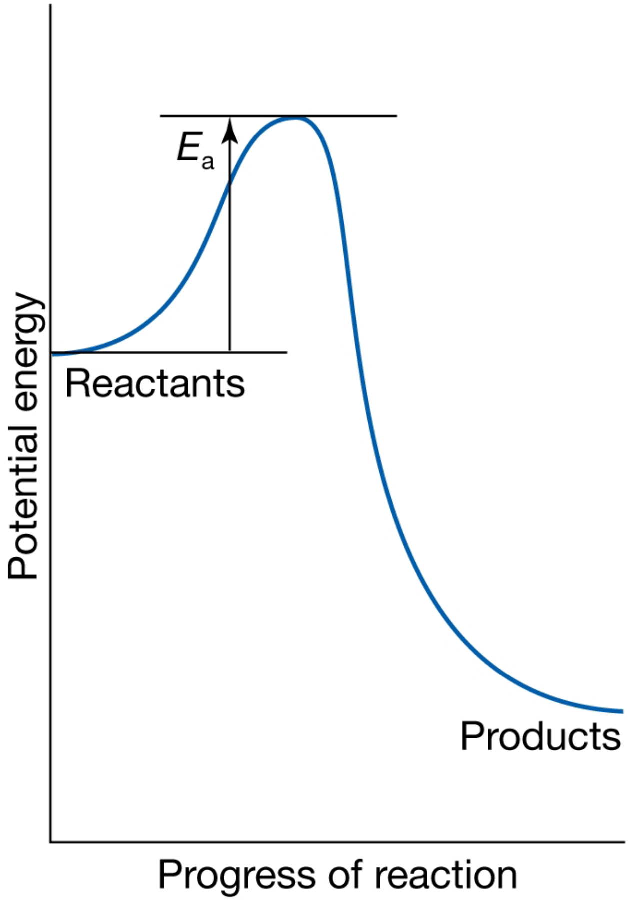
The temperature dependence of reaction rate

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

Transition state

$$k = A\underbrace{e^{-E_a/RT}}_{\text{Fraction of collision with required energy}}$$

•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.



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

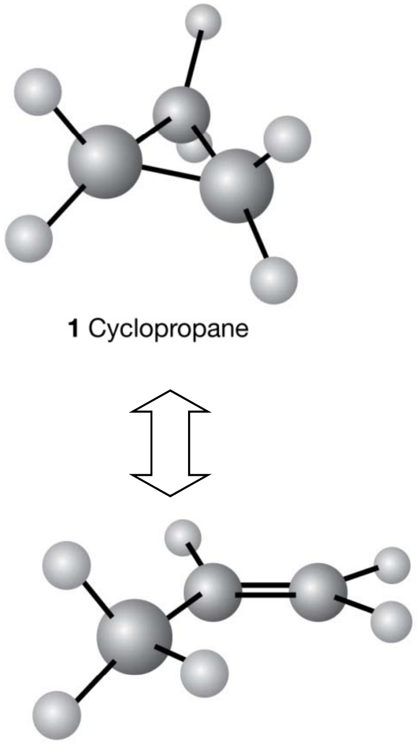
$$A \longrightarrow P \qquad \frac{d[A]}{dt} = -k[A]$$

Bimolecular: first order in the reactant

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

Proportional to collision rate

$$H + Br_2 \longrightarrow HBr + Br$$

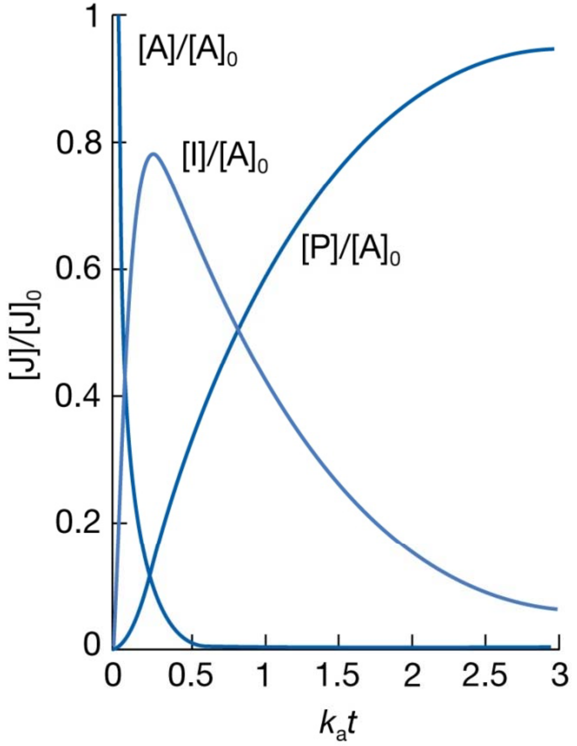


1 Cyclopropane

2 Propene

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

$$\frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \qquad [I] = \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)[A]_0$$

$$[A] + [I] + [P] = [A]_0 \qquad [P] = \left(1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a}\right)[A]_0$$

