



Univerzita Palackého
v Olomouci

**Úvod do obecné a fyzikální chemie
KFC/UOFCH
Struktura atomů a molekul
KFC/SAM**

10. Reakce molekul

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Osnova kurzu

- Úvod – půjdeme „odspodu“
- Stavba
 - Elementární částice
 - Atomy
 - Molekuly
 - Makromolekuly
- Interakce
 - V rámci molekul
 - Mezi molekulami
 - Se světlem
- Pohyby molekul

Shrnutí z minula

- Spojením I. a II. věty termodynamiky lze odvodit tzv. volné energie
- Volné energie dávají informaci o samovolnosti reakcí
- Zdroje energie se aktuálně rapidně proměňují a chemici na to musejí reagovat

Chemická kinetika

- rychlost chemických reakcí
- reakční mechanismus
 - tranzitní stav
- reakční rychlost
 - úbytek reaktantu, nebo příbytek produktu v čase
- rovnováha – kinetická definice
- katalýza
 - na pevné fázi
 - enzymatická



Časová škála chemické reakce

- Oxidace železa: $\text{Fe} + \text{vzduch} \rightarrow \text{Fe}_2\text{O}_3$



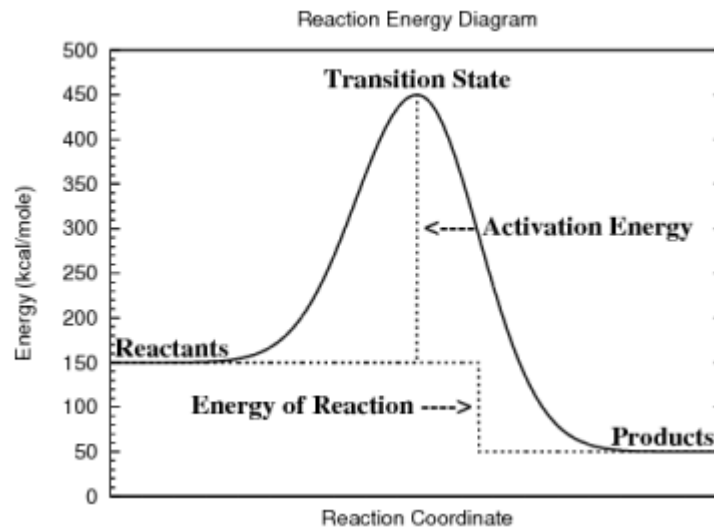
Nanočástice železa
RCPTM



Iron Pillar of Delhi
6 t, 400 n.l.

Rychlost chemické reakce

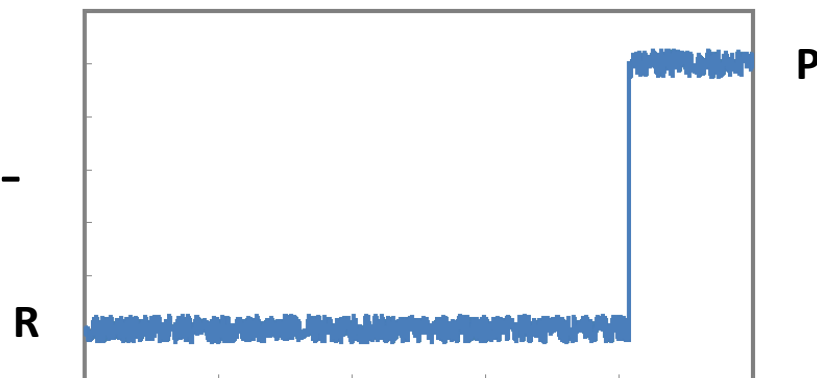
- Reaktant \rightleftharpoons Produkt



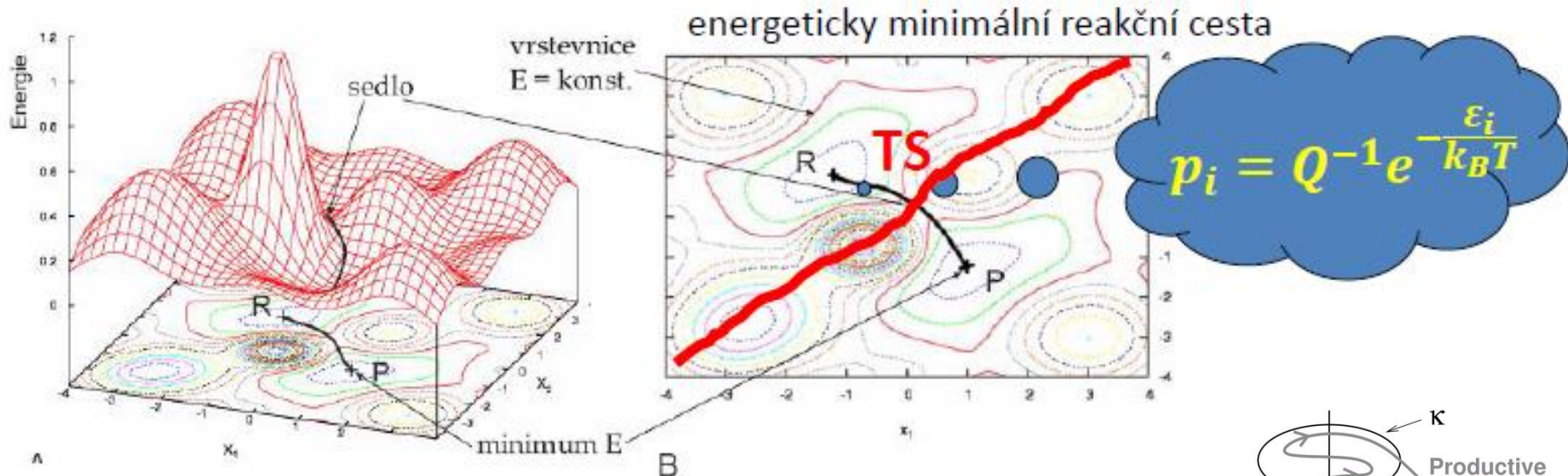
- Náhodnost reakce

~ms až roky

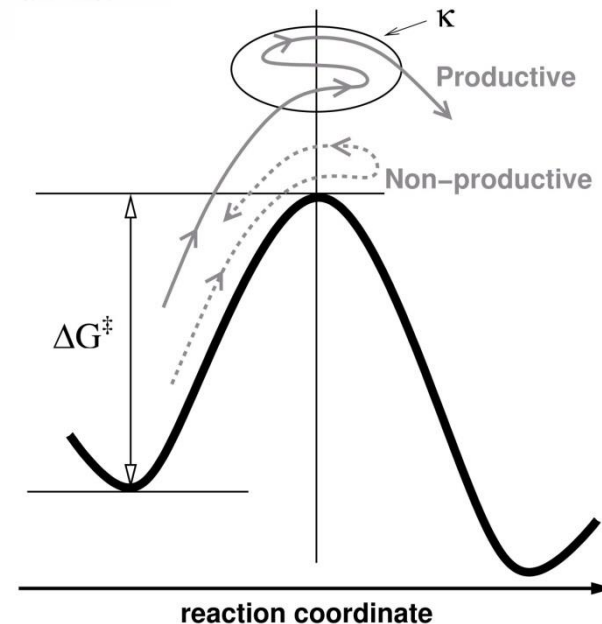
- Rare event vznik/zánik vazeb $\sim 1-10$ fs



Teorie tranzitního stavu



- Molekuly stojící na dělicí ploše a mířící do P skončí v P
- Neuvažujeme recrossing a tunelování
- Za čas dt zreaguje dn molekul \rightarrow pravděpodobnost reakce
- $dn = -k \cdot n \cdot dt$



Teorie tranzitního stavu

- $dn = -k \cdot n \cdot dt$

- Arheniova rovnice

$$k = Ae^{-\frac{E_a}{RT}}$$

- Eyringova rovnice

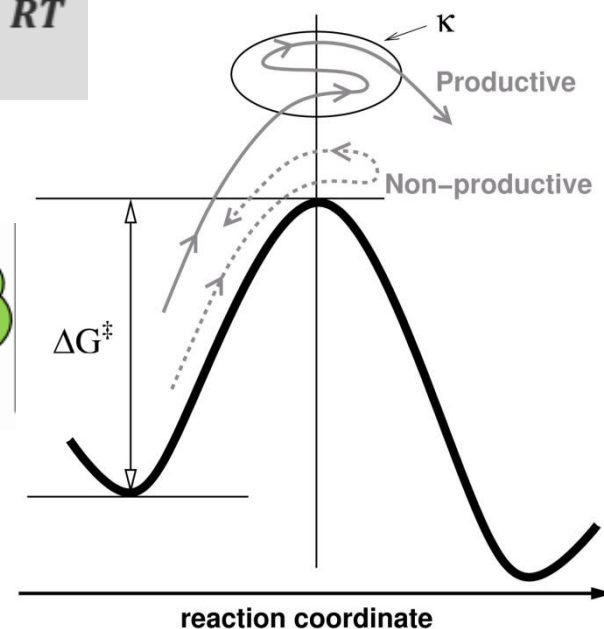
$$k = \left(\frac{k_B T}{h}\right) e^{-\frac{\Delta G^\ddagger}{RT}}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

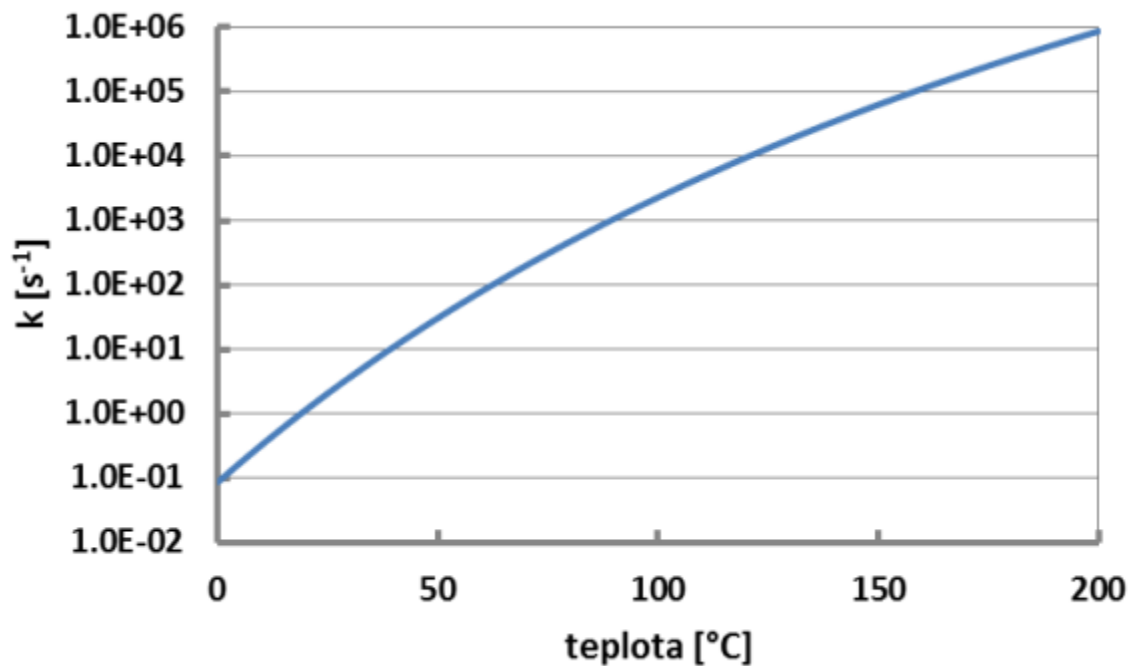
vliv
enthalpie
(energie)

$$k = \left(\frac{k_B T}{h}\right) e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

vliv
entropie



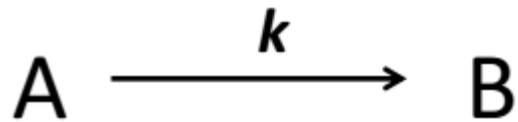
Rychlost reakce vz teplota



- Empirické pravidlo:
 - Cca co 10°C se rychlost reakce zvětší 2x

$$k = \left(\frac{k_B T}{h} \right) e^{-\frac{\Delta H^{\ddagger}}{RT}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}}$$

