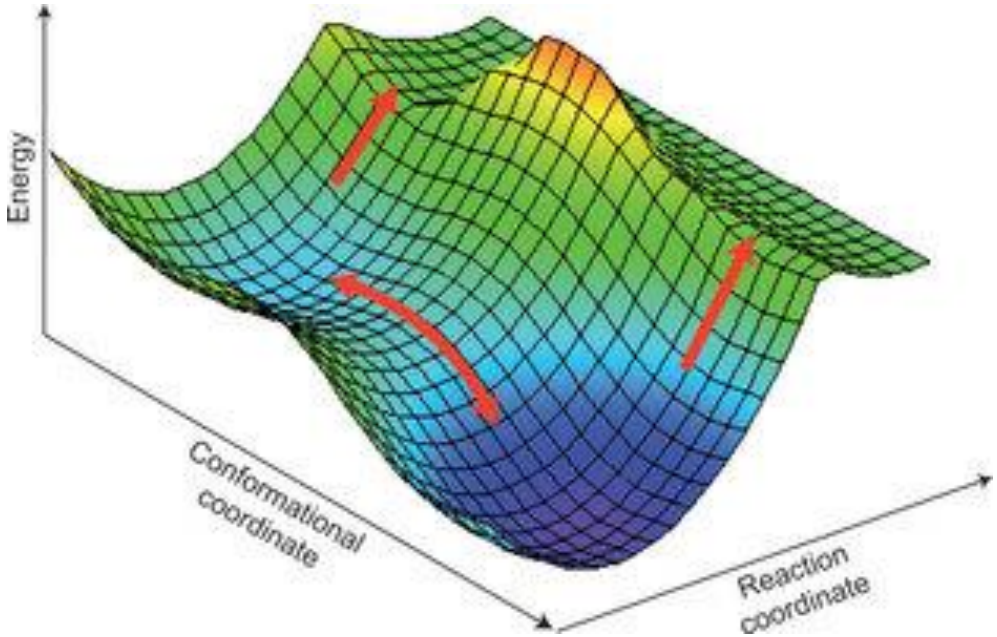
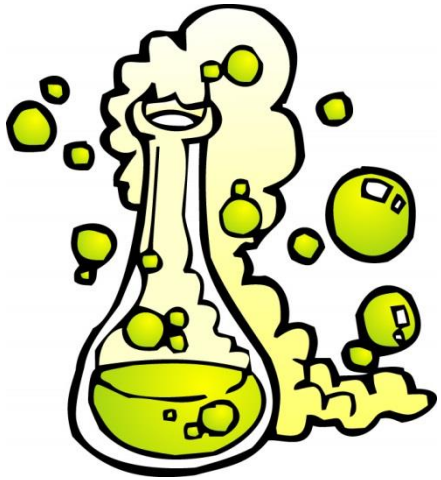
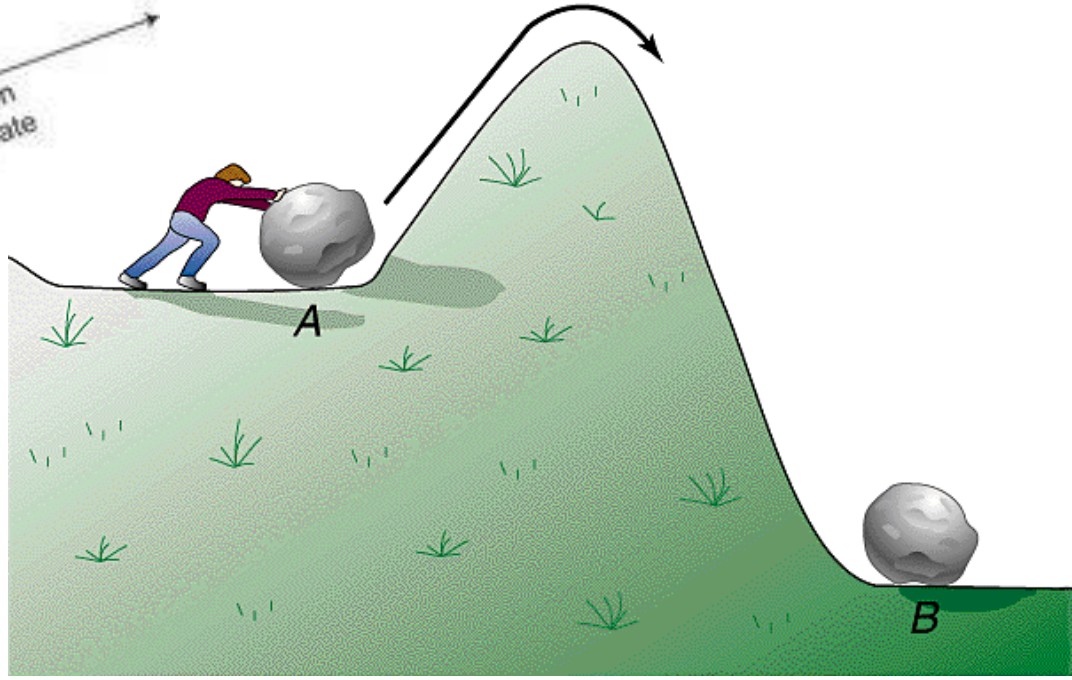
# Reakční kinetika