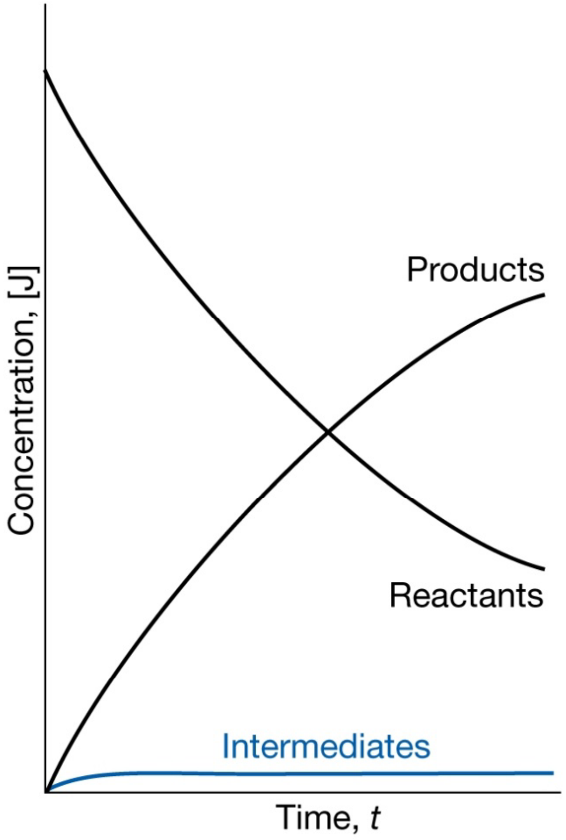
Consecutive elementary reactions

- The (quasi) steady-state approximation $\frac{d[I]}{dt} = 0$

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

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

$$[P] \approx \left(1 - e^{-k_a t}\right)[A]_0$$



Consecutive elementary reactions

- Pre-equilibria

$$A+B \xleftrightarrow{k_a, k_a'} I \xrightarrow{k_b} P$$

This condition arises when $k'_a >> k_b$.

Then $$K = \frac{[I]}{[A][B]} = \frac{k_a}{k_a'}$$

and $$\frac{d[P]}{dt} = k_b[I] = \underbrace{k_b K}_{\text{k}}[A][B]$$

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?

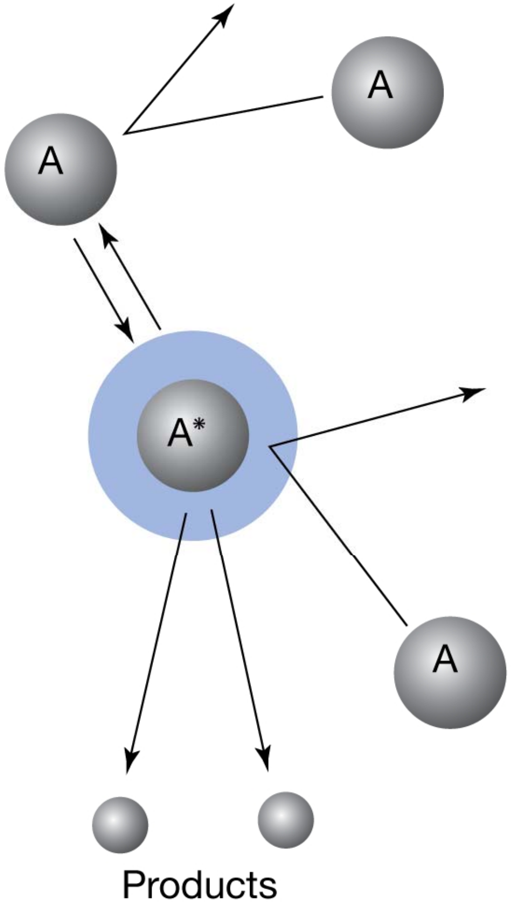
- **Lindemann-Hinshelwood mechanism**

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

$$A + A^* \xrightarrow{k_a'} A + A \qquad \frac{d[A^*]}{dt} = -k_a'[A^*][A]$$

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

If the last step is rate-limiting the overall reaction will have first order kinetics



Lindemann-Hinshelwood mechanism

$$\left.\begin{aligned}
&A + A \xrightarrow{k_a} A^* + A && \frac{d[A^*]}{dt} = k_a[A]^2 \\
&A + A^* \xrightarrow{k'} A + A && \frac{d[A^*]}{dt} = -k_a'[A^*][A] \\
&A^* \xrightarrow{k_b} P && \frac{d[A^*]}{dt} = -k_b[A^*]
\end{aligned}\right\}$$

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k_a'[A^*][A] - k_b[A^*]$$

$$[A^*] = \frac{k_a[A]^2}{k_b + k_a'[A]}$$

$$\frac{dP}{dt} = k_b[A^*] = \frac{k_b k_a[A]^2}{k_b + k_a'[A]}$$

If the rate of deactivation is much higher that unimolecular decay than:

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

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

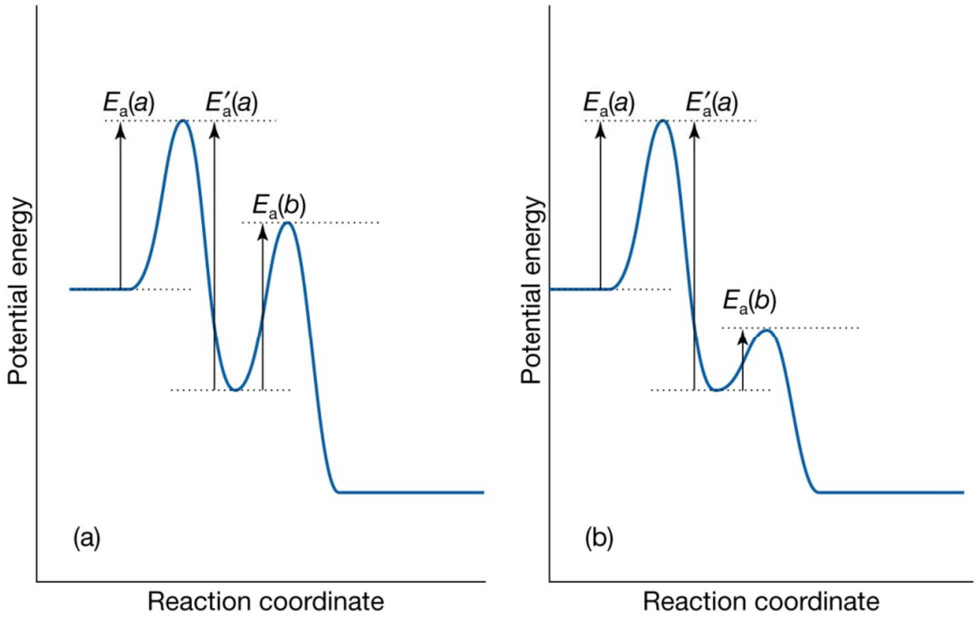
Let's consider Lindemann-Hinshelwood mechanism and apply Arrhenius-like temperature dependence to each rate constant