Teorie tranzitního stavu – dopředná reakce



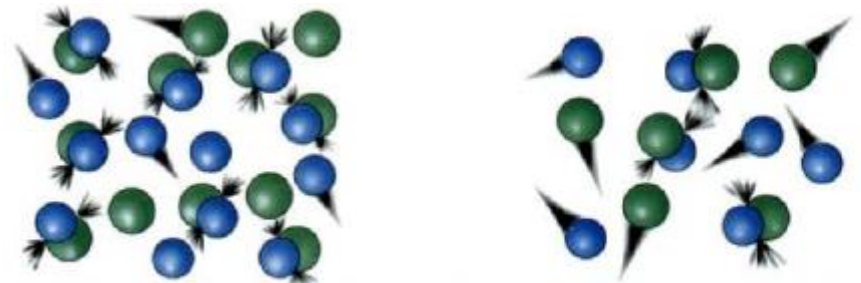
$$-\frac{dn_A}{dt} = +\frac{dn_B}{dt} = +k \cdot n_A$$

$$-dn_A = +k \cdot n_A \cdot dt$$

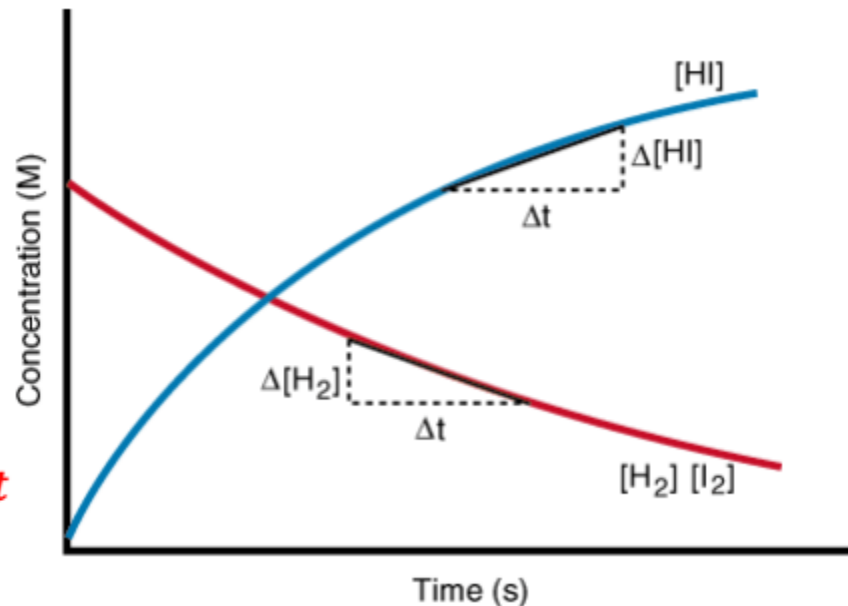
$$\int_{n_{A0}}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

$$\ln \frac{n_A}{n_{A0}} = -k \cdot t$$

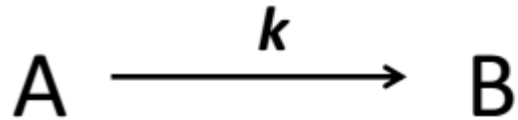
$$n_A = n_{A0} e^{-kt} \quad c_A = c_{A0} e^{-kt}$$



High concentration = More collisions Low concentration = Few collisions



Teorie tranzitního stavu – dopředná reakce



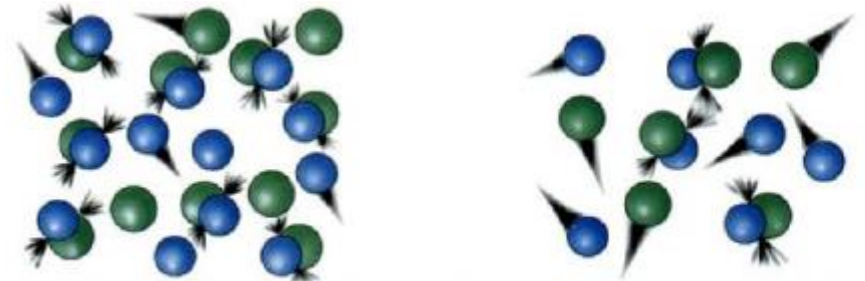
$$\frac{dn_A}{dt} = -\frac{dn_B}{dt} = -k \cdot n_A$$

$$dn_A = -k \cdot n_A \cdot dt$$

$$\int_{n_{A0}}^{n_A} \frac{dn_A}{n_A} = -k \int_0^t dt$$

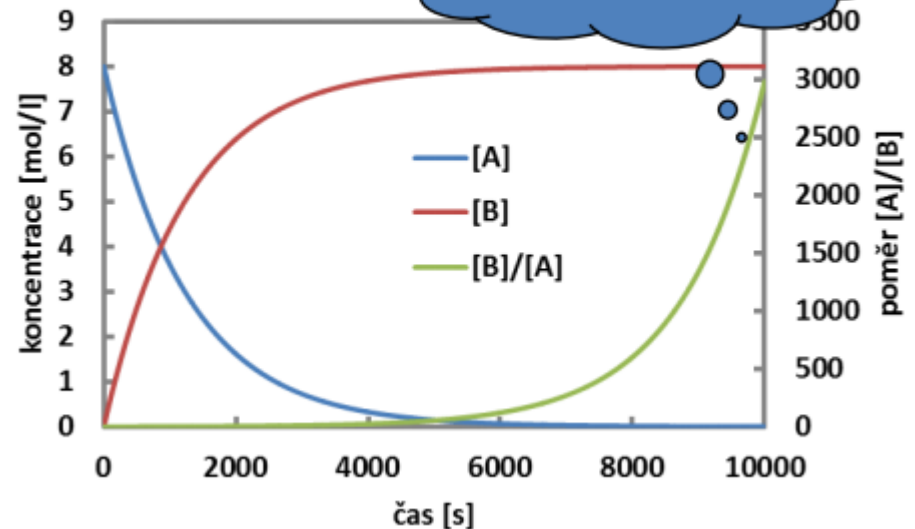
$$\ln \frac{n_A}{n_{A0}} = -k \cdot t$$

$$n_A = n_{A0} e^{-kt} \quad c_A = c_{A0} e^{-kt}$$



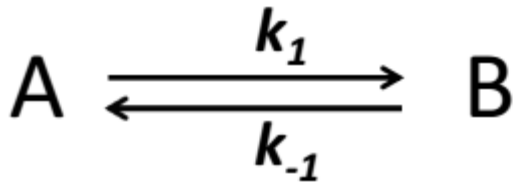
High concentration = More collisions Low concentration = Few collisions

Není v rovnováze



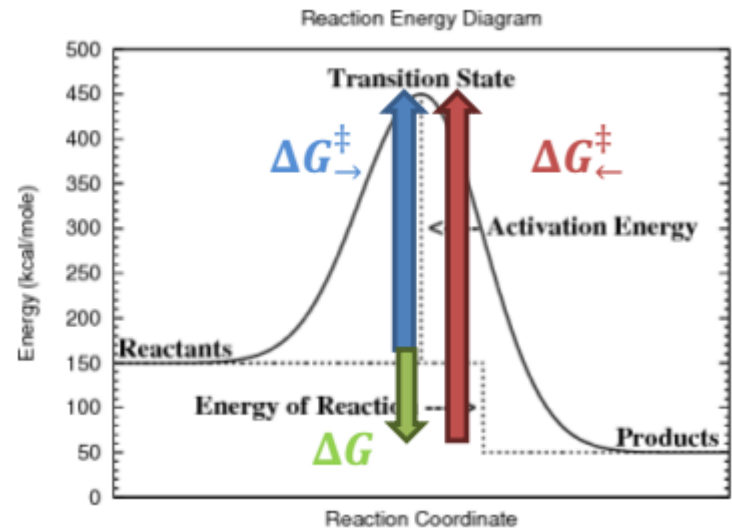
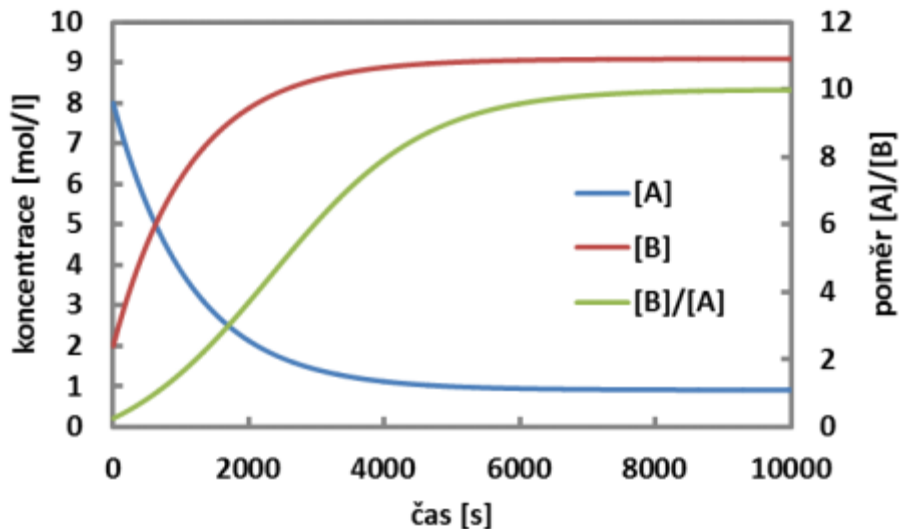
Teorie tranzitního stavu

