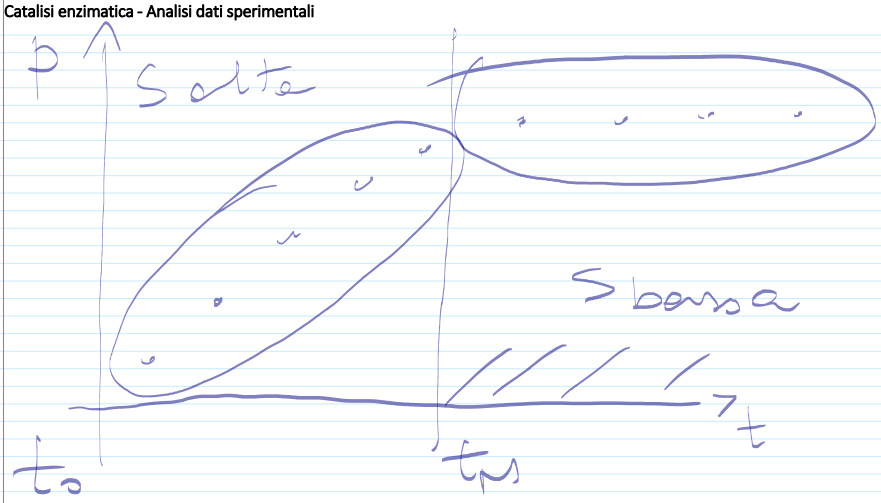


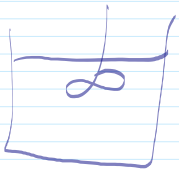
Esp. Batch

$S \rightarrow P$

E

S bassa — cinetica ordine 1 — $r = k C_S$

S alta — " ordine 0 — $r = k'$



$C_S(0) = C_{S0}$

$C_E(0) = C_{E0}$

$$\begin{cases} \frac{dC_S}{dt} = -r(C_S, C_{E0}) \\ C_S(0) = C_{S0} \end{cases}$$

$S \rightarrow P$

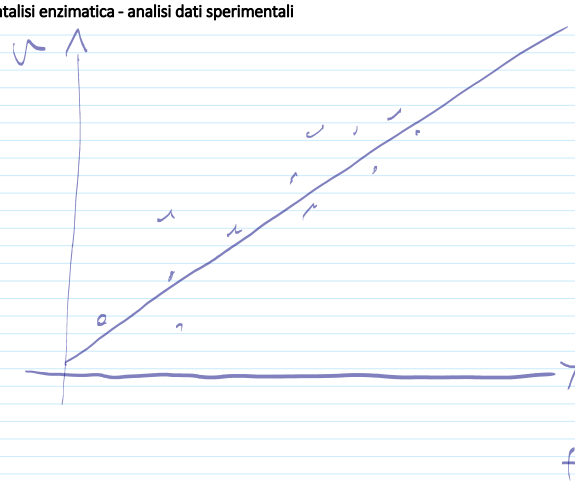
C_S bassa | t alti

$$r = -kC_S$$

$$r_2 - k(C_{S0} - C_P)$$

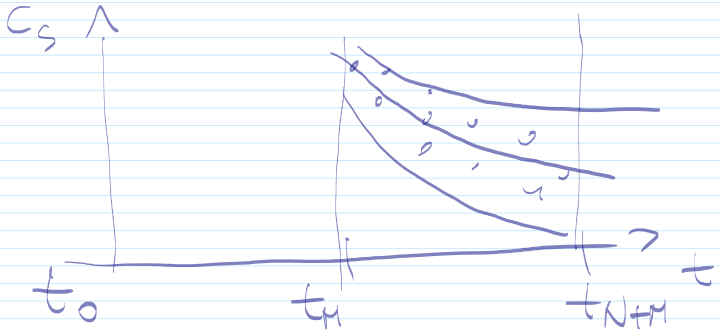
t	C_P	C_S	r
t_M	C_{PM}	$C_{S0} - C_{PM}$	
t_{M+1}	C_{PM+1}	$C_{S0} - C_{PM+1}$	$(C_{PM+1} - C_{PM})/(t_{M+1} - t_M)$
⋮	⋮	⋮	⋮
t_{M+N}	C_{PM+N}	$C_{S0} - C_{PM+N}$	$(C_{PM+N} - C_{PM+N-1})/(t_{M+N} - t_{M+N-1})$

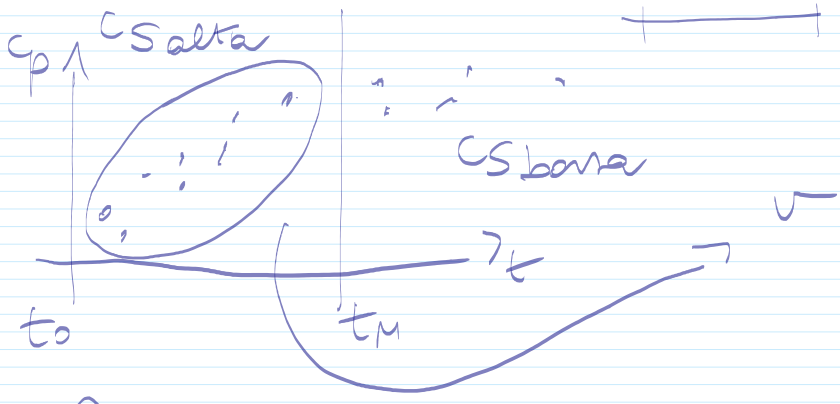
$$r = -\frac{dC_S}{dt} = \frac{dC_P}{dt}$$



