

Lecture 6: Diffusion and Reaction kinetics

12-10-2010

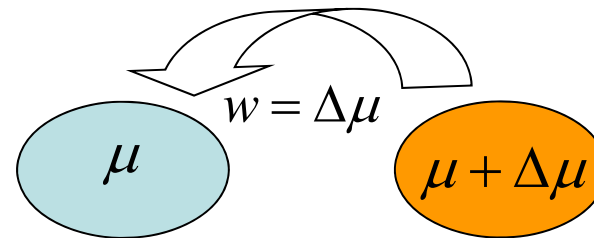
- Lecture plan:
 - diffusion
 - thermodynamic forces
 - evolution of concentration distribution
 - reaction rates and methods to determine them
 - reaction mechanism in terms of the elementary reaction steps
 - basic reaction types
 - problems

Diffusion

- **Thermodynamic force**

If the chemical potential depends on position, the maximum nonexpansion work

$$dw = d\mu = \left(\frac{\partial \mu}{\partial x} \right)_{p,T} dx$$



Comparing with $dw = -Fdx$

$$F = - \left(\frac{\partial \mu}{\partial x} \right)_{p,T} \longleftarrow \textit{Thermodynamic force}$$

Diffusion

- Thermodynamic force of concentration gradient

$$\mu = \mu_0 + RT \ln a$$

$$F = -RT \left(\frac{\partial \ln a}{\partial x} \right)_{p,T} \quad \xrightarrow{\text{For ideal solution}} \quad F = -\frac{RT}{c} \left(\frac{\partial c}{\partial x} \right)_{p,T}$$


Fick's law of diffusion:

$$\text{Particles flux: } J \sim \text{drift velocity} \sim F \sim \frac{\partial c}{\partial x}$$

Diffusion

- The Einstein relation

$$J = -D \frac{\partial c}{\partial x} \qquad J = \frac{s \Delta A t c}{A \Delta t} = s c$$



$$s c = -D \frac{\partial c}{\partial x}$$
$$s = -\frac{D}{c} \frac{\partial c}{\partial x} = \frac{DF}{RT}$$

In the case of charged particle (ion) in electric field we know drift speed vs force relation for ion mobility, so we can deduce diffusion constant

$$s = uE = \frac{DzeN_A E}{RT} \qquad \Rightarrow \qquad \boxed{D = \frac{uRT}{zF}} \qquad \text{Einstein relation}$$

For example: for $\mu = 5 \cdot 10^{-8} \text{ m}^2 / \text{sV}$ we find $D = 1 \cdot 10^{-9} \text{ m}^2 / \text{s}$

Diffusion

- The Nernst-Einstein equation

Molar conductivity of ions in the solution

$$\lambda = z\mu F = \frac{z^2 DF^2}{RT}$$

$$\Lambda_m = (v_+ z_+^2 D_+ + v_- z_-^2 D_-) \frac{F^2}{RT}$$

- The Stokes-Einstein equation

$$\begin{array}{l}
 \mu E = \frac{ezE}{f} \\
 \text{Frictional force} \rightarrow f \\
 D = \frac{\mu RT}{zF}
 \end{array}
 \rightarrow
 D = \frac{zeRT}{fzF} = \frac{zekN_A T}{fzeN_A} = \frac{kT}{f}$$

Using Stokes's law

$$D = \frac{kT}{6\pi\eta a}$$

No charge involved -> applicable to all molecules

Diffusion equation

- How concentration distribution evolves with time due to diffusion

$$\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}$$

$$J - J' = -D \frac{\partial c}{\partial x} + D \frac{\partial c'}{\partial x} = -D \frac{\partial c}{\partial x} + D \frac{\partial}{\partial x} \left(c + \left(\frac{\partial c}{\partial x} \right) l \right) = Dl \frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Diffusion with convection

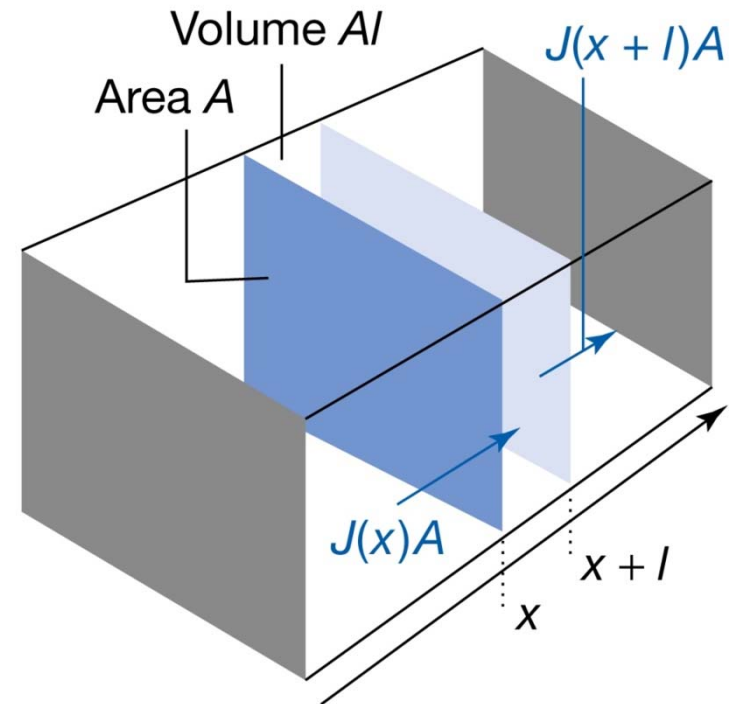
$$\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}$$

$$J - J' = cv - c'v = \left(c - \left(c + \left(\frac{\partial c}{\partial x} \right) l \right) \right) v = vl \frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = v \frac{\partial c}{\partial x}$$

due to convection only

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}$$



Solution of diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}$$

- 2nd order differential equation: two boundary condition are required for spatial dependence and single for time dependence