- zvratná reakce



$$\frac{dc_A}{dt} = -k_1 \cdot c_A + k_{-1} \cdot c_B$$

$$\frac{dc_B}{dt} = +k_1 \cdot c_A - k_{-1} \cdot c_B$$



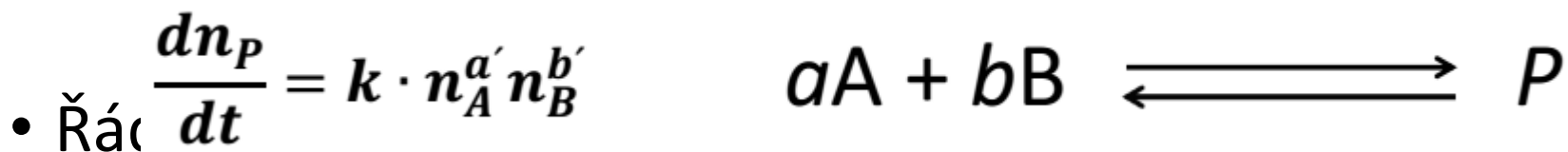
$$k_1 = \left(\frac{k_B T}{h} \right) e^{-\frac{\Delta G_{\rightarrow}^{\ddagger}}{RT}}$$

$$k_{-1} = \left(\frac{k_B T}{h} \right) e^{-\frac{\Delta G_{\leftarrow}^{\ddagger}}{RT}}$$

$$\lim_{t \rightarrow \infty} \frac{c_B(t)}{c_A(t)} = K = \frac{k_1}{k_{-1}} = e^{-\frac{\Delta G}{RT}}$$

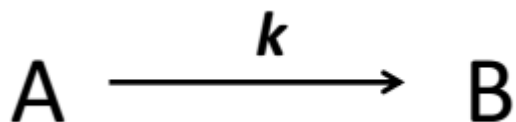
Reakční kinetika - pojmy

- Molekularita reakce – počet molekul v reakci
 - Monomolekulární – rozpady, přesmyky
 - Bimolekulární – většina reakcí
 - Trimolekulární – vzácně, např. reakce NO_x



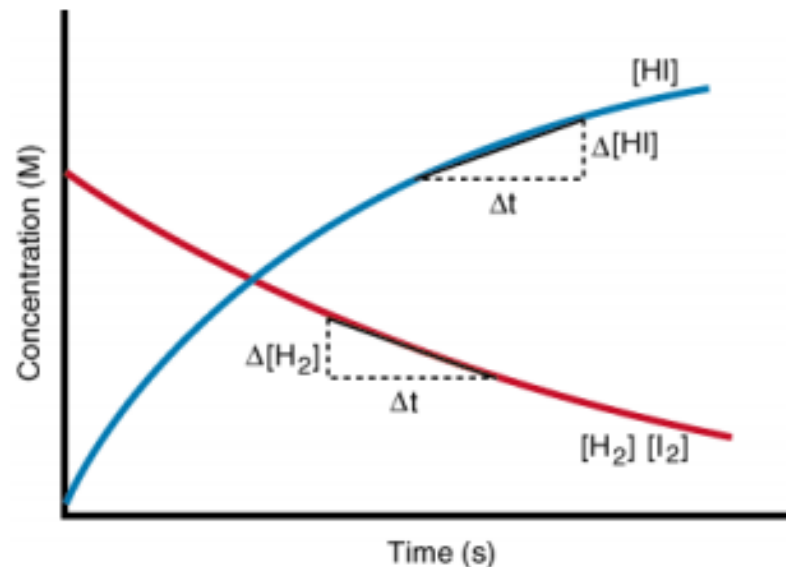
- nemusí nutně odpovídat stechiometrickým koef.
- Nemusí být nutně celá čísla

Reakce 1. řádu



$$\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -k \cdot c_A$$

$$c_A = c_{A0} e^{-kt}$$



Reakce pseudo-prvního řádu

Jedna složka v nadbytku – relativně „skoro neubývá“



$$\frac{dc_P}{dt} = k \cdot c_A \cdot c_B$$

$$c_B \gg c_A \Rightarrow k' = k \cdot c_B$$

$$\frac{dc_P}{dt} = k' \cdot c_A$$

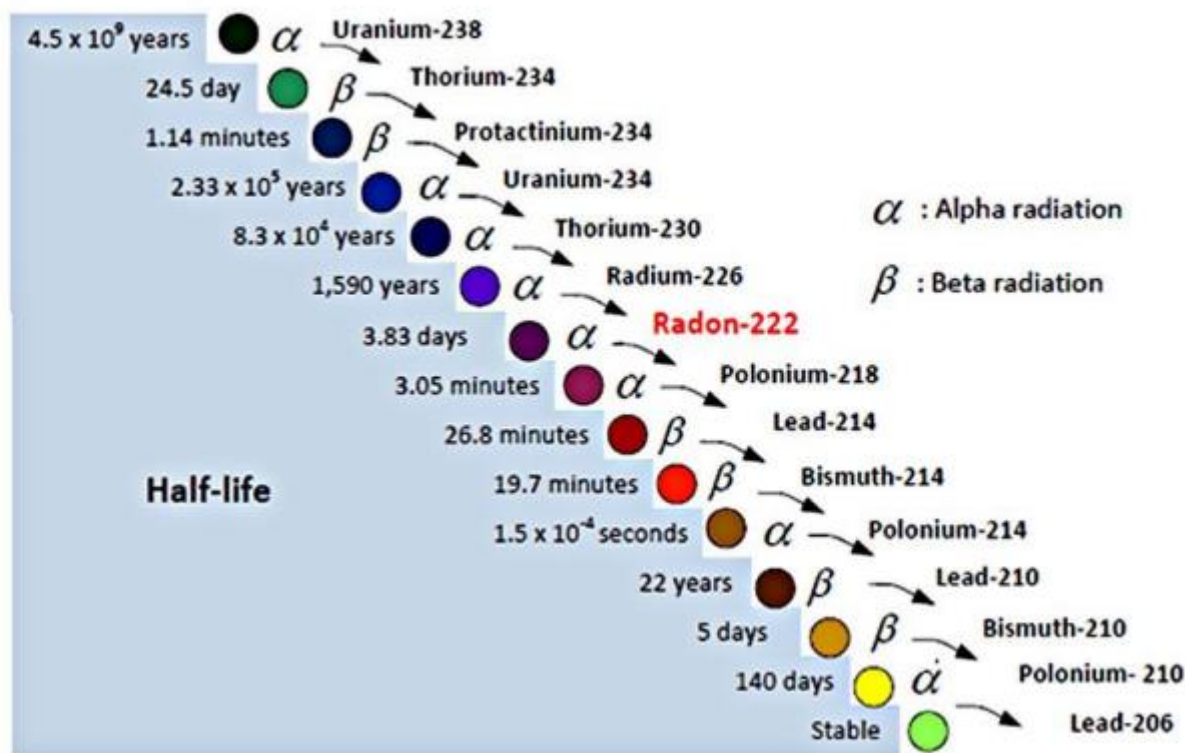
Poločas reakce

- Čas, za který zreaguje polovina látky
 - typicky radioaktivní reakce

$$n_A = n_{A0} e^{-kt}$$

$$\frac{n_{A0}}{2} = n_{A0} e^{-kT_{1/2}}$$

$$T_{1/2} = \frac{\ln 2}{k}$$



Reakce 2. řádu



$$\frac{dc_P}{dt} = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -k \cdot c_A \cdot c_B$$

$$\frac{dx}{dt} = k \cdot (c_{A0} - x) \cdot (c_{B0} - x)$$

$$\int_0^x \frac{dx}{(c_{A0} - x) \cdot (c_{B0} - x)} = \int_0^t k \cdot dt$$

$$\frac{1}{c_{A0} - c_{B0}} \ln \frac{c_{B0}(c_{A0} - x)}{c_{A0}(c_{B0} - x)} = kt$$

$$c_{B0} \gg c_{A0}$$

Pseudo-prvního řádu

Reakce 0. řádu

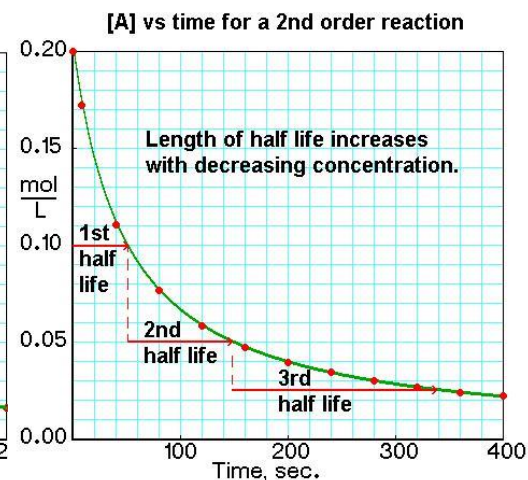
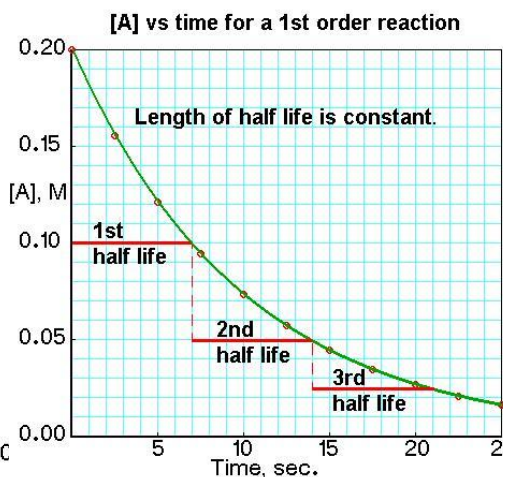
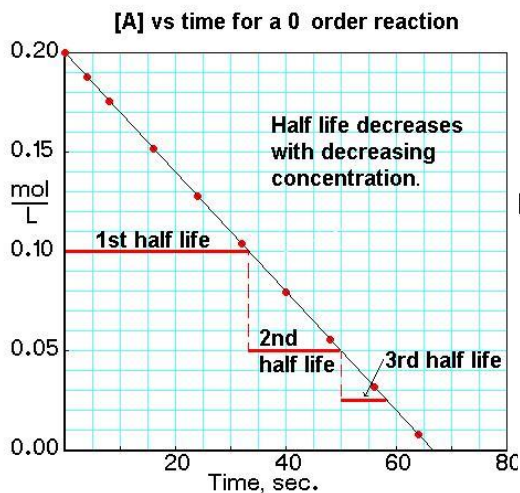
- $A^* \rightarrow P$
- nejčastěji tzv. pseudonultý řád
 - např. odbourávání alkoholu

$$\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -k$$

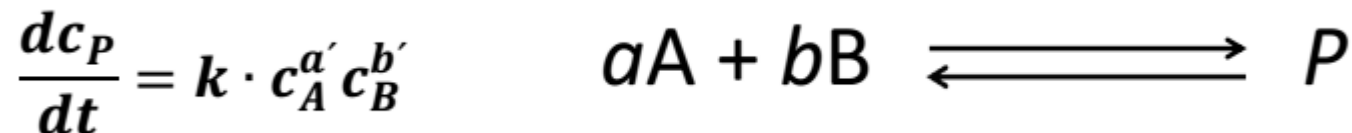
$$c_A = c_{A,0} - kt$$

Srovnání řádů reakcí

Řád	0. řád	1. řád	2. řád
Rovnice Diferenciální forma	$\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -k$	$\frac{dc_A}{dt} = -k[A]$	$\frac{dc_A}{dt} = -k[A]^2$
Integrální forma	$c_A = c_{A,0} - kt$	$c_A = c_{A,0}e^{-kt}$	$\frac{1}{c_A} = \frac{1}{c_{A,0}} + kt$
Poločas	$\tau = \frac{c_{A,0}}{2k}$	$\tau = \frac{\ln 2}{k}$	$\tau = \frac{1}{kc_{A,0}}$
Jednotka	$[\text{mol dm}^{-3}\text{s}^{-1}]$	$[\text{s}^{-1}]$	$[\text{mol}^{-1}\text{dm}^3\text{s}^{-1}]$



