



VYSOKÁ ŠKOLA
CHEMICKO-TECHNOLOGICKÁ
V PRAZE

Stechiometrická analýza sietí (SNA)

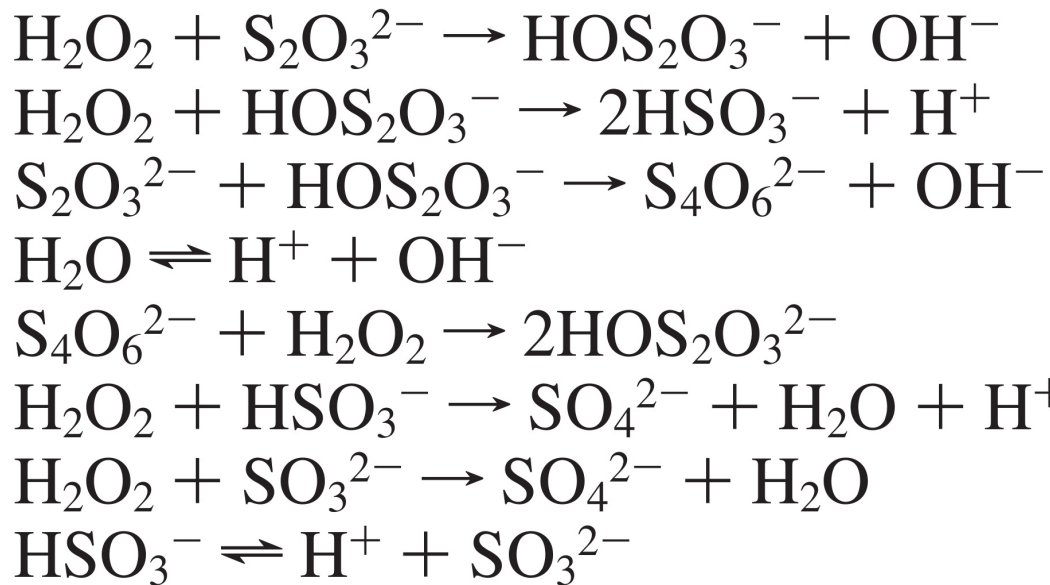
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Ústav chemického inžénýrství, VŠChT, Praha

8. 12. 2010

Zadanie úlohy

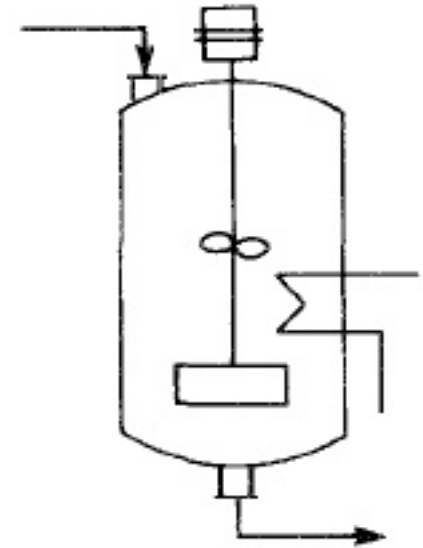


...

$$\begin{aligned} v_1 &= k_1[\text{H}_2\text{O}_2][\text{S}_2\text{O}_3^{2-}] \\ v_2 &= k_2[\text{H}_2\text{O}_2][\text{HOS}_2\text{O}_3^-] \\ v_3 &= (k_3 + k_3'[\text{H}^+])[\text{S}_2\text{O}_3^{2-}][\text{HOS}_2\text{O}_3^-] \\ v_4 &= k_4[\text{H}_2\text{O}] \\ v_{-4} &= k_{-4}[\text{H}^+][\text{OH}^-] \end{aligned}$$

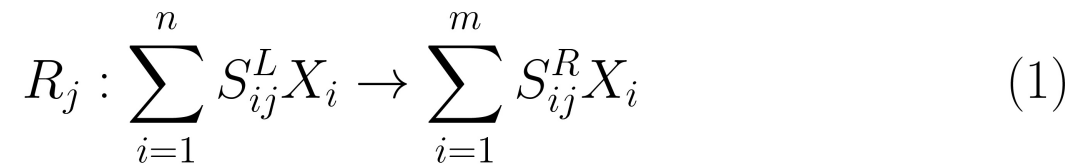
$$\begin{aligned} k_1 &= 0.019 \\ k_2 &= 0.020 \\ k_3 &= 1.0, k_3' = 1.0 \times 10^5 \\ k_4[\text{H}_2\text{O}] &= 1.0 \times 10^{-3} \text{ M s}^{-1} \\ k_{-4} &= 1.0 \times 10^{11} \end{aligned}$$

...



