

Modeli hemijskih reakcij

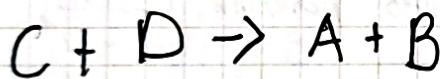
N vrst Molekul ("chem. species")

M reakcij, npr. $A + B \rightarrow C$

Naceloma: Če poznamo $\vec{r}(0)$, $\dot{\vec{r}}(0)$ za vsako molekulo
 $\Rightarrow \vec{r}(t)$, $\dot{\vec{r}}(t)$ za vsek $t > 0$
 (To je ab-initio molek. dinamika) \Rightarrow

Vektor stanja: $\vec{X}(t) = \begin{pmatrix} X_1(t) \\ \vdots \\ X_N(t) \end{pmatrix} \quad X_i(t) \geq 0$

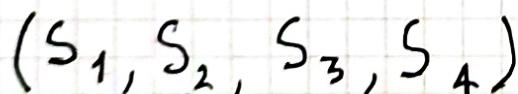
npr. $N=4$, $M=2$:



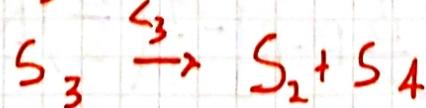
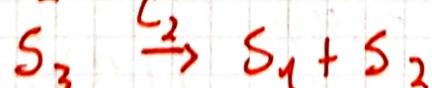
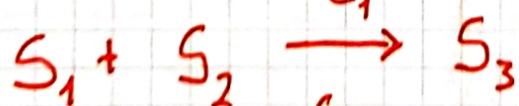
Začnemo s $\vec{X}(0) = \begin{pmatrix} K \\ K \\ 0 \\ 0 \end{pmatrix}$, $\begin{pmatrix} K-1 \\ K-1 \\ 1 \\ 1 \end{pmatrix}, \begin{pmatrix} K-2 \\ K-2 \\ 2 \\ 2 \end{pmatrix}, \dots, \begin{pmatrix} 0 \\ 0 \\ K \\ K \end{pmatrix}$

K je ponavadi ogromno število!

Zanimiv včni primer (Michaelis-Menten)



↑
Substrat ↑ enim ↑ kompleks ↑ produkt



Tu je:

$$N = 4$$

$$M = 3$$

Definiramo stoichiometrične vektorje $\vec{Y}_j \in \mathbb{R}^{N \leftarrow \# \text{ vrst molekul}}$



a M.-M. sistem imamo trije:

$$\vec{Y}_1 = \begin{pmatrix} -1 \\ -1 \\ 0 \end{pmatrix}, \quad \vec{Y}_2 = \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}, \quad \vec{Y}_3 = \begin{pmatrix} 0 \\ -1 \\ 1 \end{pmatrix}$$

\uparrow
zgimeta S_1, S_2
nastalec S_3

Kako hitra (verjetna) je posamezna realacija?

$$\text{Verjetnost} = \boxed{\uparrow} \cdot \Delta t$$

"propensity func."

$$a_j(\vec{X}(t))$$

če je realacija 1. reda $S_m \xrightarrow{c_j} \text{nekaj} : a_j(\vec{X}(t)) = c_j X_m(t)$

če je realacija 2. reda ($m \neq n$) $S_m + S_n \xrightarrow{c_j} \text{nekaj} : a_j(\vec{X}(t)) = c_j X_m(t) X_n(t)$

$$\text{ii)} \quad S_m + S_m \xrightarrow{c_j} \text{nekaj} : -\text{II-} = c_j \frac{1}{2} X_m [X_m - 1]$$

$\underbrace{}_{\# \text{ parov}}$

Poenostavimo notacijo na verjetnosti:

$$P(\vec{X}(t) = \vec{x}) = P(\vec{X}, t)$$

\uparrow
specifično
stanje

Definimo, da smo ob času $t + \Delta t$ v stanju \vec{X} .

