Note Title

V3

25.4.2019

WDH

Geschwindigkeitsgesetze 0./1./2. Ordnung

Halbwertszeiten

(Reversible Reaktionen)

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

$$c_A'(t) = \underbrace{-k_1 \cdot c_A}_{\text{Verbrauch}} + \underbrace{k_{-1} \cdot c_P}_{\text{Bildung}}$$

$$\boxed{c_A = c_{A,0} \cdot \frac{k_{-1} + k_1 e^{-(k_1+k_{-1})t}}{k_1 + k_{-1}}}$$

$$\boxed{c_P = c_{A,0} \cdot \frac{k_1 + k_1 \cdot e^{-(k_1+k_{-1})t}}{k_1 + k_{-1}}}$$

⇒ "$t \to \infty$": chem. GG

$$c_A(t \to \infty) = c_{A,eq} = c_{A,0} \cdot \frac{k_{-1}}{k_1 + k_{-1}} \qquad c_{P,eq} = c_{A,0} \cdot \frac{k_1}{k_1 + k_{-1}}$$

TD: $\boxed{K = \frac{[P]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}}}$ ⇐ Kinetik $\qquad (\Delta G = -RT \ln K \ldots)$

⇒ GG sind dynamisch: $v_1 = -\frac{dc_A}{dt} = k_1 \cdot c_A$

$v_{-1} = +\frac{dc_A}{dt} = k_{-1} c_P$

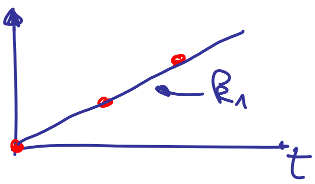
Bestimmung k_1 / k_{-1} (experimentell)

$$c_A'(t) = -k_1 c_A + k_{-1} c_P \qquad \Big| \; c_A = c_{A,0} - x, \quad dc_A/dx = -1$$

$$-x'(t) = -k_1 (c_{A,0} - x) + k_{-1} \cdot x$$

im GG: $0 = -k_1 (c_{A,0} - x_{eq}) + k_{-1} \cdot x_{eq}$

$$\longrightarrow k_1 t = \frac{x_{eq}}{c_{A,0}} \cdot \ln\left(\frac{x_{eq}}{x_{eq} - x(t)}\right)$$



Relaxationskinetik

van't Hoff: $\frac{d\ln K}{dT} = \frac{\Delta_R H}{RT^2}$

$\Delta_R H = +20\ \mathrm{kJ/mol}$

$\Delta T = 10\ \mathrm{K}$

$T = 300\ \mathrm{K}$

$d\ln K = dK/K$

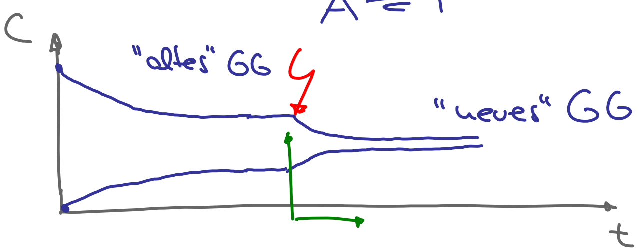
$RT_{(300K)} = 2.5\ \mathrm{kJ/mol}$

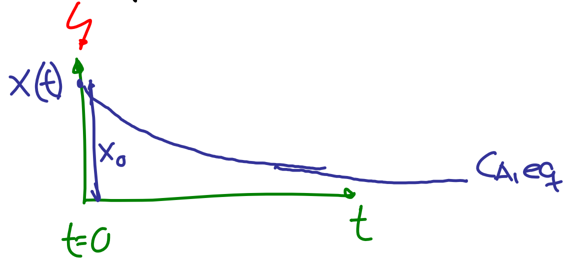
$$\frac{\Delta K}{K} = \Delta T \cdot \frac{\Delta_R H}{T \cdot RT} = 10\,\mathrm{K} \cdot \frac{20\ \mathrm{kJ/mol}}{750\ \mathrm{K\,kJ/mol}}$$

$$= 0.4 \Leftarrow 40\%?$$

T-Sprung: Kondensator, Laserpuls $\Longrightarrow$ $10\ \mu s$, $\Delta T = 10\ \mathrm{K}$