Měření řádu reakce



- Celkový řád reakce **$a' + b'$**
 - Nemusí nutně odpovídat stechiometrickým koef.
 - Nemusí být nutně celá čísla
- Oswaldova metoda měření rádu reakce
 - Nadbytek všech složek kromě jedné

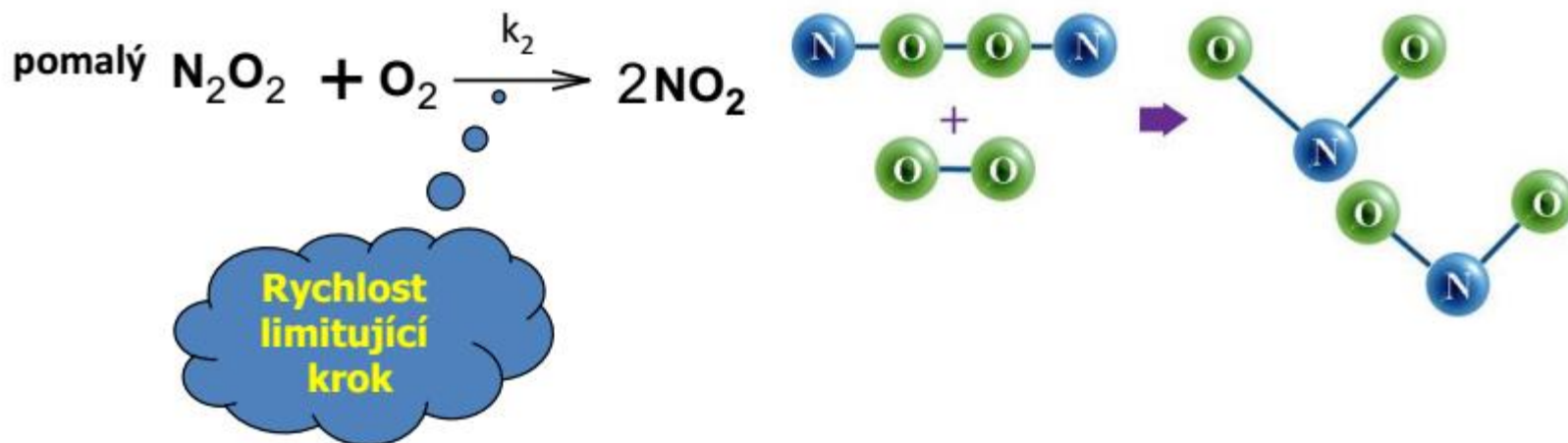
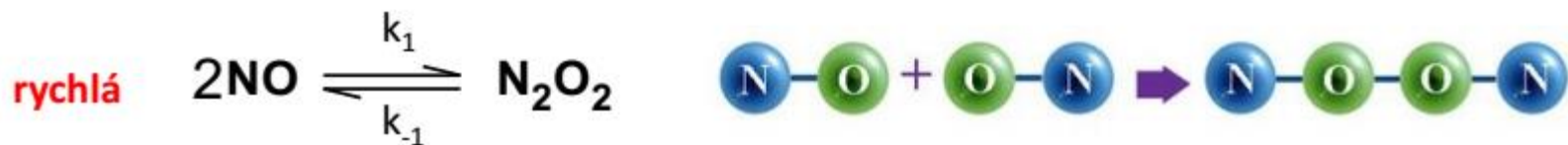
$$\frac{dc_P}{dt} = k' \cdot c_A^{a'}$$

Reakční mechanismus

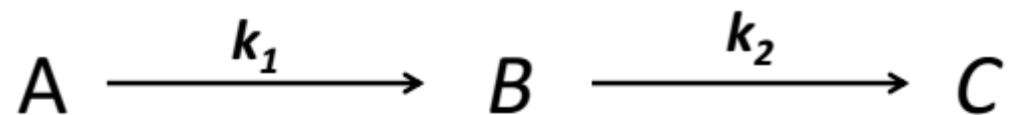
- Sled dílčích elementárních reakcí



$$k = k_2 \frac{k_1}{k_{-1}}$$



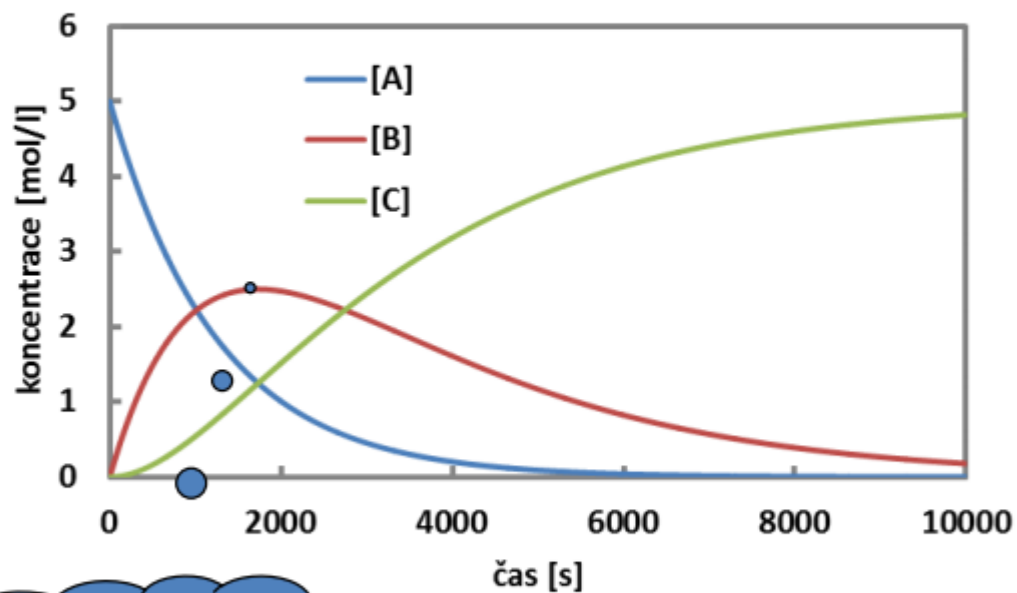
Následné reakce



$$\frac{dc_A}{dt} = -k_1 c_A$$

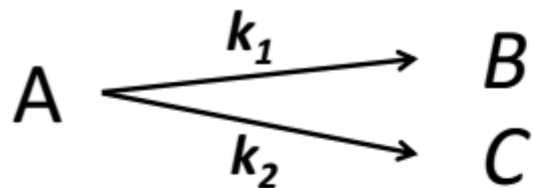
$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B$$