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

Overall activation energy can be positive or negative

$$E_a(a) + E_a(b) > E'_a(a)$$

$$E_a(a) + E_a(b) < E'_a(a)$$

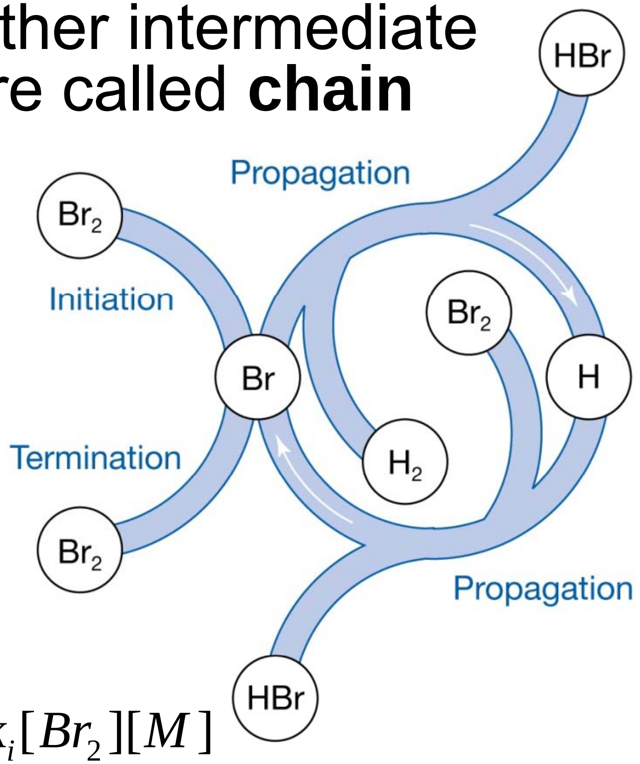


The kinetics of complex reactions

- 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



$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

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

collision with Br_2 or H_2.

Initiation:	$Br_2 + M \longrightarrow Br\bullet + Br\bullet + M$	$v = k_i[Br_2][M]$
Propagation:	$Br\bullet + H_2 \longrightarrow HBr + H\bullet$	$v = k_p[Br\bullet][H_2]$
Propagation:	$H\bullet + Br_2 \longrightarrow HBr + Br\bullet$	$v = k_{p'}[H\bullet][Br_2]$
Retardation:	$H\bullet + HBr \longrightarrow H_2 + Br\bullet$	$v = k_r[H\bullet][HBr]$
Termination:	$Br\bullet + Br\bullet + M \longrightarrow Br_2 + M$	$v = k_t[Br\bullet]^2[M]$

Chain Reactions

Initiation:	$Br_2 + M \longrightarrow Br\bullet + Br\bullet + M$	$v = k_i[Br_2][M]$
Propagation:	$Br\bullet + H_2 \longrightarrow HBr + H\bullet$	$v = k_p[Br\bullet][H_2]$
Propagation:	$H\bullet + Br_2 \longrightarrow HBr + Br\bullet$	$v = k_{p'}[H\bullet][Br_2]$
Retardation:	$H\bullet + HBr \longrightarrow H_2 + Br\bullet$	$v = k_r[H\bullet][HBr]$
Termination:	$Br\bullet + Br\bullet + M \longrightarrow Br_2 + M$	$v = k_t[Br\bullet]^2[M]$

$$\frac{d[HBr]}{dt} = k_p[Br\bullet][H_2] + k_{p'}[H\bullet][Br_2] - k_r[H\bullet][HBr]$$

Steady-state approximation:

$$\frac{d[H\bullet]}{dt} = k_p[Br\bullet][H_2] - k_{p'}[H\bullet][Br_2] - k_r[H\bullet][HBr] = 0$$

$$\frac{d[Br\bullet]}{dt} = 2k_i[Br_2][M] - k_p[Br\bullet][H_2] + k_{p'}[H\bullet][Br_2] + k_r[H\bullet][HBr] - 2k_t[Br_2][M] = 0$$

$$[Br\bullet] = \left(\frac{k_i}{k_t}\right)^{1/2}[Br_2]^{1/2} \qquad [H\bullet] = \frac{k_p\sqrt{k_i/k_t}[H_2][Br_2]^{1/2}}{k_{p'}[Br_2] + k_r[HBr]}$$

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

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 $2H_2(g)+O_2(g)\longrightarrow 2H_2O(g)$

Initiation: $H_2 \longrightarrow H\bullet + H\bullet$ $v = const$

Propagation: $H_2 + \bullet OH \longrightarrow H\bullet + H_2O$ $v = k_p[H_2][\bullet OH]$

Branching: $O_2\bullet + H\bullet \longrightarrow \bullet O\bullet + \bullet OH$ $v = k_b[\bullet O_2\bullet][H\bullet]$