Formalizmus analýzy

- Stechiometriu siete zapíšeme stochiometrickou maticou



- Hľadáme vektory rýchlostí, ktoré nám dajú stacionárne stavy

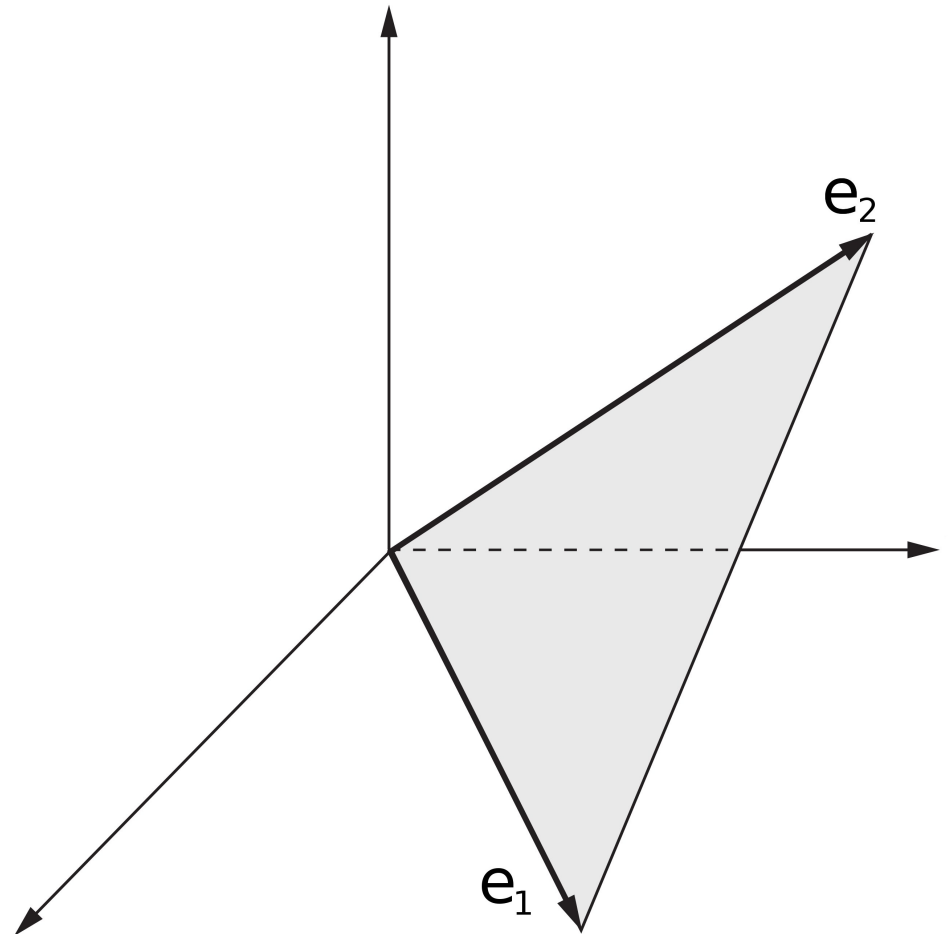
$$Sv = \dot{x} \quad (2)$$

- Matica linearizácie sústavy obsahuje aj informáciu o danom stacionárnom stave

$$J(x_s) = S(\text{diag}v_s)\kappa^T(\text{diag}x_s)^{-1} \quad (3)$$

Hľadanie hrán ihlanu

- SVD
- Lineárnou kombináciou bázy získame hrany = 1D steny
- Viacdimenziálne steny sú podpriestory generované vybranými n -ticami hrán