Example 1:

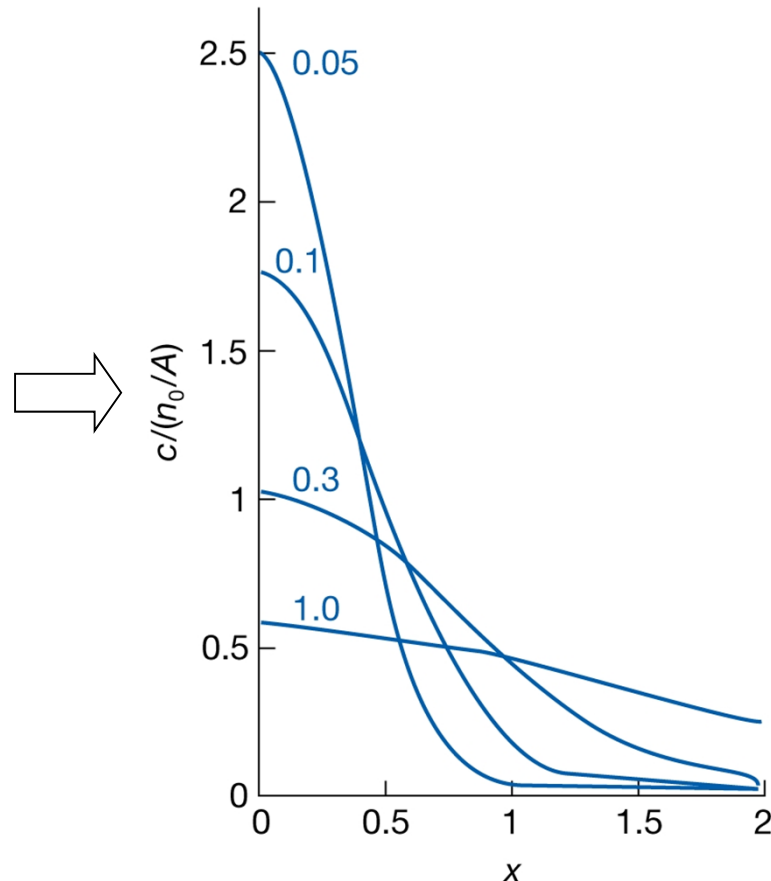
one surface of a container ($x=0$) is coated with N_0 molecules at time $t=0$

$$c(x, t) = \frac{n_0}{A(\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

Example 2:

dissolution infinitely small solid containing N_0 molecules at time $t=0$ in 3D solvent

$$c(r, t) = \frac{n_0}{8(\pi Dt)^{3/2}} e^{-r^2/4Dt}$$



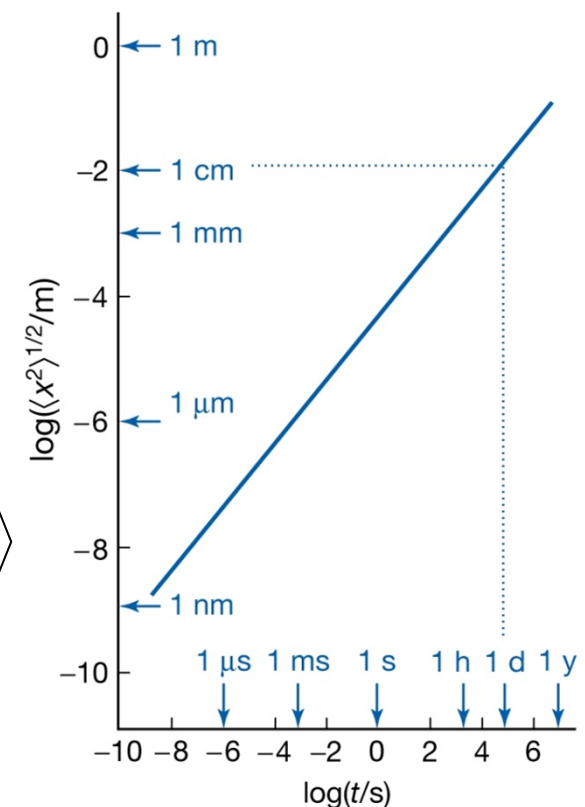
Diffusion probabilities

- Probability to find a particle at a given slab of thickness dx is proportional to the concentration there: $p(x) = c(x)AN_A dx / N_0$
- The mean distance traveled by the particles:

$$\langle x \rangle = \int_0^{\infty} \frac{c(x)AN_A dx}{N_0} = \frac{1}{(\pi Dt)^{1/2}} \int_0^{\infty} x e^{-x^2/4Dt} dx = 2 \left(\frac{Dt}{\pi} \right)^{1/2}$$

$$\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}$$

Diffusion in unstirred solution, $D=5 \times 10^{-10} \text{ m}^2/\text{S}$



Random Walk

- Apparently diffusion can be modeled as a random walk, where particle is jumping distance λ in a time τ . Direction of the jump is chosen randomly
- One dimensional walk:

$$p = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2\tau/2t\lambda^2}$$

Comparing with the solution of diffusion equation

$$D = \frac{\lambda^2}{2\tau}$$

Einstein-Smoluchowski equation

Connection between microscopic and macroscopic parameters.