Torej je bil v ob času t sistem: i) v istem stanju \vec{X}

ii) v enem od stanj $\vec{X} - \vec{Y}_j$

Spominimo se Bayesovega teorema:

$$P(A) = \sum_{j=0}^{M+1} P(A|H_j) P(H_j)$$

A... dogodek, da je sistem v stanju \vec{x} ob $t + \Delta t$

$H_0 \dots - II -$

$H_M \dots - II -$

$\vec{x} - \vec{y}_j$ ob t ($j = 1, \dots, M$)

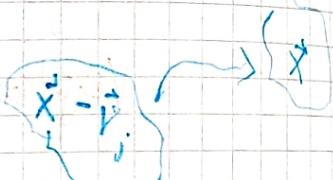
ukaterom holi drugem stanju

Torej:

$$P(A|H_j) = a_j(\vec{x} - \vec{y}_j) \cdot \Delta t ; 1 \leq j \leq M$$

$$P(A|H_0) = 1 - \sum_{j=1}^M a_j(\vec{x}) \Delta t$$

$$P(A|H_{M+1}) = 0 \quad \text{Zanemarimo}$$



↑ tu calc
prop. fun.

Prepisemo to sedaj v Bayesovo formulo:

$$P(\vec{x}, t + \Delta t) = \left[1 - \sum_{j=1}^M a_j(\vec{x}) \Delta t \right] P(\vec{x}, t) + \\ + \left[\sum_{j=1}^M a_j(\vec{x} - \vec{y}_j) \Delta t \right] P(\vec{x} - \vec{y}_j, t)$$

Nesemo vse to na eno stran:

$$\frac{P(\vec{x}, t + \Delta t) - P(\vec{x}, t)}{\Delta t} = \sum_{j=1}^M \left[a_j(\vec{x} - \vec{y}_j) P(\vec{x} - \vec{y}_j, t) - a_j(\vec{x}) P(\vec{x}, t) \right]$$

Sedaj pa $\Delta t \rightarrow 0$ in dobimo:

$$\frac{dP(\vec{x}, t)}{dt} = \dots$$

glozno!

To se imenuje "Chemical master eq."

Sistem ODE s toliko komponentami kolikor je možnih stanj sistema.

npr. $\vec{x} = \begin{pmatrix} 12766350 \\ 12766350 \\ 106 \\ 106 \end{pmatrix}$

→ Nujno potrebujemo, kakošen priblizek:

Shocimo za veliki čas γ , ki ne sme biti ne prekratek (da se nica ne

Povprečje za \sim $(a_j(\vec{x}(t)) \cdot \gamma)$ ne pridega (da se q ne spremeni) zgodil

$$\vec{x}(t + \gamma) = \vec{x}(t) + \sum_{j=1}^M P_j^{\uparrow} \cdot \gamma_j$$

↑ poissonsko porazdeljeno nalj. st.

1. Primer na listih:

1) Izrabuj poissonskie $\{P_j\}_{j=1}^M$
s parametrom $\lambda = a_j(\vec{x}(t)) \gamma$

$$(P_j = \frac{e^{-\lambda} \lambda^j}{j!})$$

2) $\vec{x}(t + \gamma) = \vec{x}(t) + \dots$

Tav-leap aproksimacija

↳ Slika kuže primer

$$\vec{x}(0) = \begin{pmatrix} 312 \\ 125 \\ 0 \\ 0 \end{pmatrix}$$

3) GOTO 1

Pejmo zdaj še z aproksimacijo naprej. Če je $a_j(\vec{x}(t)) \cdot \gamma$ dovolj veliko \Rightarrow poisson \approx lahko nadomeščimo z Gaussom $\sim N(\delta, 1)$

$$P_j(a_j(\vec{x}(t)) \gamma) \rightarrow a_j(\vec{x}(t)) \gamma + \sqrt{a_j(\vec{x}(t)) \gamma} \tilde{Z}_j$$

Kar smo naredili je essentially:

$$X \sim N(\mu, \sigma^2) = X \sim \mu + \sigma N(0, 1)$$

$\sqrt{\mu}$ za poisson

Takto zdej pri sholu dobimo:

$$\vec{X}(t+\gamma) = \vec{X}(t) + \gamma \sum_{j=1}^M a_j(\vec{X}(t)) \vec{v}_j + \sqrt{\gamma} \sum_{j=1}^M \sqrt{a_j(\vec{X}(t))} z_j \vec{v}_j$$

To je Chemical Langevin equation.