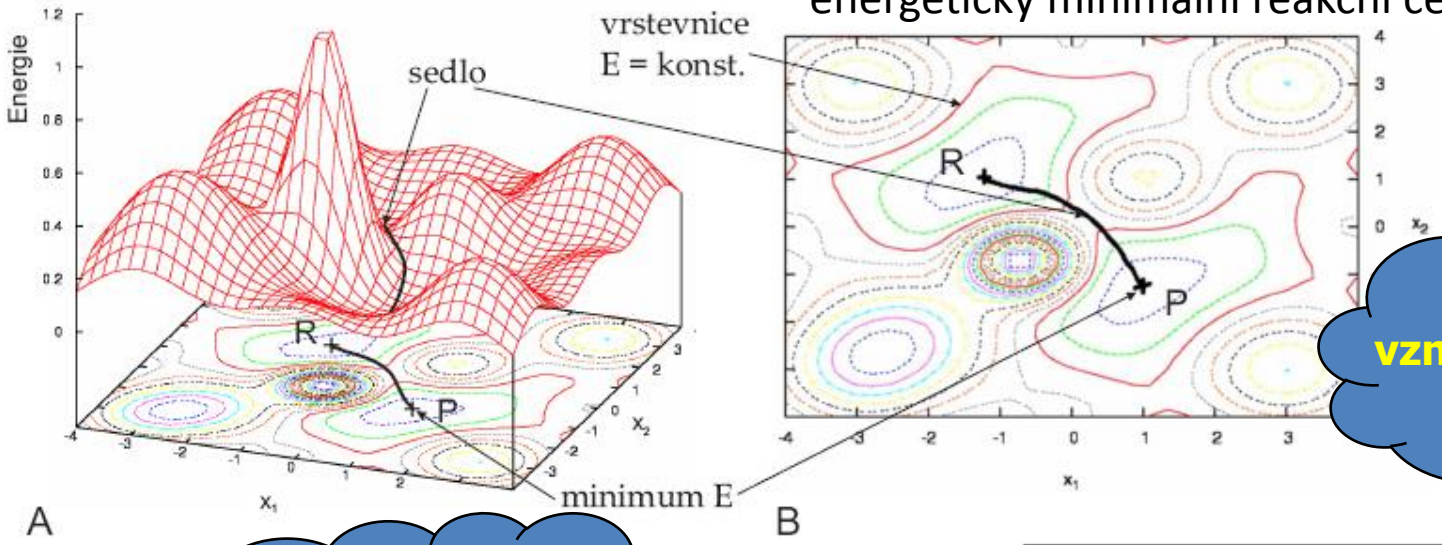




# Rychlost chemické reakce

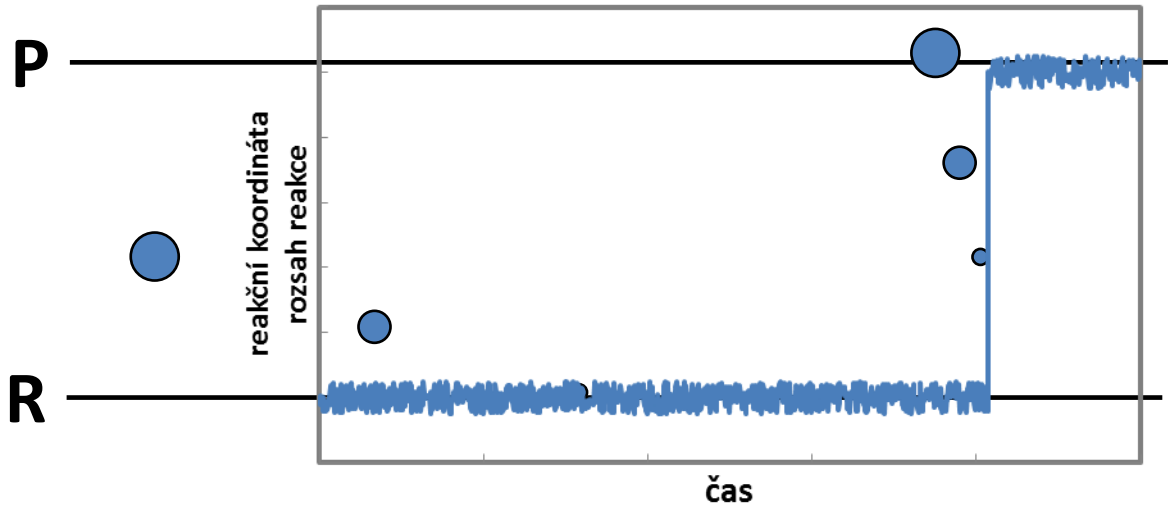
A ⇌ B

energeticky minimální reakční cesta




**Rare event**
**vznik/zánik vazeb**
**~1-10 fs**

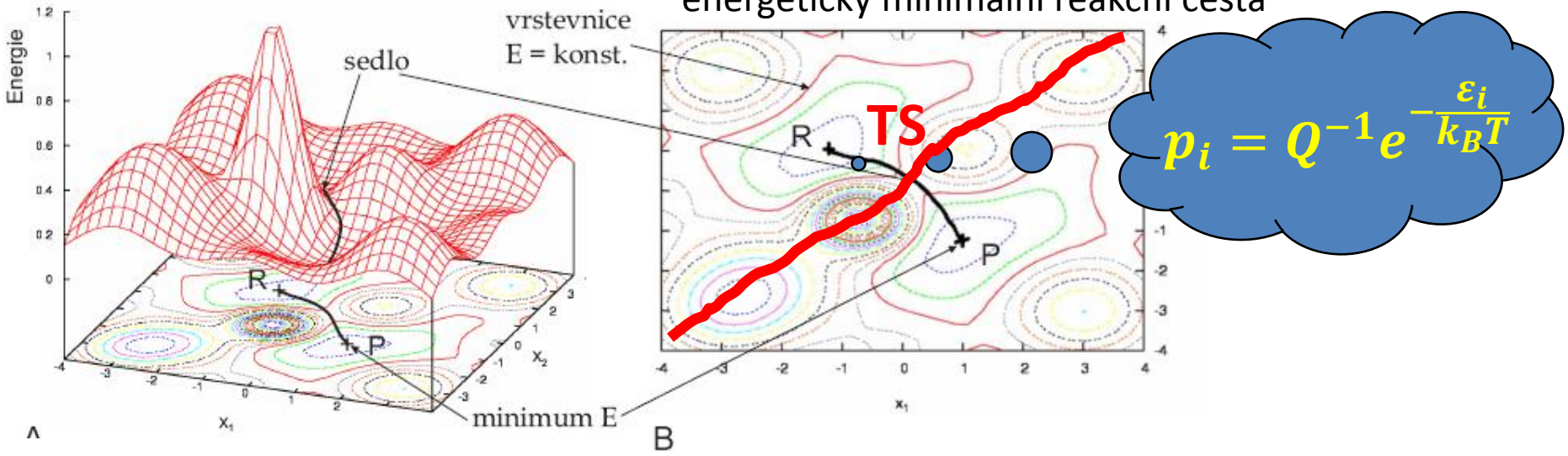
**Náhodnost reakce**
**~ms až roky**

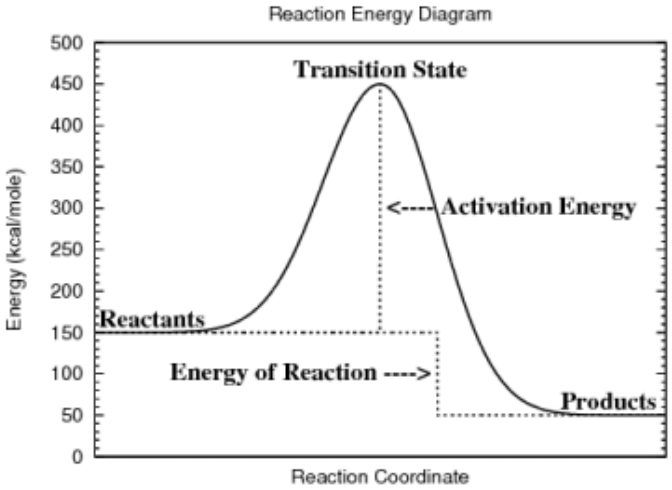


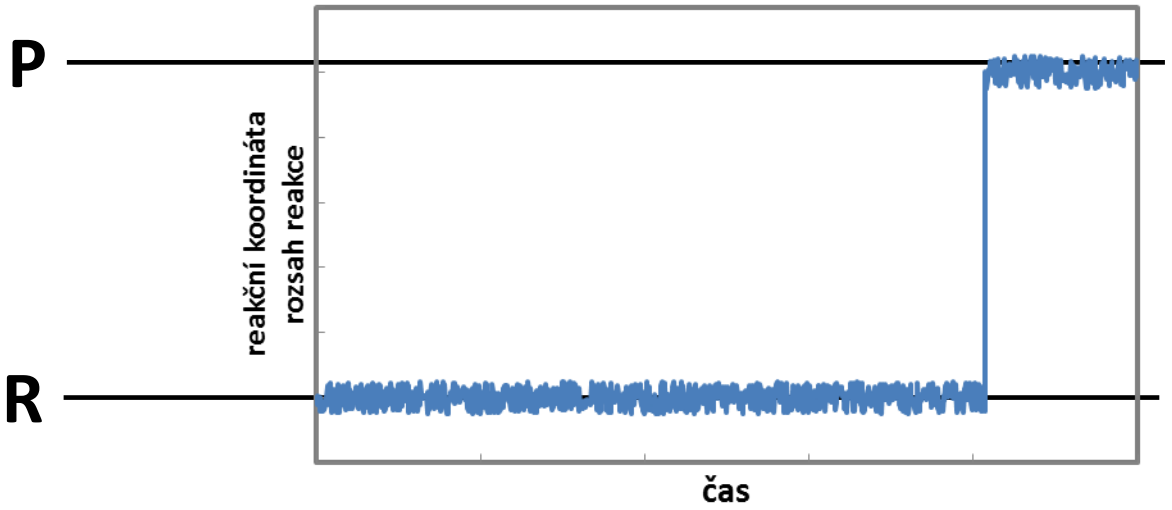
# Rychlost chemické reakce

A ⇌ B

energeticky minimální reakční cesta

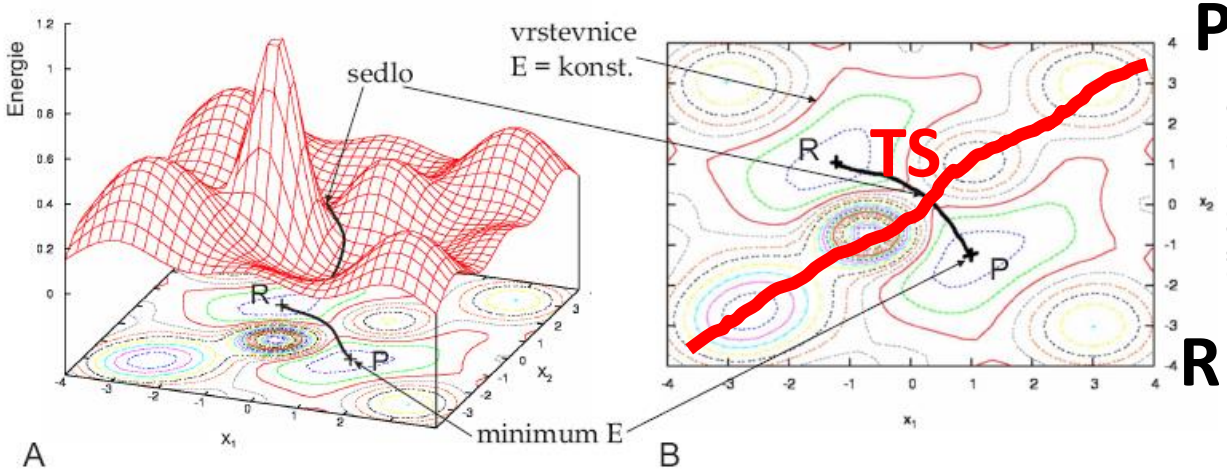


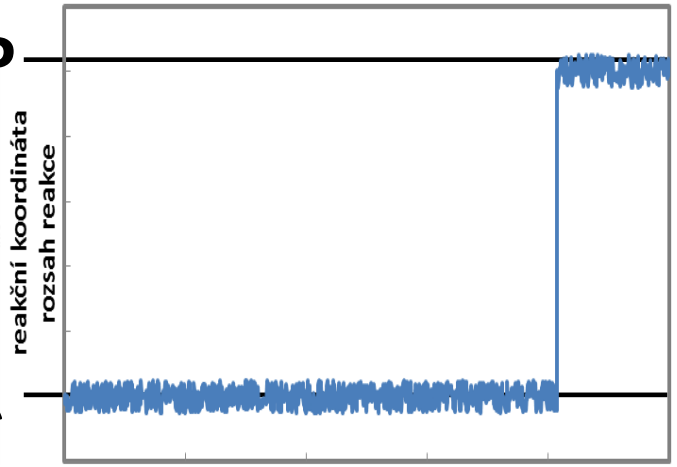



# Teorie tranzitního stavu

$$A \rightleftharpoons B$$



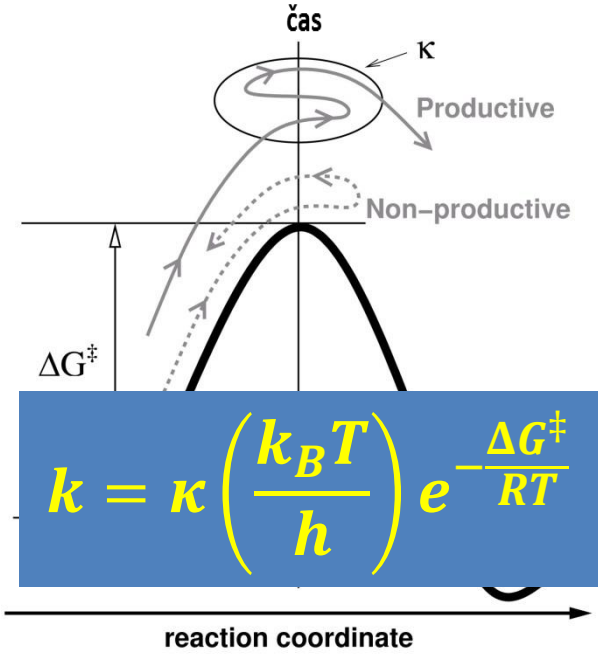

- **Molekuly stojící na dělící ploše a mířící do P skončí v P**
- **Neuvažujeme recrossing a tunelování**
- **Za čas dt zreaguje dn molekul → pravděpodobnost reakce**

**Eyringova rovnice**

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

**Arheniova rovnice**

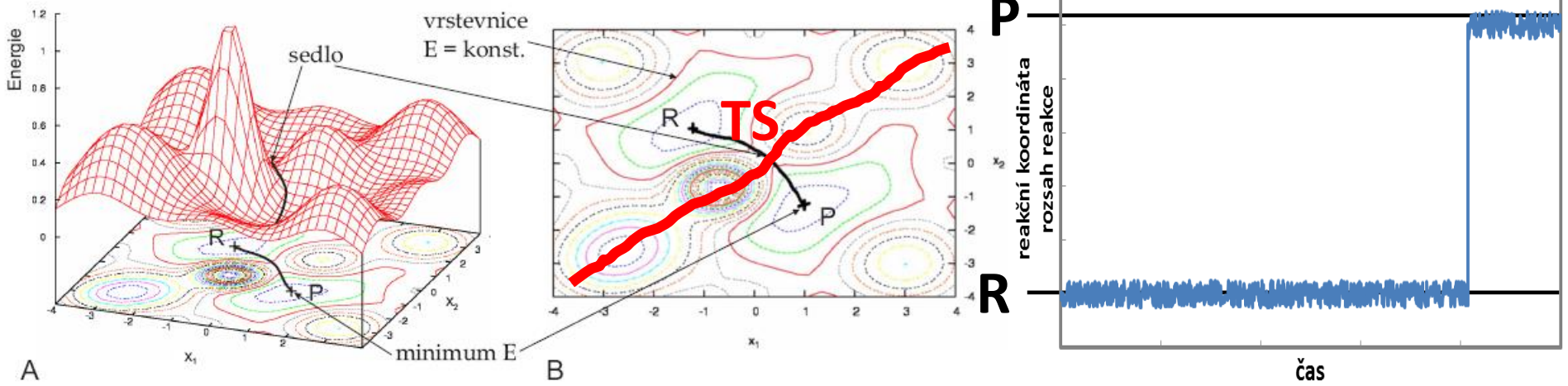
$$k = A e^{-\frac{E_a}{RT}}$$




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

# Teorie tranzitního stavu

$$A \rightleftharpoons B$$



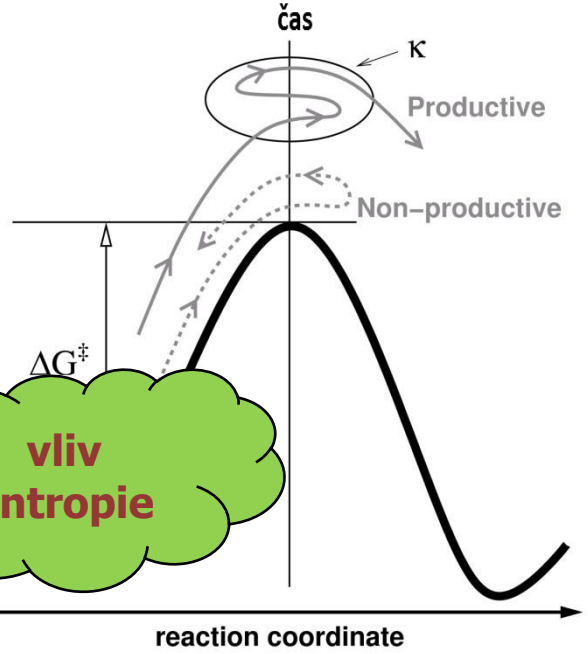

## Eyringova rovnice

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

vliv enthalpie (energie)

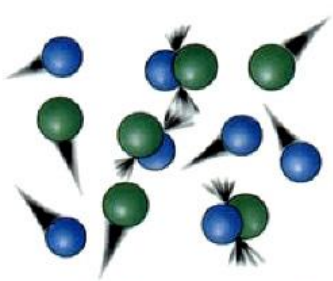
$$k = \left(\frac{k_B T}{h}\right) e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}}$$

vliv entropie

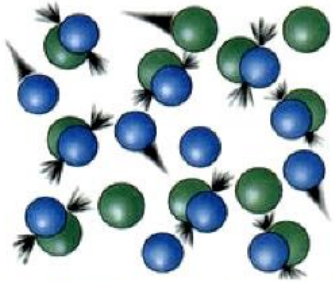


# Teorie tranzitního stavu

$$A \xrightarrow{k} B$$



Low concentration = Few collisions



High concentration = More collisions

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

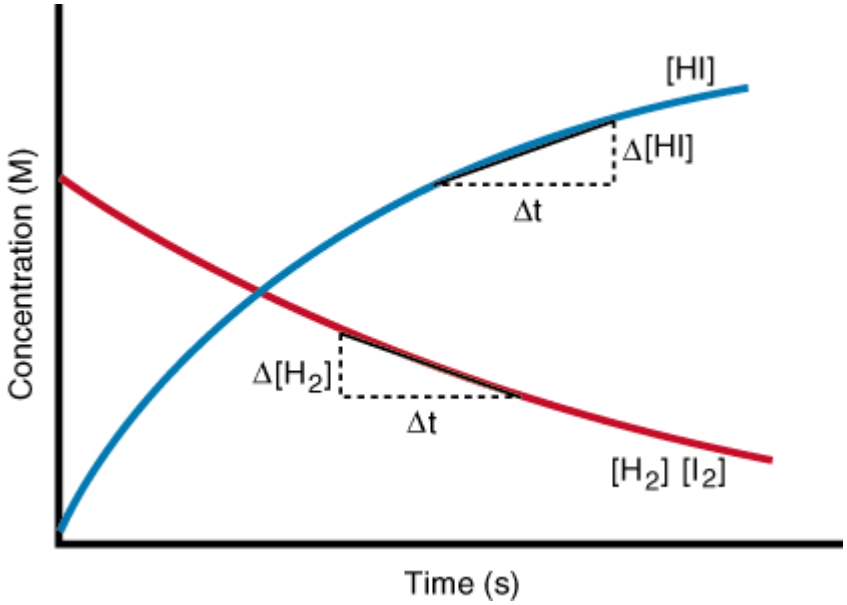
$$dn_A = -k \cdot n_A \cdot dt$$

$$k = \left(\frac{k_B T}{h}\right) e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad [s^{-1}]$$

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

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

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



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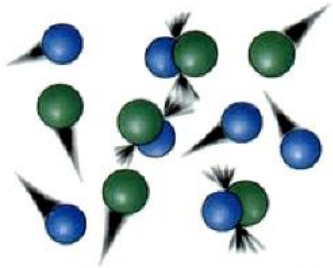
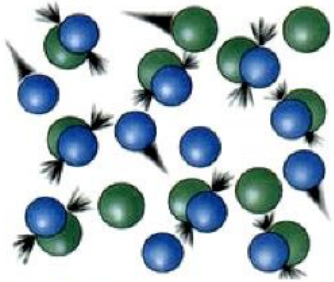
$$A \xrightarrow{k} B$$



