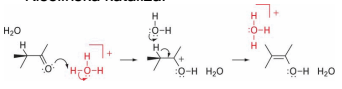
Homogena kataliza

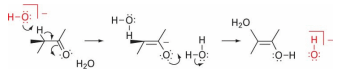
$$2\,H_2O_2\,(aq) \xrightarrow{I^-} 2\,H_2O\,(aq) + O_2\,(g)$$

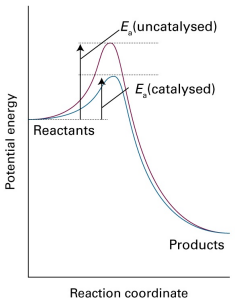
$$\frac{dc_{O_2}}{dt} = k \cdot c_{I^-} \cdot c_{H_3O^+} \cdot c_{H_2O_2}$$

Kiselinska kataliza: $X + HA \rightarrow HX^+ + A^-$ $HX^+ \rightarrow$ products



Bazna kataliza: $XH + B \rightarrow X^- + BH^+$ $X^- \rightarrow$ products

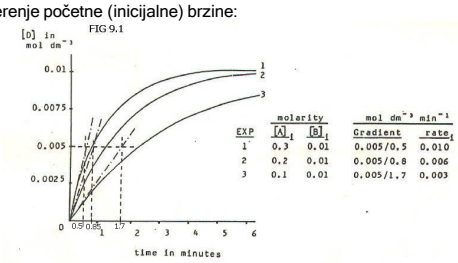




1

Enzimska kataliza

Mjerenje početne (inicijalne) brzine:



2

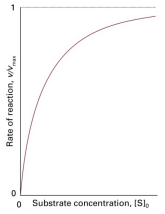
Michaelis-Mentenov mehanizam

•za različite $c_{S,0}$, početna brzina stvaranja produkta razmjerna je $c_{E,0}$.

•za neku $c_{E,0}$ i pri malim $c_{S,0}$, brzina stvaranja produkta razmjerna je $c_{S,0}$.

•za neku $c_{E,0}$ i pri velikim $c_{S,0}$, brzina stvaranja produkta je neovisna o $c_{S,0}$ i doseže najveću (maksimalnu) brzinu v_{max}.

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES \xrightarrow{k_b} E + P$$

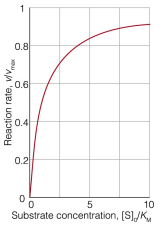


3

Michaelis-Mentenova jednadžba

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES \xrightarrow{k_b} E + P$$

$$v = \frac{k_b \cdot c_{E,0} \cdot c_{S,0}}{c_{S,0} + K_M} = \frac{v_{max} \cdot c_{S,0}}{c_{S,0} + K_M} \qquad v = \frac{k_b \cdot c_{E,0}}{1 + \frac{K_M}{c_{S,0}}}$$



Michaelisova konstanta: $K_M = \frac{k_a' + k_b}{k_a}$

Kada je $c_{S,0} << K_M$, v je razmjerna $c_{S,0}$: $v = \frac{k_b}{K_M} \cdot c_{S,0} \cdot c_{E,0}$

Kada je $c_{S,0} >> K_M$, v doseže najveću brzinu v_{max}: $v = v_{max} = k_b \cdot c_{E,0}$

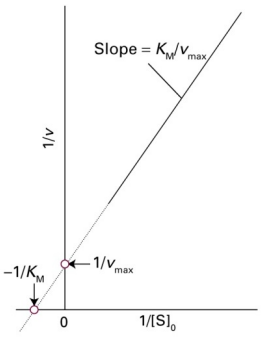
Kada je $c_{S,0} = K_M$: $v = \frac{v_{max}}{2}$

4

Lineweaver-Burk jednadžba

Kada je $c_{S,0} >> K_M$:

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \cdot \frac{1}{c_{S,0}}$$



5

Katalitička efikasnost enzima

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES \xrightarrow{k_b} E + P$$

Katalitička konstanta: $k_{cat} = k_b = \frac{v_{max}}{c_{E,0}}$

Katalitička efikasnost: $\eta = \frac{k_{cat}}{K_M} = \frac{k_a \cdot k_b}{k_a' + k_b}$