RATES OF CHEMICAL REACTIONS

Rates of chemical reactions



Instantaneous rate of consumption of a reactant:

$$-d[R]/dt$$

Instantaneous rate of formation of a product:

$$d[P]/dt$$

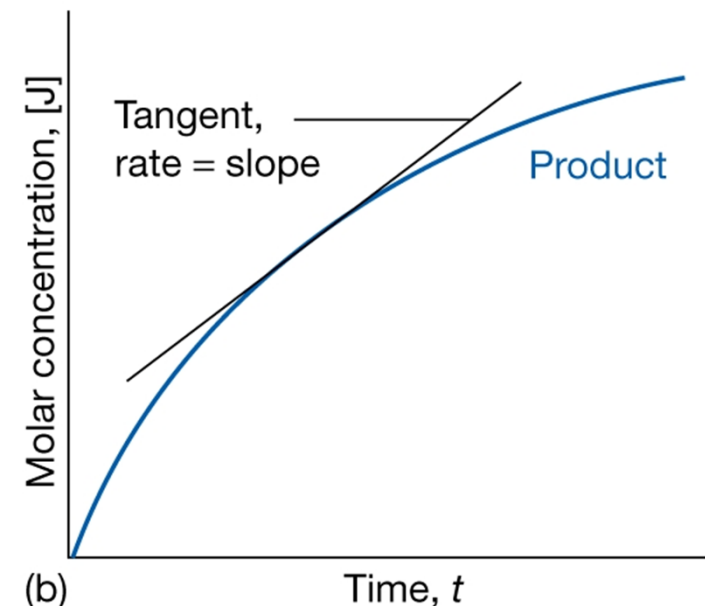
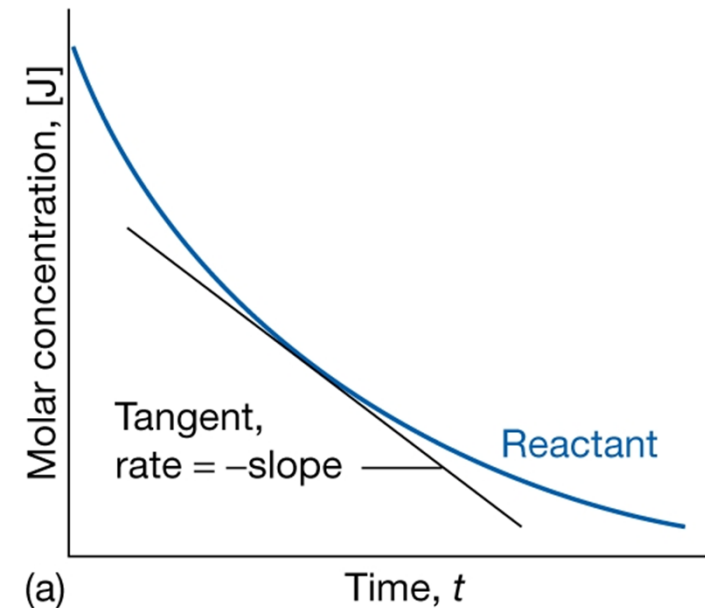
From stoichiometry

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

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/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:

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

algebraic dependence on the reagent concentration raised to some power

reaction order with respect to species A: α

overall reaction order: $\alpha + \beta \dots$

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:

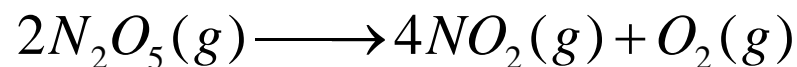
$$v = k \quad \longrightarrow \quad \text{Zero order.} \quad [M \cdot s^{-1}]$$

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

$$v = k[A]^{1/2}[B] \quad \longrightarrow \quad \text{Halforder in A, first order in B, overall three-halves order.}$$

Measuring the rates of chemical reactions

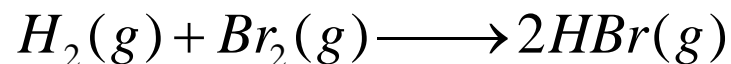
- Experimental measuring progress of the reaction
 - Monitoring pressure in the reaction involving gases



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

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

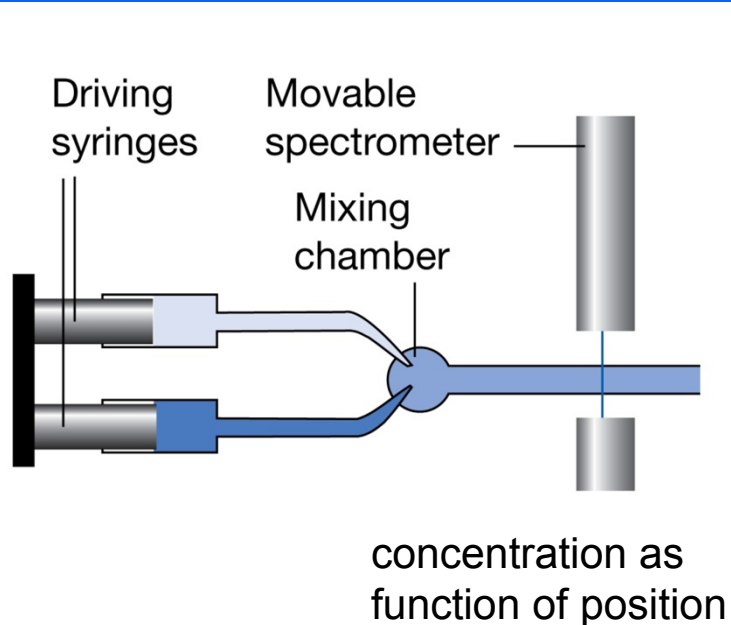
- Absorption at particular wavelength (e.g. Br₂ below)