SNA na dlani

| Veličina | symbol | rád |
|-----------------------------------|--------------------------|---------------------------------|
| Počet reakcií | r | 1 |
| Počet zložiek | n | 1 |
| Počet väzieb | f | 1 |
| Stechiometrická matica | S | $n \times r$ |
| Stacionárny stav | x_s | $1 \times n$ |
| Rýchlosť akumulácie zložiek | \dot{x} | $1 \times n$ |
| Matica linearizácie v okolí x_s | $J(x_s)$ | $n \times n$ |
| Hodnosť S | $\text{rank}(S) = n - f$ | 1 |
| Nulový priestor S | V | $r \times (r - \text{rank}(S))$ |
| Kinetická matica | κ | $n \times r$ |
| Hrana | e_i | $1 \times r$ |
| Stena dimenzie 2 | f_{ij} | $2 \times r$ |
| Stena dimenzie 3 | f_{ij} | $3 \times r$ |
| Prúd (vektor rýchlostí) | v_s | $1 \times r$ |
| Matica hrán | E | $(r - \text{rank}(S)) \times r$ |

Stabilita podsietí

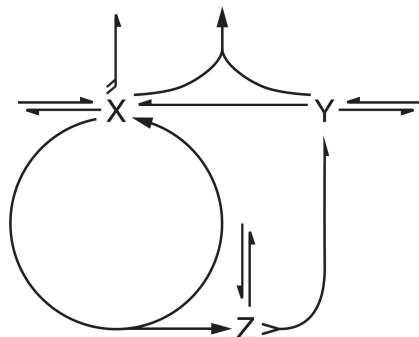
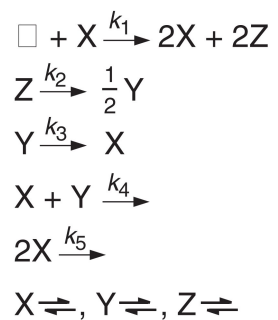
- Skúmame maticu obsahujúcu informáciu len o stechiometrii siete a molekularite reakcií

$$B = -S(\text{diag}v_s)\kappa^T \quad (4)$$

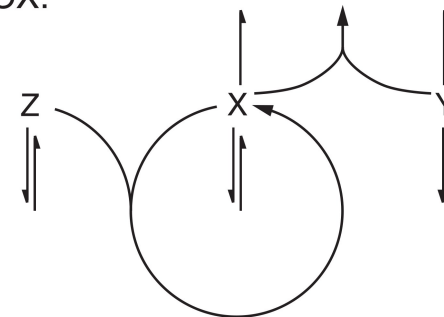
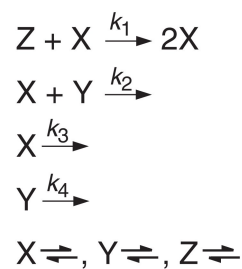
- Ak aspoň jeden hlavný subdeterminant záporný, aspoň 1 vlastné číslo J je kladné a podsieť je nestabilná
- Záporný hlavný subdeterminant je postačujúcou podmienkou pre enstabilitu, nie nutnou - Hopfova bifurkácia aj bez toho

Klasifikácia oscilátorov

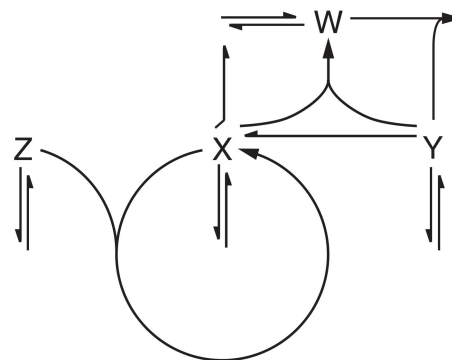
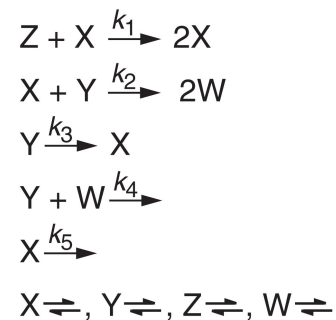
(a) Category 1B:



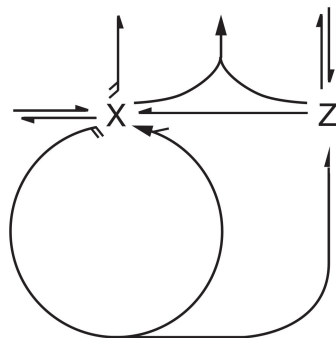
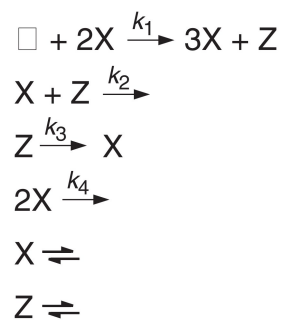
(b) Category 1CX:



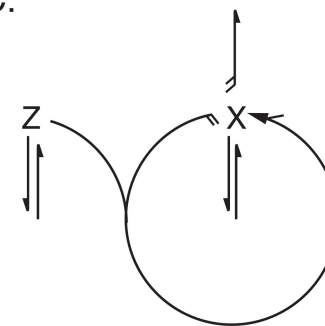
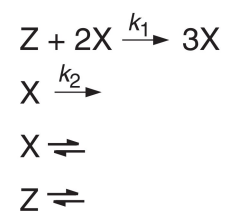
(c) Category 1CW:



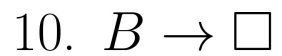
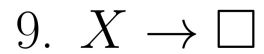
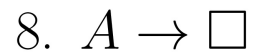
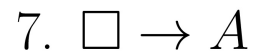
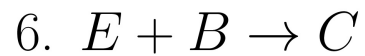
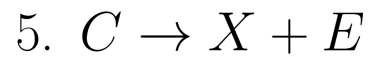
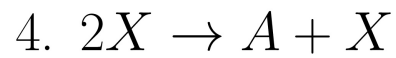
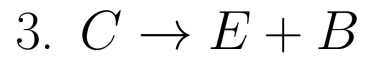
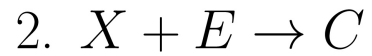
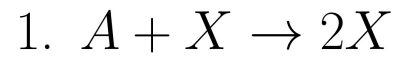
(d) Category 2B:



(e) Category 2C:



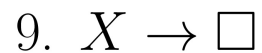
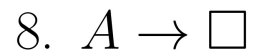
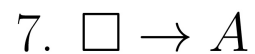
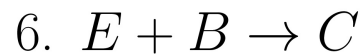
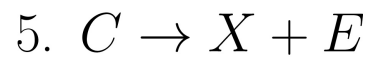
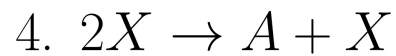
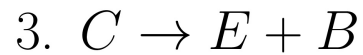
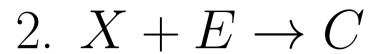
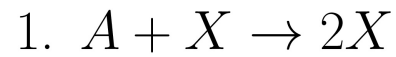
JR model



$$S^L = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 2 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$S^R = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

JR model



$$S^L = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 2 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$S^R = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$E = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix}$$

Obmedzenia

- V prípade veľkej sústavy je výpočtovo zdĺhavé nájsť hrany ihlana
- Prejsť všetky steny všetkých rozmerov je zdĺhavé
- Implementovaný algoritmus reprezentuje steny 1 vektorom - stredovým
- Opísanou metodológiou nemožno s istotou vo všeobecnosti vylúčiť nestabilitu

Zdroje

- Determination of complex reaction mechanisms. Ross J., Schreiber I., Vlad M.O. Oxford University Press. 2006
- Stability of Complex Reaction networks. Clarke B.L., Advances in Chemical Physics, 1980, 43, 1
- Oscillatory Reactions Involving Hydrogen Peroxide and Thiosulfate Kinetics of the Oxidation of Tetrathionate by Hydrogen Peroxide. Voslar M, Matejka P, Schreiber I. Inorganic Chemistry, 2006, 45 (7), 2824-2834
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