6

Reverzibilna inhibicija enzima

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES \xrightarrow{k_b} E + P$$

$$EI \overset{K_I}{\rightleftharpoons} E + I \qquad K_I = \frac{c_E \cdot c_I}{c_{EI}}$$

$$ESI \overset{K_I'}{\rightleftharpoons} ES + I \qquad K_I' = \frac{c_{ES} \cdot c_I}{c_{ESI}}$$

$$v = \frac{v_{max}}{\alpha' + \alpha K_M / c_{S,0}} \qquad \alpha = 1 + \frac{c_I}{K_I} \qquad \alpha' = 1 + \frac{c_I}{K_I'}$$

Reverzibilna inhibicija enzima

$$v = \frac{v_{max}}{\alpha' + \alpha K_M / c_{S,0}} \qquad \alpha = 1 + \frac{c_I}{K_I} \qquad \alpha' = 1 + \frac{c_I}{K_I'}$$

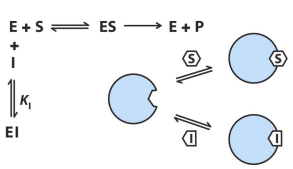
Kompetitivna inhibicija: $\alpha > 1, \alpha' = 1$

Akompetitivna inhibicija: $\alpha = 1, \alpha' > 1$

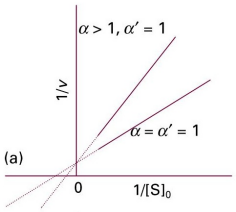
Nekompetitivna (miješana) inhibicija: $\alpha > 1, \alpha' > 1$

Lineweaver-Burk jednadžba s inhibicijom: $\frac{1}{v} = \frac{\alpha'}{v_{max}} + \frac{\alpha \cdot K_M}{v_{max}} \cdot \frac{1}{c_{S,0}}$

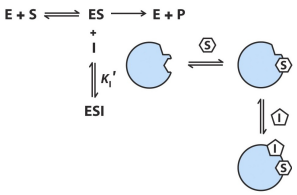
Kompetitivna inhibicija



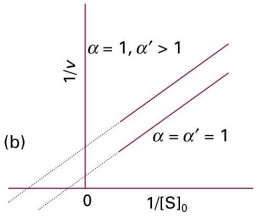
$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{\alpha \cdot K_M}{v_{max}} \cdot \frac{1}{c_{S,0}}$$



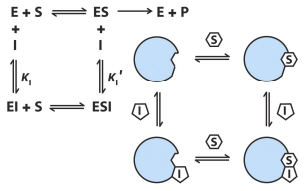
Akompetitivna inhibicija



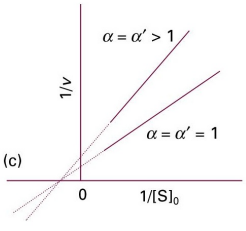
$$\frac{1}{v} = \frac{\alpha'}{v_{max}} + \frac{K_M}{v_{max}} \cdot \frac{1}{c_{S,0}}$$



Nekompetitivna inhibicija



$$\frac{1}{v} = \frac{\alpha'}{v_{max}} + \frac{\alpha \cdot K_M}{v_{max}} \cdot \frac{1}{c_{S,0}}$$



Michaelis-Mentenov mod. mehanizam

$$E + S \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES \underset{k_b'}{\overset{k_b}{\rightleftharpoons}} E + P$$

$$v = \frac{(v_{max} / K_M) \cdot c_{S,0} - (v'_{max} / K_M') \cdot c_P}{1 + c_{S,0} / K_M + c_P / K_M'}$$

$$v_{max} = k_b \cdot c_{E,0} \qquad v'_{max} = k_a' \cdot c_{E,0}$$

$$K_M = \frac{k_a' + k_b}{k_a} \qquad K_M' = \frac{k_a' + k_b}{k_b'}$$

Uzastopne (konsekutivne) enz. reakcije

$$E + S_1 \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} ES_1 \qquad K_{M1} = \frac{c_E \cdot c_{S_1}}{c_{ES_1}} \qquad K_{M2} = \frac{c_E \cdot c_{S_2}}{c_{ES_2}}$$

$$ES_1 + S_2 \underset{k_b'}{\overset{k_b}{\rightleftharpoons}} ES_1S_2 \qquad K_{M12} = \frac{c_{ES_1} \cdot c_{S_2}}{c_{ES_1S_2}} \qquad K_{M21} = \frac{c_{ES_2} \cdot c_{S_1}}{c_{ES_1S_2}}$$

$$ES_1S_2 \underset{k_c'}{\overset{k_c}{\rightleftharpoons}} E + P \qquad v = k_b \cdot c_{ES_1S_2}$$

$$v = \frac{v_{max} \cdot c_{S_1,0} \cdot c_{S_2,0}}{K_{M1} \cdot K_{M2} + K_{M12} \cdot c_{S_1,0} + K_{M12} \cdot c_{S_2,0} + c_{S_1,0} \cdot c_{S_2,0}}$$

$$\frac{1}{v} = \frac{1 + K_{M12}/c_{S_2,0}}{v_{max}} + \frac{K_{M21} + K_{M1} \cdot K_{M12}/c_{S_2,0}}{v_{max}} \cdot \frac{1}{c_{S_1,0}}$$