- Conductance of the ionic solution

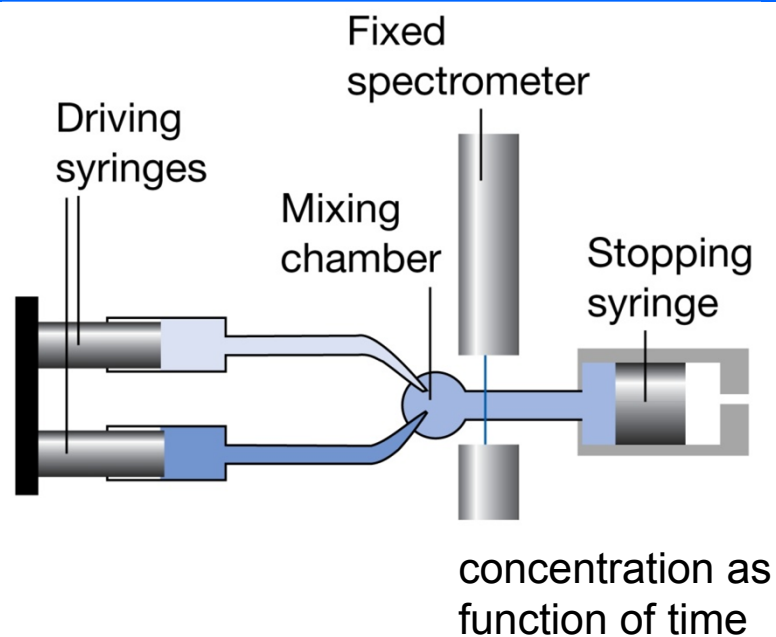


Measuring the Rates of chemical reactions



- 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)

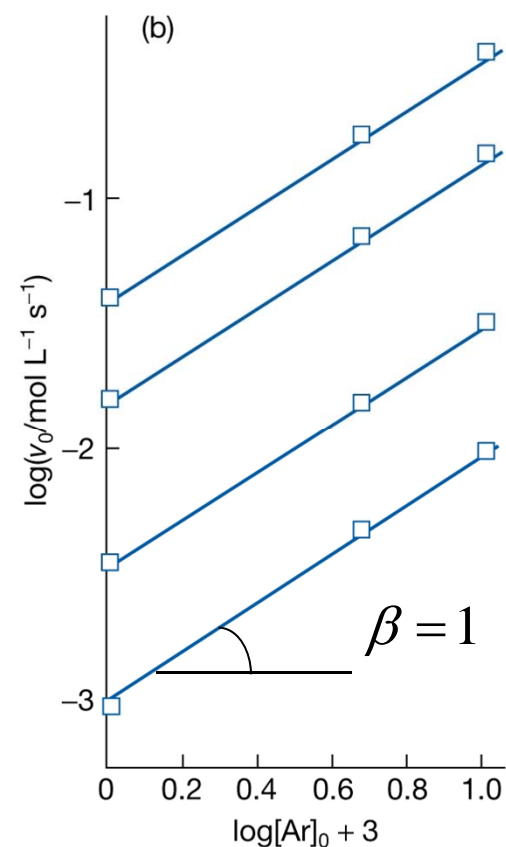
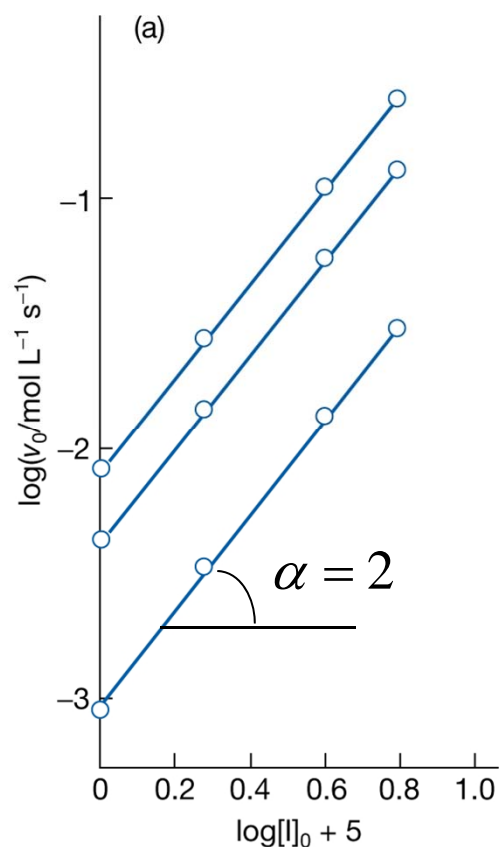
$$v_0 = k'[A_0]^a \quad \log v_0 = \log k' + a \log[A_0]$$

Measuring the rates of chemical reactions

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

A

B



Integrated rate laws

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

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

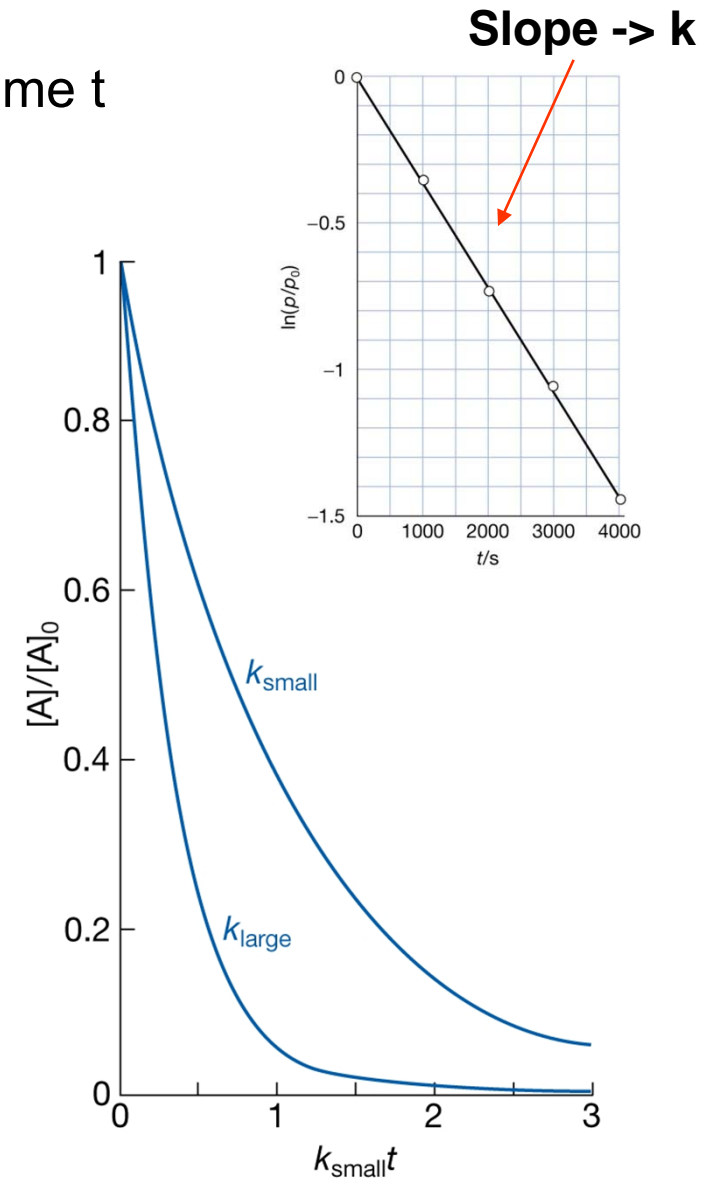
$$\Rightarrow \ln\left(\frac{[A]}{[A_0]}\right) = -kt \quad \Rightarrow \quad [A] = [A_0]e^{-kt}$$