$$\frac{dc_C}{dt} = k_2 c_B$$



Stacionární stav
Ale ne v rovnováze

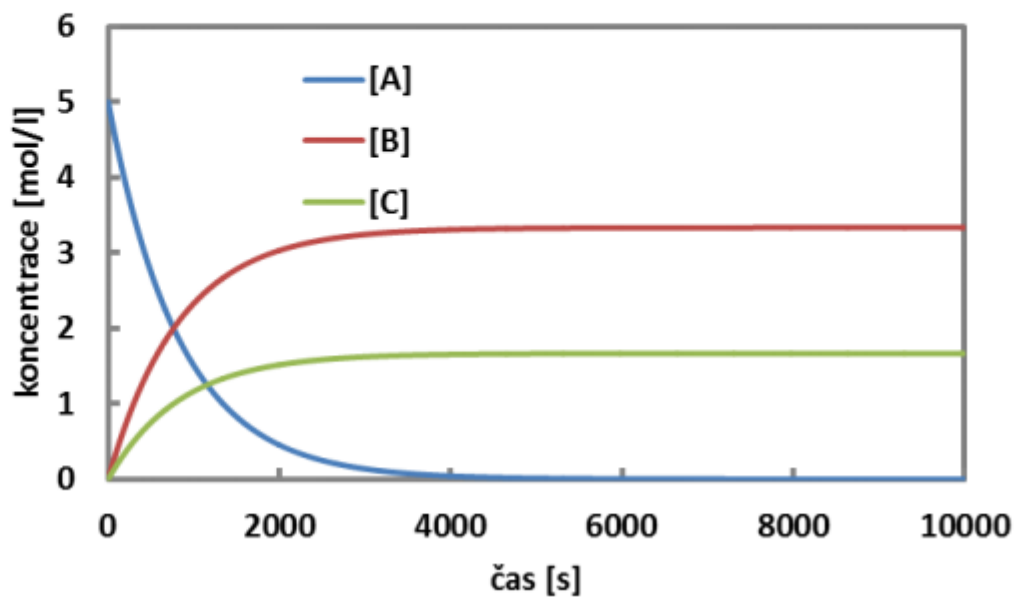
Bočné reakce



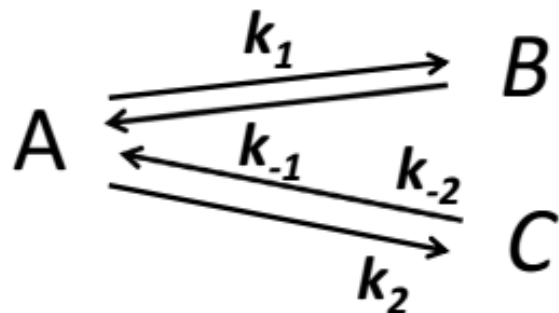
$$\frac{dc_A}{dt} = -k_1c_A - k_2c_A$$

$$\frac{dc_B}{dt} = k_1c_A$$

$$\frac{dc_C}{dt} = k_2c_A$$



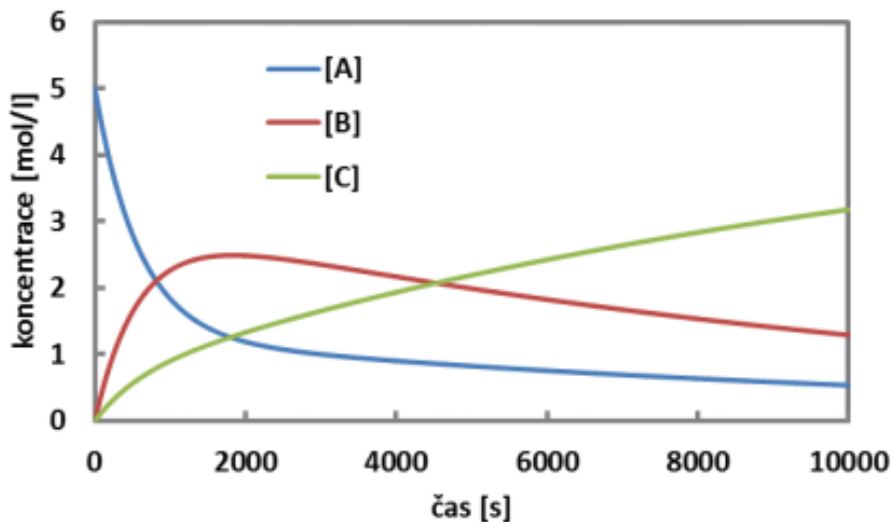
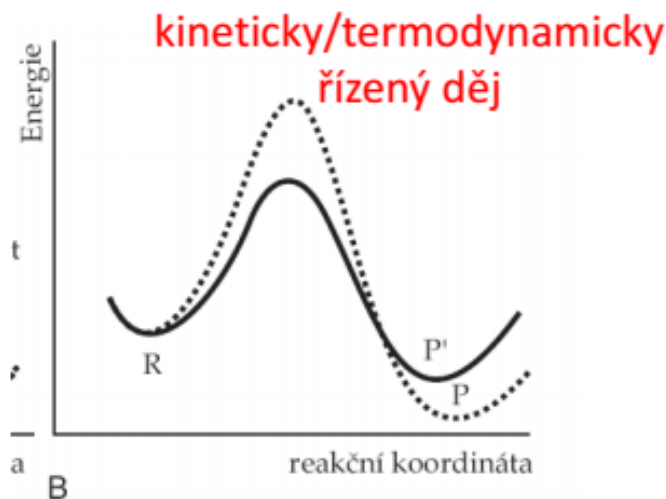
Vratné bočné reakce



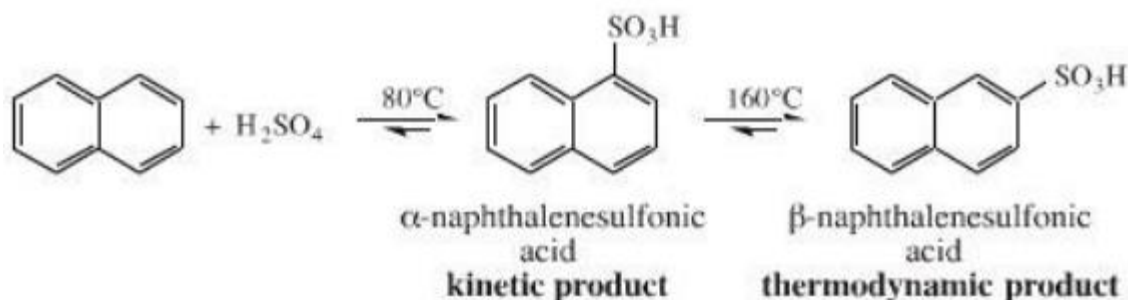
$$\begin{aligned}
 \frac{dc_A}{dt} &= -(k_1 + k_2)c_A \\
 &\quad + k_{-1}c_B \\
 &\quad + k_{-2}c_C
 \end{aligned}$$

$$\frac{dc_B}{dt} = k_1c_A - k_{-1}c_B$$

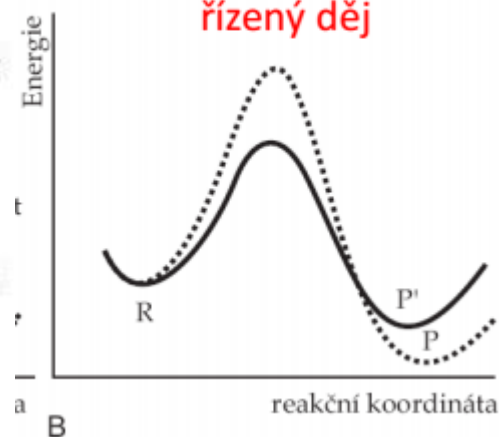
$$\frac{dc_C}{dt} = k_2c_A - k_{-2}c_C$$



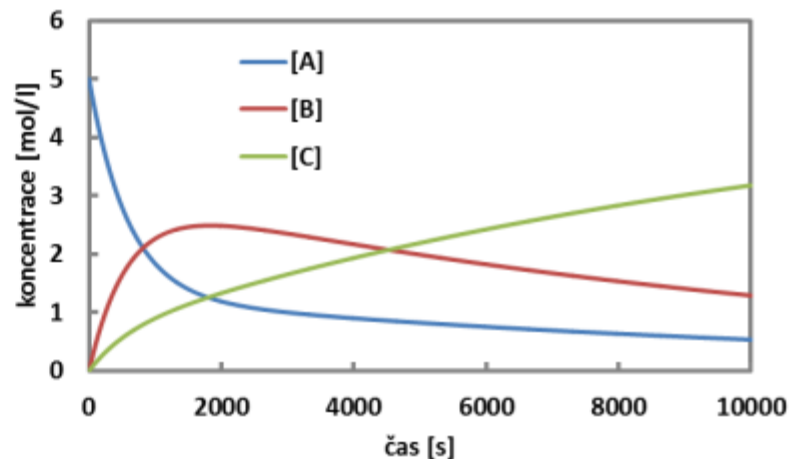
Kineticky vz. Termodynamicky řízené vratné reakce



kineticky/termodynamicky řízený děj



Teplota [°C]	α -naftolsulfon. kys		Reakční doba [hod]
	Reakce	rovnováha	
80	96%	3%	>1000
120	95%	5%	500
160	15%	15%	4



Briggs–Rauscherova oscilační reakce

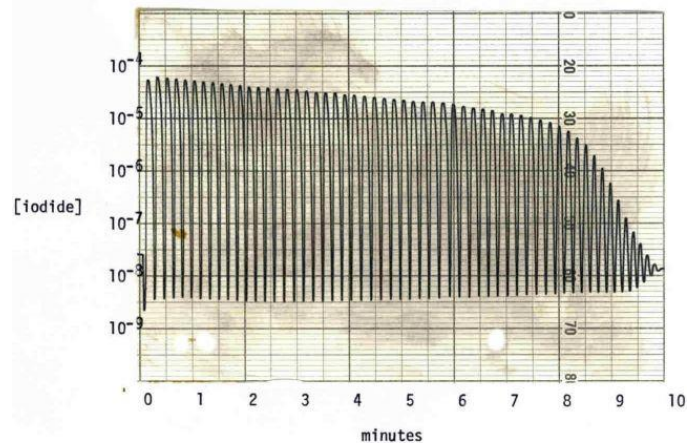
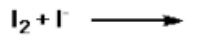
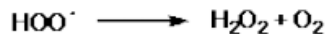
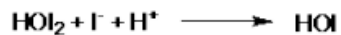
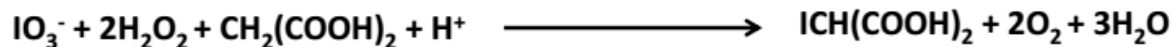
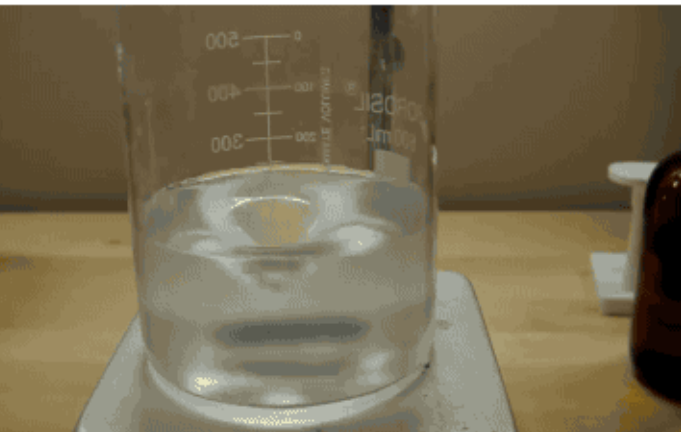


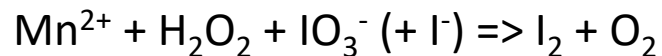
Figure . Oscillations produced by a solution of 0.050M potassium iodate, 0.038M malonic acid, 0.0050M manganese II sulfate, 0.88M hydrogen peroxide, 0.035M perchloric acid and 0.01% starch.



A ("non-radical process"): slow (high conc.)



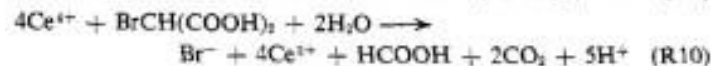
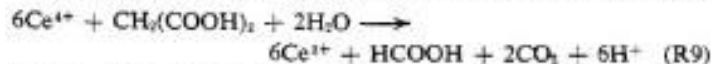
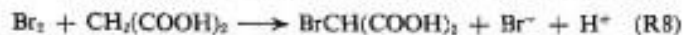
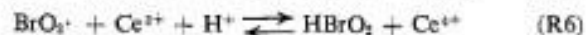
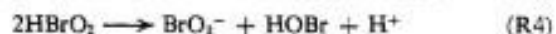
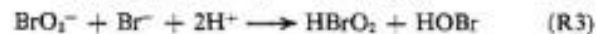
B ("radical process"): fast auto-catalytic (low conc.)