Low concentration = Few collisions



High concentration = More collisions

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

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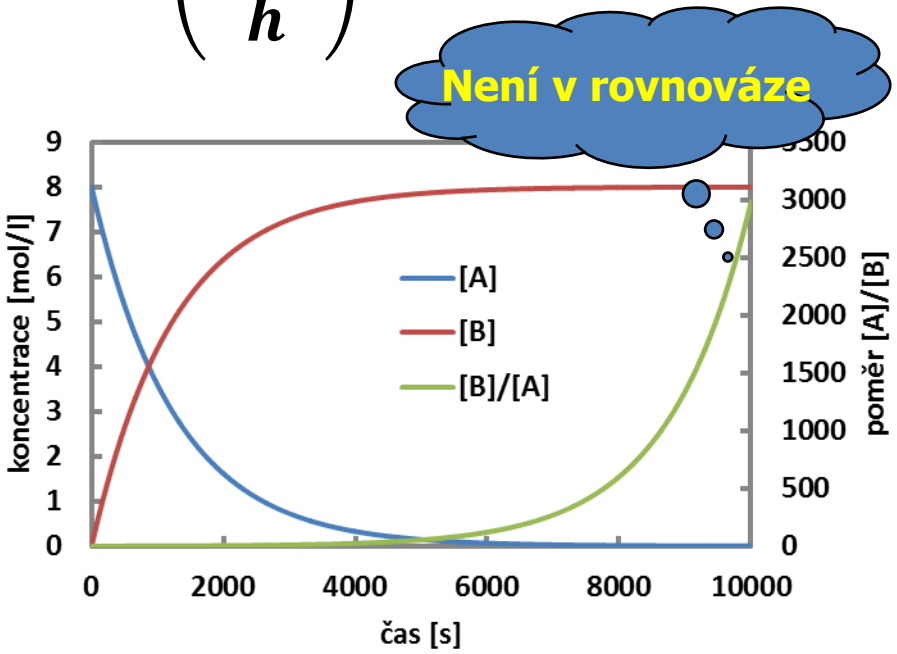
$$\ln \frac{n_A}{n_{A0}} = -k \cdot t$$

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

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

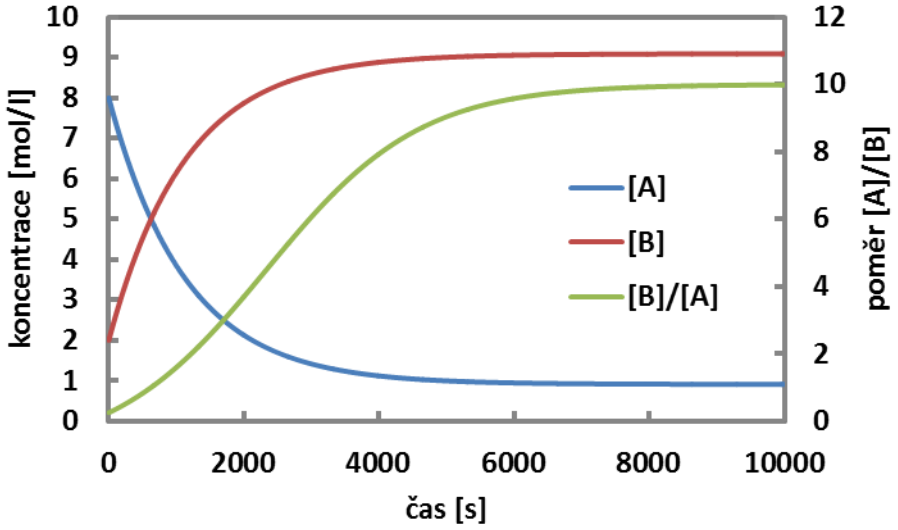


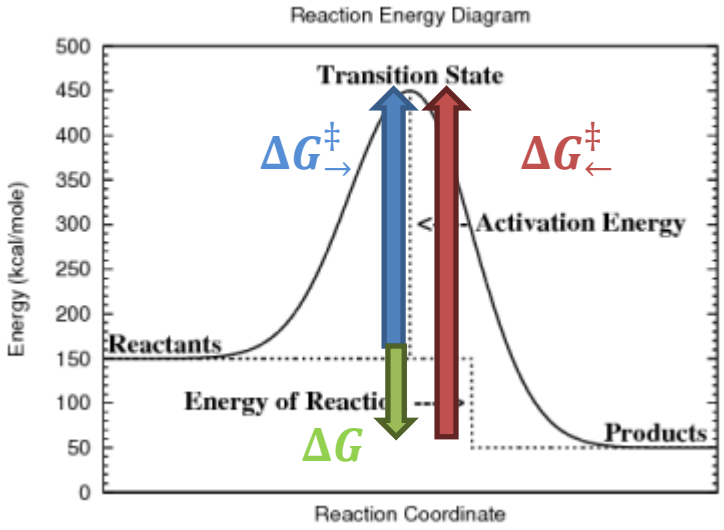
# Teorie tranzitního stavu

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

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

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




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

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

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

# Reakční kinetika

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

$$\frac{dn_P}{dt} = k \cdot n_A^{a'} n_B^{b'}$$

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons P$$

- Řád reakce $a'+b'$
  - Nemusí nutně odpovídat stechiometrickým koef.
  - Nemusí být nutně celá čísla

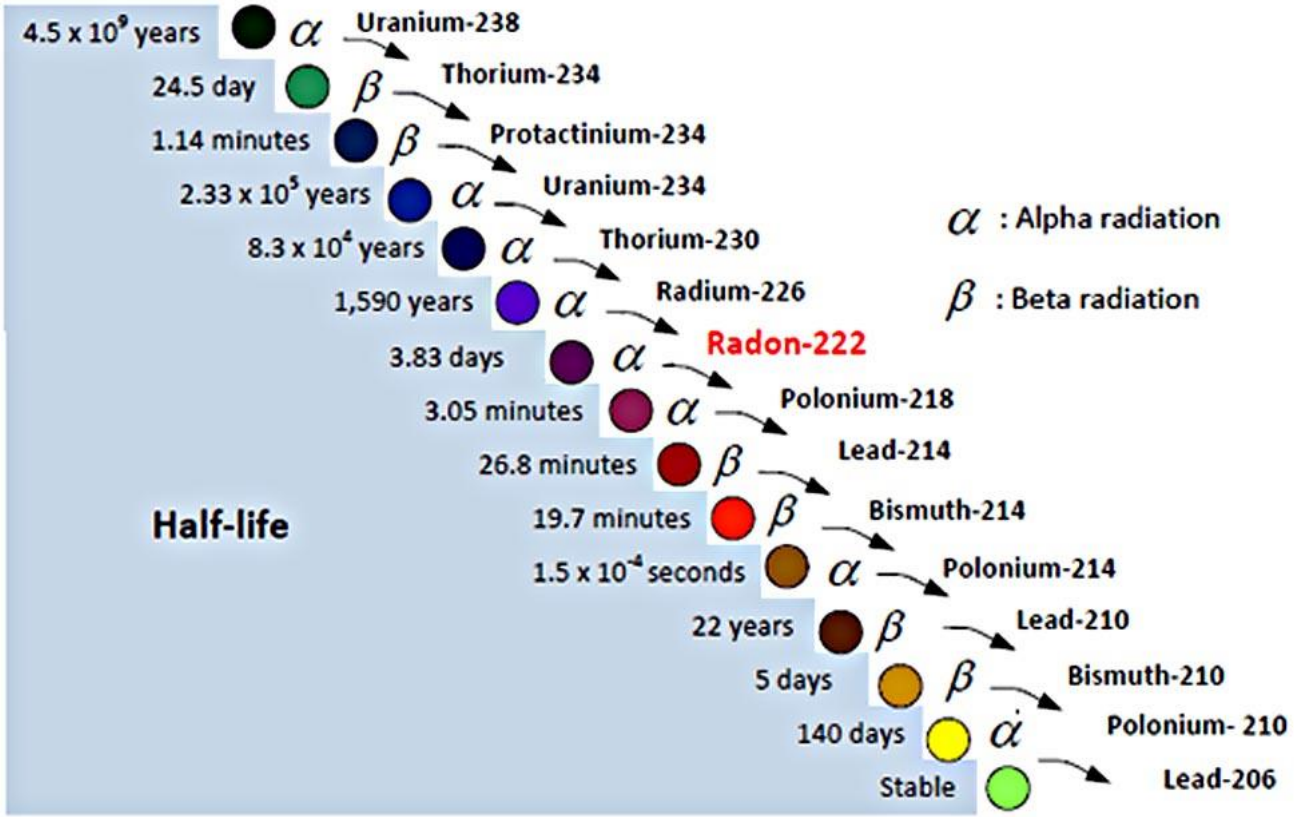
# Poločas reakce

- Čas, za který zreaguje polovina látky

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

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

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

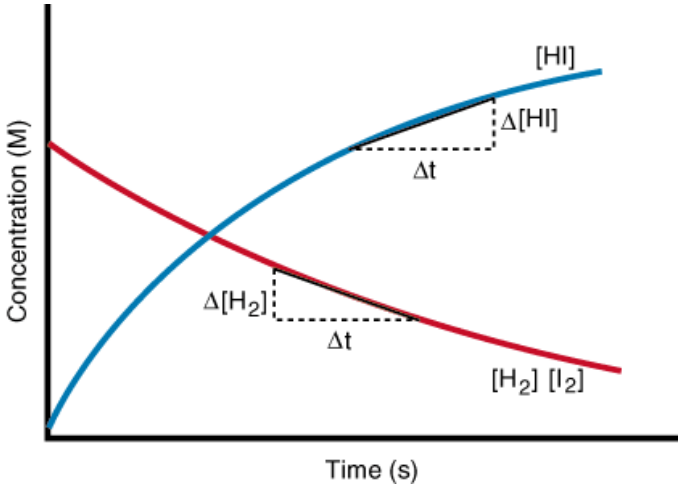


# Reakce 1. řádu

A $\rightleftharpoons$ B

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

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




- Reakce pseudo-prvního řádu
  - Jedna složka v nadbytku – relativně „skoro neubývá“

A + B $\rightleftharpoons$ *P*

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

$$c_B \gg c_A \Rightarrow k' = k \cdot c_B \qquad \frac{dc_P}{dt} = k' \cdot c_A$$

# Reakce 2. řádu

A + B $\rightleftharpoons$ *P*

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

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

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

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

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

**Pseudo-prvního řádu**

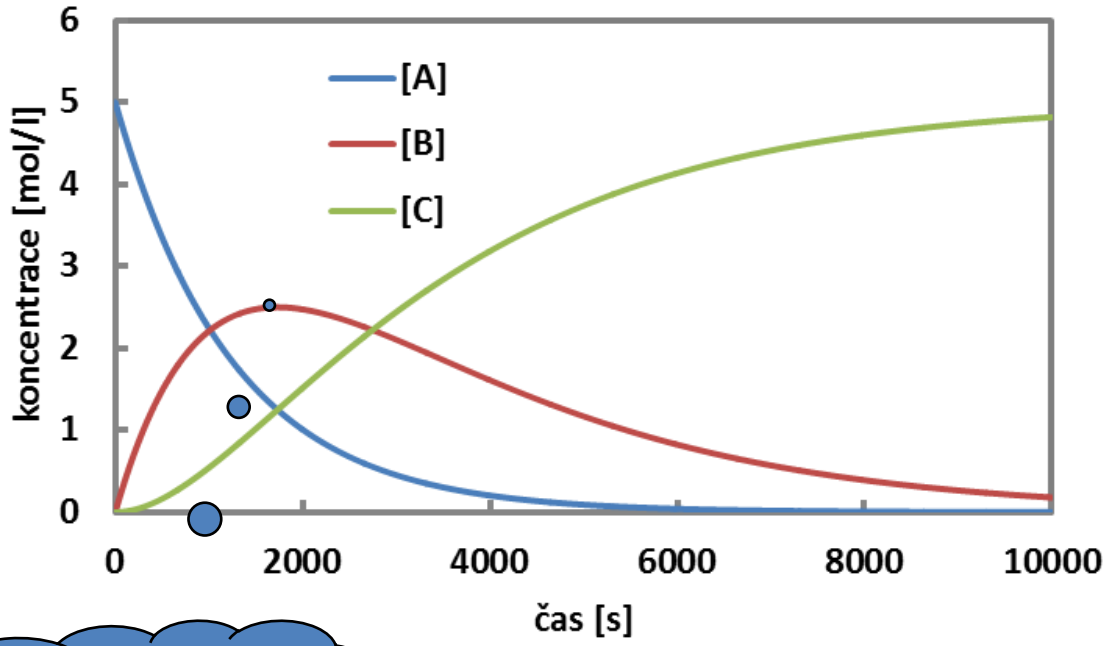
# Následné reakce

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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

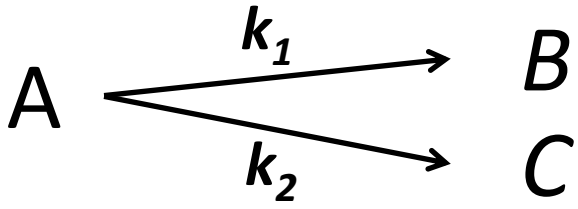
$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B$$

