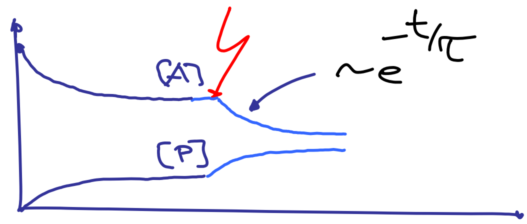
V4
30.4.2019

Note Title

WDH: Relaxation

(1) T-Sprung

$$\frac{dK/K}{dT} = \frac{\Delta_R H}{RT^2} \qquad \Delta H \neq 0$$



$A \rightleftharpoons P, \quad \tau = \frac{1}{k_1 + k_{-1}}$

$A + B \rightleftharpoons P, \quad 1/\tau = k_1 \cdot (c_{A,eq} + c_{B,eq}) + k_{-1}$

(2) p-Sprung

$$\frac{dK/K}{dp} = \frac{-\Delta V}{RT}$$

Stoßwelle ($\Delta p > 0$)
Membran ($\Delta p < 0$)

→ Ladungsneutralisation

$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_{3(aq)} \qquad \Delta V = 28\,cm^3/mol$

(3) Dissoziationsfeld
(E-Feld)

$H^+ + OH^- \rightleftharpoons H_2O \qquad \sim 100\,kV/cm,$ 20 µs

$k_1 = 1{,}35 \cdot 10^{11}\,L/mol \cdot s$

(4) zusammengesetzte Reaktionen

$A \underset{}{\overset{k_1}{\rightleftharpoons}} I_1 \overset{k_2}{\rightleftharpoons} I_2 \rightleftharpoons$

$\tau = \sum_i \alpha_i \cdot e^{-t/\tau_i}$

$A + B \rightleftharpoons C \rightleftharpoons D$

$1/\tau = k_1 (c_{A,eq} + c_{B,eq}) + \frac{k_{-1}}{1 + K_2}$

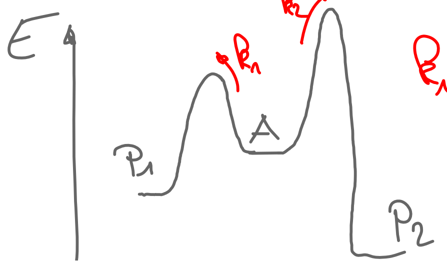
WDH

$A \xrightarrow{k_1} P_1$

$A \xrightarrow{k_2} P_2$

$\Rightarrow c_{P,i} = \frac{k_i}{\sum_j k_j} \cdot c_{A,0}\left(1 - e^{-\sum_j k_j t}\right)$

$\frac{[P_1]}{[P_2]} = \frac{k_1}{k_2}$



$k_1 \gg k_2$

Folgereaktionen

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

unimolekular, irreversibel

$$C_A = C_{A,0} \cdot e^{-k_1 t}$$

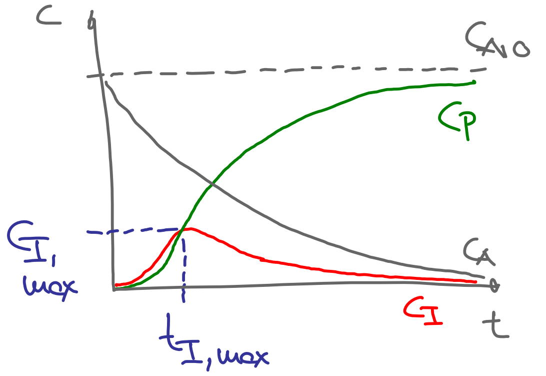
$$C_I' = +k_1 \cdot C_A - k_2 C_I$$

$$\Rightarrow \quad C_I' + k_2 C_I = k_1 C_{A,0} \cdot e^{-k_1 t} \quad / \cdot e^{k_2 t}$$

$$\int d\left(C_I \cdot e^{k_2 t}\right) = \int k_1 \cdot C_{A,0} \cdot e^{(k_2 - k_1)t}\, dt$$

$$\Rightarrow \quad \boxed{C_I(t) = \frac{k_1}{k_2 - k_1} \cdot C_{A,0} \cdot \left(e^{-k_1 t} - e^{-k_2 t}\right)}$$

$$\Rightarrow \quad \boxed{C_P(t) = C_{A,0} \cdot \left(1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right)}$$



$\boxed{k_1 \gg k_2}$

$$\left.\begin{aligned} C_I &\approx C_{A,0} \cdot e^{-k_2 t} \\ C_P &\approx C_{A,0} \cdot \left(1 - e^{-k_2 t}\right) \end{aligned}\right\} \quad \text{„}A \xrightarrow{k_2} P\text{“}$$

($I \xrightarrow{k_2} P$, geschwindigkeitsbestimmend)