Belousov-Zhabotinsky reaction

Mechanism of the Oscillating Reaction

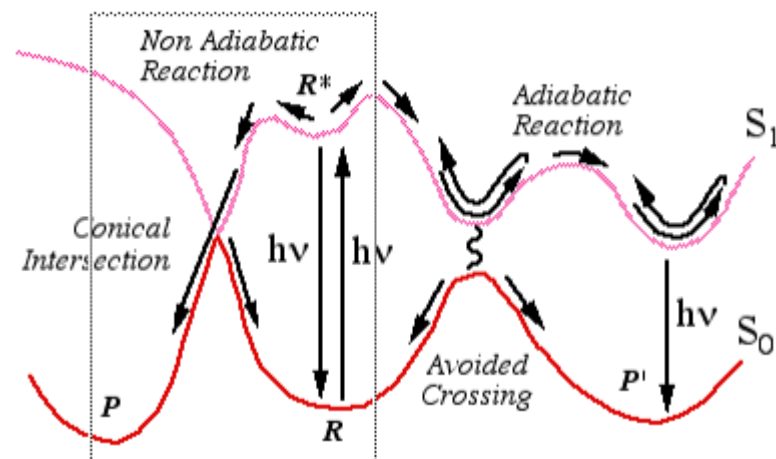
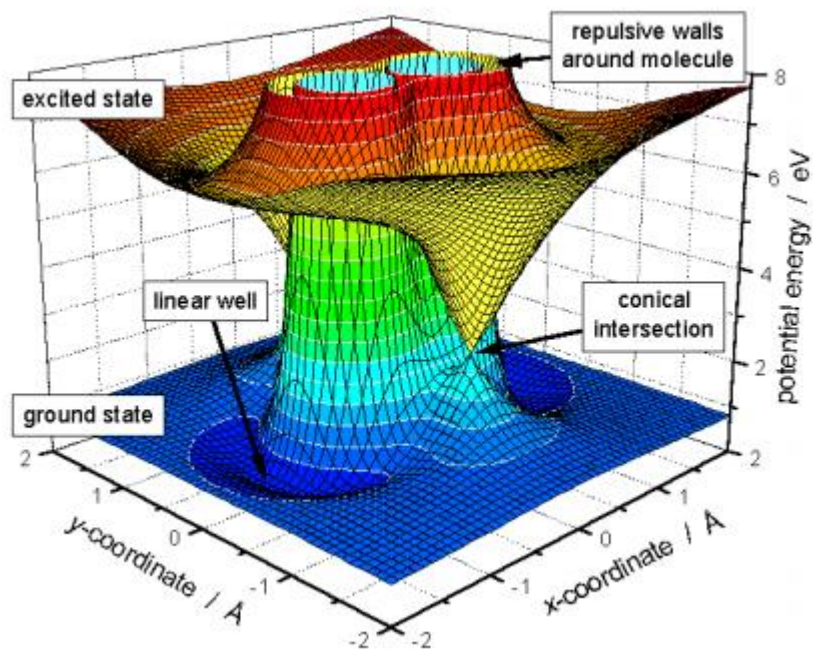
Component Processes. As a result of the evidence discussed above, we propose that the mechanism of the oscillating reaction can be described by ten processes, each of which is elementary or at least has clearly defined kinetics. Unless a double arrow is included in an equation, the process may be regarded as virtually irreversible under our conditions.



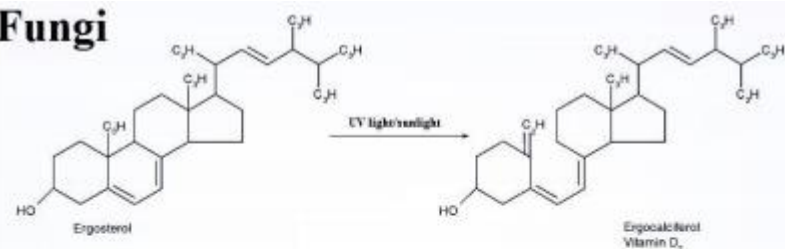
process A: $\rightarrow \text{Br}_2$ (red)

process B: $\text{Br}_2 \rightarrow \text{Br}^-$ (white)

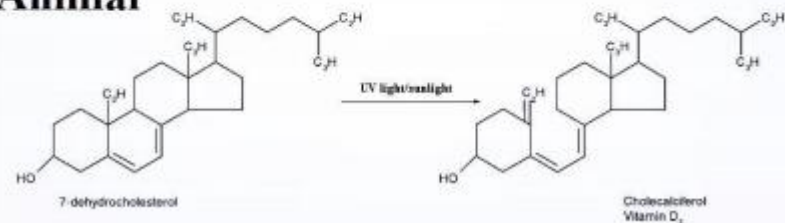
Fotochemické reakce



Fungi

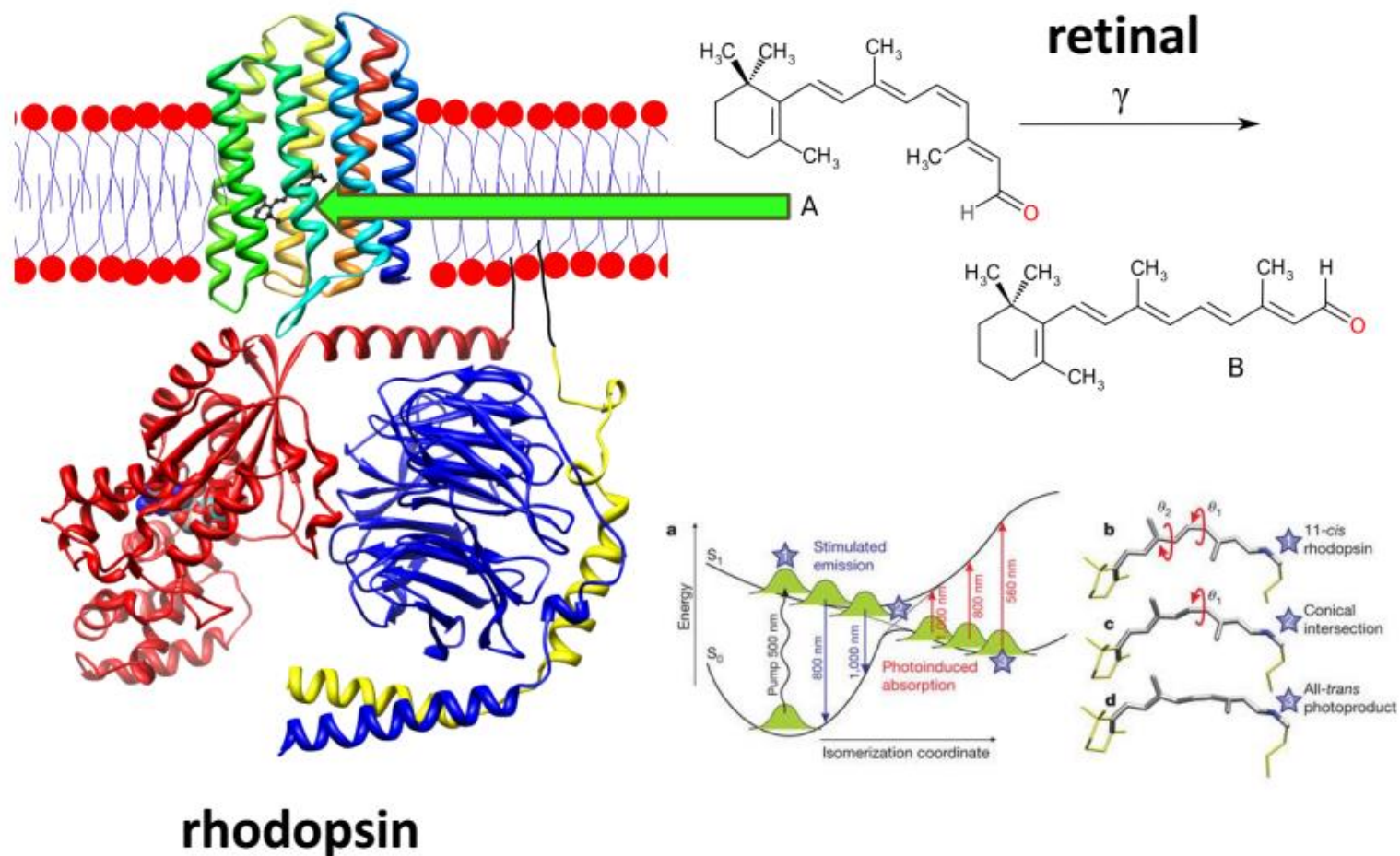


Animal



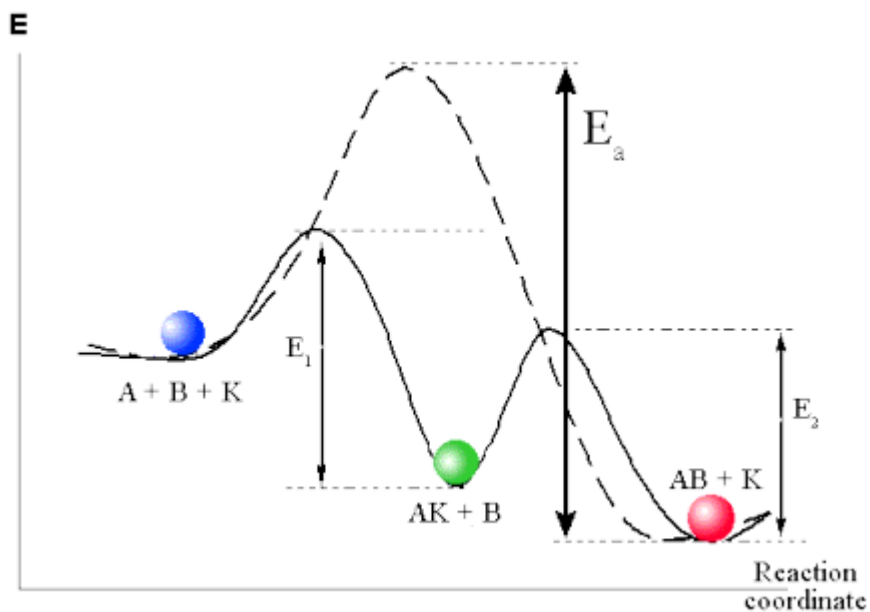
Plants do not directly synthesize vitamin D, lacking the necessary precursors.

Fotochemické reakce – vidění



Katalýza

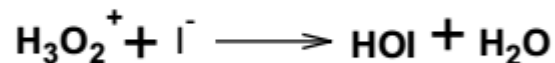
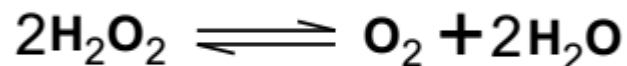
IUPAC: *Catalyst* is a substance that **increases the rate of a reaction without modifying the overall standard Gibbs energy change** in the reaction; the process is called *catalysis*. The catalyst is **both a reactant and product** of the reaction.



