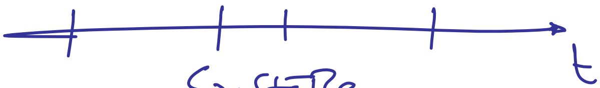
Note Title

V10
18.6.2019

10. Molekulare Reaktionskinetik

$$A + B \xrightarrow{k_2} P$$

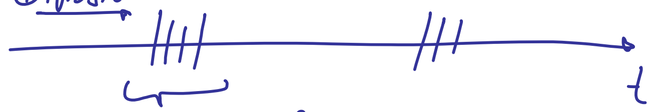
Gasphase



↳ Stöße

$\sim \bar c,\ \sigma_{AB}$

Lösung

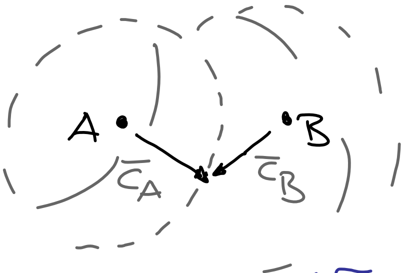


LM-Komplex

$\{AB\}_{LM}$

A. Stoßtheorie

$$\bar c = \sqrt{\frac{8k_BT}{\pi m}}$$



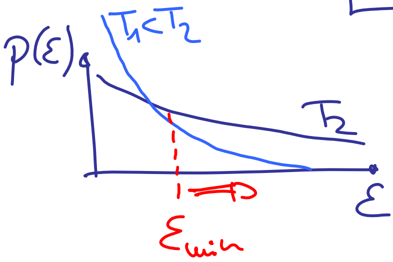
⇒ Oberflächenintegral

$$\bar c_{AB} = \sqrt{2}\cdot\bar c$$

Stoßdichte: $z_{AB} = \bar c_{AB}\cdot\sigma_{AB}\cdot\left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right) = \bar c_{AB}\cdot\sigma_{AB}\cdot N_A^2\cdot[A][B]$

$\frac{N_B}{V} = [B]\cdot N_A$

Energie: $\varepsilon \overset{!}{>} \varepsilon_{min}$



$$f(\varepsilon) = e^{-E_{min}/RT}$$

⇒ molekulare RG: $\tilde v = f\cdot\bar c_{AB}\cdot\sigma_{AB}\cdot N_A^2\,[A][B]$ $\left(\frac{1}{L\cdot s}\right)$

(mit $1/N_A$)

$$\boxed{v = \underbrace{\sigma_{AB}\,\bar c_{AB}\,N_A\cdot e^{-E_{min}/RT}}_{k_2}\,[A][B]}$$

↳ $\bar c_{AB}\sim\sqrt{T}$ ⇒ $E_A/RT^2 = \frac{\partial}{\partial T}\ln k_2 = \frac{\partial}{\partial T}\left(\ln\sigma_{AB}N_A + \ln\sqrt{2}\sqrt{\frac{8R}{\pi m}} + \ln\sqrt{T} - \frac{E_{min}}{RT}\right)$

$= \frac{1}{2T} + \frac{E_{min}}{RT^2}$ ⇒ $E_A = E_{min} + \frac{1}{2}RT$

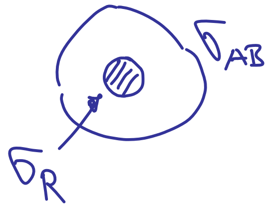
⇒ $\boxed{k_2 = N_A\,\sigma_{AB}\,\bar c_{AB}\cdot\sqrt{e}\cdot e^{-E_A/RT}}$

(bei 300K: $RT = 2.5$ kJ/mol)

$\sim 10^{11}\ \mathrm{l/mol\cdot s}$

„Erweiterung"

Reaktionsquerschnitts: $\sigma_R\ (\sigma^*, \sigma^*(E))$

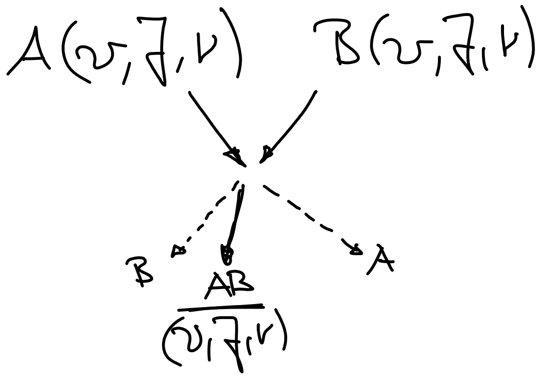


sterischer Faktor $P = \dfrac{\sigma_R}{\sigma_{AB}}$

Molekularstrahlexperimente

$\Rightarrow$ Messung $\sigma_R(E)$

(Hinweis: RRK(M))



„Harpuneneffekt"

$$K + Br_2 \xrightarrow[\bar{e}\text{-Transfer}]{\text{Tunneleffekt}} K^+ + Br_2^- \xrightarrow[\text{Coulomb}]{} KBr + Br$$

$(P = 4.8)$

$\Rightarrow P > 1$

Stöße im LM

$$\rightleftharpoons^{K_D} \underbrace{\{AB\}_{LM}}_{\text{Intermediat}} \xrightarrow{k_2} P \qquad k_D,\ k_{-D}$$

$$[AB] = \frac{k_D[A][B]}{k_{-D} + k_2}$$

$$\Rightarrow \boxed{v_p = k_2 \cdot \frac{k_D[A][B]}{k_{-D} + k_2}}$$

geschw. best.