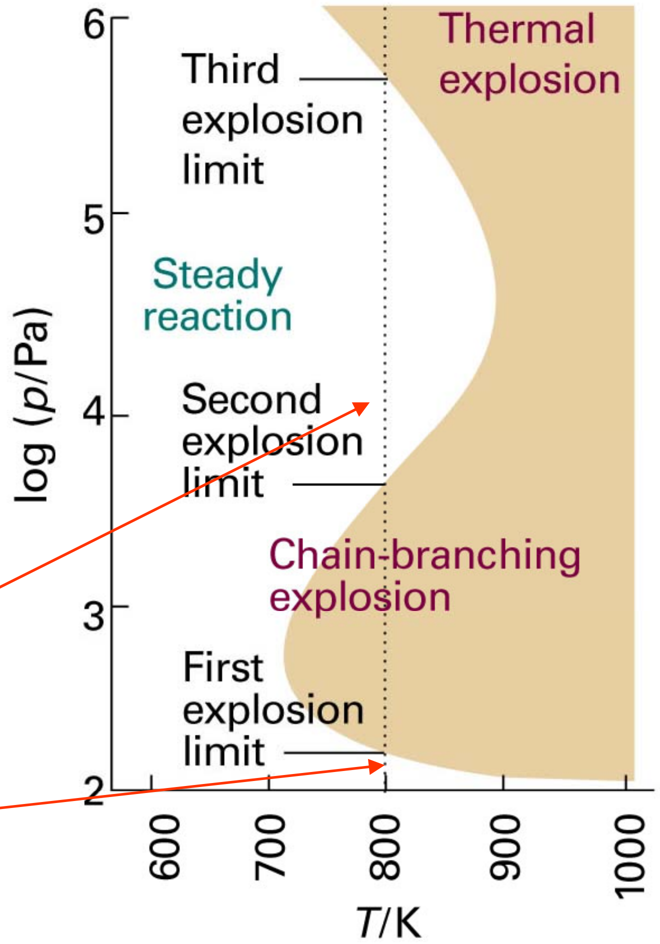
$\bullet O\bullet + H_2 \longrightarrow \bullet OH + H\bullet$ $v = k_b'[\bullet O\bullet][H_2]$

Termination: $H\bullet + wall \longrightarrow \frac{1}{2}H_2$ $v = k_t[H\bullet]$

$H\bullet + O_2 + M \longrightarrow HO_2\bullet + M$ $v = k_t'[H\bullet][O_2][M]$

Above 3rd explosion limit

Regeneration: $HO_2\bullet + H_2 \longrightarrow H\bullet + H_2O_2$



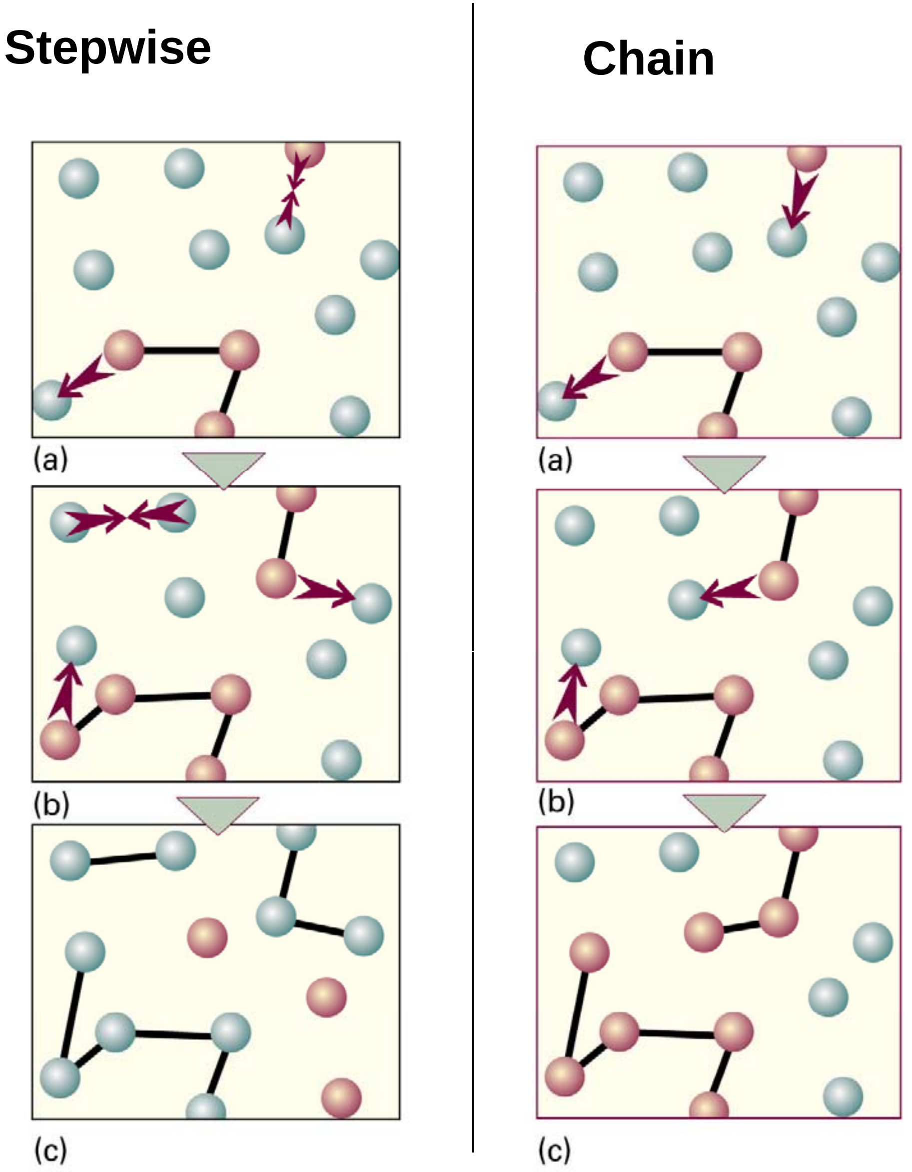
Three-particle collisions are important

Recombination on the walls is dominant

Polymerization Kinetics

- **Stepwise polymerization**:
  any two monomers ca
  link together, growth of
  polymer is not confined
  to already formed chai
  Average mass increasi
  with time