Typy katalýzy

- Homogenní

- Reakce probíhá v jedné fázi (např. jeden roztok)



- Heterogenní

- Reakce probíhá na/poblíž fázového rozhraní (adsorbované látky na pevné fázi)
- Hraje roli i difuze látky k fázovému rozhraní
- Reakce na zeolitech, oxidech kovů, **nanočástice**

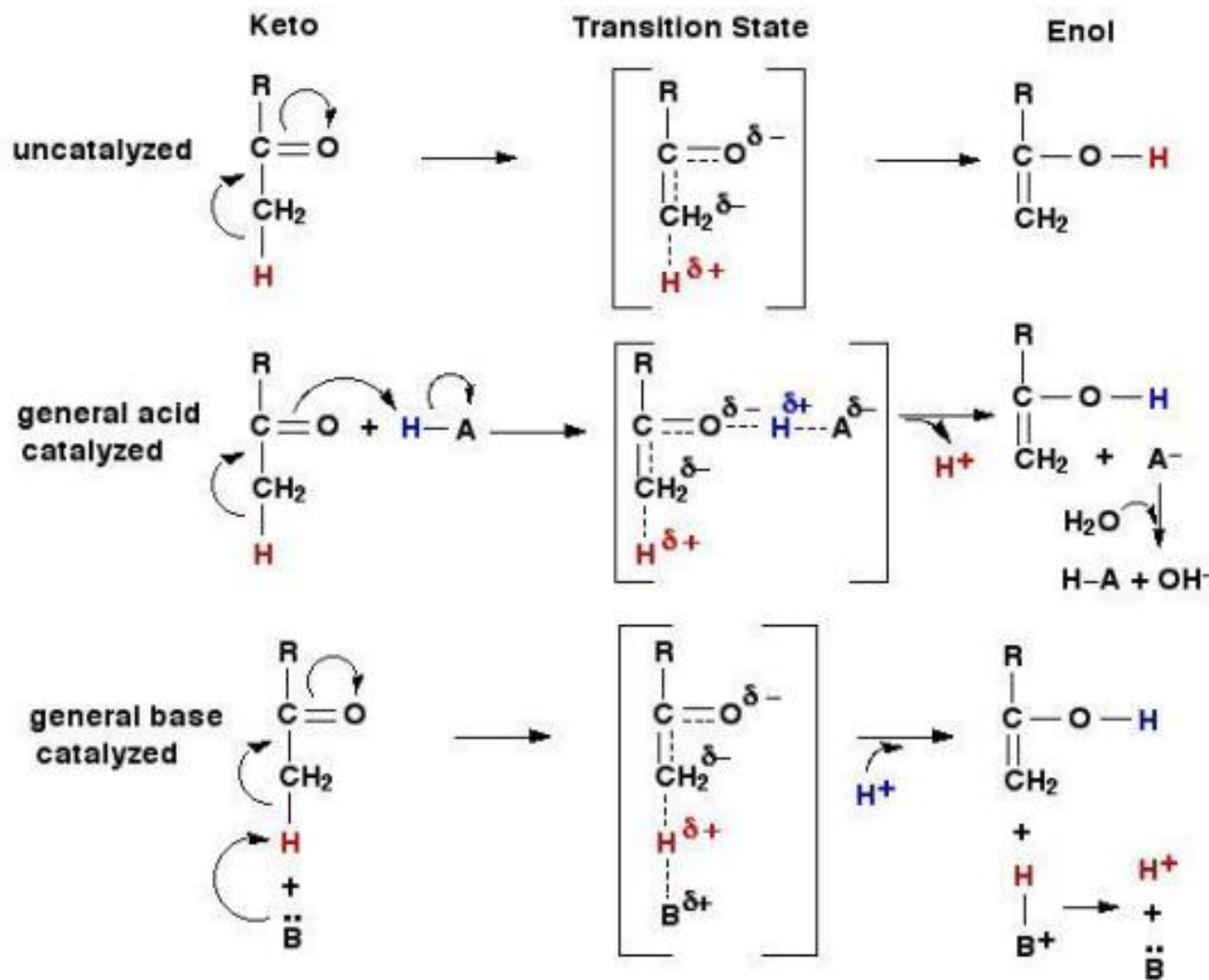
Aktivátor katalytické reakce

IUPAC

The term catalysis is also often used when the substance is consumed in the reaction (for example: base-catalysed hydrolysis of esters). Strictly, such a substance should be called an **activator**.

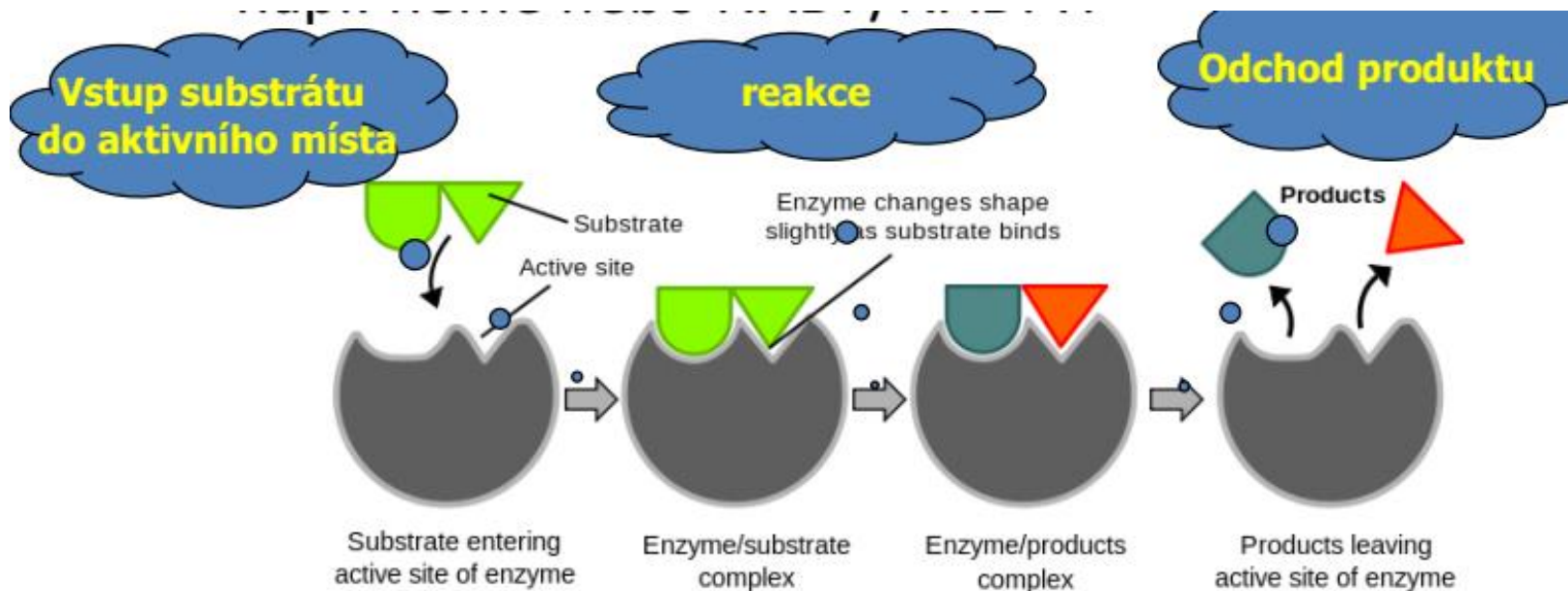
Příklad:

acidobazická katalýza



Enzymatická katalýza

- Katalýza pomocí proteinů
 - Protein
 - Kofaktor – neproteinová skupina v aktivním místě např. heme nebo NADP/NADPH+



(Enzymová) kinetika

Michaelis-Mentenová



Za předpokladu rovnováhy vazby substrátu

$$k_{in}[E][S] = k_{out}[ES] \quad [E] + [ES] = c_E$$

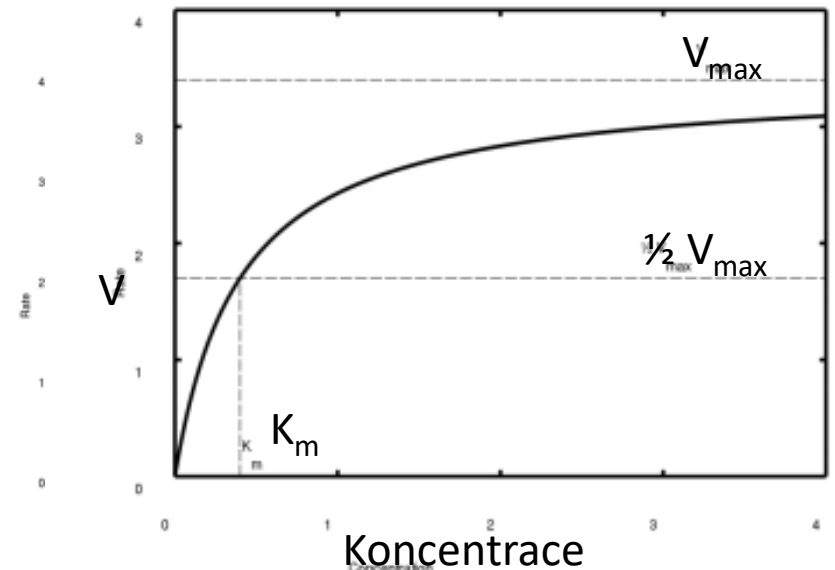
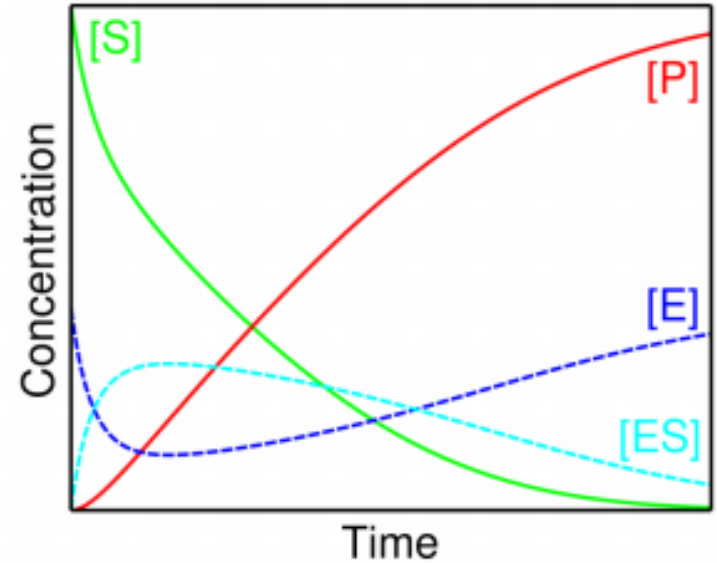
$$[ES] = \frac{c_E[S]}{K_m + [S]} \quad K_m = \frac{k_{out}}{k_{in}}$$