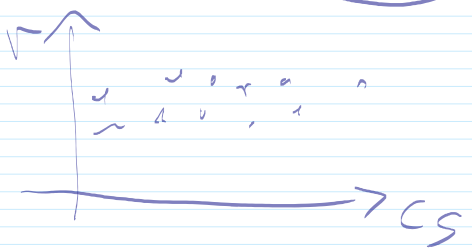
$v = k c_S$

$v = k c_S \;\; ; \;\; (\Leftrightarrow) \begin{cases} \frac{dc_S}{dt} = -k c_S \\ c_S(0) = c_{S_M} \end{cases} \;\; (\Rightarrow) \;\; c_S = c_{S_M} \exp(-kt)$





$v = k'$



$S \rightarrow P$

S bassa $\quad r = k C_S$

S alta $\quad r = k'$

$$r = -\frac{dC_S}{dt} = \frac{dC_P}{dt}$$

Batch

$$\begin{cases} E + S = ES \\ ES \rightarrow P + E \end{cases}$$

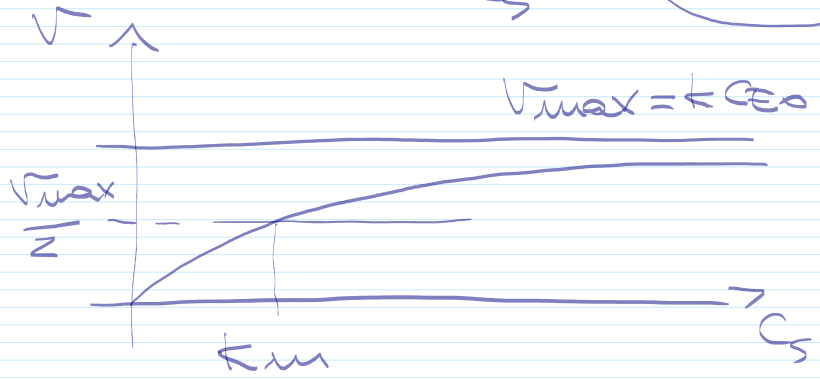
$$K_M = \frac{C_E \cdot C_S}{C_{ES}}$$

$$r = k C_{ES} = \frac{dC_P}{dt} = -\frac{dC_S}{dt}$$

$$C_{E0} = C_E + C_{ES} = \frac{K_M}{C_S} \cdot C_{ES} + C_{ES} =$$

$$= C_{ES}\left(\frac{K_M}{C_S} + 1\right) \Rightarrow C_{ES} = \frac{C_{E0}}{\frac{K_M}{C_S} + 1} = \frac{C_{E0} C_S}{K_M + C_S}$$

$$r = \frac{k C_{E0} C_S}{K_M + C_S}$$



$$r = \frac{r_{max} C_S}{K_M + C_S}$$

$C_S \ll K_M \quad r \simeq \left(\frac{r_{max}}{K_M}\right) C_S$

$C_S \gg K_M \quad r \simeq r_{max}$

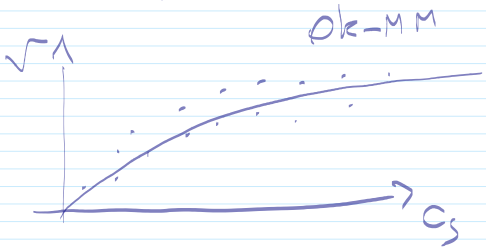
Parametri r_{max}, K_M

Michaelis-Menten

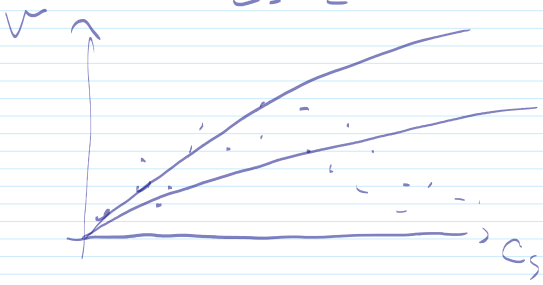
Modello MM - stima parametri e soluzione equazioni di bilancio in batch

$$r = \frac{r_{max}\, c_S}{k_M + c_S}$$ può andar bene?

$$r = -\frac{dc_S}{dt}$$ Es-1



Es-2



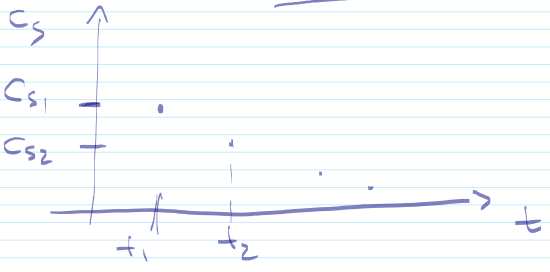
$$r = \frac{r_{max}\, c_S}{k_M + c_S}\,; \qquad c_S(t) = ? \qquad c_S(0) = c_{S0}$$