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




Stacionární stav
Ale ne v rovnováze

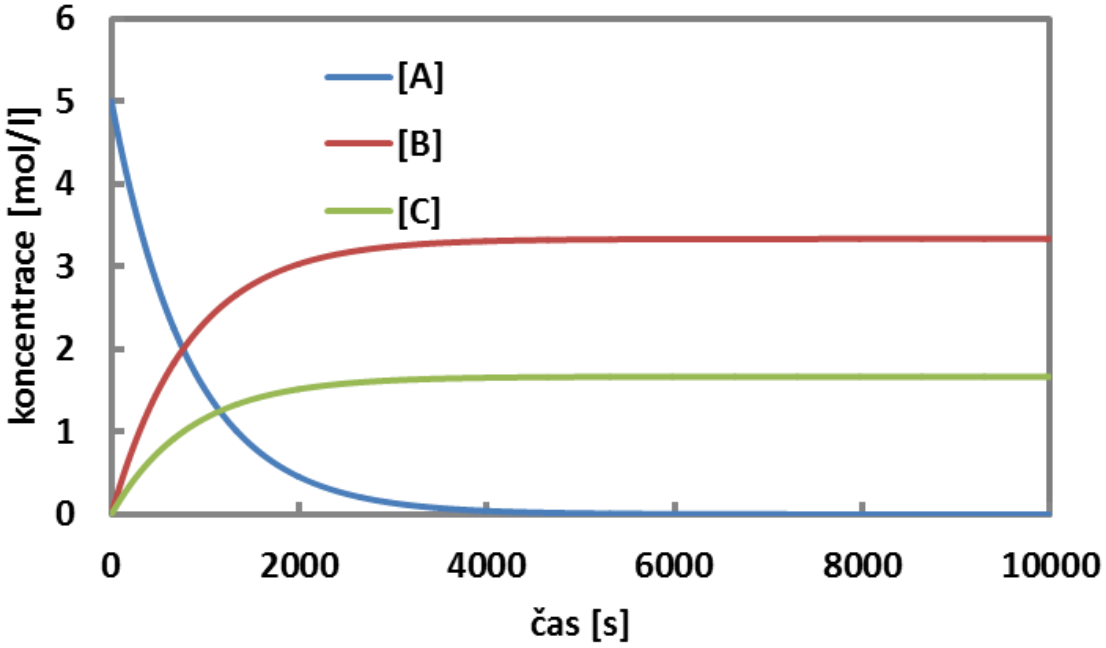
# Bočné reakce



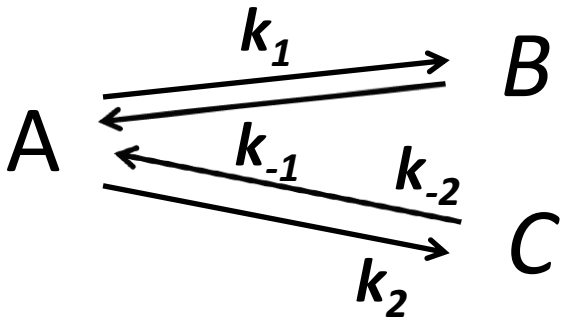

$$\frac{dc_A}{dt} = -k_1 c_A - k_2 c_A$$

$$\frac{dc_B}{dt} = k_1 c_A$$

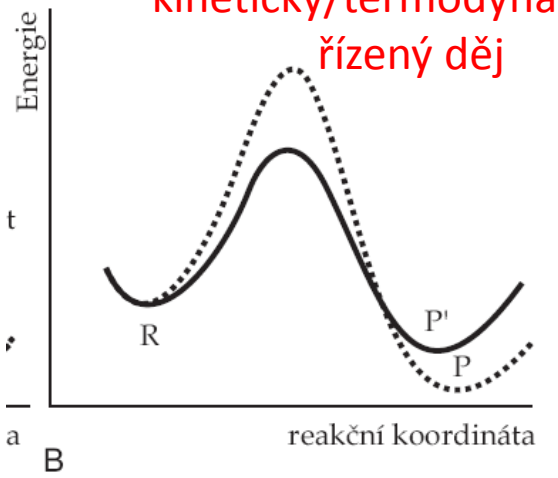
$$\frac{dc_C}{dt} = k_2 c_A$$



# Vratné bočné reakce



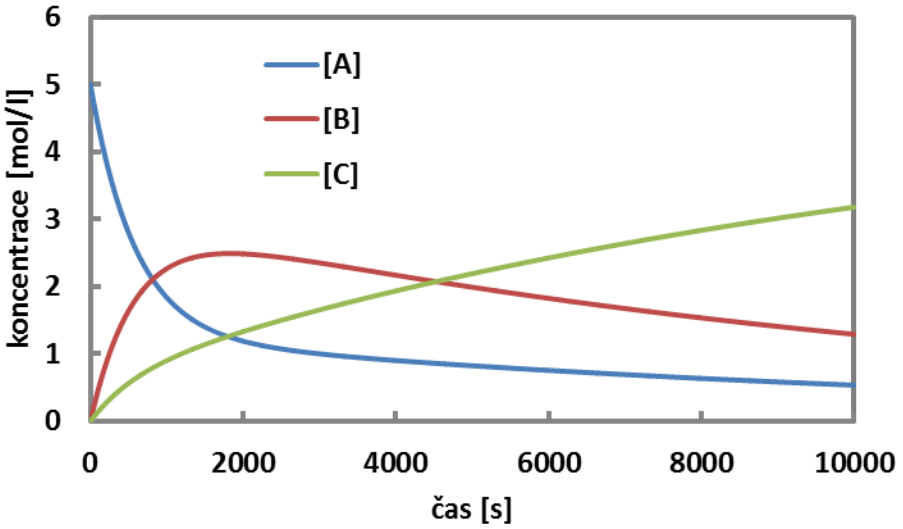

kineticky/termodynamicky řízený děj



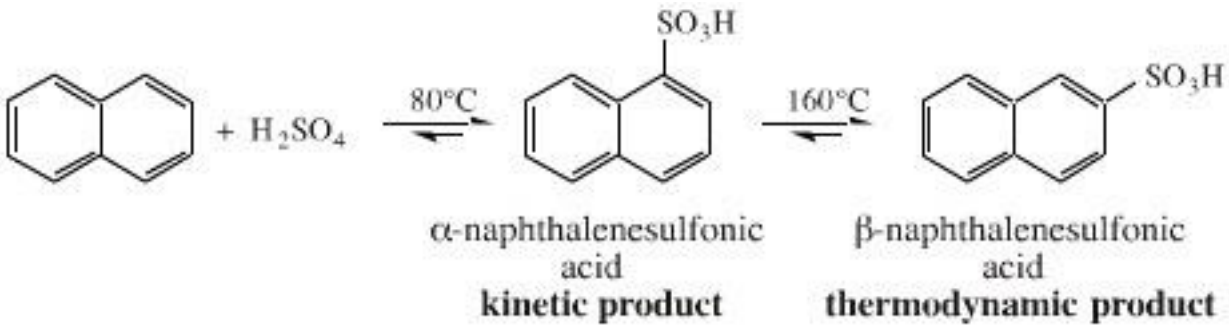

$$\frac{dc_A}{dt} = -(k_1 + k_2)c_A + k_{-1}c_B + k_{-2}c_C$$

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

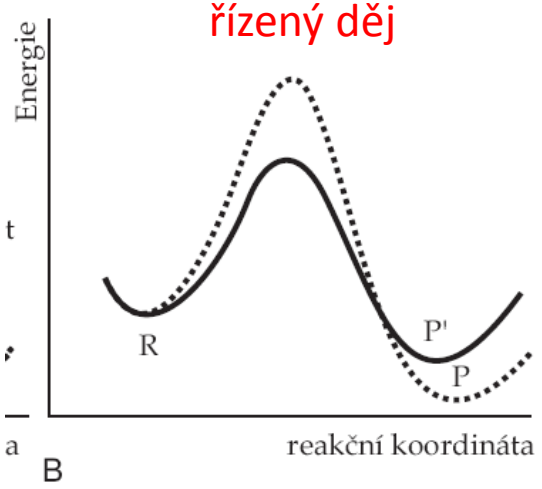
$$\frac{dc_C}{dt} = k_2 c_A - k_{-2} c_C$$



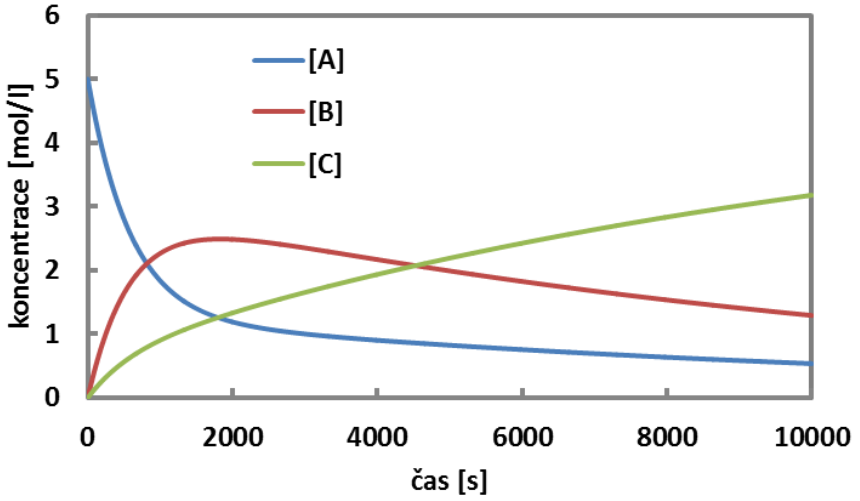
# Kineticky vs. Termodynamicky řízené reakce




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 reakce

$$IO_3^- + 2H_2O_2 + CH_2(COOH)_2 + H^+ \longrightarrow ICH(COOH)_2 + 2O_2 + 3H_2O$$

$$IO_3^- + I^- + H^+ \longrightarrow HIO_2 + HOI$$
$$HOI_2 + I^- + H^+ \longrightarrow HOI$$
$$HOI + H_2O_2 \longrightarrow I^- + O_2 + H^+ + H_2O$$
$$IO_3^- + HIO_2 + H^+ \longrightarrow IO_2^{\cdot} + H_2O$$
$$IO_2^{\cdot} + Mn^{2+} + H_2O \longrightarrow HIO_2 + Mn(OH)^{2+}$$
$$Mn(OH)^{2+} + H_2O_2 \longrightarrow Mn^{2+} + H_2O + HOO^{\cdot}$$

$$HOO^{\cdot} \longrightarrow H_2O_2 + O_2$$
$$HIO_2 \longrightarrow IO_3^- + HOI + H^+$$
$$I^- + HOI + H^+ \longrightarrow I_2 + H_2O$$
$$I_2 + CH_2(CO_2H)_2 \longrightarrow ICH(CO_2H)_2 + H^+ + I^-$$
$$I_2 + I^- \longrightarrow I_3^-$$
$$I_3^- + \text{starch} \longrightarrow I_5^- \text{ complex} + I^-$$

**Prozess I: $c(I^-) > c_{krit}$**

$$5I^- + IO_3^- + 6H_3O^+ \longrightarrow 3I_2 + 9H_2O$$
$$3I_2 + 3CH_2(COOH)_2 + 3H_2O \longrightarrow 3ICH(COOH)_2 + 3I^- + 3H_3O^+$$
$$\mathbf{3CH_2(COOH)_2 + IO_3^- + 2I^- + 3H_3O^+ \longrightarrow 3ICH(COOH)_2 + 6H_2O}$$

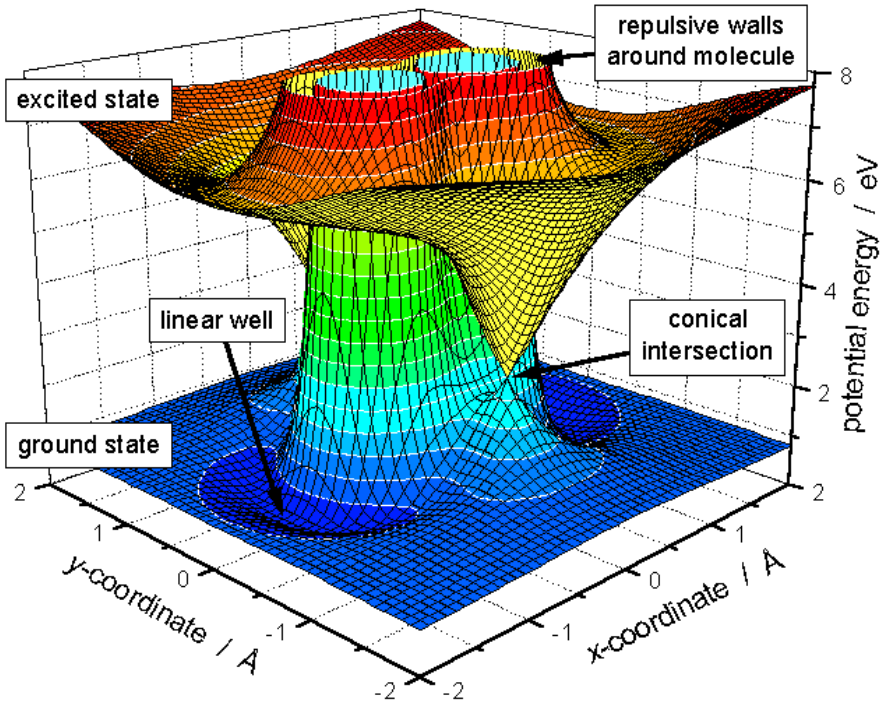
**Prozess II: $c(I^-) < c_{krit}$**

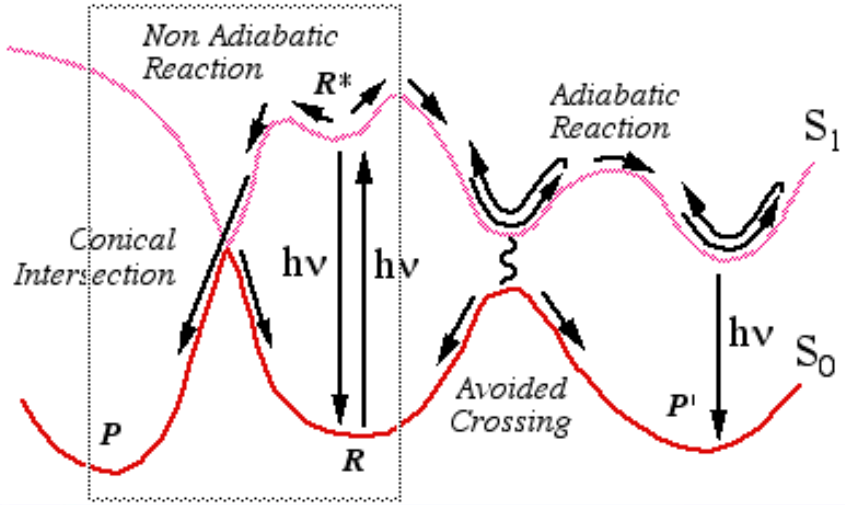
$$IO_3^- + HIO_2 + 2[Mn(OH_2)_6]^{2+} + H_3O^+ \rightleftharpoons 2HIO_2 + 2H_2O + 2[Mn(OH_2)_5OH]^{2+}$$
$$2HIO_2 + H_2O \rightleftharpoons HIO + IO_3^- + H_3O^+$$
$$\mathbf{IO_3^- + 4[Mn(OH_2)_6]^{2+} + H_3O^+ \rightleftharpoons HIO + IO_3^- + H_3O^+ + 4[Mn(OH_2)_5OH]^{2+}}$$