• Dimenzionalnost smo zmanjšali iz st. stanj na št. vrst molekul.
(N = množina)

• Opravka imamo z R holicinami, ne Z

• Namesto diskretnega nabora stanj imamo zvezne holicine

Eliminirajmo že vsa nahajčnost (zadnjih len preostalo):

$$\dot{\vec{X}} = \sum_{j=1}^M a_j(\vec{X}(t)) \vec{v}_j$$

Reaction rate equations!

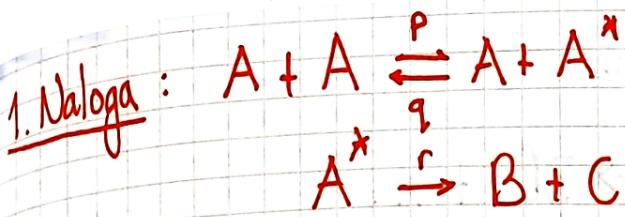
Za M-M sistem:

$$\dot{X}_1 = -k_1 X_1 X_2 + k_2 X_3$$

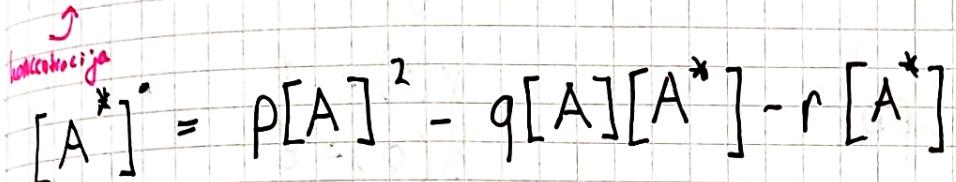
$$\dot{X}_2 = -k_1 X_1 X_2 + (k_2 + k_3) X_3$$

$$\dot{X}_3 = k_1 X_1 X_2 - (k_2 + k_3) X_3$$

$$\dot{X}_4 = k_3 X_3$$



$$\dot{[A]} = -p[A]^2 + q[A][A^*]$$



$$\dot{[B]} = \dot{[C]} = r[A^*]$$

Brez dimenzijske:

$$a(t) = \frac{[A](t)}{[A](0)} \text{ podobno } a^*$$

$$a(0) = 1, a^*(0) = 0 \text{ zac pog } t \Rightarrow \gamma = p \cdot [A](0)t$$

$$b = \frac{q}{p}, S = \frac{r}{q[A](0)}$$

go against what if this does not hold!

Znana je zaceta konc. $[A](0)$ in razmerje $q/p = 1000$. Integriraj sistem

$$\text{za } \frac{r}{q[A](0)} = 10, 1, 0.1$$

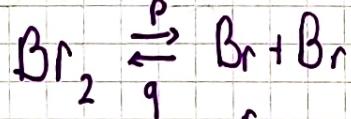
Integriraj "ehsaltno" \rightarrow kolikor gre

izrazi in poprijem
nor sistem enak.