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Uzastopne (konsekutivne) enz. reakcije

"ping-pong" mehanizam

$$E + S_1 \rightleftharpoons ES_1 \qquad K_{M1} = \frac{c_E \cdot c_{S_1}}{c_{ES_1}}$$

$$ES_1 \xrightarrow{k_{b1}} E^* + P_1 \qquad v_1 = k_{b1} \cdot c_{ES_1}$$

$$E^* + S_2 \rightleftharpoons E^*S_2 \qquad K_{M2} = \frac{c_{E^*} \cdot c_{S_2}}{c_{E^*S_2}}$$

$$E^*S_2 \xrightarrow{k_{b2}} E + P_2 \qquad v_2 = k_{b2} \cdot c_{E^*S_2}$$

$$v_2 = \frac{v_{2max} \cdot c_{S_1} \cdot c_{S_2}}{K_{M2} \cdot c_{S_1} + K_{M1} \cdot c_{S_2} + c_{S_1} \cdot c_{S_2}}$$

$$\frac{1}{v_2} = \frac{1 + K_{M2}/c_{S_{2,0}}}{v_{2max}} + \frac{K_{M1}}{v_{2max}} \cdot \frac{1}{c_{S_{1,0}}}$$

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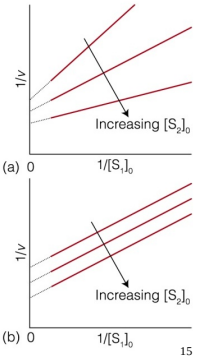
Uzastopne (konsekutivne) enz. reakcije

$$\frac{1}{v} = \frac{1 + K_{M12}/c_{S_2,0}}{v_{max}} + \frac{K_{M21} + K_{M1} \cdot K_{M12}/c_{S_2,0}}{v_{max}} \cdot \frac{1}{c_{S_1,0}}$$

$$\frac{1}{v_2} = \frac{1 + K_{M2}/c_{S_{2,0}}}{v_{2max}} + \frac{K_{M1}}{v_{2max}} \cdot \frac{1}{c_{S_{1,0}}}$$



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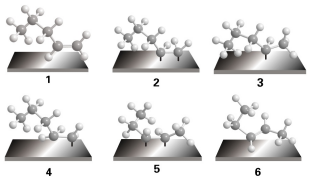
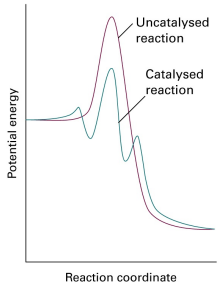
Heterogena kataliza

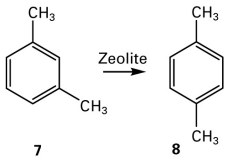


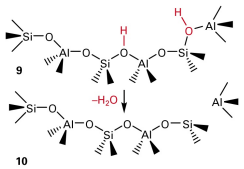


16

Heterogena kataliza

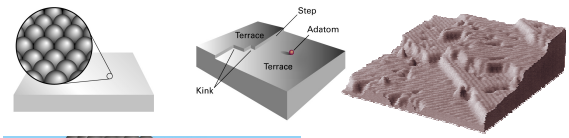
Zeolit (Si, Al, O)

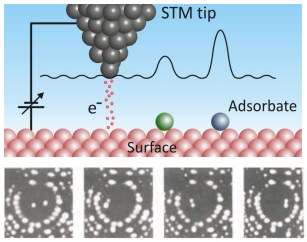


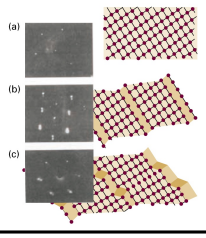


17

Površina







18

Fizička i kemijska adsorpcija

Prekrivenost površine: $\theta = \dfrac{N_{\text{Zauzetih adsorpcijskih mjesta}}}{N_{\text{Ukupnih adsorpcijskih mjesta}}}$

Fizička adsorpcija (fizisorpcija): $\Delta_{\text{ad}}H \approx -20\ \text{kJ mol}^{-1}$

