V2

23.4.2019

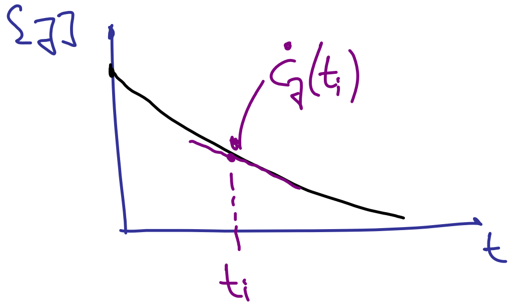
Note Title

WDH

$$\xi(t) = \frac{\Delta n_j}{\nu_j} = 0 \ldots 1\,\text{mol}$$

$\Longrightarrow$ molekulare RG: $\tilde{\nu} = \dot{\xi}(t)$

$\Longrightarrow$ $\nu = \frac{1}{V} \cdot \dot{\xi}(t) = \frac{1}{\nu_j} \cdot \dot{c}_j(t)$



Zeitgesetz: $\nu = k(T) \cdot [A]^{\alpha} [B]^{\beta} \cdot [C]^{\gamma} \cdot \ldots$

Reaktionsordnung

Bestimmung der Reaktionsordnung

(i) differentielle Methode

(ii) Isolationsmethode $\longrightarrow$ $\nu = k[A]^{\alpha}[B]^{\beta}$

mit $[A]\uparrow \approx [A](t=0) = \text{const} \longrightarrow \nu = k'[B]^{\beta}$

$\Longrightarrow$ differentielle Methode

(iii) Integrationsmethode

Ziel: $c_A(t) = f(k(T), c_{A,0} \ldots)$

1. Ordnung

$A \longrightarrow P$

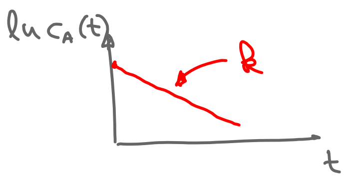
$A \rightarrow P + P$, $\nu_P = +2$
$\rightarrow P + Q$

$$\nu_A(t) = -\frac{dc_A(t)}{dt} = k \cdot c_A(t)$$

für $t=0$ ist $c_A(t=0) = c_{A,0}$
$\Rightarrow C = -\ln c_{A,0}$

$$\Longrightarrow \int \frac{dc_A(t)}{c_A(t)} = \int -k\,dt \Longrightarrow \ln c_A(t) + C = -kt$$

$$\boxed{\ln c_A(t) = \ln c_{A,0} - kt}$$ (linear bzgl. t)

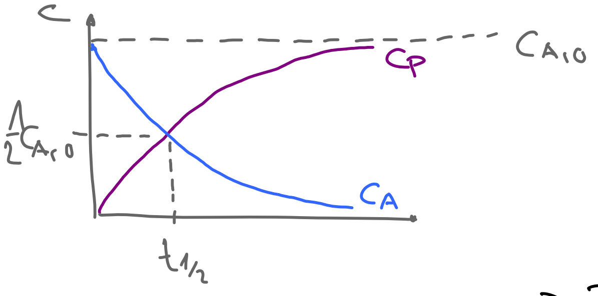


$$\boxed{c_A(t) = c_{A,0} \cdot e^{-kt}}$$

Produkt: $\nu_P(t) = +\frac{dc_P(t)}{dt} = k \cdot c_A(t) = k \cdot c_{A,0} \cdot e^{-kt}$

$\Longrightarrow \Longrightarrow \boxed{c_P(t) = c_{A,0} - c_{A,0} \cdot e^{-kt}}$

$c_A(t) + c_P(t) = c_{A,0}$



Halbwertszeit: $c_A(t_{1/2}) = \frac{1}{2}\cdot c_{A,0}$

$$\Rightarrow \boxed{t_{1/2} = \frac{\ln 2}{k}}$$

→ Fluoreszenz, Radioaktivität

→ Zuckerinversion, $N_2O_5 \xrightarrow{\Delta}$, $\nearrow \rightarrow \Delta$

2. Ordnung "A → P"

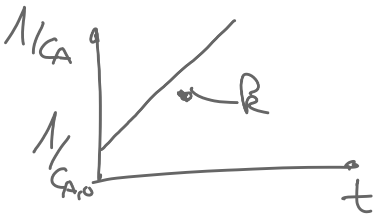
$$v_A(t) = -\frac{dc_A(t)}{dt} = k\cdot c_A^2 \longrightarrow \int \frac{dc_A(t)}{c_A(t)^2} = \int -kt$$

$$\Rightarrow -\frac{1}{c_A(t)} + C = -kt$$

$c_A(t=0) = c_{A,0}$

$\hookrightarrow C = 1/c_{A,0}$

$$\boxed{\frac{1}{c_A(t)} = \frac{1}{c_{A,0}} + kt} \qquad \boxed{c_A(t) = \frac{c_{A,0}}{1 + c_{A,0}\cdot kt}}$$



für c_P? $\Rightarrow v_P(t) = +\frac{dc_P(t)}{dt} = k\cdot c_A(t)^2 =$

Halbwertszeit: $\boxed{t_{1/2} = \frac{1}{c_{A,0}\cdot k}}$

Bsp: $H_3C\cdot + \cdot CH_3 \longrightarrow C_2H_6$

$\nu_{CH_3} = -2$

$$v_{CH_3}(t) = -\frac{1}{2}\frac{dc_{CH_3}}{dt} = k\cdot c_{CH_3}^2$$

$$\frac{1}{c_{CH_3}(t)} = \frac{1}{c_{CH_3,t=0}} + 2kt, \quad t_{1/2} = \frac{1}{2k\cdot c_{CH_3,t=0}}$$