- **Chain polymerization**
  an activated monomer
  attacks another
  monomer to form
  growing chain. Yield, n
  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:

$$-CH_2CHX\bullet + CH_2=CHX \longrightarrow -CH_2CHXCH_2CHX\bullet$$

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

$$\begin{array}{lll}
\text{Initiation:} & I \longrightarrow R\bullet + R\bullet & v = k_i[I] \\
 & M + R\bullet \longrightarrow \bullet M_1 & (fast) \\
\text{Propagation:} & M + \bullet M_1 \longrightarrow \bullet M_2 & \\
 & M + \bullet M_2 \longrightarrow \bullet M_3 & \\
 & \vdots & \\
 & M + \bullet M_n \longrightarrow \bullet M_{n+1} & v = k_p[M][\bullet M]
\end{array}$$

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

$$\left(\frac{d[M\bullet]}{dt}\right)_{production} = 2fk_i[I]$$

Polymerization Kinetics

Termination: $\bullet M_n + \bullet M_m \longrightarrow M_{n+m}$ (mutual termination)

$\bullet M_n + \bullet M_m \longrightarrow M_n + M_m$ (disproportionation)

$M + \bullet M_n \longrightarrow \bullet M + M_n$ (chain transfer)

Assuming only mutual termination occurs:

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

In a steady-state approximation:

$$\left(\frac{d[M\bullet]}{dt}\right) = 2\,fk_i[I] - k_t[M\bullet]^2 = 0 \qquad [M\bullet] = \left(\frac{fk_i}{k_t}\right)^{1/2}[I]^{1/2}$$

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

Propagation: $M + \bullet M_n \longrightarrow \bullet M_{n+1}$ $\quad v = k_p[M][\bullet M]$

$$v_p = k_p[M\bullet][M] = k_p\left(\frac{fk_i}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

Polymerization Kinetics

Kinetic chain length:

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

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

$$v = k_p\left(fk_ik_t\right)^{-1/2}[I]^{-1/2}$$

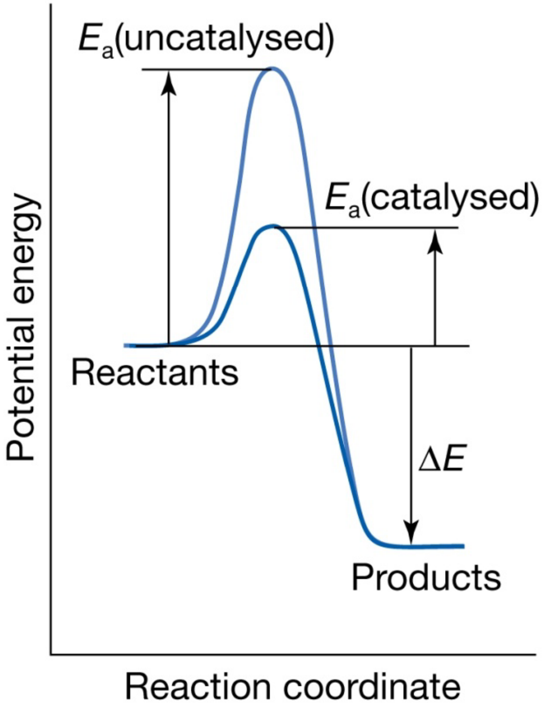
In chains are terminated by mutual termination, than the average chain length is the length of two chains combining:

$$\langle n\rangle = 2v = 2k_p\left(fk_ik_t\right)^{-1/2}[M][I]^{-1/2}$$

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 and 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

	Activation energy	Rate increase at 298K
Non-catalyzed:	E_a=76 kJ/mol	1
Iodide catalyzed	E_a=57 kJ/mol	2000
Enzyme catalase	E_a=8 kJ/mol	10^{15}.

Homogeneous Catalysis

$$2H_2O_2(aq)\xrightarrow{Br^-}2H_2O(l)+H_2(g)$$

Pre-equilibrium

$$H_3O^+ + H_2O_2(aq) \longleftrightarrow H_3O_2{}^+ + H_2O \qquad K=\frac{[H_3O_2{}^+]}{[H_2O_2][H_3O^+]}$$

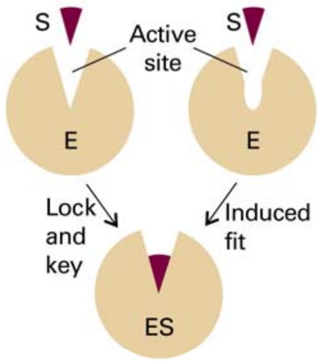
$$H_3O_2{}^+ + Br^- \longrightarrow HOBr + H_2O \qquad v=k[H_3O_2{}^+][Br^-]$$