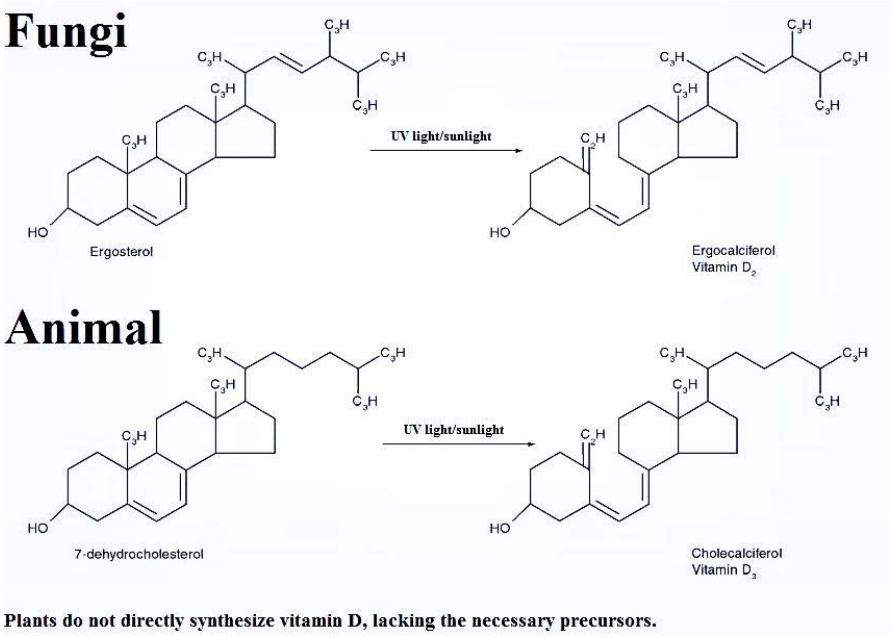
**Prozess III:**

$$2H_2O_2 + 2[Mn(OH_2)_5OH]^{2+} + HIO \longrightarrow 2O_2 + 2[Mn(OH_2)_6]^{2+} + I^- + H_3O^+$$