- **Half-life** – time required for concentration to drop by 1/2.

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

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

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



Integrated rate laws

- Second-order reactions

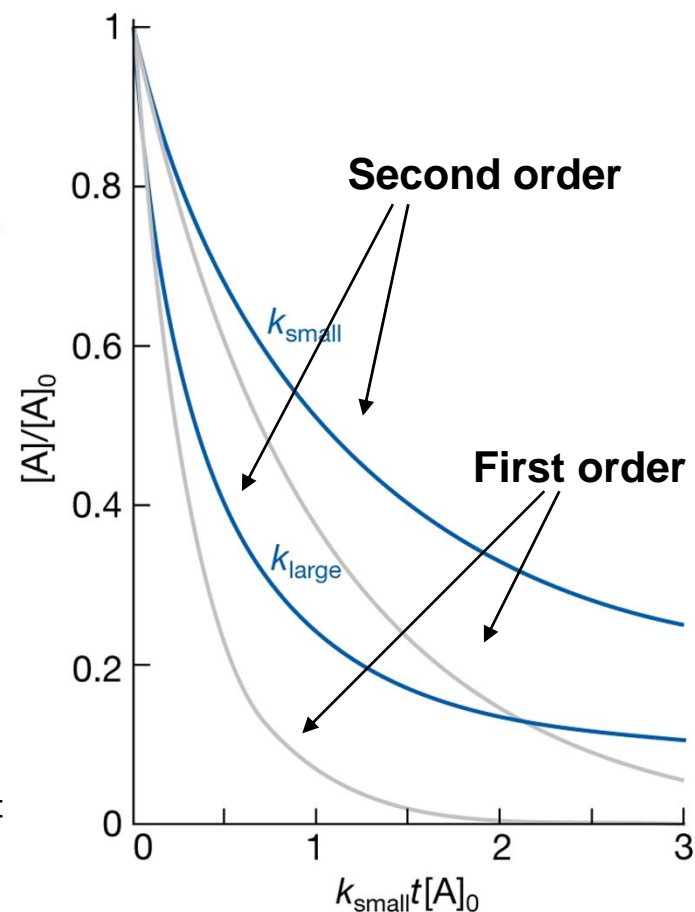
$$\frac{d[A]}{dt} = -k[A]^2 \quad \Rightarrow \quad \int_{A_0}^A \frac{d[A]}{[A]^2} = -k \int_0^t dt \quad \Rightarrow$$

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

– **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**.



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

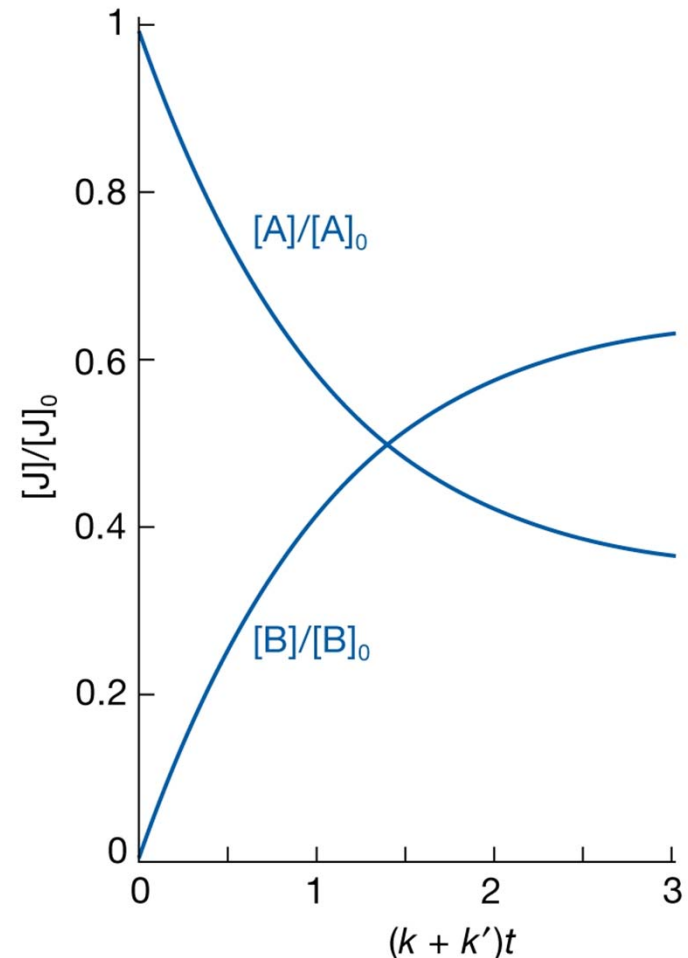
$$\frac{dA}{dt} = -k[A] + k'([A]_0 - [A])$$