$$HOBr + H_2O_2 \longrightarrow H_3O^+ + O_2 + Br^- \qquad (fast)$$

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

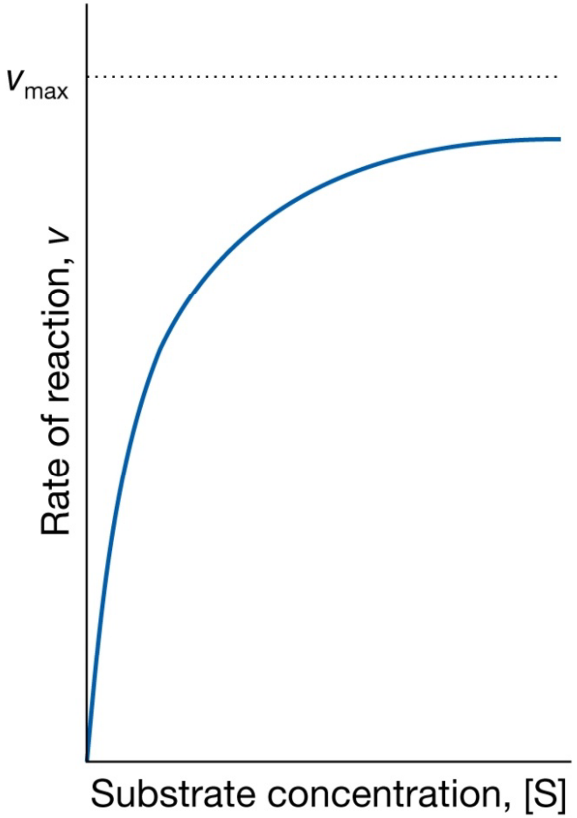
Enzymes

- 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 concentrationof 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

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

$$ES \longrightarrow P \qquad k_b$$

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

$$[E]_0 = [E] + [ES]$$

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

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

v_{max}

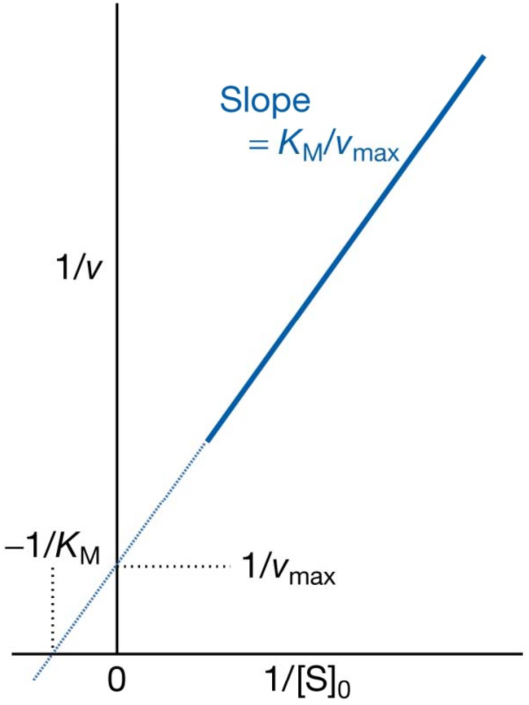
K_M – Michaelis constant

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

Enzymes

- Experimental analysis of enzyme catalysed reaction

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

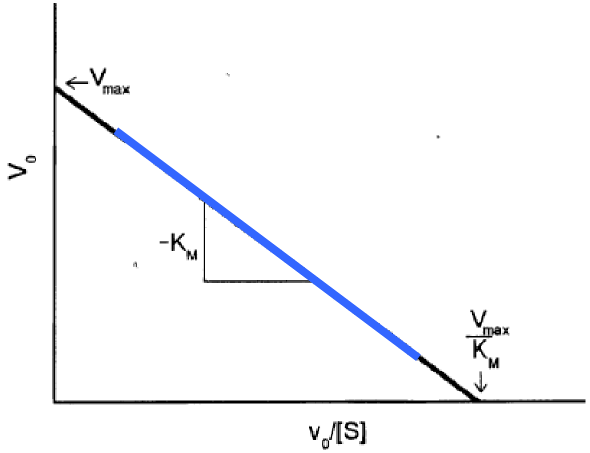


Lineweaver-Burk plot

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

Eadie-Hofstee plot

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



Enzymes

- Catalytic efficiency of enzymes

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

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

Catalytic efficiency of an enzyme is defined as k_{cat}/K_M .

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

$$\varepsilon \xrightarrow{k_b \gg k_a} k_a$$

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

$$ES \longrightarrow P \qquad k_b$$

Enzymes

- Mechanism of enzyme inhibition

Inhibition occurs to the enzyme or to ES complex, or to both:

$$E + S \longleftrightarrow ES \qquad k_a, k'_a$$

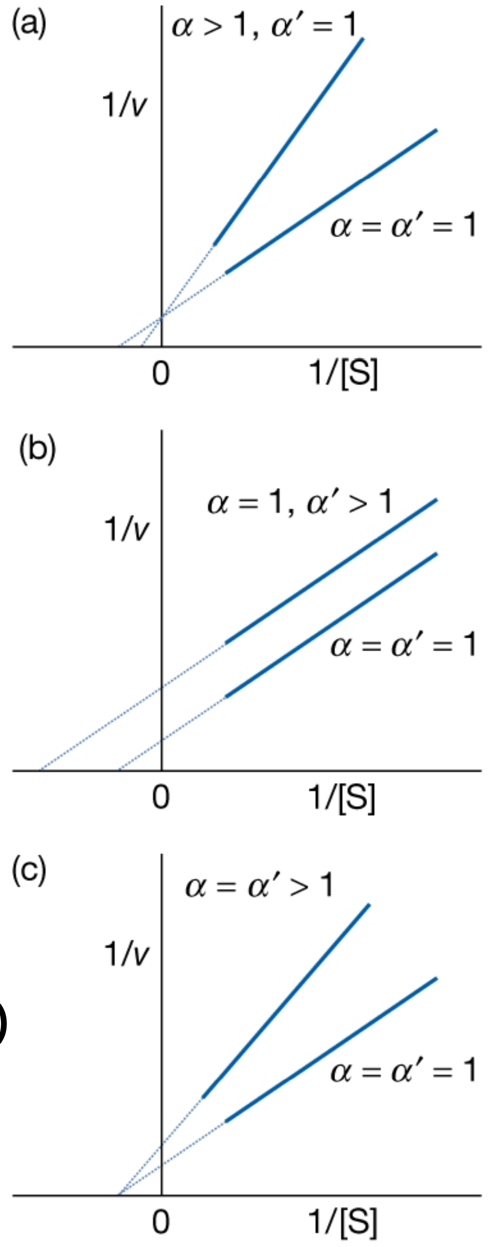
$$ES \longrightarrow P \qquad k_b$$

$$EI \longleftrightarrow E + I \qquad K_I = \frac{[E][I]}{[EI]}$$

$$ESI \longleftrightarrow ES + I \qquad K'_I = \frac{[ES][I]}{[ESI]}$$

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

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



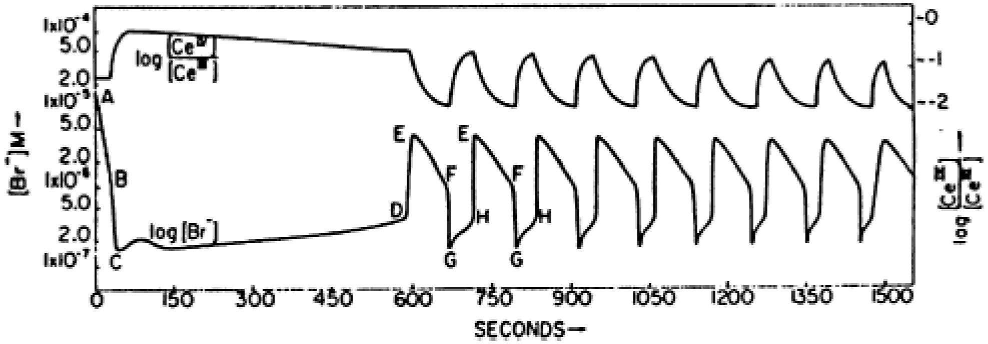
Inhibition modes:

- **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

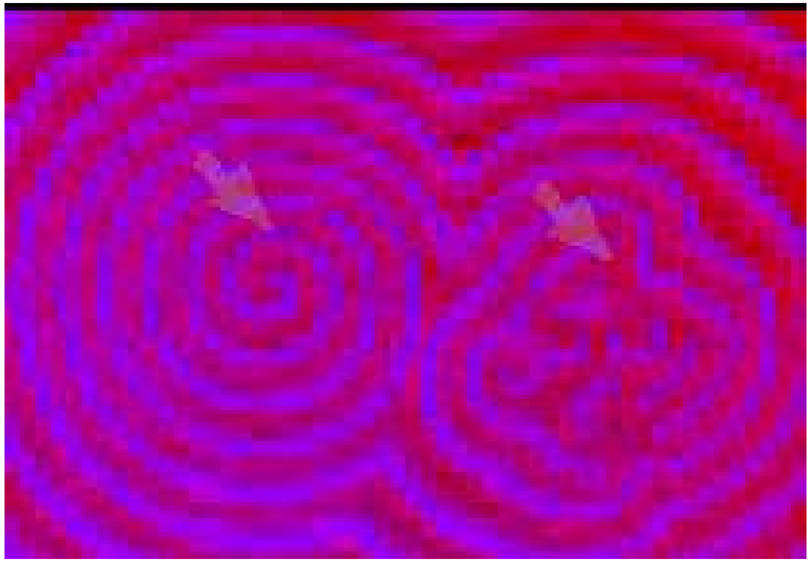
- Belousov-Zhabotinsky reaction

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 Oscillatins

- Autocatalysis – catalysis of a reaction by the products.