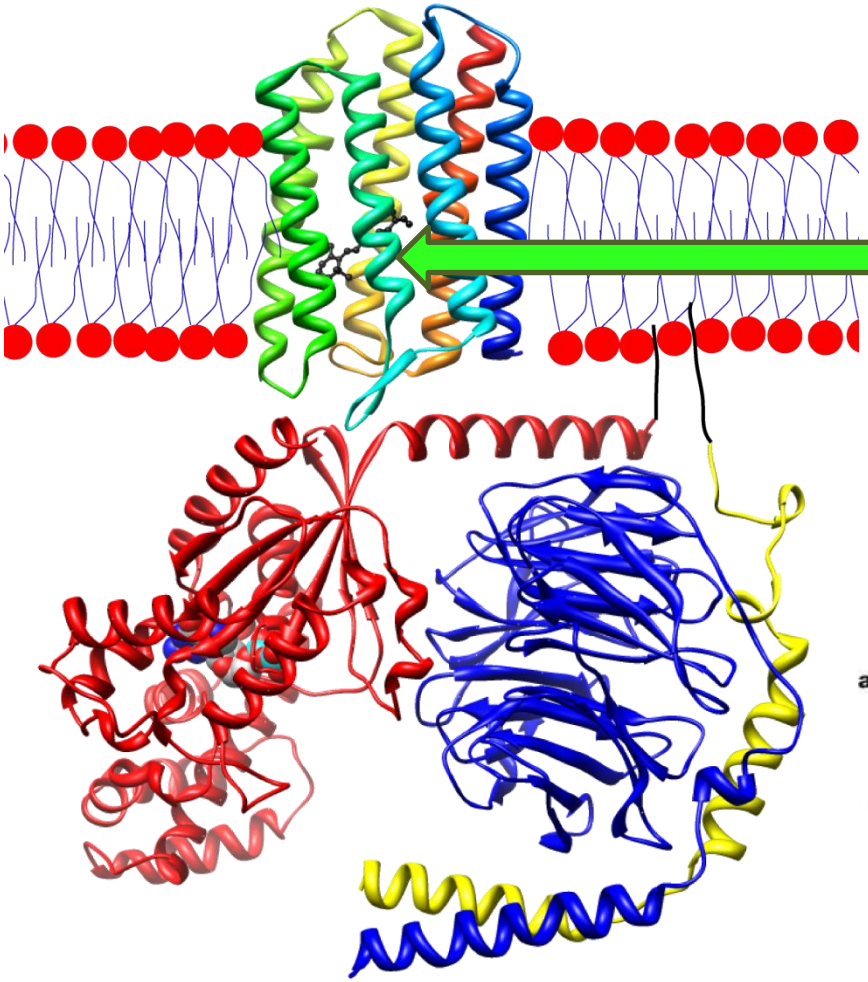
# Fotochemické reakce



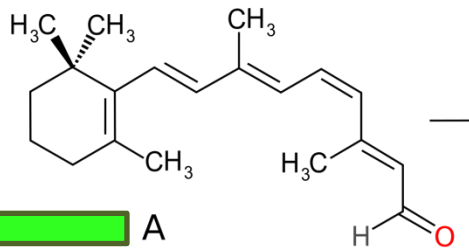



# Fotochemické reakce



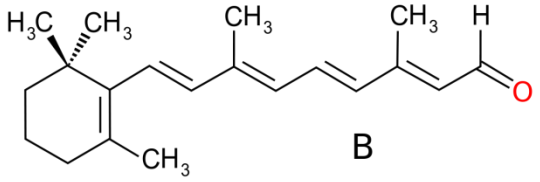
**rhodopsin**

**retinal**

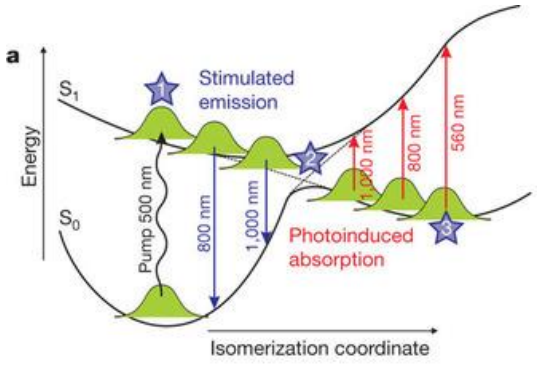


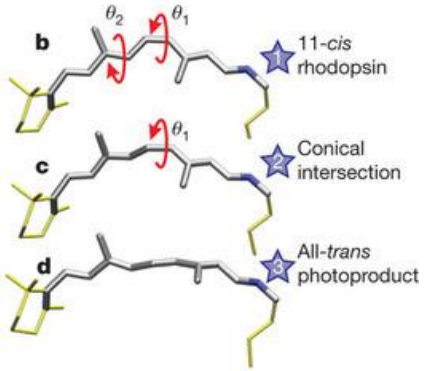

γ

A

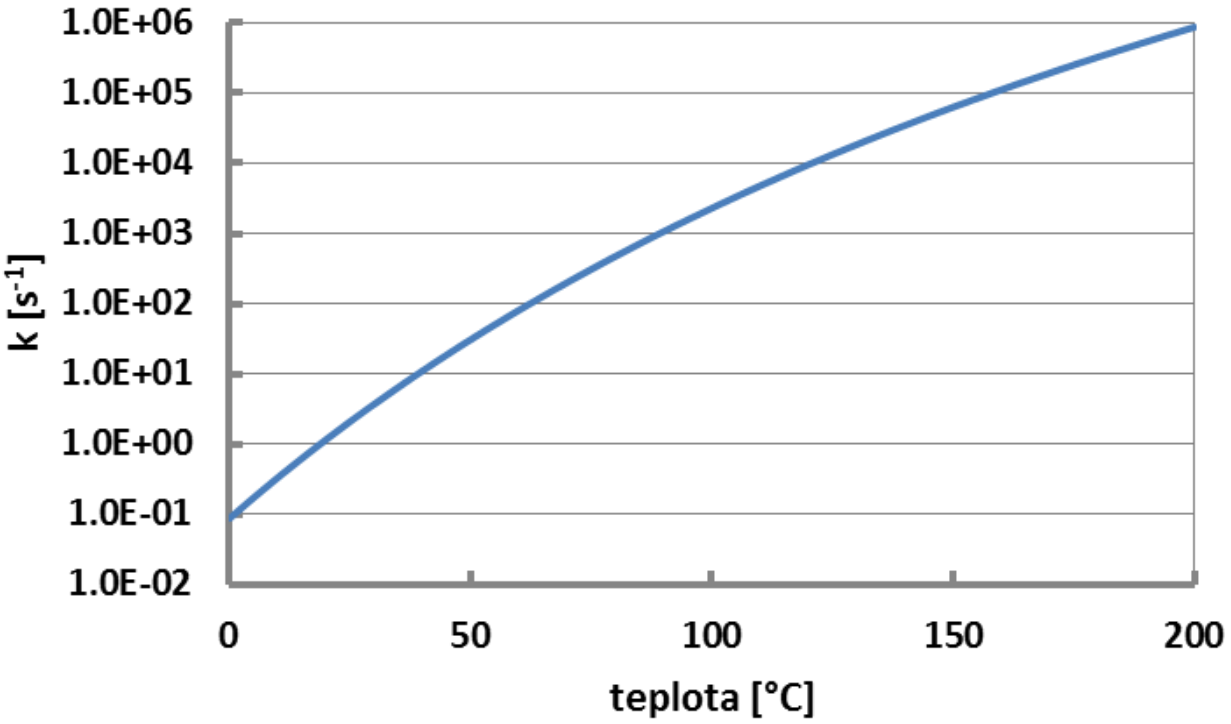



B



# Rychlost reakce vs. teplota

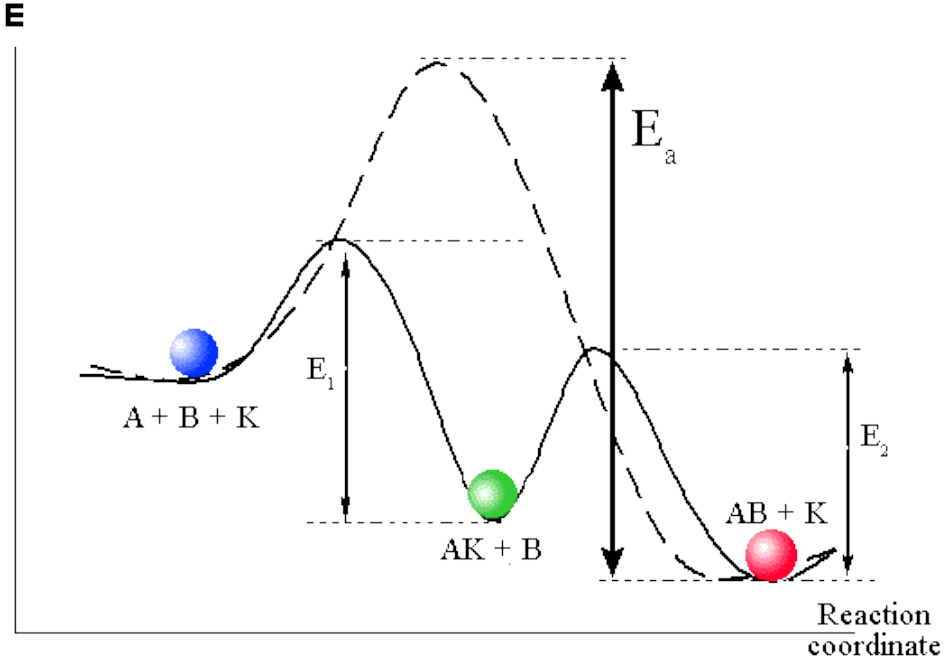



**Cca co 10°C se rychlost reakce zvětší 2x**

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

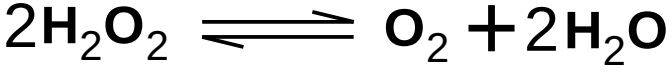
# katalýza


**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.

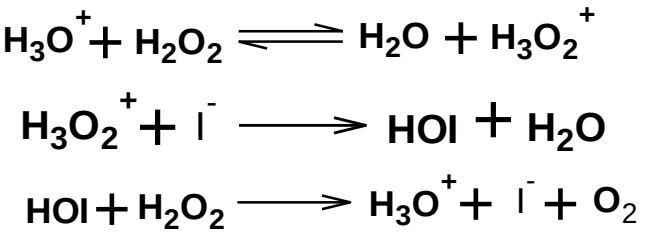


# katalýza

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



$$2H_2O_2 \rightleftharpoons O_2 + 2H_2O$$



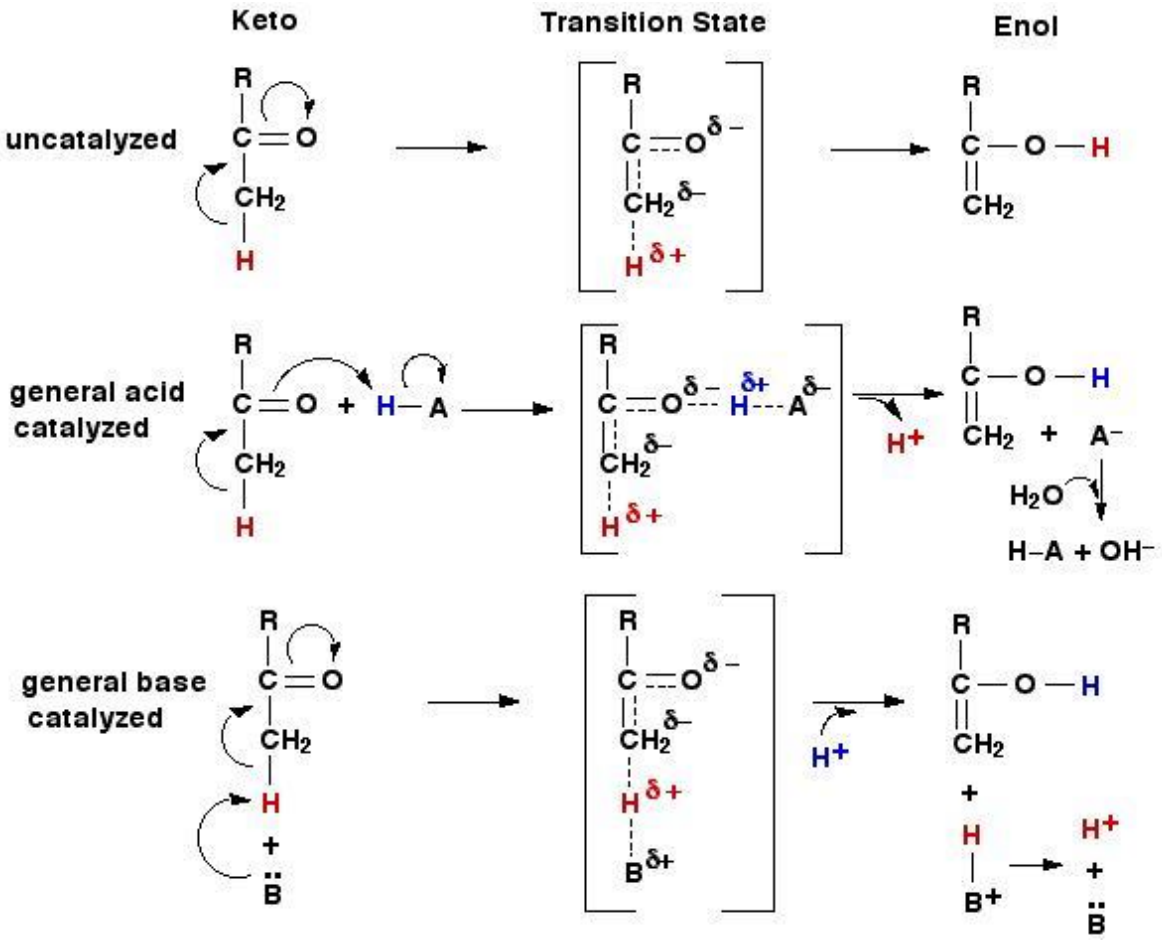
$$H_3O^+ + H_2O_2 \rightleftharpoons H_2O + H_3O_2^+$$

$$H_3O_2^+ + I^- \longrightarrow HOI + H_2O$$

$$HOI + H_2O_2 \longrightarrow H_3O^+ + I^- + O_2$$

- 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**

# Acidobazická katalýza

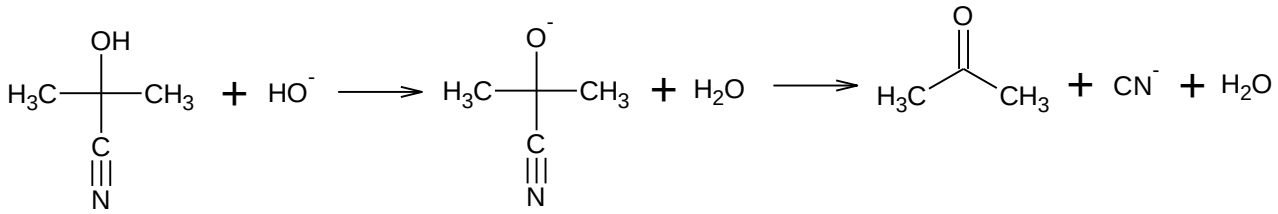



**IUPAC**

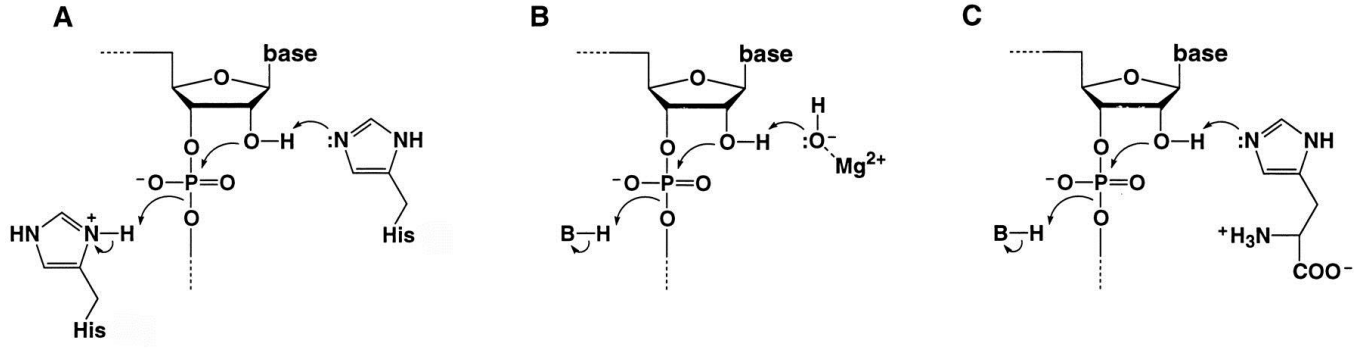
The term catalysis is also often used when the substance is consumed in the reaction (for example: base-catalysed hydrolysis of esters). Strictly, such a substance should be called an activator.

# Acidobazická katalýza

- Specifická acidobazická katalýza
  - Reaktant je plně protonovaný/deprotonovaný v reakci
  - Vyžaduje silnou kyselinu/zásadu

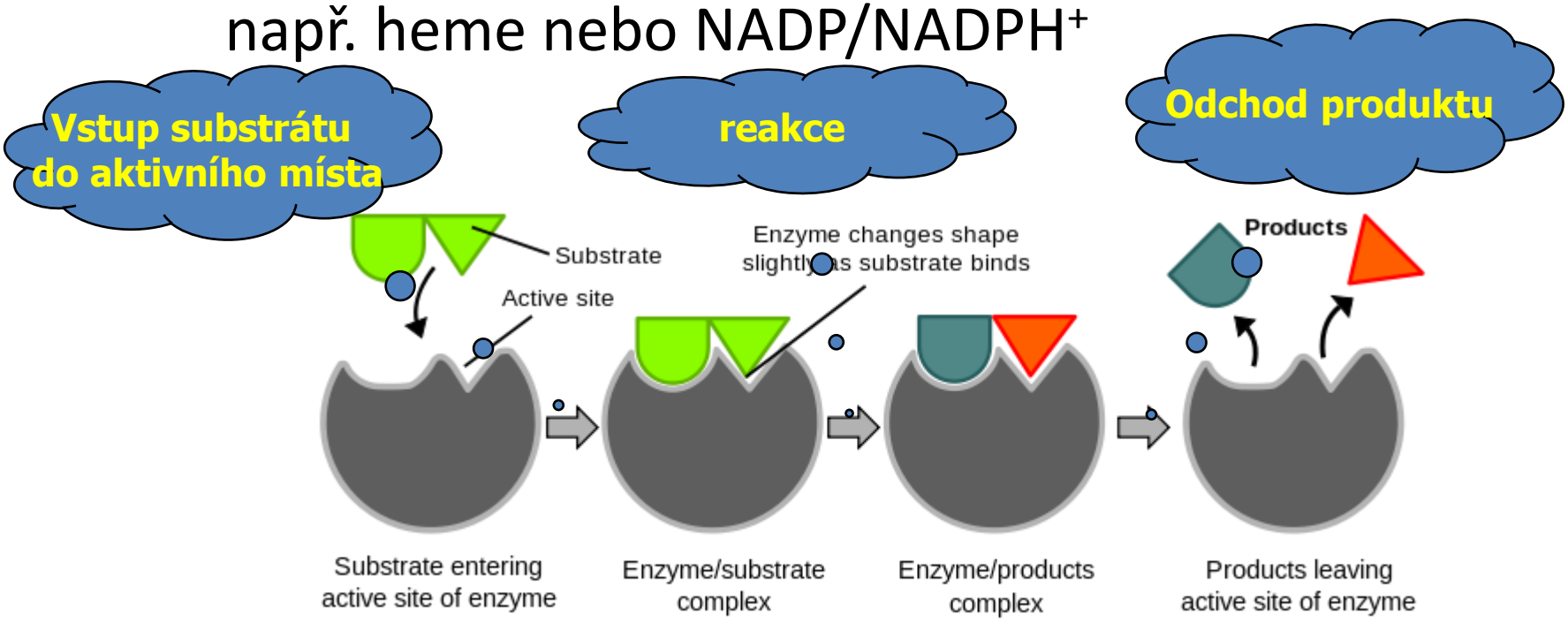



- Obecná acidobazická katalýza
  - Proton transfer probíhá v průběhu reakce
  - Proton ($H^+$ ion) je částečně přenesen v tranzitním stavu
  - Vyžaduje spíše slabou kyselinu/zásadu



# Enzymatická katalýza

- Katalýza pomocí proteinů
  - Protein – 21 aminokyselin
  - Kofaktor – neproteinová skupina v aktivním místě např. heme nebo NADP/NADPH$^+$