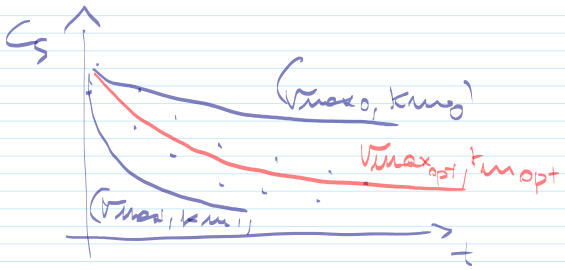
$$\frac{dc_S}{dt} = -\frac{r_{max}\, c_S}{(k_M + c_S)}\,; \qquad \frac{dc_S}{c_S \cdot dt} = -\frac{r_{max}}{(k_M + c_S)}\,;$$

$$\frac{(k_M + c_S)}{c_S}\frac{dc_S}{dt} = -r_{max}\,; \qquad \int_{c_{S0}}^{c_S(t)} \frac{(k_M + c_S)}{c_S}\, dc_S = \int_0^t -r_{max}\, dt$$

$$\int_{c_{S0}}^{c_S} \frac{k_M}{c_S}\, dc_S + \int_{c_{S0}}^{c_S} dc_S = -r_{max} \cdot t\,;$$

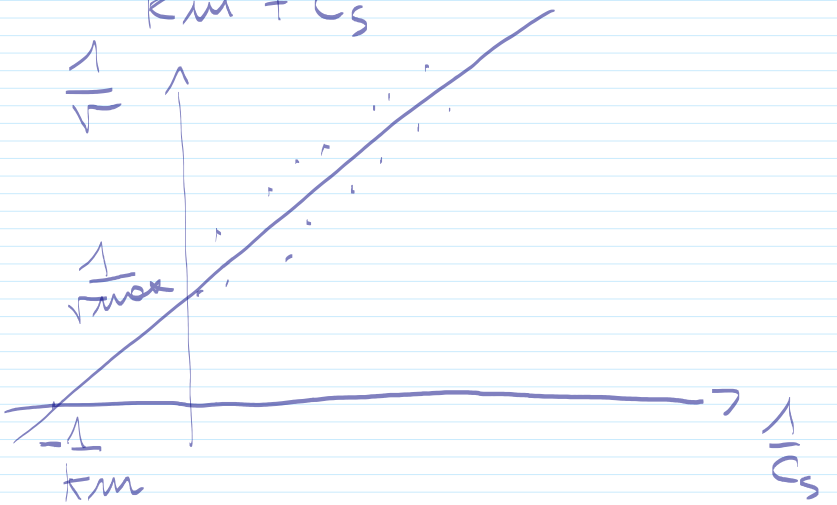
$$k_M \ln\left(\frac{c_S}{c_{S0}}\right) + (c_S - c_{S0}) = -r_{max} \cdot t\,; \qquad c_S(t)$$



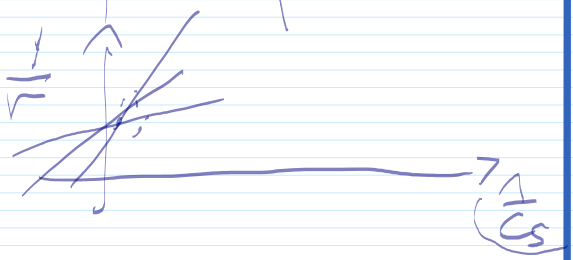


Modello MM - Stima parametri cinetici mediante linearizzazione

$$r = \frac{r_{max} C_S}{K_M + C_S} \qquad \frac{1}{r} = \frac{1}{r_{max}} + \frac{K_M}{r_{max}} \cdot \frac{1}{C_S} \quad (*)$$



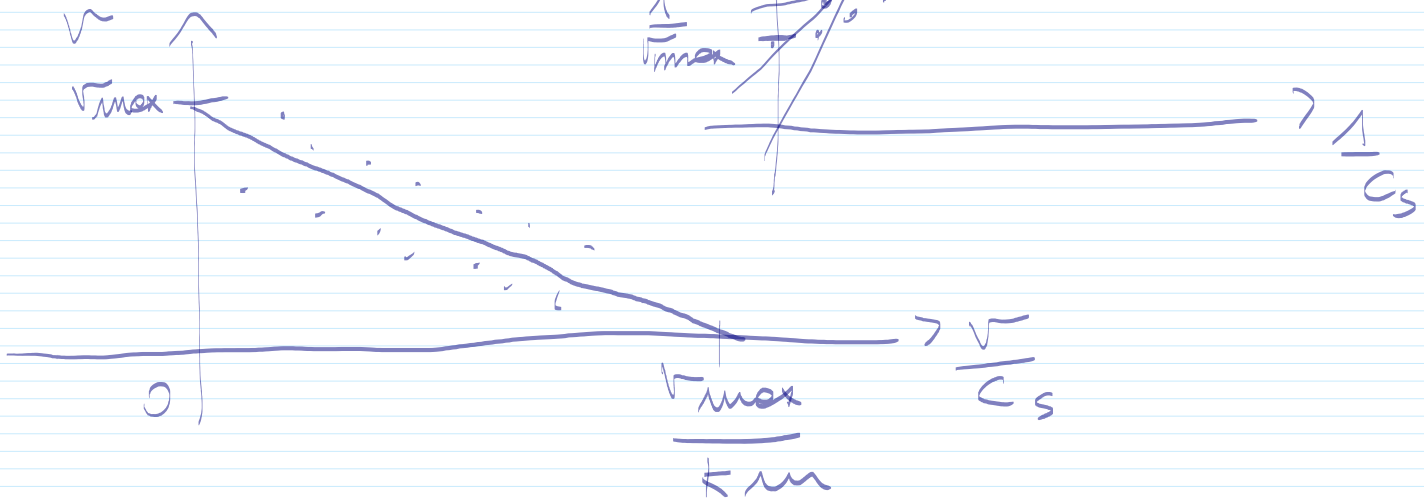
t	C_S	r
t_0	C_{S0}	
t_1	C_{S1}	$(C_{S0} - C_{S1})/(t_1 - t_0)$
t_2	C_{S2}	$(C_{S1} - C_{S2})/(t_2 - t_1)$
t_3	C_{S3}	