Kemijska adsorpcija (kemisorpcija): $\Delta_{\text{ad}}H \approx -200\ \text{kJ mol}^{-1}$

Table 23.1* Maximum observed enthalpies of physisorption

Adsorbate	$\Delta_{\text{ad}}H^{\ominus}$/(kJ mol^{-1})
CH_4	−21
H_2	−84
H_2O	−59
N_2	−21

* More values are given in the *Data section.*

Table 23.2* Enthalpies of chemisorption, $\Delta_{\text{ad}}H^{\ominus}$/(kJ mol^{-1})

Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
C_2H_4	−427	−285	−243
CO		−192	
H_2	−188	−134	
NH_3		−188	−155

* More values are given in the *Data section.*

19

Langmuirova izoterma

$$\text{A}_{\text{(plin,otopina)}} + \text{P}_{\text{(površina)}} \underset{k_{\text{d}}}{\overset{k_{\text{a}}}{\rightleftharpoons}} \text{AP}_{\text{(površina)}}$$

- Adsorpcijom nastaje monomolekularni sloj.
- Površina je uniformna i sva adsorpcijska mjesta su ekvivalentna.
- Ne postoji interakcija između susjednih adsorbiranih molekula.

Brzina adsorpcije: $\dfrac{d\theta}{dt} = k_{\text{a}} \cdot c_{\text{A,sol}} \cdot N(1-\theta)$

Brzina desorpcije: $\dfrac{d\theta}{dt} = -k_{\text{d}} \cdot N \cdot \theta$

$$K = \frac{k_{\text{a}}}{k_{\text{d}}}$$

$$\theta = \frac{K \cdot c_{\text{A,sol}}}{1 + K \cdot c_{\text{A,sol}}} \qquad K \cdot c_{\text{A,sol}} = \frac{\theta}{1-\theta}$$

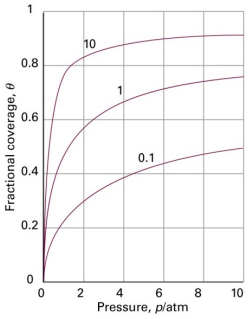
20

Langmuirova izoterma

$$\theta = \frac{K \cdot p_{\text{A}}}{1 + K \cdot p_{\text{A}}}$$

$$K \cdot c_{\text{A,sol}} = \frac{\theta}{1-\theta}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_{\theta} = \frac{\Delta_{\text{ad}}H}{RT^2}$$



21

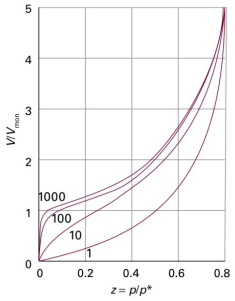
BET izoterma

Adsorpcijom nastaje više slojeva molekula.

$$\frac{V}{V_{\text{mono}}} = \frac{e^{(\Delta_{\text{des}}H^{-} - \Delta_{\text{vap}}H^{-})/RT} \cdot c_{\text{A,sol}}}{(1-c_{\text{A,sol}}) \cdot \{1 - (1 - e^{(\Delta_{\text{des}}H^{-} - \Delta_{\text{vap}}H^{-})/RT}) \cdot c_{\text{A,sol}}\}}$$

Ako je $e^{(\Delta_{\text{des}}H^{-} - \Delta_{\text{vap}}H^{-})/RT} >> 1$

$$\frac{V}{V_{\text{mono}}} = \frac{1}{1-c_{\text{A,sol}}}$$



22

Temkin i Freundlich izoterme

Dolazi do međusobne interakcije između adsorbiranih molekula.

Temkinova izoterma: $\theta = c_1 \cdot \ln(c_2 \cdot c_{\text{A,sol}})$

Freundlichova izoterma: $\theta = c_1 \cdot c_{\text{A,sol}}^{1/c_2}$

c_1 i c_2 su empirijske konstante.

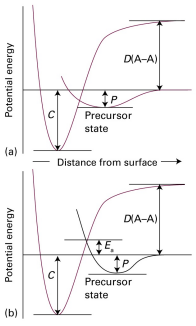
23

Brzina katalizirane reakcije

$$v = k \cdot \theta = \frac{k \cdot K \cdot c_{\text{A,sol}}}{1 + K \cdot c_{\text{A,sol}}}$$

Kada je $K \cdot c_{\text{A,sol}} << 1$: $v = k \cdot K \cdot c_{\text{A,sol}}$

Kada je $K \cdot c_{\text{A,sol}} >> 1$: $v = k$



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