Note Title

V9

11.6.2019

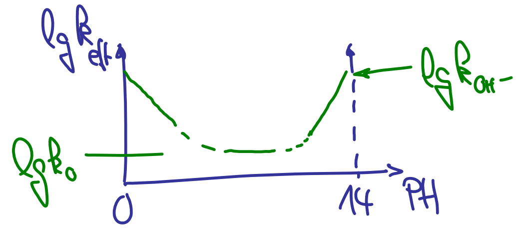
WDH

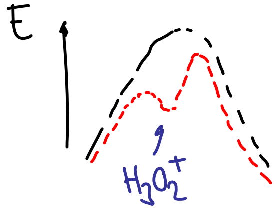
Homogene Katalyse

M^+, H^+/OH^-, Halogenide

$v_{cat} \sim \underbrace{[Kat]}_{\approx \text{const}}$

H^+/OH^-





Arrhenius-Intermediat

Heterogene Katalyse

A (B) $\quad$ ($\downarrow$ +B) $\quad$ $\xrightarrow{k_T}$ P

$\rightleftharpoons$ A_{ads} $(+B_{ads})$ $\Longleftarrow$ $\Theta_A (\Theta_B)$ $\quad$ Langmuir, BET

unimolekular: $\Theta_A = \frac{k_A p_A}{1 + k_A p_A} \Rightarrow$ $k_A p_A \gg 1$, $E_A = E_r$

$k_A p_A \ll 1$, $E_A = E_r + \underbrace{\Delta H_{ads}}_{<0}$

C. Enzymkinetik

$$S + E \underset{}{\overset{K_1}{\rightleftharpoons}} ES \underset{(EP)}{\xrightarrow{k_2}} P$$

$[E] = [E_0] - [ES]$

$[ES]' = k_1 [S] ([E_0] - [ES]) - k_{-1} [ES] - k_2 [ES] \approx 0 \quad$ (QS)

$$\Rightarrow [ES] = \frac{k_1 [S][E_0]}{k_1 [S] + k_{-1} + k_2} = \frac{[S][E_0]}{[S] + \underbrace{\frac{k_{-1} + k_2}{k_1}}_{=: K_M}}$$

$$\boxed{v_p = k_2 \cdot \frac{[E_0][S]}{K_M + [S]}}$$

Michaelis-Menten-Gleichung

$[S] \gg K_M$:

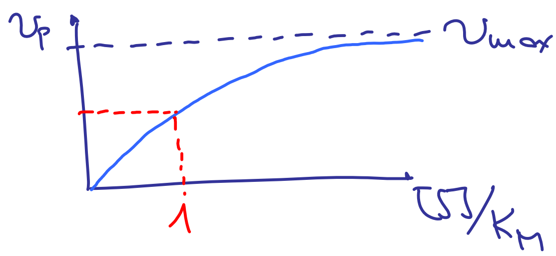
$v_p = k_2 [E_0] \approx \text{const}$

$=: v_{max}$ $\quad$ $\boxed{\text{0. Ordnung}}$

$[S] \ll K_M$:

$v_p = \frac{k_2}{K_M} [S][E_0]$

$$\longrightarrow \boxed{v_p = v_{max} \cdot \frac{[S]}{K_M + [S]}}$$



Lineweaver-Burk $\rightarrow$ $1/v_p \sim 1/[S]$ $\quad$ (s. Folien)

Wechselzahl: $k_{cat} = \frac{v_{max}}{[E_0]}$ $\left(\frac{1}{s}\right)$ $1 \dots 10^6 \ \frac{1}{s}$

(turnover number/rate)

Katalytische Effizienz: $\eta = \frac{k_{cat}}{K_M} = \frac{k_2 \cdot k_1}{k_{-1} + k_2}$ $\left[\frac{L}{mol \cdot s}\right]$

für $[S] \gg K_M$ $(v_p \rightarrow v_{max})$: $\eta = 10^9 \ \frac{L}{mol \cdot s}$

(Diffusionskontrolle)

Inhibition von Enzymreaktion

$$E + S \underset{}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P$$

$E + S \rightleftharpoons^{+J} EJ$ $K_J = \frac{[E][J]}{[EJ]}$

$\alpha = \left(1 + \frac{[J]}{K_J}\right)$ kompetitive Hemmung

$ES \rightleftharpoons^{+J} JES \ (ESJ)$ K_J', α' unkompetitiv

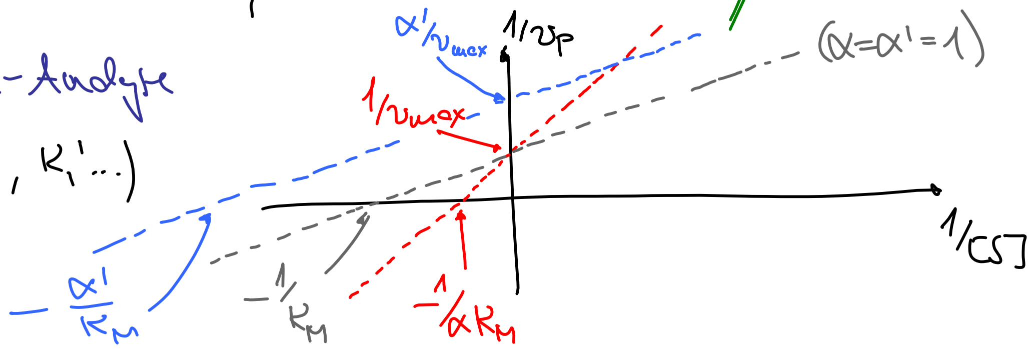
JES (ESJ) } katalytisch inaktiv

$$\Longrightarrow v_p = \frac{v_{max}[S]}{\alpha \cdot K_M + [S]} \qquad v_p = \frac{v_{max}[S]}{K_M + \alpha'[S]}$$

nicht-kompetitiv $\alpha, \alpha' > 1$

$\Longrightarrow$ Lineweaver-Burk-Analyse

$(\Rightarrow K_M, v_{max}, K_I, K_I' \dots)$



D. Oszillierende Reaktionen

LOTKA – VOLTERRA – MODELL :

– 2 Intermediate

X autokatalytisch

$$
\begin{array}{llcl}
(1) & A + X & \longrightarrow & X + X \\
(2) & X + Y & \longrightarrow & Y + Y \\
(3) & Y & \longrightarrow & P \\
\hline
 & 'A & \longrightarrow & P'
\end{array}
$$

Intermediate :

$$[X]' = 2k_1[A][X] - k_2[X][Y]$$

"theoretisches GG": $2k_1[A][X_{eq}] = k_2[X_{eq}][Y_{eq}] \quad // : [X_{eq}]$

$$\Leftrightarrow [X]' = k_2[X][Y_{eq}] - k_2[X][Y]$$

$$\Longrightarrow \boxed{\begin{aligned} [X]'(t) &= k_2[X](t)\cdot\left([Y_{eq}] - [Y](t)\right) \\ [Y]'(t) &= 2k_2[Y](t)\left([X](t) - [X_{eq}]\right) \end{aligned}}$$

gekoppelte DGL, $\longrightarrow$ Jacobi-Matrix

$\Longrightarrow$ Eigenwerte

(0, 0)

$\longrightarrow$ GG $(t \to \infty)$

konjugiert-komplex

$e^{i\lambda_i} = \cos t + i \sin t$

$\Longrightarrow \omega = \sqrt{k_1 k_3 [A]}$

$\lambda_1 = i k_1$

$\lambda_2 = i k_3 [A]$