$k_2 \gg k_{-D}$:

$$v_p = k_D[A][B]$$

Diffusionskontrolle

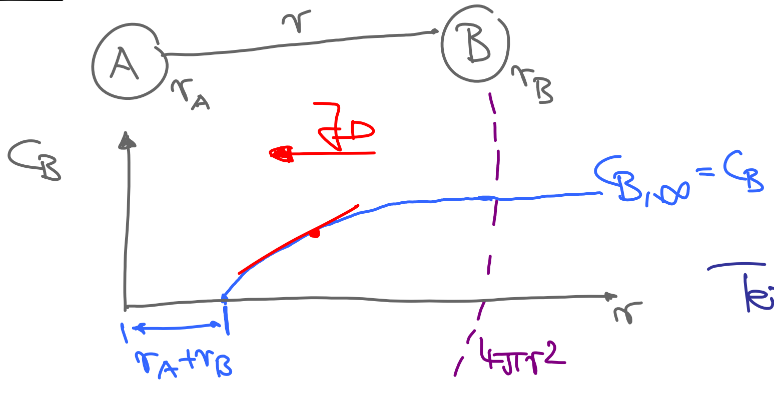
$k_2 \ll k_{-D}$:

$$v_p = k_2 \cdot K_D[A][B]$$

Reaktionskontrolle

(Thermodynamik!)

MODELL:



Teilchenstrom

$$j_B = \frac{dn_B}{dt} \quad \left(\frac{\mathrm{mol}}{\mathrm{s}}\right)$$

Teilchenstromdichte:

$$J = j/A \quad \left(\frac{\mathrm{mol}}{\mathrm{s\cdot m^2}}\right)$$

$j_B/A = +D\,\frac{dc_B}{dr}$ Diffusion: $J_D = -D\cdot\frac{dc}{dr} = j/A$

$\longrightarrow \quad j_B = +D_B\cdot\frac{dc_B}{dr}\cdot 4\pi r^2$

$j_B \int_{r_A+r_B}^{\infty}\frac{dr}{r^2} = 4\pi D_B\int_0^{\infty} c_B \Longrightarrow j_B\cdot\frac{1}{(r_A+r_B)} = 4\pi D_B\,[B]$

$\hookrightarrow \quad j_B = \underset{(D_A+D_B)}{D_B}\cdot 4\pi(r_A+r_B)\underset{\cdot[A]N_A}{[B]} \Longrightarrow \underbrace{(D_A+D_B)4\pi(r_A+r_B)N_A}_{=k_D}[A][B] = v_p \quad \left[\frac{mol}{L\cdot s}\right]$

Abschätzung: $D_A = D_B = 10^{-9}\,m^2/s$, $r_A = r_B = 0.5\,nm$

$\hookrightarrow k_D = 1.5\cdot 10^{10}\,L/mol\cdot s$

$D = \frac{kT}{6\pi\eta r} \Longrightarrow k_D = 4\pi N_A\left(\frac{k_BT}{6\pi\eta}\right)\underbrace{\left(\frac{1}{r_A}+\frac{1}{r_B}\right)(r_A+r_B)}_{\frac{(r_A+r_B)^2}{r_A r_B}}$

mit $\eta = \eta_0\cdot e^{E/RT}$

$E = 15\,kJ/mol$ in H_2O

Stoffbilanzgleichung

$$\boxed{\frac{\partial c_A(t,x)}{\partial t} = D\,\frac{\partial^2 c_A}{\partial x^2} - v\cdot\frac{\partial c_A}{\partial x} - k\cdot c_A}$$

Diffusion Konvektion Reaktion

B. Theorie des ÜZ (Eyring, Polanyi)

$A + BC \overset{K_{\neq}}{\rightleftharpoons} [\neq] \xrightarrow{k_{\neq}} AB + C$

$v = \underbrace{k_{\neq}\cdot K_{\neq}}_{k_2}[A][BC]$

$K_{\neq}$: $K_{\neq} = \frac{[\neq]}{[A][BC]} = \boxed{\frac{q_{\neq}\cdot N_A}{q_A\cdot q_{BC}}\cdot e^{-\Delta E_0/RT}}$

statistische TD

"bei ‡": 1 FG (vib) wird "aufgegeben"

$$\hookrightarrow K_{\ddagger} = \left(\frac{kT}{h\nu^{\ddagger}}\right) \cdot \overline{K}_{\ddagger}$$

für "‡" ohne Schwingungs-FG

<u>$k_{\ddagger}$:</u> $k_{\ddagger} = \kappa \cdot \nu^{\ddagger}$ (κ = Transmissionskoeffizient, i.d.R. $\kappa = 1$)

$$\Rightarrow \boxed{k_2 = k_{\ddagger} \cdot K_{\ddagger} = \kappa \cdot \underbrace{\frac{kT}{h}}_{6 \cdot 10^{12}\, 1/s} \cdot \overline{K}_{\ddagger}}$$

($\rightarrow$ vgl. RRKM)

Ergänzung: $\ln \overline{K}_{\ddagger} = \frac{-\Delta G^{\ddagger}}{RT} = -\left(\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right)$

$$\rightarrow \boxed{k_2 = \kappa \frac{kT}{h} \cdot e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT}}$$

s. sterischer Faktor, $\Delta S^{\ddagger} = (\Delta S^{\ddagger}_{A+B \to AB} + \Delta S^{\ddagger}_{ster})$

(s. Eyring-Plots)

C. Potentialhyperflächen

($\rightarrow$ Folien)