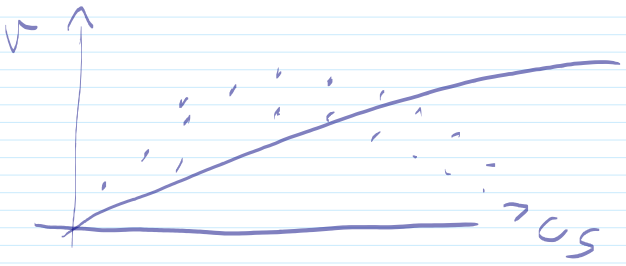
$$r = \left(\frac{r_{max} C_S}{K_M + C_S}\right) = r_{max} - \left(\frac{r_{max} K_M}{K_M + C_S}\right) = r_{max} - \left(\frac{r}{C_S}\right) K_M$$

$$\frac{r}{2} = r_{max} - \left(\frac{r}{C_S}\right) K_M \quad (*)$$

$$y = a - x \cdot b$$



Modello con inibizione da substrato



$$v = \frac{v_{max} C_S}{K_M + C_S}$$

$$E + S = ES \qquad K_1 = \frac{C_E \cdot C_S}{C_{ES}}$$

$$ES + S = ES_2 \qquad K_2 = \frac{C_{ES} \cdot C_S}{C_{ES_2}}$$

$$ES \rightarrow E + P$$

$$v = -\frac{dC_S}{dt} = \frac{dC_P}{dt} = k C_{ES}$$

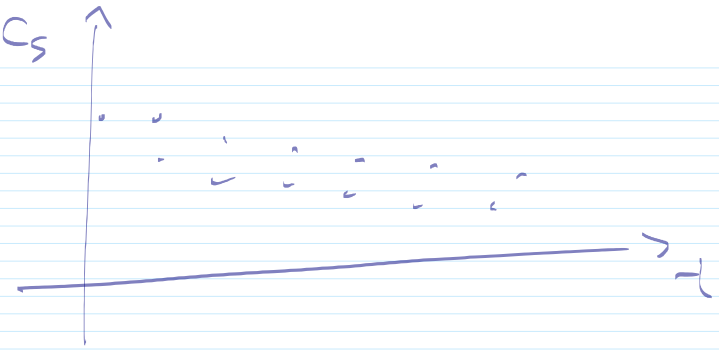
$$C_{E_0} = C_E + C_{ES} + C_{ES_2} = \frac{K_1 C_{ES}}{C_S} + C_{ES} + \frac{C_{ES} \cdot C_S}{K_2} =$$

$$= C_{ES}\left(\frac{K_1}{C_S} + 1 + \frac{C_S}{K_2}\right);$$

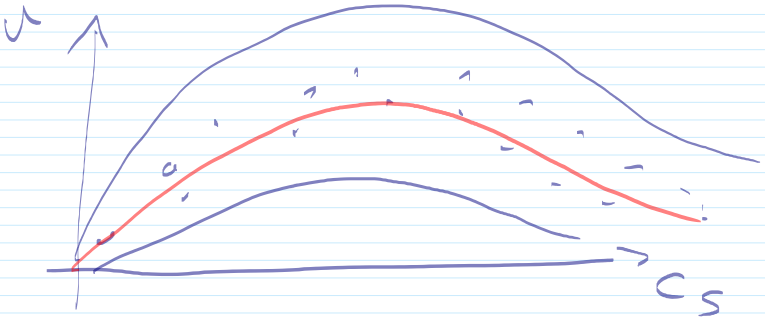
$$C_{ES} = \frac{C_{E_0}}{\frac{K_1}{C_S} + 1 + \frac{C_S}{K_2}} = \frac{C_{E_0} C_S}{K_1 + C_S + \frac{C_S^2}{K_2}}$$

$$v = k C_{ES} = \frac{k C_{E_0} C_S}{K_1 + C_S + \frac{C_S^2}{K_2}} = \frac{v_{max} C_S}{K_1 + C_S + \frac{C_S^2}{K_2}};$$

$$r = \frac{r_{max} c_S}{K_1 + c_S + \frac{c_S^2}{K_2}}$$



(r_{max}, K_1, K_2)