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

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

Generally:

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



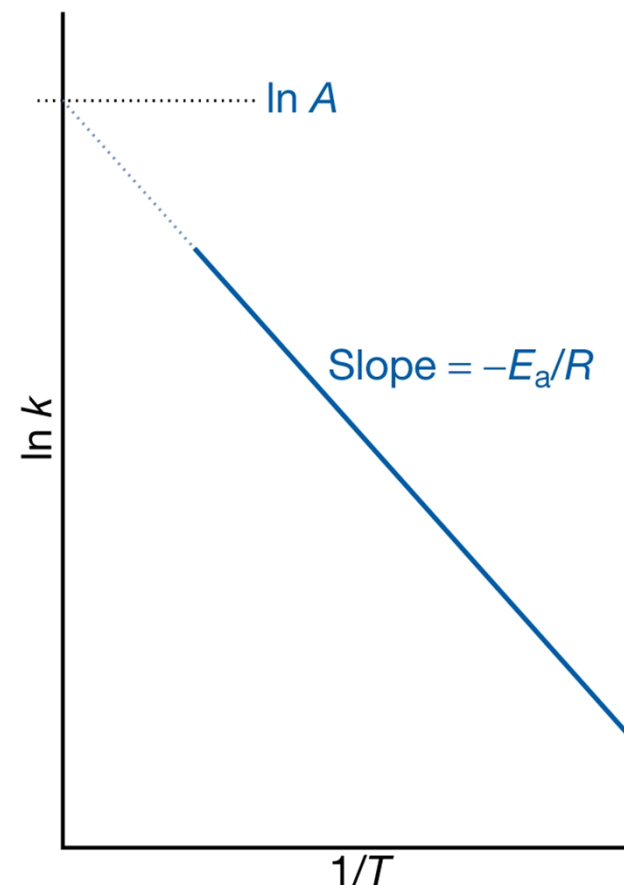
The temperature dependence of reaction rate

- 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



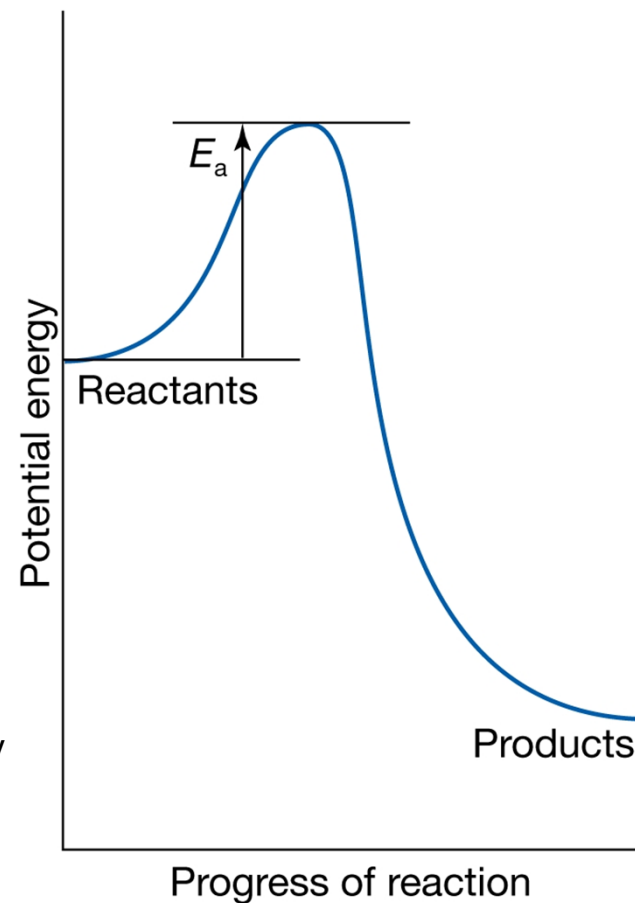
The temperature dependence of reaction rate

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

$$k = A e^{-E_a/RT}$$

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.

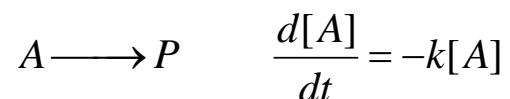


reaction coordinate: e.g. changes of interatomic distances or angles

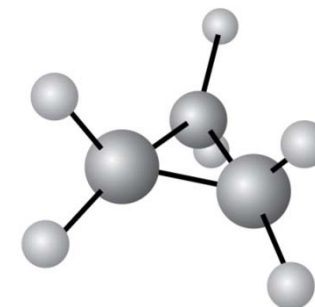
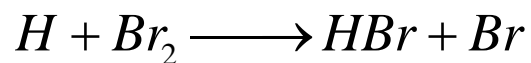
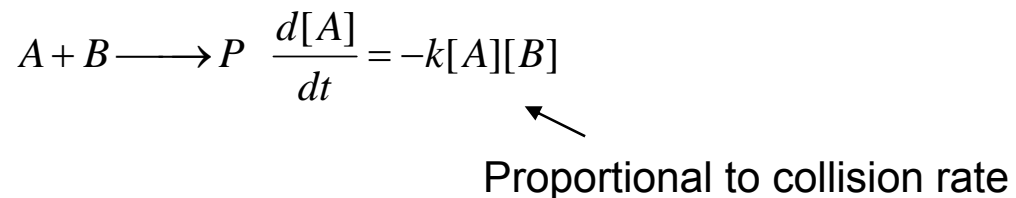
Elementary reactions

- 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**)

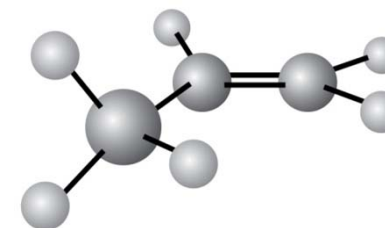
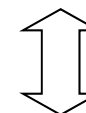
Uni-molecular: first order in the reactant



