

① Reaktionen  
Simpliz  
Gen Expression

② Models of Reactions

③ Basics: Chemical Kinetics / Physical Chemistry



$$\frac{d[A]}{dt} = -2 v_1 \quad \frac{d[B]}{dt} = +v_1 \quad \left| \begin{array}{l} \text{also:} \\ \frac{d[B]}{dt} = -\frac{1}{2} \frac{d[A]}{dt} \end{array} \right.$$

Stöchiometrische Koeffizienten  
-2      +1

Beispiel



	A	B	C	<del>D</del>	<del>E</del>
Stöch. Koeff	-1	-1	+1		

enthält nicht alle  
Komplett Info

④ Reaktionssraten

$$v = f([A], [B], \text{etc...}) \quad \text{hier: intensive}$$

⑤ Rassenanzahlsgesetz

## Rassenwirkungsgesetz



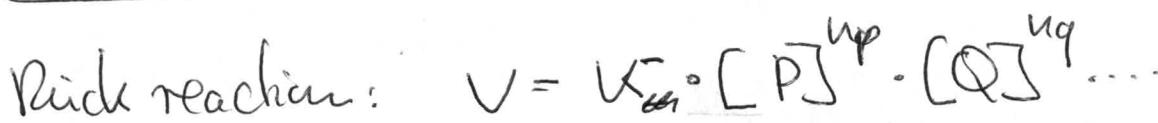
$$\frac{d[A]}{dt} = -v$$

$$v = k \cdot [A]$$

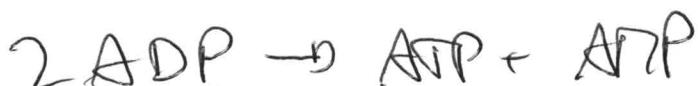


$$v = k^+ \cdot [A]^{n_A} \cdot [B]^{n_B}$$

Rass-aktive Kinetics!



Bsp



$$v^+ = k^+ \cdot [ADP]^2$$

$$v^- = k^- \cdot [ATP] \cdot [ADP]$$

Chemical equilibrium

Bsp



$$v^+ = k^+ \cdot [A]$$

$$v^- = k^- \cdot [B]$$

$$v = v^+ - v^- \stackrel{!}{=} 0$$

$$\Rightarrow k^+ [A]^0 = k^- [B]^0$$

$$\Rightarrow \frac{k^+}{k^-} = \frac{[B]^0}{[A]^0} = \underline{\underline{k_{eq}}}$$

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free

$$V_{eq} = \frac{[P]^{u_p} \cdot [Q]^{u_q}}{[A]^{u_a} \cdot [B]^{u_b}} = \frac{V^+}{V^-}$$

## ⑥ Detakild Balancee ("detaillierte Gleichgewicht")



$$\frac{V_1^+}{V_1^-} = \frac{B^0}{A^0} = V_{eq1} \quad \frac{V_2^+}{V_2^-} = \frac{C^0}{B^0} = V_{eq2} \quad \frac{V_3^+}{V_3^-} = \frac{A^0}{C^0} = V_{eq3}$$

$$V_{eq1} \cdot V_{eq2} \cdot V_{eq3} = 1 = \frac{V_1^+}{V_1^-} \frac{V_2^+}{V_2^-} \frac{V_3^+}{V_3^-}$$

for any cycle: product of forward rate  
 constant = prod of rev.  
 rate · const.

$$\prod V_i^+ = \prod V_i^- \quad \text{or} \quad \prod V_{eq} = 1$$

"Wegscheider Condition"

gilt auch für metabolische

Netzwerke!

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## Mass-action ratio

$$V = V^+ - V^- = V^+ (1 - \frac{V^-}{V^+})$$

$$\frac{V^-}{V^+} = \frac{K^-}{K^+} \frac{\overbrace{[A]^a [Q]^b}^{u_a u_b}}{\overbrace{[A]^a [B]^b}^{u_a u_b}}$$

Mass-action ratio =  $\Gamma$

$$V = V^+ \left( 1 - \frac{\Gamma}{K_{eq}} \right)$$

## Thermodynamic

~~+~~

⑦ Slides: Models of Neutralism

verb R.R. Beechey

Stationärer Zustand

$$\frac{dx}{dt} = N \cdot V$$

Bsp glykolyse

• Eigenschaften von  $N$

• Prozessmatrix

die doppelte rows!

rank( $N$ )

Ques Neumann  $E \cdot N = 0$

$$[0 \ 0 \ 0 \ 1] \cdot N = 0$$

$$E \cdot \dot{x} = E \cdot N \cdot V = 0$$

$$E \cdot \begin{bmatrix} \dot{x} \\ ATP \\ ADP \end{bmatrix} = \frac{d}{dt}(ATP + ADP) = 0$$

Beispiel



	$\tau_1$	$\tau_2$	$\tau_3$
A	-1	0	+1
B	-1	+2	-1
C	+1	-1	0

$$\text{rank}(N) = 2$$

$$E = (1 \ 1 \ 2)$$

$$E \cdot N = 0$$

$$\Rightarrow \frac{d}{dt} \underbrace{\begin{bmatrix} \dot{A} \\ \dot{B} \\ \dot{C} \end{bmatrix}}_{\dot{V}} = N \cdot V$$

$$\dot{A} = -\tau_1 + \tau_3$$

$$\dot{B} = -\tau_1 + 2\tau_2 - \tau_3$$

$$\dot{C} = +\tau_1 - \tau_2$$

$$\Rightarrow E(\cdot) = E \cdot N \cdot V = 0$$

$$\frac{d}{dt}(A + B + 2C) = 0 \Rightarrow A + B + 2C = \text{const}$$

$$-\tau_1 + \tau_3 - \tau_1 + 2\tau_2 - \tau_3 + 2(\tau_1 - \tau_2) = 0$$

Rechts Nullraum

$$N \cdot V \Leftrightarrow N \cdot V^0 = 0$$

$$\tau - \text{rank}(N)$$

typisch  $\tau > m$