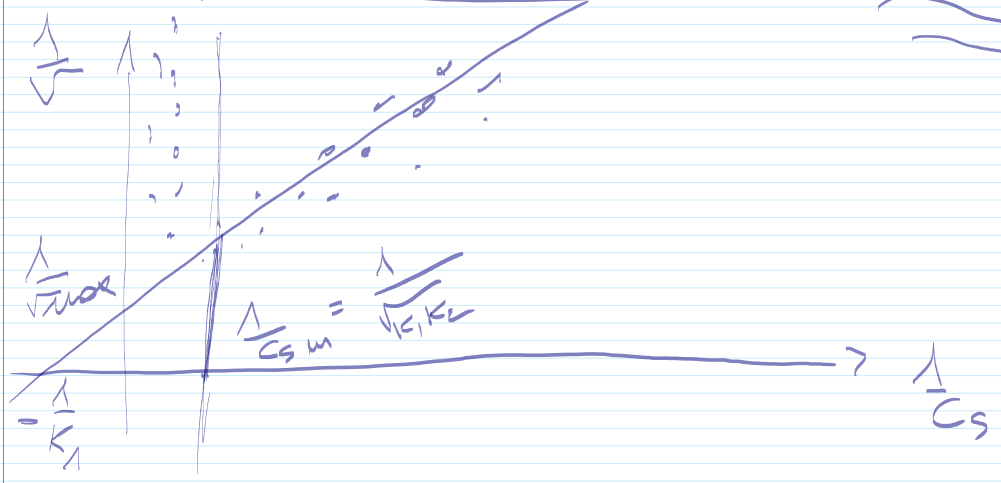


$c_S(t)$?

$$\begin{cases} \frac{dc_S}{dt} = -\frac{r_{max} c_S}{K_1 + c_S + \frac{c_S^2}{K_2}} \\ c_S(0) = c_{S0} \end{cases}$$

Risolvendo trovo $c_S(t)$

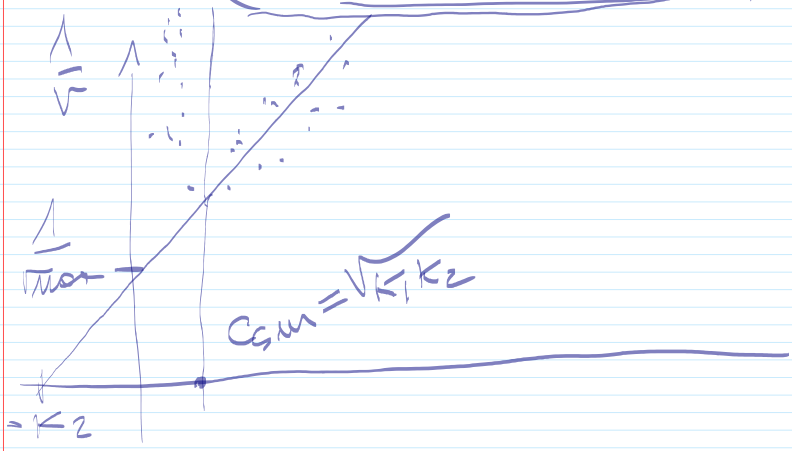
$$\frac{1}{r} = \left(\frac{1}{r_{max}} + \frac{K_1}{r_{max}} \cdot \frac{1}{c_S}\right) + \frac{1}{K_2 r_{max}} \cdot \left(\frac{1}{c_S}\right)^{-1}$$



Modello con inibizione da substrato - stima parametri cinetici

$$\frac{1}{r} = \left(\frac{1}{r_{max}} + \frac{k_1}{r_{max}} \cdot \frac{1}{c_S} + \frac{1}{r_{max} \cdot k_2} \cdot c_S\right) =$$

$$= \left(\frac{1}{r_{max}} + \frac{1}{r_{max} k_2} \cdot c_S\right) + \frac{k_1}{r_{max}} \cdot \frac{1}{c_S} \quad (*)$$



r_{max}, k_2, c_{SM}

$$k_1 = \frac{c_{SM}^2}{k_2}$$

$$E + C = EC \qquad K_C = \frac{C_E C_C}{C_{EC}} \; ; \; K_S = \frac{C_{EC} \cdot C_S}{C_{ECS}}$$

$$EC + S = ECS$$

$$ECS \rightarrow EC + P \qquad r = k\, C_{ECS}$$

$$C_{E0} = C_E + C_{EC} + C_{ECS} = \frac{K_C C_{EC}}{C_C} + \frac{K_S \cdot C_{ECS}}{C_S} + C_{ECS} =$$

$$= \frac{K_C}{C_C} \cdot \frac{K_S}{C_S} \cdot C_{ECS} + K_S \frac{C_{ECS}}{C_S} + C_{ECS} =$$

$$= C_{ECS} \left(\frac{K_C K_S}{C_C C_S} + \frac{K_S}{C_S} + 1 \right)$$

$$\Rightarrow \quad C_{ECS} = \frac{C_{E0}}{\frac{K_C K_S}{C_C C_S} + 1 + \frac{K_S}{C_S}} \qquad (A)$$

$$r = k\, C_{ECS} = \frac{k\, C_{E0}\, C_S}{\frac{K_C K_S}{C_C} + C_S + K_S} = \frac{k\, C_{E0}\, C_S}{K_S \left(\frac{K_C}{C_C} + 1 \right) + C_S} =$$

$$= \frac{r_{max}\, C_S}{K^* + C_S} \qquad K^* = \left(\frac{K_C}{C_C} + 1 \right) K_S$$