$$A \longrightarrow P$$

$$v = k[A][P]$$

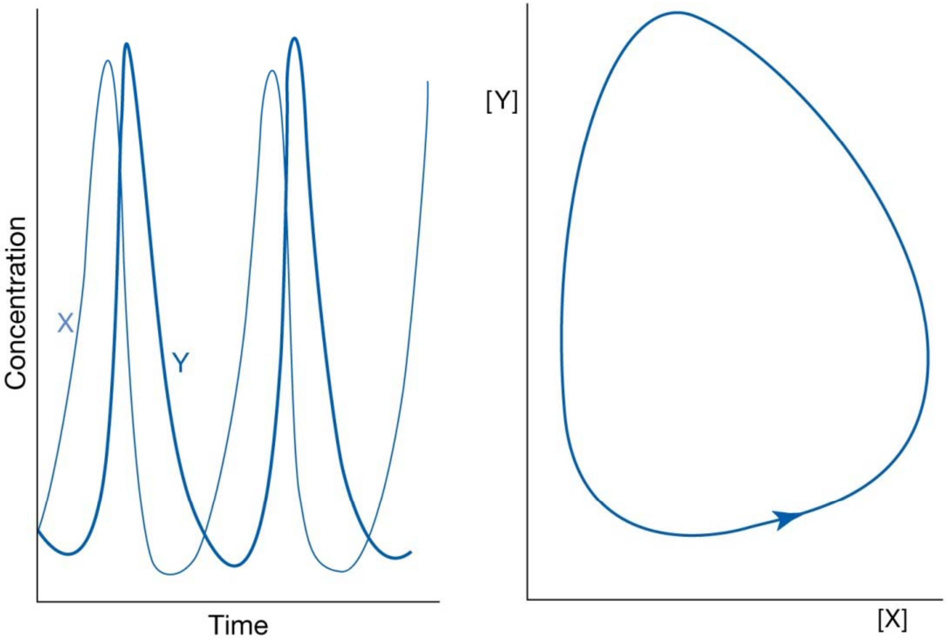
- The Lotka-Volterra mechanism

$$A + X \longrightarrow X + X \qquad \frac{d[A]}{dt} = -k_a[A][X]$$

$$X + Y \longrightarrow Y + Y \qquad \frac{d[X]}{dt} = -k_b[X][Y]$$

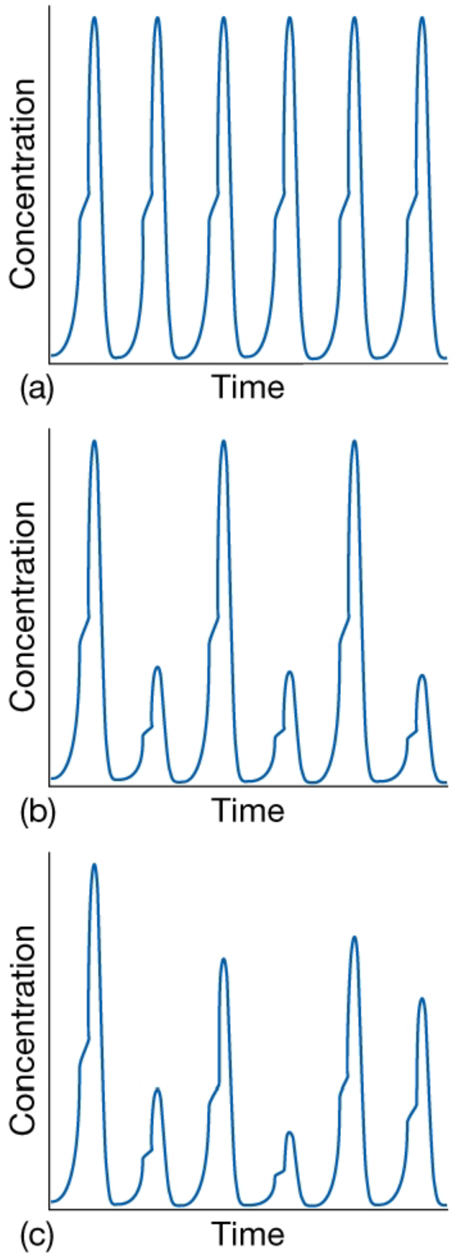
$$Y \longrightarrow B \qquad \frac{d[B]}{dt} = k_c[Y]$$

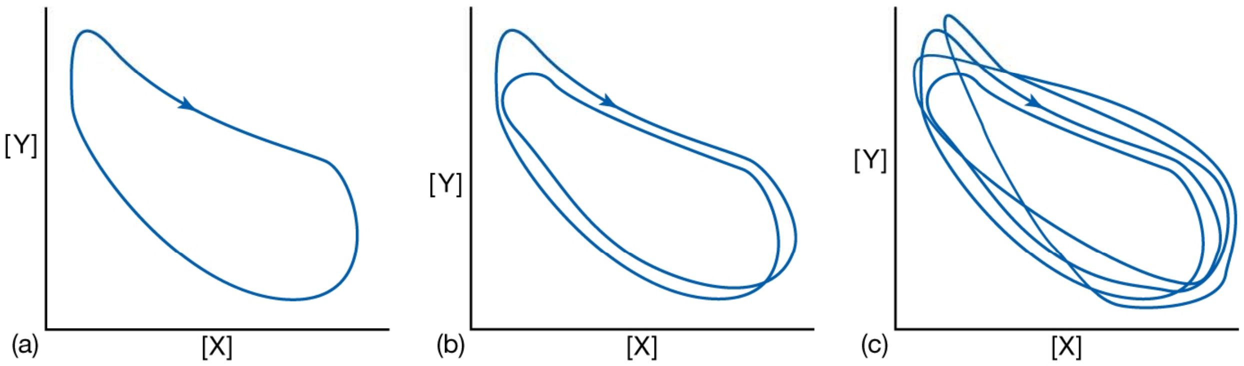
Concentration of A is held constant, product B is not participating in the reaction but is normally removed as well.



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





Problems

- **E22.10a** The second-order rate constant for the reaction

  $CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + CH_3CH_2OH(aq)$

  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 $[CH_3COOC_2H_5]$ = 0.100 mol dm^{-3}?
- **E22.16a** The effective rate constant for a gaseous reaction that has a Lindemann–Hinshelwood mechanism is $2.50 \times 10^{-4}\ s^{-1}$ at 1.30 kPa and $2.10 \times 10^{-5}\ s^{-1}$ 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 $2\ O_3(g) \rightarrow 3\ O_2(g)$ on the basis of the following proposed mechanism:

(1) $O_3 \leftrightarrow O_2 + O$ k_1, k_1'
(2) $O + O_3 \rightarrow O_2 + O_2$ 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=1.78x10^{-7} s^{-1} at 25ºC.
  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

(1) $N_2O \rightarrow N_2 + O$

(2) $O + SiH_4 \rightarrow SiH_3 + OH$

(3) $OH + SiH_4 \rightarrow SiH_3 + H_2O$

(4) $SiH_3 + N_2O \rightarrow SiH_3O + N_2$

(5) $SiH_3O + SiH_4 \rightarrow SiH_3OH + SiH_3$

(6) $SiH_3 + SiH_3O \rightarrow (H_3Si)_2O$

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