$\boxed{k_1 \ll k_2}$

$$\left.\begin{aligned} C_I &\approx 0 \\ C_P &\approx C_{A,0}\left(1 - e^{-k_1 t}\right) \end{aligned}\right\} \quad \text{„}A \xrightarrow{k_1} P\text{“}$$

Quasistationarität (Max Bodenstein)

$$\boxed{C_I(t) \approx \text{const} \iff C_I'(t) \approx 0}$$

$$C_I'(t) = k_1 C_A(t) - k_2 C_I(t) \overset{QS}{\approx} 0$$

$$\Rightarrow \quad C_I(t) = \frac{k_1}{k_2} \cdot C_{A,0} \cdot e^{-k_1 t} \qquad (k_2 > k_1)$$

$$\Rightarrow \quad C_P'(t) = k_2 \cdot C_I(t) = k_1 C_{A,0} \cdot e^{-k_1 t} \quad \Rightarrow \quad \boxed{C_P(t) = C_{A,0}\left(1 - e^{-k_1 t}\right)}$$

! $C_I(t=0) = \frac{k_1}{k_2} C_{A,0}$!

Vorgelagertes GG

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P \qquad C_I' = k_1 C_A - k_{-1} C_I - k_2 C_I \overset{QS}{\approx} 0$$

$$\Rightarrow \quad C_I = C_A \cdot \frac{k_1}{k_{-1} + k_2} \quad \ldots \quad C_A,\ C_P$$

$\Rightarrow$ häufig: $A + B \underset{(K_1)}{\overset{H^+/OH^-}{\rightleftharpoons}} I \xrightarrow[k_2]{} P$ "schneller" GG $\Rightarrow k_2 \ll \{k_1, k_{-1}\}$

$$\Rightarrow c_I = K_1 \cdot c_A$$

$$K_1 = \frac{[I]}{[A][B]}$$

Bsp.:

$$H_3C\text{–}OH + H^+ \rightleftharpoons H_3C\text{–}OH_2^+ \qquad K_1$$

$$H_3C\text{–}OH_2^+ + Cl^- \longrightarrow H_3C\text{–}Cl + H_2O \qquad k_2$$

① Intermediat: $$[H_3C\text{–}OH_2^{\oplus}]' = k_1 [H_3C\text{–}OH][H^+] - k_{-1}[H_3C\text{–}OH_2^{\oplus}] - k_2 [H_3C\text{–}OH_2^+][Cl^-] \overset{QS}{\approx} 0$$

$$\longrightarrow [H_3C\text{–}OH_2^{\oplus}] = \frac{k_1 [H_3C\text{–}OH][H^+]}{k_{-1} + k_2 [Cl^-]}$$

② Produkt: $$[H_3C\text{–}Cl]' = k_2 \cdot [H_3C\text{–}OH_2^+] \cdot [Cl^-] = \boxed{\frac{k_1 k_2 [H_3C\text{–}OH][Cl^-][H^+]}{k_{-1} + k_2 [Cl^-]}}$$

mit "schnellem" GG: $v_p = K_1 k_2 [H_3C\text{–}OH][Cl^-][H^+]$

oder: $$K_1 = \frac{[H_3C\text{–}OH_2^+]}{[H^+][H_3C\text{–}OH]} \iff [H_3C\text{–}OH_2^+] = K_1 [H^+][H_3C\text{–}OH]$$

Allgemeine kinetische Modelle

$$[S_1]' = -(k_{21} + k_{11})[S_1] + k_{12}[S_2]$$

$$[S_2]' = +k_{21}[S_1] - (k_{12} + k_{22} + k_{32})[S_2] + k_{23}[S_3]$$

$$[S_3]' = +k_{32}[S_2] - (k_{23} + k_{33})[S_3]$$

$$\begin{tikzcd} S_1 \arrow[r, shift left, "k_{21}"] \arrow[d, "k_{11}"] & S_2 \arrow[l, shift left, "k_{12}"] \arrow[r, shift left, "k_{32}"] \arrow[d, "k_{22}"] & S_3 \arrow[l, shift left, "k_{23}"] \arrow[d, "k_{33}"] \\ P_1 & P_2 & P_3 \end{tikzcd}$$

$$\overrightarrow{[S]}' = T \cdot \overrightarrow{[S]}$$

$$T = \begin{bmatrix} -(k_{21} + k_{11}) & k_{12} & 0 \\ k_{21} & -(k_{12} + k_{22} + k_{32}) & k_{23} \\ 0 & k_{32} & -(k_{23} + k_{33}) \end{bmatrix}$$

Ansatz: ① Eigenwerte $\lambda_i \Rightarrow$ Eigenvektoren

$\longrightarrow$ Fundamentalsystem: $\overrightarrow{[S]}_i = e^{\lambda_i t} \vec{v}_i$