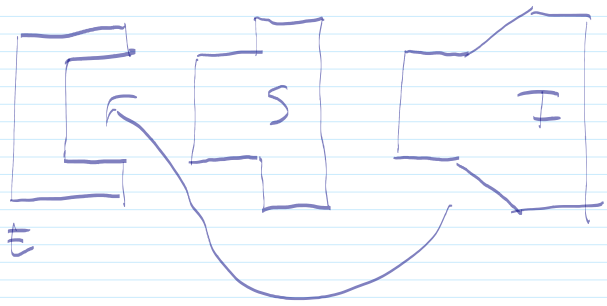
$$r = \frac{k\, C_{E0}\, C_S \cdot C_C}{K_C K_S + C_S C_C + K_S C_C} = \frac{k\, C_{E0}\, C_S \cdot C_C}{K_C K_S + C_C (K_S + C_S)} =$$

$$= \left(\frac{k\, C_{E0} \cdot C_S}{K_S + C_S} \right) \cdot C_C$$

$$\left(\frac{k_c k_s}{k_s + c_s} \right) + c_c \qquad c_s \gg k_s$$

$$\simeq \left(\frac{k_{CE0} \cdot c_c}{\left(\frac{k_c k_s}{c_s} \right) + c_c} \right)$$

Inibizione dell'attività enzimatica



$E + I = EI$

$E + S = ES$

$ES \rightarrow E + P$

$v = k C_{ES}$

$K_I = \frac{C_E C_I}{C_{EI}}$; $K_S = \frac{C_E C_S}{C_{ES}}$

$C_{E0} = C_E + C_{ES} + C_{EI} =$

$= \left(\frac{K_S}{C_S} \cdot C_{ES}\right) + C_{ES} + \frac{C_E \cdot C_I}{K_I} =$

$= \frac{K_S}{C_S} \cdot C_{ES} + C_{ES} + \frac{K_S}{C_S} \cdot C_{ES} \cdot \frac{C_I}{K_I} =$

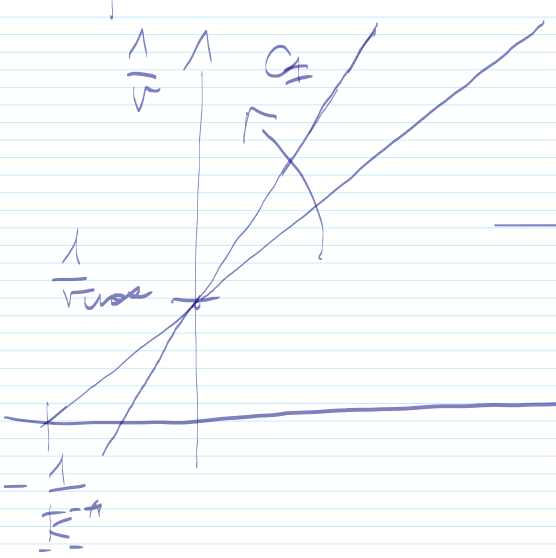
$= C_{ES}\left(\frac{K_S}{C_S} + 1 + \frac{K_S}{K_I} \cdot \frac{C_I}{C_S}\right)$

$C_{ES} = \frac{C_{E0}}{\frac{K_S}{C_S} + 1 + \frac{K_S}{K_I}\frac{C_I}{C_S}} = \frac{C_{E0} \cdot C_S}{K_S + C_S + \frac{K_S}{K_I} \cdot C_I}$

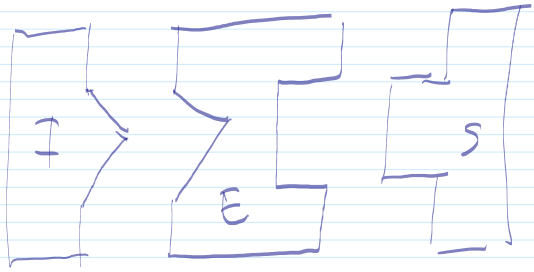
$v = k C_{ES} = \frac{k C_{E0} \cdot C_S}{\underbrace{K_S\left(1 + \frac{C_I}{K_I}\right)}_{K^*} + C_S} = \frac{V_{max} C_S}{K^* + C_S}$

$$v = \frac{v_{max} c_S}{K_S^* + c_S}$$

$$K_S^* = k_S \left(1 + \frac{c_I}{k_I}\right)$$



$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_S^*}{v_{max}} \frac{1}{c_S}$$



1) $E + S = ES$

2) $E + I = EI$

3) $ES + I = EIS$

4) $EI + S = EIS$

5) $ES \rightarrow P + E$

$K_S = \frac{C_E C_S}{C_{ES}}$; $K_I = \frac{C_E C_I}{C_{EI}}$ (*)

$K_I = \frac{C_{ES} C_I}{C_{EIS}}$, $K_S = \frac{C_{EI} C_S}{C_{EIS}}$

$C_{E0} = C_{ES} + C_{EIS} + C_E + C_{EI}$

$$C_{E0} = C_{ES} + \frac{C_{ES} \cdot C_I}{K_I} + \left(\frac{K_S}{C_S} \cdot C_{ES}\right) + \frac{C_I}{K_I} \cdot \frac{K_S}{C_S} \cdot C_{ES}$$

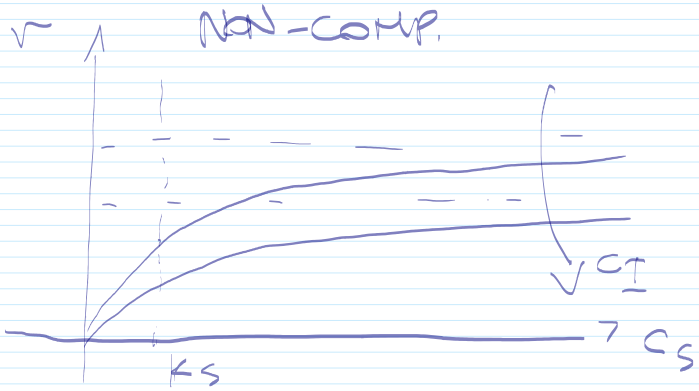
$$= C_{ES}\left(1 + \frac{C_I}{K_I} + \frac{K_S}{C_S} + \frac{K_S}{K_I} \cdot \frac{C_I}{C_S}\right)$$