$$A + B \longrightarrow P + Q$$

$$v = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = k\cdot c_A\cdot c_B = k\cdot\underbrace{(c_{A,0} - x(t))}_{c_A(t)}(c_{B,0} - x(t))$$

$$\frac{dx}{dt} = k(c_{A,0} - x)(c_{B,0} - x)$$

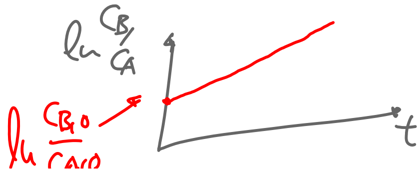
Partialbruch

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\cdot\ln\frac{b-x}{a-x}$$

$$\frac{dc_A}{dt} = -\frac{dx}{dt}$$

$$\hookrightarrow \frac{1}{c_{B,0} - c_{A,0}}\cdot\ln\frac{c_B}{c_A} - \frac{1}{c_{B,0} - c_{A,0}}\cdot\ln\frac{c_{B,0}}{c_{A,0}} = kt$$

$$\Rightarrow \boxed{\ln\frac{c_B}{c_A} - \ln\frac{c_{B,0}}{c_{A,0}} = kt(c_{B,0} - c_{A,0})}$$



"allg. Formulierung" für bel. Konz. [A], [B]

Vereinfachung: $|\nu_A| A + |\nu_B| B \longrightarrow \dots$

$$\frac{c_A}{\nu_A} = \frac{c_B}{\nu_B} \longrightarrow c_B = c_A \cdot \left(\frac{\nu_B}{\nu_A}\right)$$

$$\Rightarrow v_A = \frac{1}{\nu_A} \cdot \frac{dc_A}{dt} = k \cdot c_A c_B = k \cdot c_A^2 \cdot \left(\frac{\nu_B}{\nu_A}\right) \Rightarrow \boxed{\frac{1}{c_A} = \frac{1}{c_{A,0}} - \nu_B k t}$$

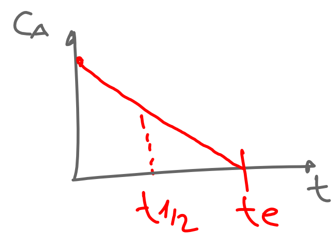
(Reaktanden im stöchiometr. Verhältnis ν_A / ν_B)

0. Ordnung

$$H_3C-CH_2-OH \xrightarrow{ADH} H_3C-C(=O)H \qquad PH_3 \xrightarrow{Pt}$$

$$v_A = -\frac{dc_A}{dt} = k \cdot c_A^0 = k$$

$$\boxed{c_A = c_{A,0} - kt} \qquad t_{1/2} = \frac{c_{A,0}}{2k}, \quad t_e = \frac{c_{A,0}}{k}$$



(iv) Halbwertszeiten

Ordnung	0	1	2
$t_{1/2}$ =	$\frac{c_{A,0}}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k \cdot c_{A,0}}$

charakteristische Zeiten: $t_{1/4} \longrightarrow c_A(t_{1/4}) = \frac{1}{4} \cdot c_{A,0}$

$$t_{1/2} / t_{1/4} = \quad \text{Ordnung} = 1: \ 1/2 \qquad = 2: \ 1/3$$

3. Reversible Reaktionen

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P \qquad \frac{dc_A}{dt} =$$

(1) $A \xrightarrow{k_1} P$ $\qquad v_A = -\frac{dc_A}{dt} = k_1 \cdot c_A$

(-1) $P \xrightarrow{k_{-1}} A$ $\qquad v_A = +\frac{dc_A}{dt} = k_{-1} \cdot c_P = k_{-1} \cdot (c_{A,0} - c_A)$

$$\Rightarrow \frac{dc_A}{dt} = -k_1 \cdot c_A + k_{-1} \cdot c_{A,0} - k_{-1} \cdot c_A$$

$$\Longrightarrow \quad C_A'(t) + (k_1+k_{-1}) \cdot C_A(t) = k_{-1} \cdot C_{A,0} \quad \Big/ \cdot e^{(k_1+k_{-1})t}$$

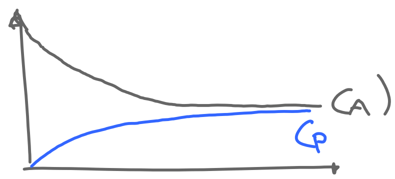
$$\underbrace{C_A'(t) \cdot e^{(k_1+k_{-1})t} + C_A(t) \cdot (k_1+k_{-1}) \cdot e^{(k_1+k_{-1})t}} = k_{-1} \cdot C_{A,0} \cdot e^{(k_1+k_{-1})t}$$

$$\frac{d}{dt}\left(C_A(t) \cdot e^{(k_1+k_{-1})t}\right) = k_{-1} \cdot C_{A,0} \cdot e^{(k_1+k_{-1})t}$$

$$\int d\left(C_A(t) \cdot e^{(k_1+k_{-1})t}\right) = k_{-1} C_{A,0} \int e^{(k_1+k_{-1})t} \, dt$$

$$C_A(t) \cdot e^{(k_1+k_{-1})t} + C = \frac{k_{-1} C_{A,0}}{k_1+k_{-1}} \cdot e^{(k_1+k_{-1})t}$$

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



PROBE: $\quad k_1 \gg k_{-1} \;:\; \underline{\underline{C_A(t) = C_{A,0} \cdot e^{-k_1 t}}} \qquad A \xrightarrow{k_1} P$

$\qquad\quad\; k_1 \ll k_{-1} \;:\; C_A(t) = C_{A,0}$