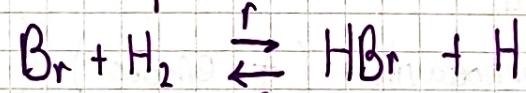
Integriraj v približku stac. stanja ($[A^*]^\circ \equiv 0$)

2. Naloga Spajanje vodika in bromata

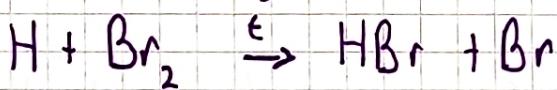
$$u = [H_2]$$



$$v = [Br_2]$$



$$x = [HBr]$$



$$y = [H]$$

Sistem ODE:

integriraj i) ehsaltno

$$z = [Br]$$

$$\dot{u} = Sxy - ruz$$

ii) v približku $y \approx 0$

$$\dot{v} = qz^2 - pr - evy$$

iii) v približku $z \approx 0$

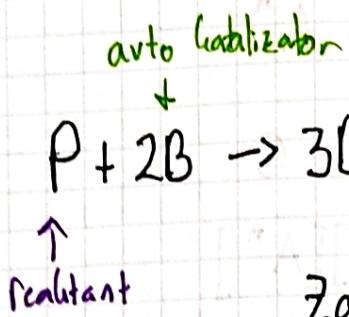
$$\dot{x} =$$

$$\dot{y} =$$

$$\dot{z} =$$

Kemijske ure

Kubična autohataliza



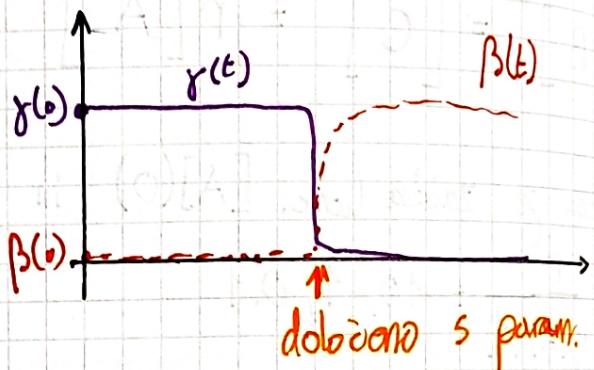
Zač. pogoji.

Rate eqs:

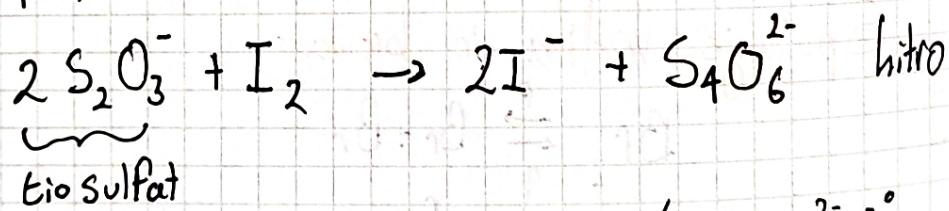
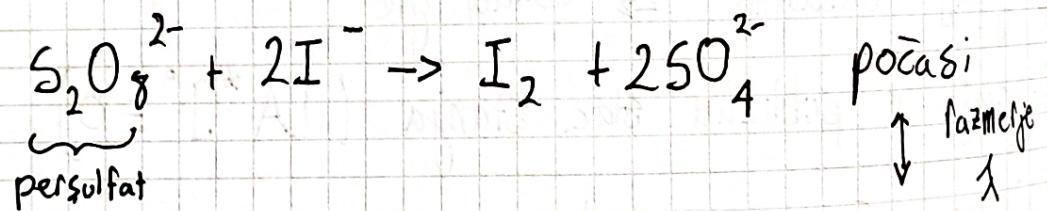
$$\dot{P} = -k_P b^2$$

$$\dot{b} = k_P b^2$$

$$\begin{aligned} \text{Poenostavimo } & \rightarrow \dot{y} = -y \beta^2 \\ \text{Na eno parametreno. } & \dot{\beta} = y \beta^2 \end{aligned}$$



3. Naloga jodova ure



Pametno je potem poenostaviti (4 enačbe) ($[S_2O_8^{2-}]^* = 0$)?

Za probleme z ODE liger so reakcije hitrosti v posameznih procesih procesih zelo različne (redi velikosti !!!)

↪ Stiff ODE!

(your ghetto RK8(9)?)