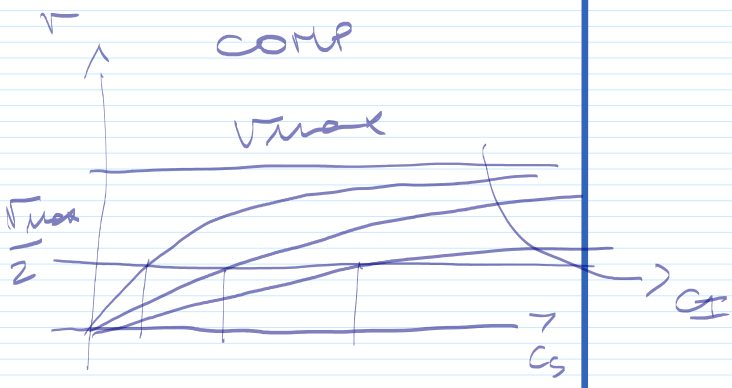
$$C_{ES} = \frac{C_{E0}}{1 + \frac{C_I}{K_I} + \frac{K_S}{C_S} + \frac{K_S}{K_I} \cdot \frac{C_I}{C_S}} \quad (**)$$

$$V = kC_{ES} = \frac{kC_{E0} C_S}{\left(C_S + \frac{C_I C_S}{K_I}\right) + K_S + \frac{K_S}{K_I} \cdot C_I} = \frac{kC_{E0} \cdot C_S}{C_S\left(1 + \frac{C_I}{K_I}\right) + K_S\left(1 + \frac{C_I}{K_I}\right)}$$

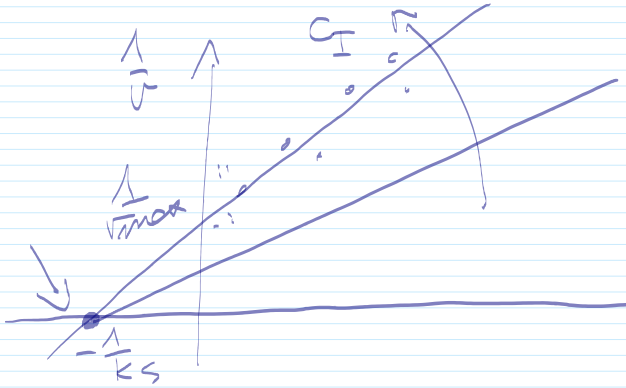
$$v = \frac{k\, c_{E0}\, c_S}{c_S\left(1 + \frac{c_I}{K_I}\right) + K_S\left(1 + \frac{c_I}{K_I}\right)} = \frac{\frac{k\, c_{E0}}{\left(1 + \frac{c_I}{K_I}\right)} \cdot c_S}{K_S + c_S}$$

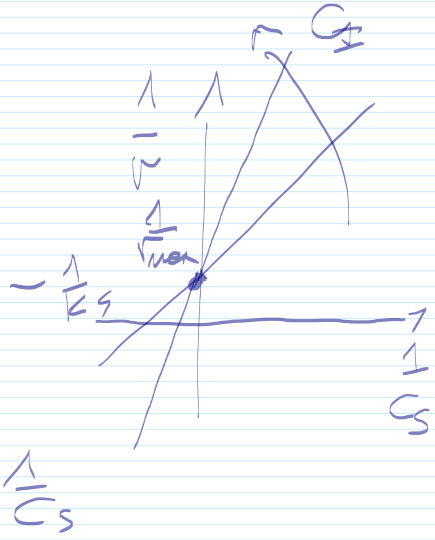
$$v \overset{(*1)}{=} \frac{v_{max}^{*} \cdot c_S}{K_S + c_S} \qquad v_{max}^{*} = \frac{k\, c_{E0}}{1 + \frac{c_I}{K_I}}$$