Bimolecular: first order in the reactant



1 Cyclopropane



2 Propene

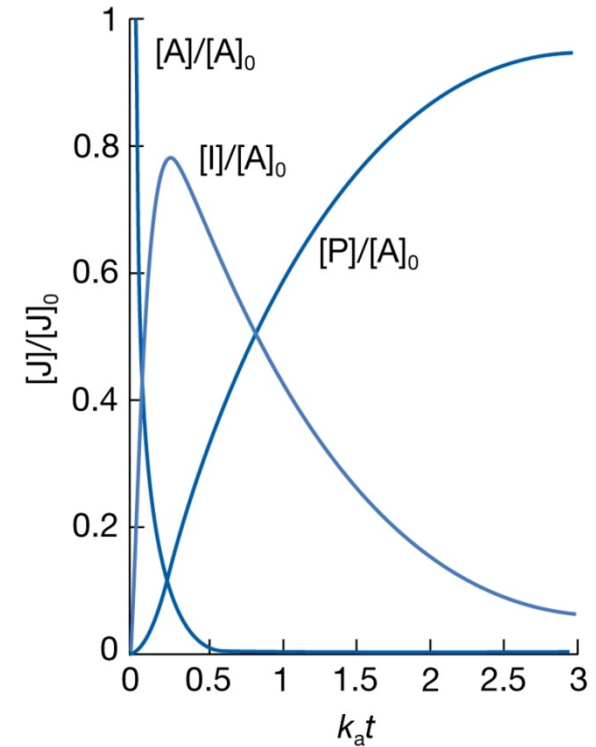
Consecutive elementary reactions



$$\frac{d[A]}{dt} = -k_a[A]$$

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

$$\frac{d[P]}{dt} = k_b[I]$$



Solution for A should be in a form: $[A] = [A]_0 e^{-k_a t}$

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

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

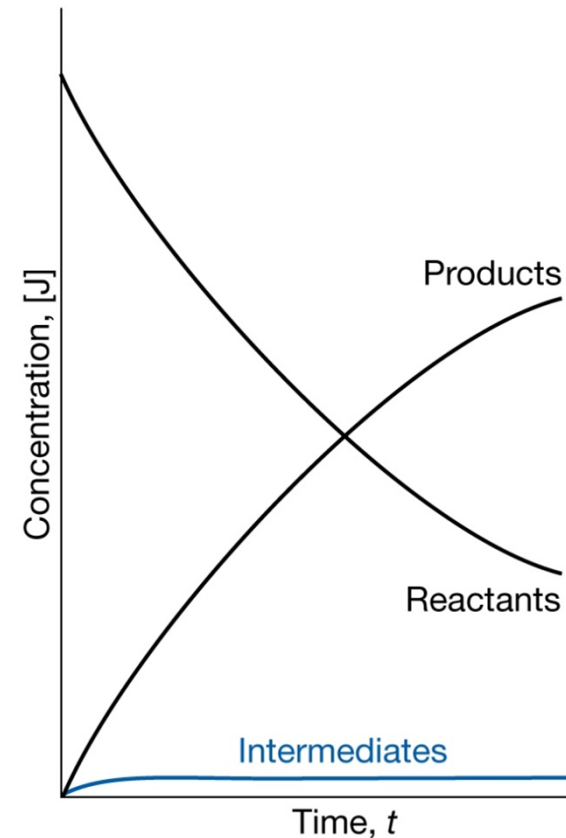
Consecutive elementary reactions

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

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

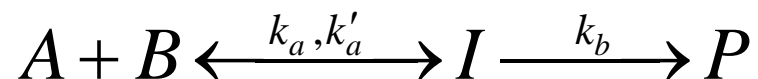
and $\frac{d[P]}{dt} = k_b[I] \approx k_a[A]$

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



Consecutive elementary reactions

- Pre-equilibria



This condition arises when $k'_a \gg k_b$.

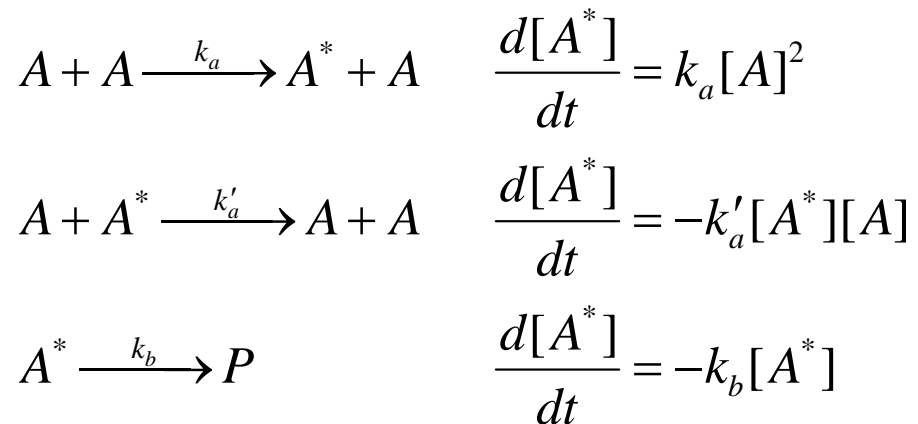
Then
$$K = \frac{[I]}{[A][B]} = \frac{k_a}{k'_a}$$