# Enzymatická katalýza

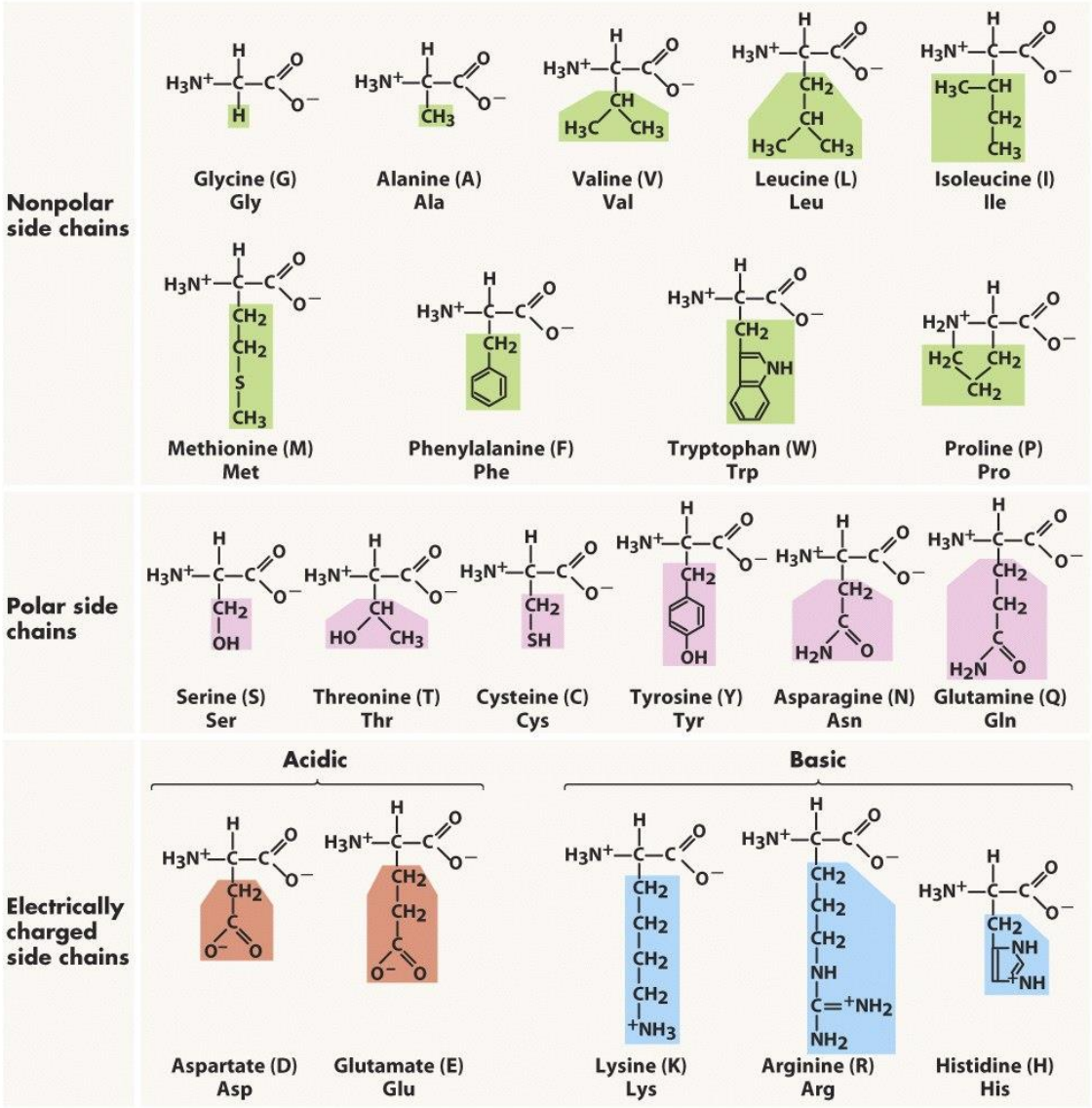
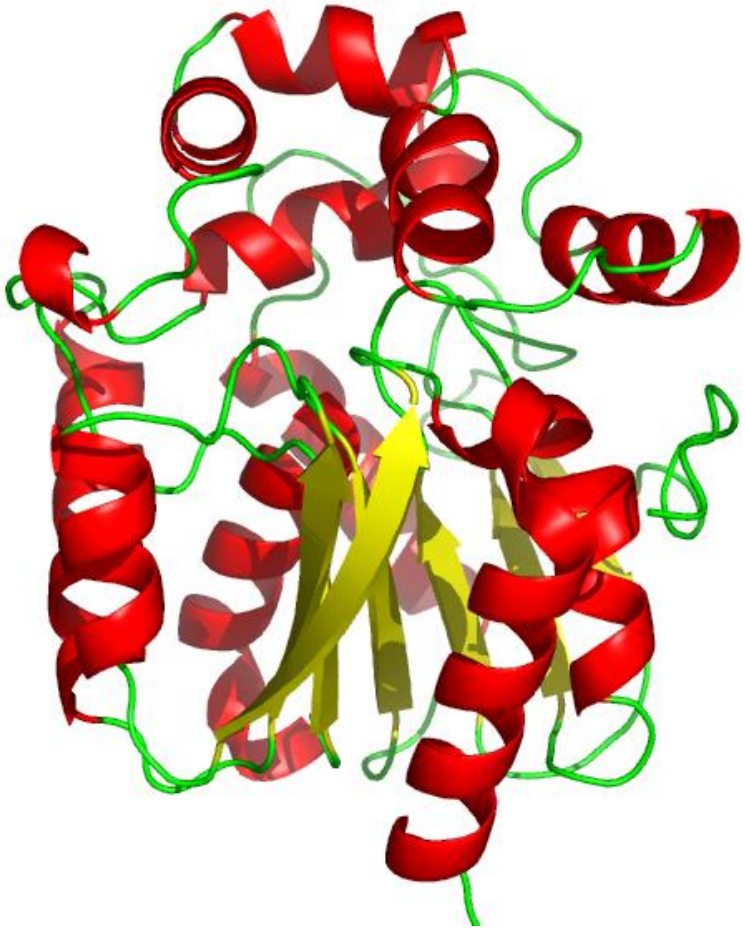
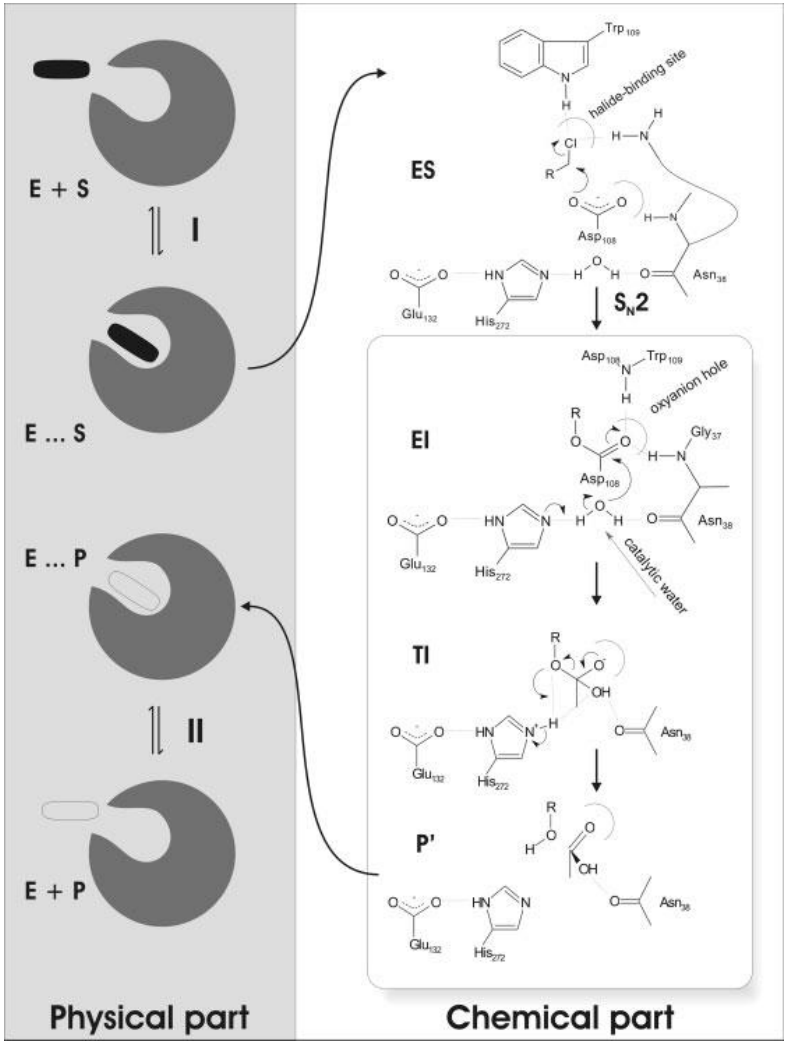


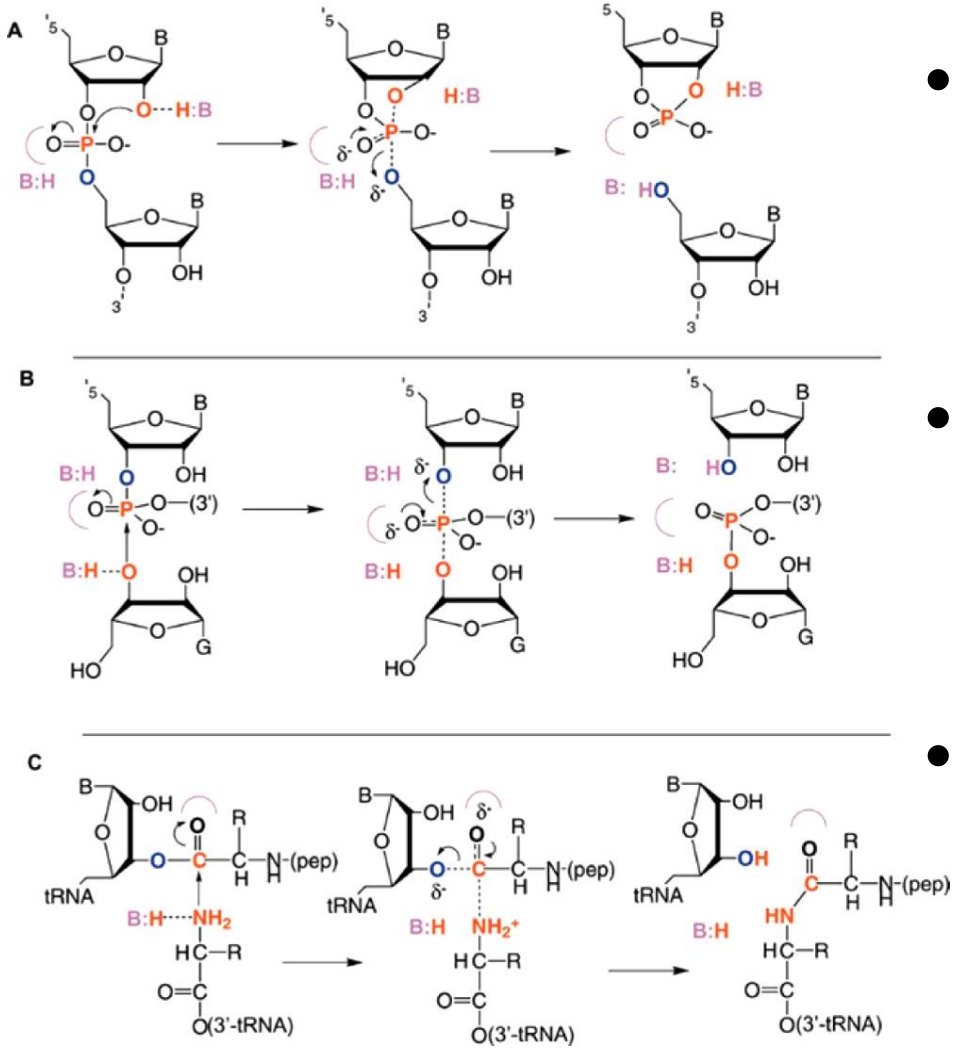

Figure 3-5 Biological Science, 2/e

# Enzymy - halogenalkandehalogenázy





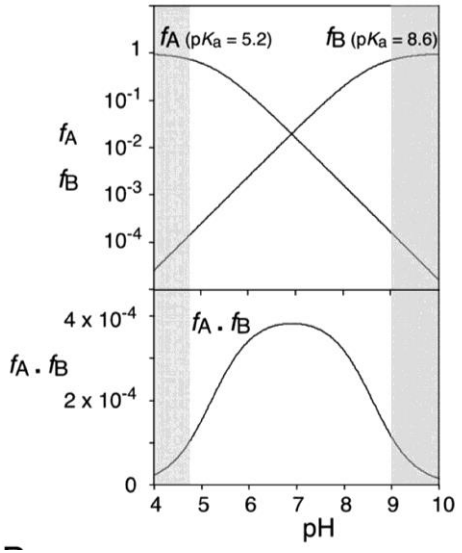
# RNA enzymy – RNA katalýza

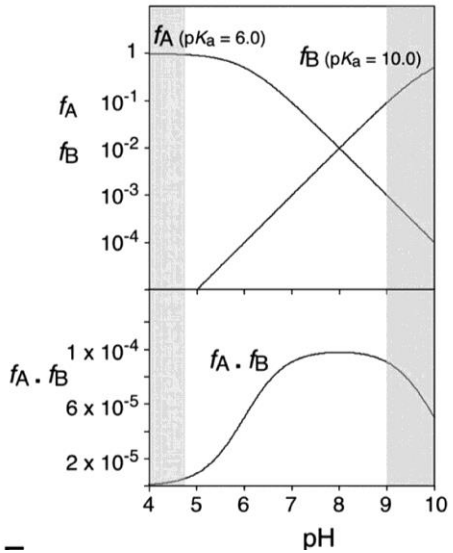



- malé ribozymy
  - 30-200 nts
  - Replikace virů
- Velké ribozymy
  - Self-splicing
  - Alternativní splice
- Peptidyl transfer
  - Syntéza proteinů
  - Katalyzováno pouze RNA

# RNA katalýza – acidobazická rovnováha

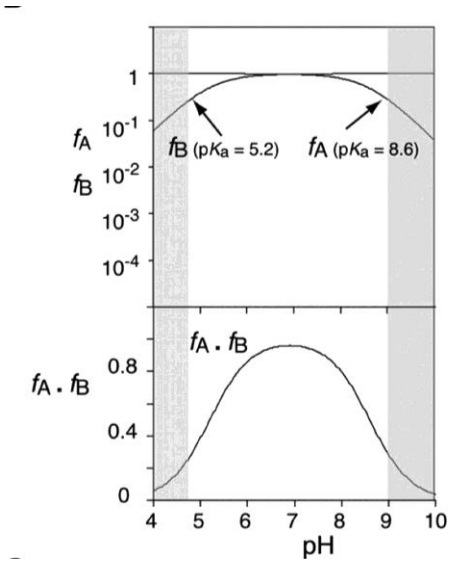
- Obecná acidobazická katalýza

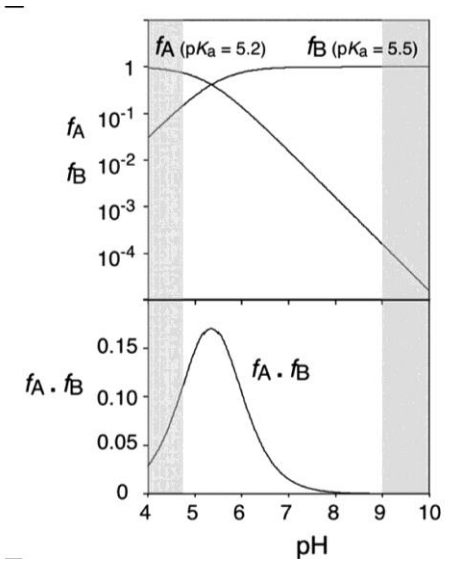



$\mathrm{p}\boldsymbol{K_a(base)} > \mathrm{p}\boldsymbol{K_a(acid)}$

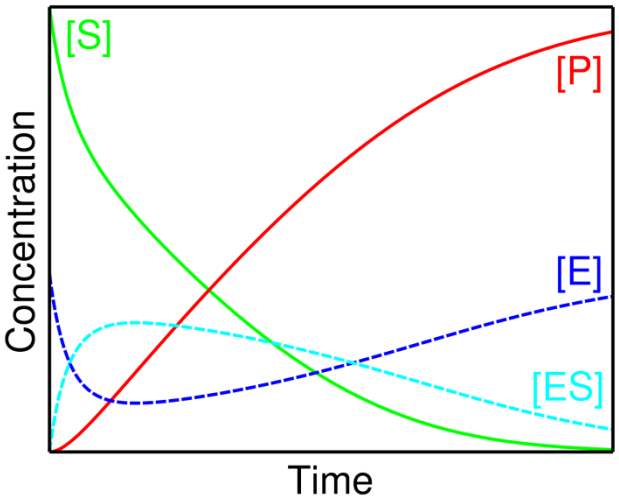
$\mathrm{p}\boldsymbol{K_a(base)} < \mathrm{p}\boldsymbol{K_a(acid)}$