$$v = \frac{d[P]}{dt} = k_{cat}[ES] = \frac{v_{max}[S]}{K_m + [S]}$$

Quasi-steady state aproximace

$$k_{in}[E][S] = k_{out}[ES] + k_{cat}[ES]$$

$$K_m = \frac{k_{out} + k_{cat}}{k_{in}}$$



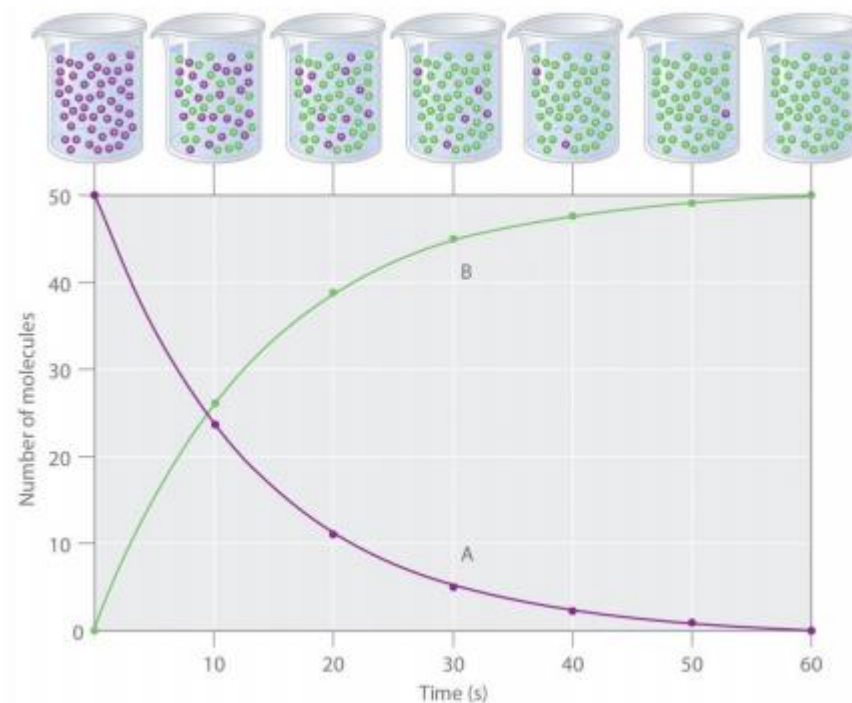
Enzymatická katalýza

Efektivita enzymu

Enzym	Katalyzovaná reakce	K_m [mol/l]	k_{cat} [s^{-1}]	K_{cat}/K_m [$l\text{mol}^{-1}s^{-1}$]
Chymotrypsin	Ac-Phe-Ala \rightarrow Ac-Phe+Ala	1.5×10^{-2}	0.14	9.3
Pepsin	Phe-Gly \rightarrow Phe+Gly	3.0×10^{-4}	0.5	1.7×10^3
Tyrosyl-tRNA syntaza	Tyrosin+tRNA \rightarrow tyrosyl-tRNA	9.0×10^{-4}	7.6	8.4×10^3
Ribonukleáza	Cytidine-2',3' cyclic phosphate \rightarrow cytidine-3'-phosphate	7.9×10^{-3}	7.9×10^2	1×10^5
Carbonic anhydráza	$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$	2.6×10^{-2}	4×10^5	1.5×10^7
Fumaráza	Fumarát \rightarrow malát	5.0×10^{-6}	8×10^2	1.6×10^8

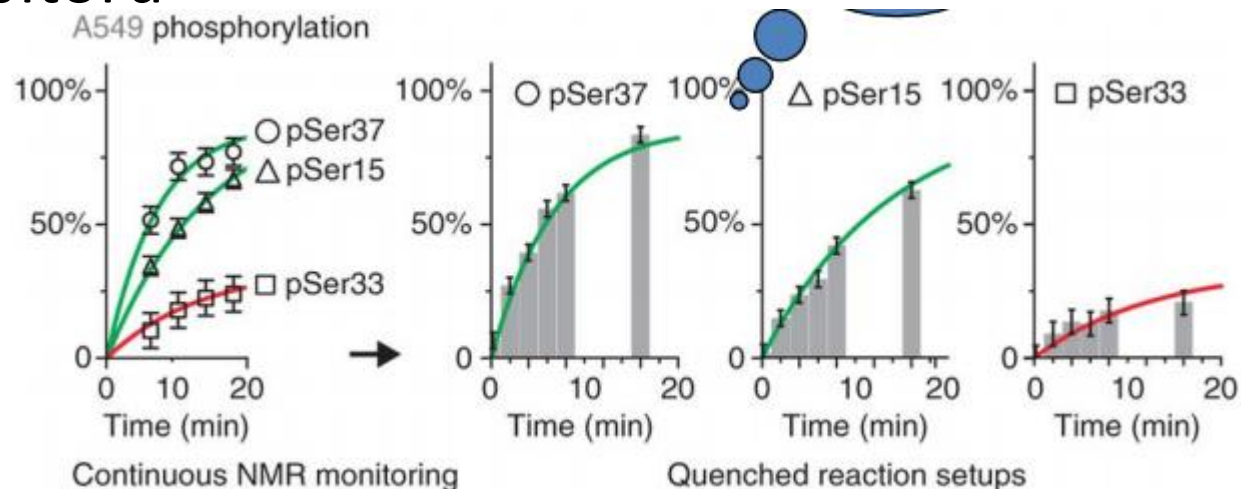
Měření kinetiky reakce

- Sledování průběhu reakce
 - Pomalé a velmi pomalé reakce
- Měření signálu
 - Spektrofotometricky
 - absorpce/emise
 - UV-Vis, IČ,...
 - Elektrochemicky
 - pH
 - vodivost



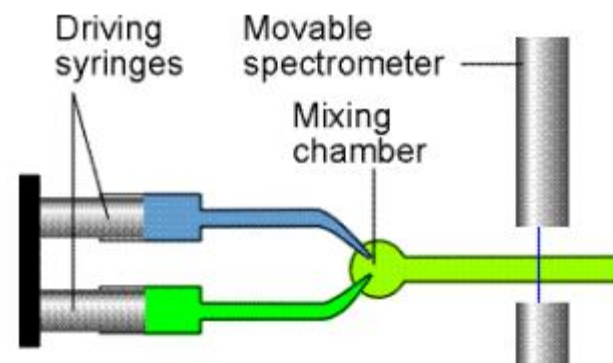
Měření kinetiky reakce

- quenched reaction – metoda zastavení reakce
 - Jednodušší měření
 - Vhodné pro velmi pomalé reakce
- Zastavení reakce
 - Přidání inhibitoru
 - zamrazení

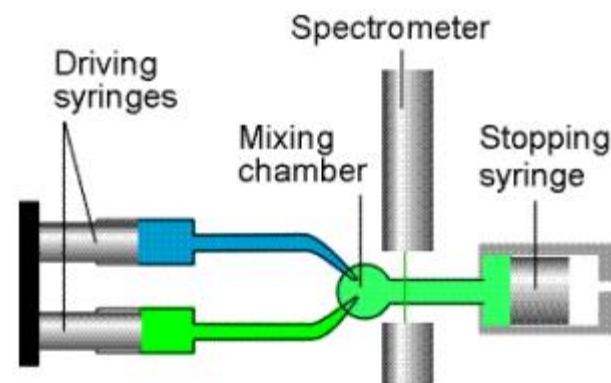
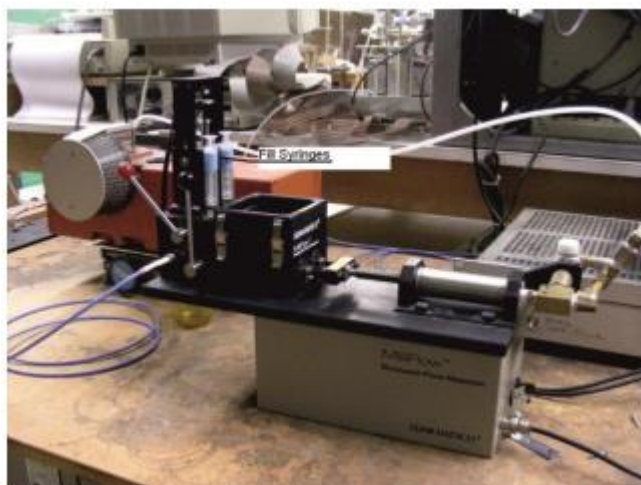


Měření kinetiky reakce

- Rychlé a velmi rychlé reakce
 - Flow (průtokové) metody



- Stopped-flow metody



MAKING CHEMICAL REACTIONS HAPPEN FASTER

There are a number of different things that we can change to make a chemical reaction faster. Here, we explain the concept of collision theory, and how it can be used to explain the effects of five different factors on the rate of a chemical reaction.

COLLISION THEORY



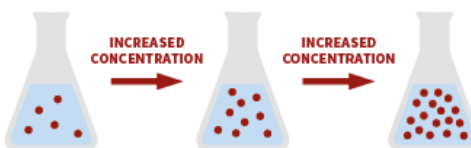
CORRECT ORIENTATION
SUFFICIENT ENERGY

WRONG ORIENTATION

INSUFFICIENT ENERGY

Collision theory states that, for a reaction to occur, particles must collide with the correct orientation and with sufficient energy for a reaction to occur. Different factors affect the rate of the reaction by affecting the frequency of particle collisions, and/or the proportion of collisions that have enough energy to react.

INCREASE CONCENTRATION OF REACTANTS

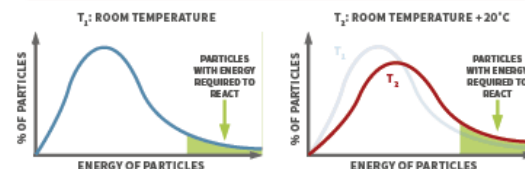


↑ FREQUENCY OF COLLISIONS

↑ % SUCCESSFUL COLLISIONS

Increasing the concentration of reactants in solution increases the rate of reaction as there are a greater number of particles available to react. This increases the frequency of collisions between particles.

INCREASE TEMPERATURE OF REACTION



↑ FREQUENCY OF COLLISIONS

↑ % SUCCESSFUL COLLISIONS

Increasing the temperature increases the kinetic energy of particles. This increases the frequency of particle collisions, and a greater proportion of collisions will have the energy required to react.

INCREASE SURFACE AREA OF REACTANTS

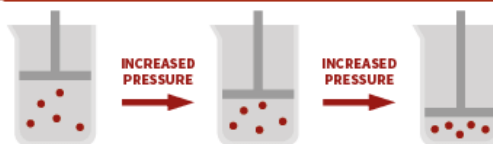


↑ FREQUENCY OF COLLISIONS

↑ % SUCCESSFUL COLLISIONS

Increasing the surface area of solid reactants increases the number of particles that are exposed and available to react, and as a consequence this increases the frequency of particle collisions, increasing rate.

INCREASE PRESSURE OF REACTION

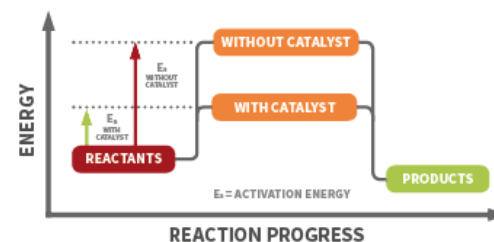


↑ FREQUENCY OF COLLISIONS

↑ % SUCCESSFUL COLLISIONS

Increasing the pressure of a reaction involving gases forces the gas particles closer together. This will increase the frequency of particle collisions, and therefore increase the rate of reaction.

USE A CATALYST IN THE REACTION



A catalyst provides an alternative route for the reaction, with a lower activation energy. This means that particle collisions need less energy in order for a reaction to occur, increasing the rate of the reaction.



Shrnutí chemická kinetika

- Řeší rychlost chemických reakcí
- reakční mechanismus
 - tranzitní stav
- reakční rychlost
 - úbytek reaktantu, nebo příbytek produktu v čase
 - Řády reakce 0., 1., 2. řádu
- rovnováha je definována i kineticky
- Katalýza – změna rychlosti reakce změnou mechanismu

Požadavky na splnění

- Zkouška
 - online test (>50%)
 - ústní zkoušení (3 průřezové otázky)

Doporučená literatura

- Otyepka M., Struktura atomů a molekul, 2. opravené a rozšířené vydání, VUP Olomouc, 2010
- YouTube kanál přednášky
- Studijní materiály na stránkách KFC

Poděkování

- Vytvořeno na základě podkladů
 - Prof. Otyepka
 - Doc. Banáš
 - Dr. Kührová