$A \rightleftharpoons P$





$$c_A' = -k_1 c_A + k_{-1} c_P \qquad \left| \begin{array}{l} c_A = c_{A,eq} + x(t) \\ c_P = c_{P,eq} - x(t) \end{array} \right.$$

$$\Rightarrow\ x'(t) = -\underbrace{k_1 \cdot (c_{A,eq}}_{v_{1,eq}} + x) + \underbrace{k_{-1} \cdot (c_{P,eq}}_{v_{-1,eq}} - x)$$

$$x'(t \to \infty) = 0 = -k_1 c_{A,eq} + k_{-1} c_{P,eq}$$

$$\Rightarrow\ x'(t) = -x \cdot (k_1 + k_{-1})$$

$$\boxed{x(t) = x_0 \cdot e^{-(k_1+k_{-1})t}}$$

Relaxationszeit $\tau = 1/(k_1 + k_{-1})$ $\left(K = \frac{k_1}{k_{-1}}\right)$

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

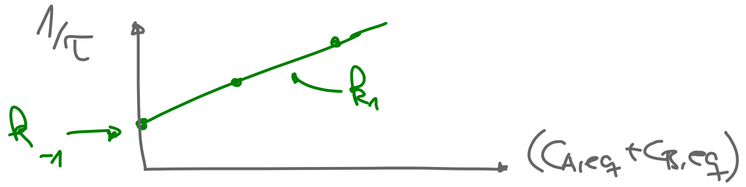
im GG: $\boxed{\begin{array}{l} v_1 = k_1 c_A c_B \\ v_{-1} = k_{-1} c_P \end{array}}$

$$x'(t) = -k_1 (c_{A,eq} + x)(c_{B,eq} + x) + k_{-1}(c_{P,eq} - x)$$

$$= -k_1 x (c_{A,eq} + c_{B,eq}) \underbrace{-k_1 x^2}_{\approx 0} \underbrace{-k_1 c_{A,eq} c_{B,eq}}_{v_{1,eq}} \underbrace{+k_{-1} c_{P,eq}}_{v_{-1,eq}} - k_{-1} \cdot x$$

$$\boxed{x'(t) = -x \cdot \left[(c_{A,eq} + c_{B,eq}) k_1 + k_{-1}\right]} \longrightarrow x(t) = x_0 \cdot e^{-t/\tau}$$

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



$\Rightarrow$ Eigen, Norrish, Porter NP 1967

Bsp: $I_2 + I^- \rightleftharpoons I_3^-$

($A + B \rightleftharpoons P$)

$K_1(258K) = 720\,M^{-1}$

Turner et al. 1972, JACS $\rightarrow$ Folien

NMR: $k_1 = 5 \times 10^{10}\ L/mol \cdot s$

↳ schneller als Diffusion im LM

$I_{2,eq}$, $I^-_{,eq}$

Raman-Laser, 1.4 µm, 20 ns $\Delta T = 3.4K$ (T-Sprung)

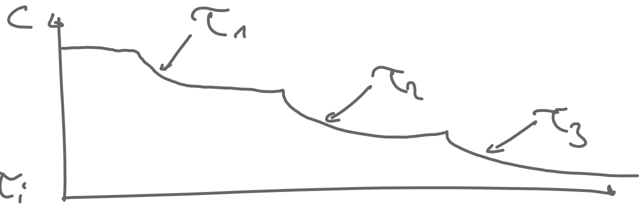
Absorption, $\lambda_{I_3^-} \sim 350\,nm$

$\Rightarrow \tau = 30 \ldots 70\,ns$

$\Rightarrow k_1 = 6.2 \cdot 10^9\ L/mol \cdot s$

(p-Sprung $\frac{\partial K/K}{\partial p} = \ldots$)

Zusammengesetzte Reaktion:



$$X = X_0 \sum_i \omega_i \cdot e^{-t/\tau_i}$$

4. Zusammengesetzte Reaktion

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

$$c_A'(t) = -k_1 c_A - k_2 c_A$$

$$\Rightarrow c_A(t) = c_{A,0} \cdot e^{-(k_1+k_2)t}$$

$$c_P' = k_1 \cdot c_{A,0} \cdot e^{-(k_1+k_2)t}$$

$$\int dc_P = k_1 c_{A,0} \int e^{-(k_1+k_2)t}\, dt$$

$$\Rightarrow c_P = \frac{k_1}{k_1+k_2} \cdot c_{A,0} \cdot \left(1 - e^{-(k_1+k_2)t}\right)$$

$$c_Q \sim \frac{k_2}{k_1+k_2} \cdot \quad "$$

$$\frac{[P]}{[Q]} = \frac{k_1}{k_2}$$ $\rightarrow$ Kinetische Reaktionskontrolle