# (Enzymová) Michaelis-Mentenová kinetika

$$\mathbf{E + S} \underset{k_{out}}{\overset{k_{in}}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_{cat}} \mathbf{E + P}$$

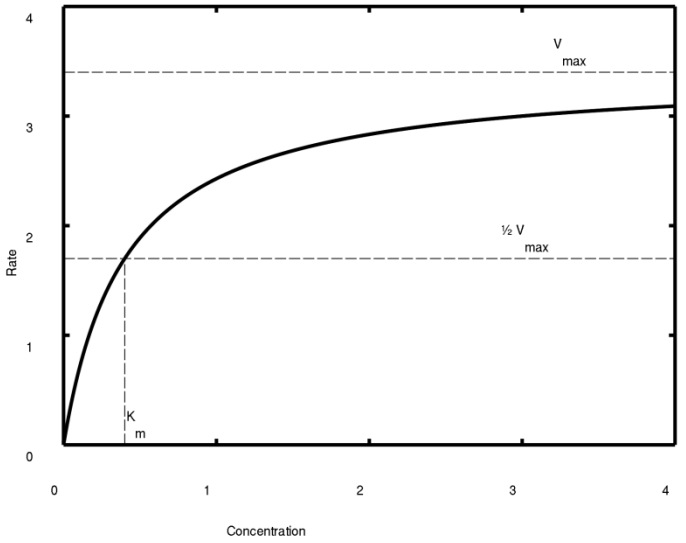



**Za předpokladu rovnováhy vazby substrátu**

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

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

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




**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


| Enzym | Katalyzovaná reakce | $K_m$ [mol/l] | $k_{cat}$ [$s^{-1}$] | $K_{cat}/K_m$ [$lmol^{-1}s^{-1}$] |
|---|---|---|---|---|
| Chymotrypsin | Ac-Phe-Ala→Ac-Phe+Ala | $1.5x10^{-2}$ | 0.14 | 9.3 |
| Pepsin | Phe-Gly→Phe+Gly | $3.0x10^{-4}$ | 0.5 | $1.7x10^{3}$ |
| Tyrosyl-tRNA syntaza | Tyrosin+tRNA→tyrosyl-tRNA | $9.0x10^{-4}$ | 7.6 | $8.4x10^{3}$ |
| Ribonukleáza | Cytidine-2´,3´cyclic phospate →cytidine-3´-phosphate | $7.9x10^{-3}$ | $7.9x10^{2}$ | $1x10^{5}$ |
| Carbonic anhydráza | $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ | $2.6x10^{-2}$ | $4x10^{5}$ | $1.5x10^{7}$ |
| Fumaráza | Fumarát → malát | $5.0x10^{-6}$ | $8x10^{2}$ | $1.6x10^{8}$ |

# Reakční mechanismus

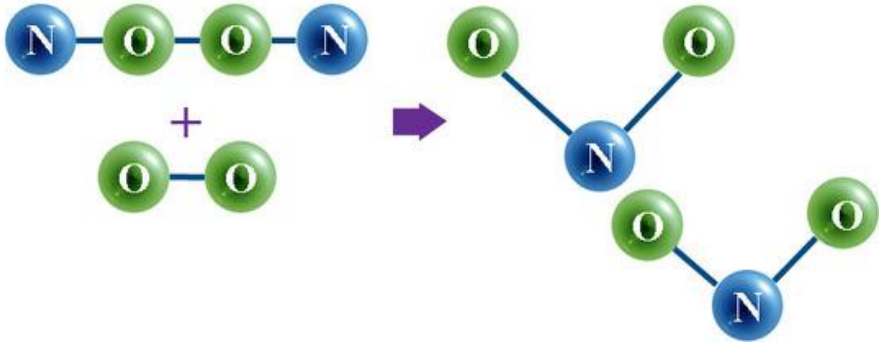
- Sled dílčích elementárních reakcí

$$2NO + O_2 \rightleftharpoons 2NO_2$$

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

**rychlá** $2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

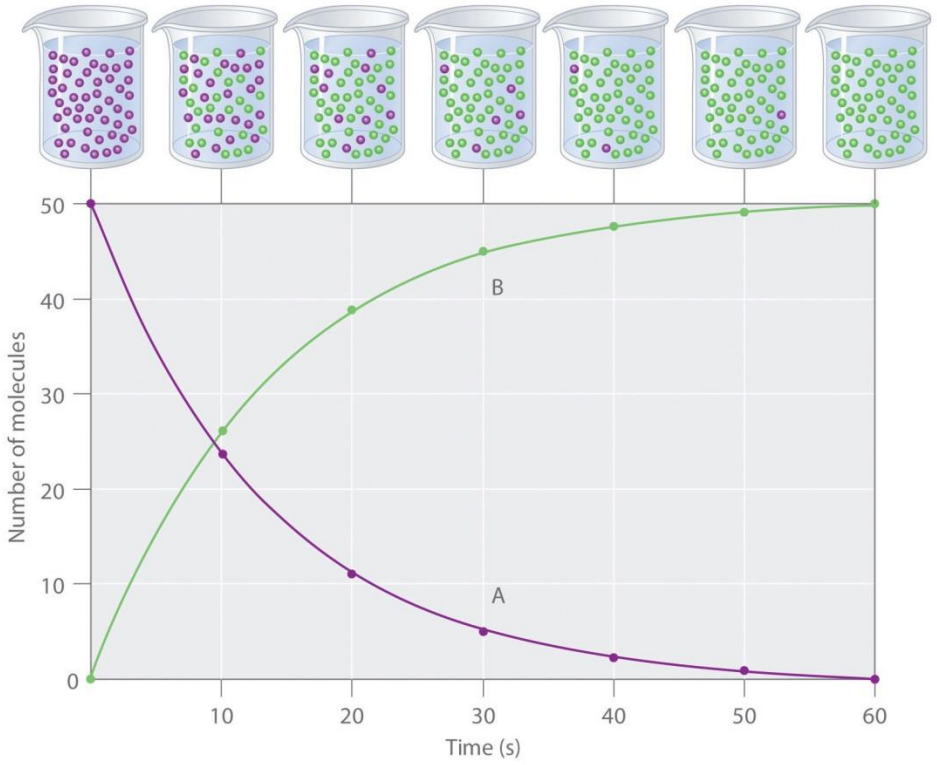

**pomalý** $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$




**Rychlost limitující krok**

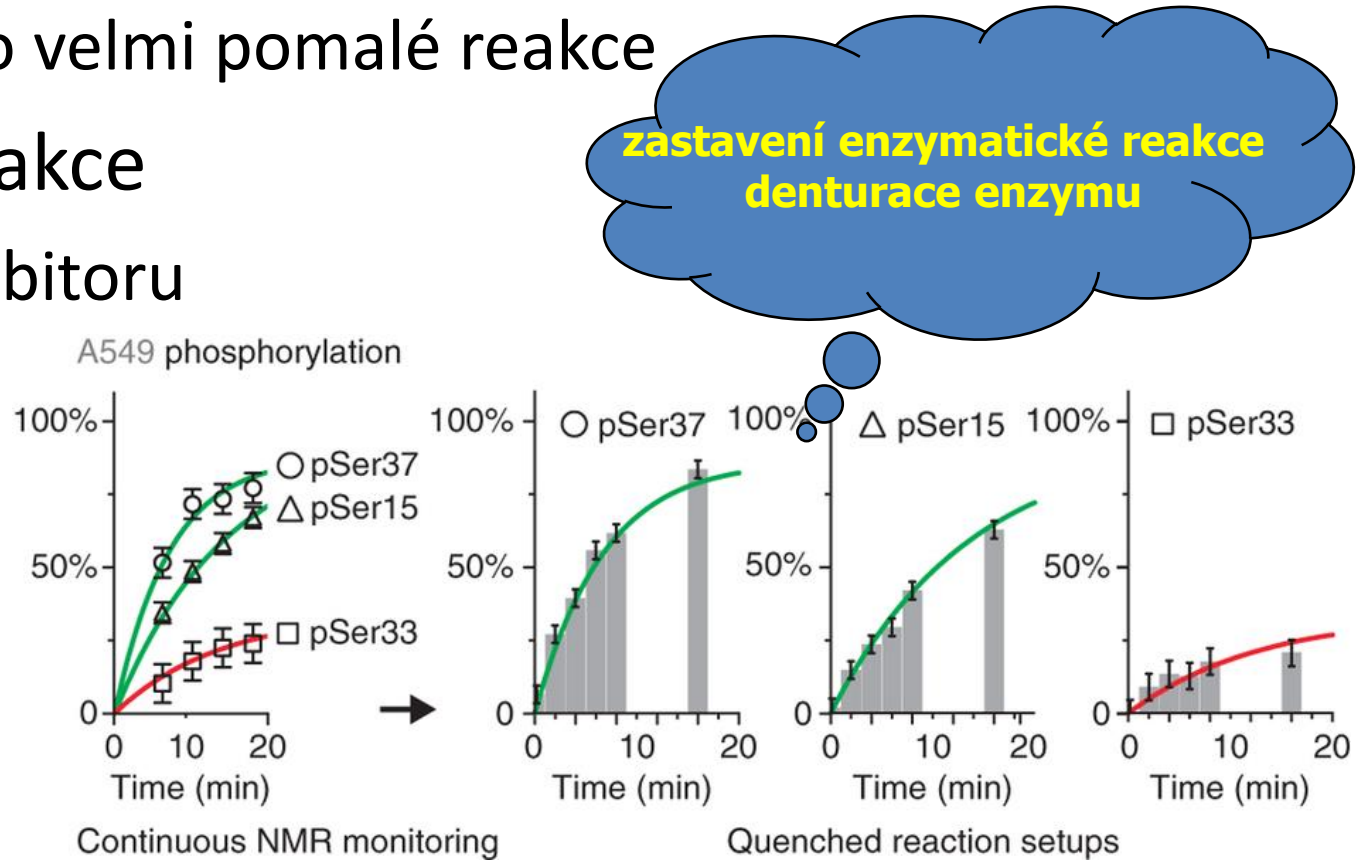
# Měření kinetiky reakce

- Sledování průběhu reakce
  - Pomalé a velmi pomalé reakce
- Měření signálu
  - Spektrofotometricky
    - absorpce/emise
    - UV-vis, IČ,…
  - elektrochemicky
    - pH
    - vodivost



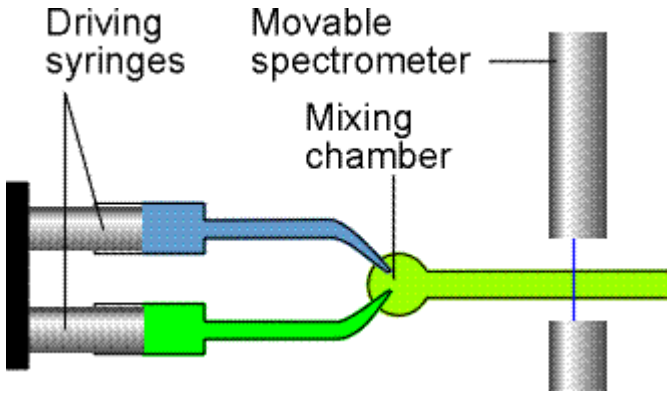
# Měření kinetiky reakce

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

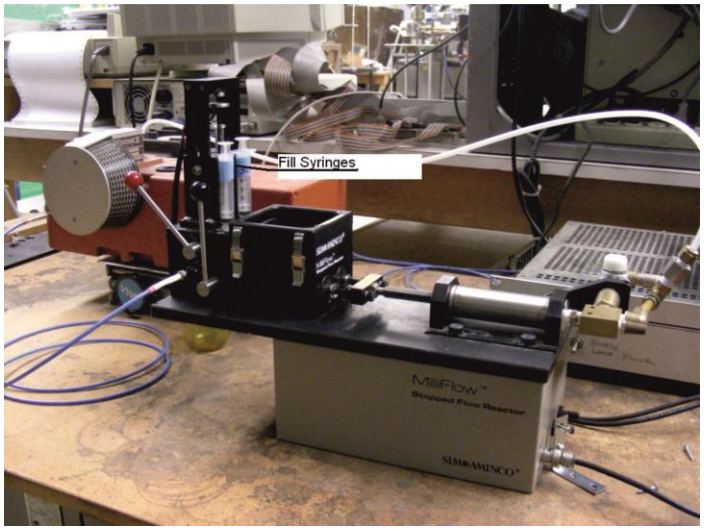


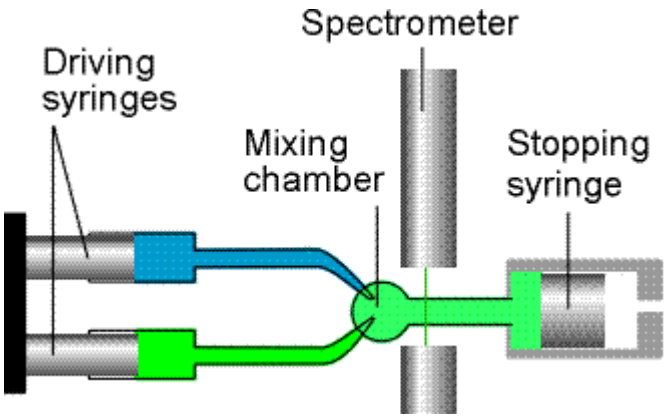
# Měření kinetiky reakce

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




  - Stopped-flow metody



# Měření řádu reakce

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

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons P$$

- 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

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