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

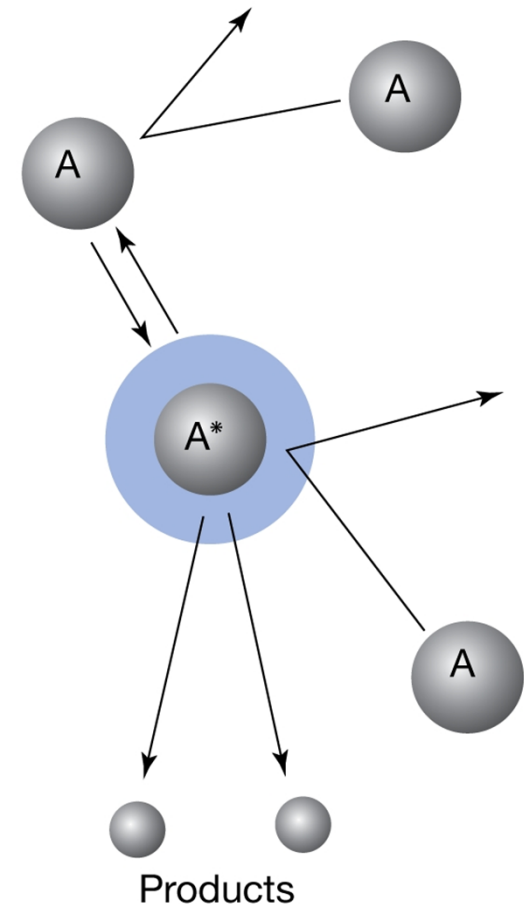
Second order form with composite rate constant

Unimolecular reactions

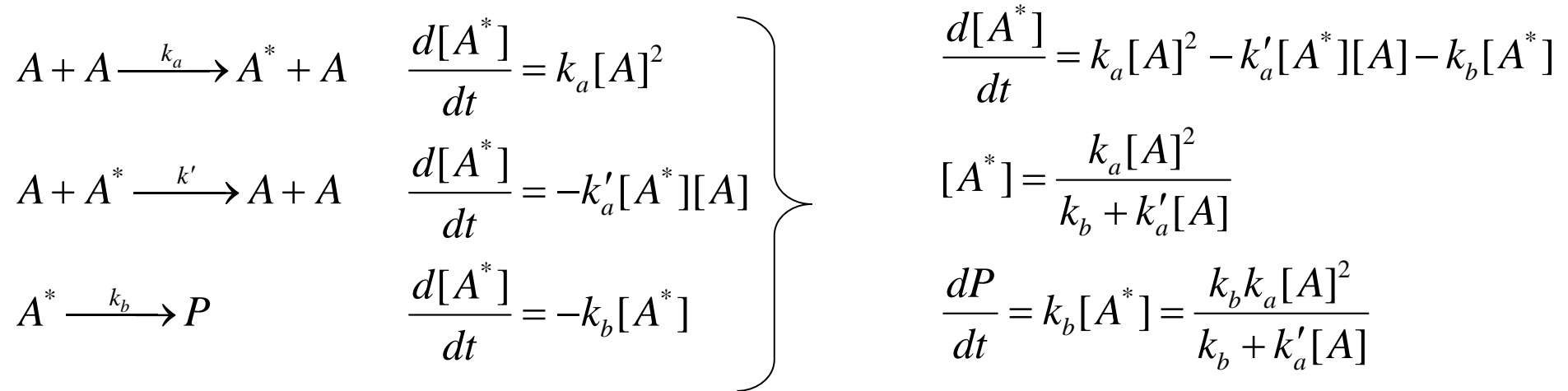
- As the molecule acquires the energy as a result of collision why the reaction is still a first order?
- **Lindemann-Hinshelwood mechanism**



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



Lindemann-Hinshelwood mechanism



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

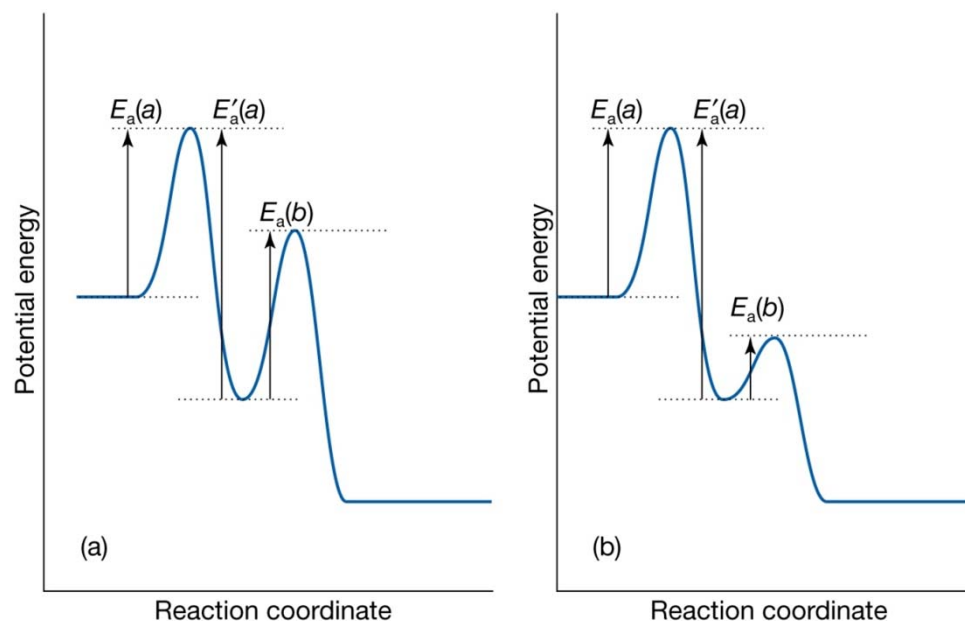
Let's consider Lindemann-Hinshelwood mechanism and apply Arrhenius-like temperature dependence to each rate constant

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

Overall activation energy can be positive or negative

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

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



Problems

- **P20.35.** The diffusion coefficient of particular RNA molecule is $1.0 \times 10^{-11} \text{ m}^2/\text{s}$. Estimate time required for a molecule to diffuse 1 μm from nucleus to the cell wall
- **E21.11a** 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 $0.11 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. 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 $[\text{NaOH}] = 0.050 \text{ mol dm}^{-3}$ and $[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.100 \text{ mol dm}^{-3}$?
- **E21.17a** 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.