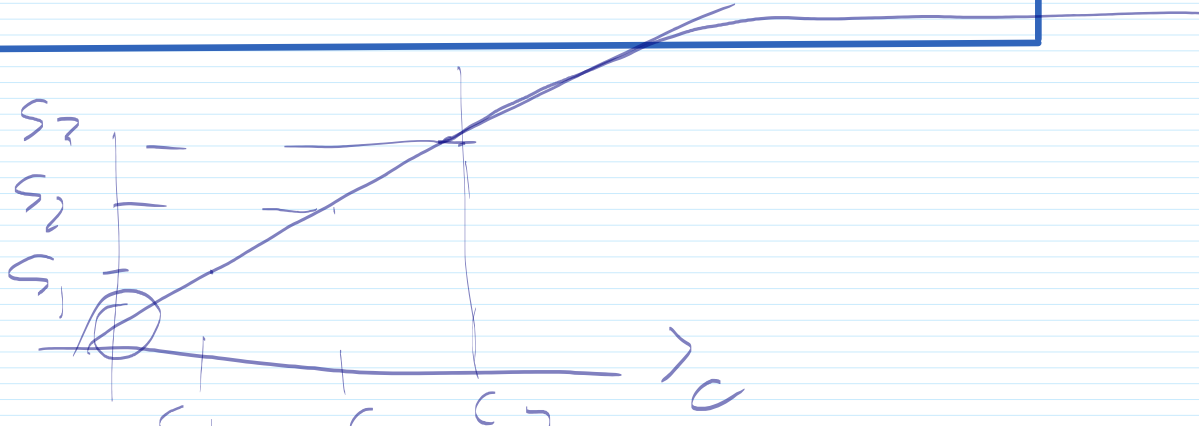


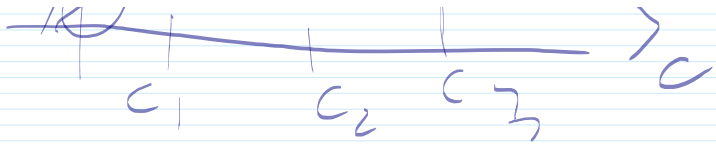


$$\frac{1}{v} = \frac{1}{v_{max}^{*}} + \frac{K_S}{v_{max}^{*}} \cdot \frac{1}{c_S}$$








C1
C2
C3
C

Effetto pH

1) $E = (E^-) + H^+$

2) $E^- = E^{2-} + H^+$

$$K_1 = \frac{(e^-)\cdot h^+}{e} \quad (*)$$

$$K_2 = \frac{e^{2-}\cdot h^+}{e^-} \quad (**)$$

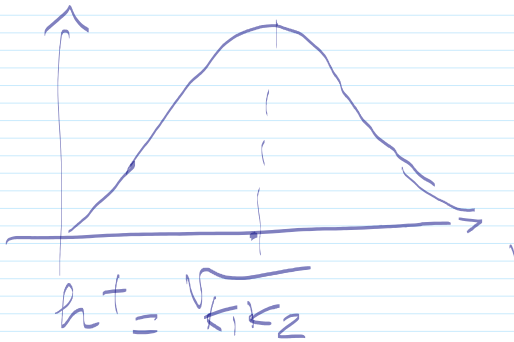
$$e_0 = e + e^- + e^{2-} = \frac{e^-\cdot h^+}{K_1} + e^- + \frac{K_2}{h^+}\cdot e^- =$$

$$= e^-\left(\frac{h^+}{K_1} + 1 + \frac{K_2}{h^+}\right)$$

$$\frac{e^-}{e_0} = \frac{1}{\frac{h^+}{K_1} + 1 + \frac{K_2}{h^+}} \Leftrightarrow \frac{e^-}{e_0} = \frac{h^+}{\frac{(h^+)^2}{K_1} + h^+ + K_2}$$

$$\frac{e^-}{e_0} \simeq \frac{h^+}{K_2} \qquad h^+ << K_2$$

$$\lim_{h^+ \to +\infty} \frac{e^-}{e_0} = 0$$



$h^+ = \sqrt{K_1 K_2}$

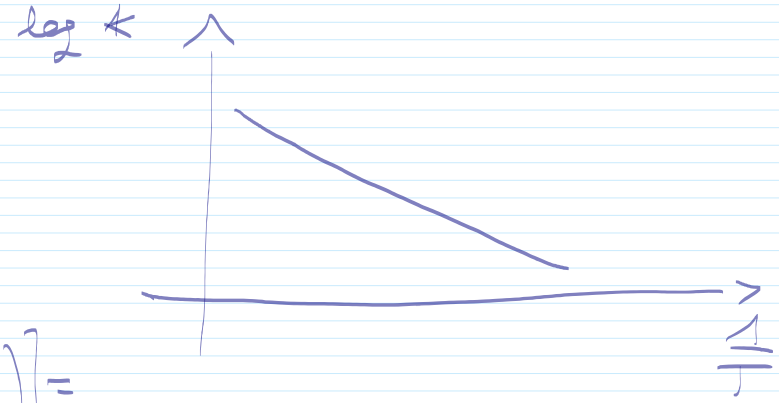
$$pH = -\log_{10}\sqrt{K_1 K_2}$$

$$v(S) = \frac{v_{max}\, S}{K_1 + S + S^2/K_2}$$

$S \rightarrow P$; $E + S = ES$

$ES \rightarrow P + E$

$$r = -\frac{dC_S}{dt} = \frac{dC_P}{dt} = +kC_{ES}$$



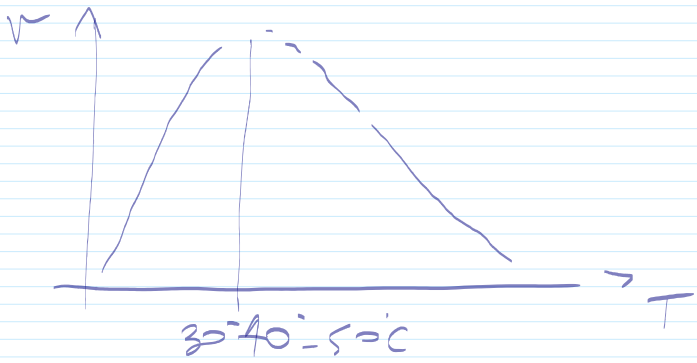
$$k = A \exp\left(-\frac{E}{RT}\right) ;$$

$$\log k = \log A + \log\left[\exp\left(-\frac{E}{RT}\right)\right] =$$

$$= \log A - E/RT = \log A - \left(\frac{E}{R}\right)\cdot\frac{1}{T}$$

a b x

$y = a - bx$



$E_a \rightarrow E_i$

$r = k\, l_a$

$$\begin{cases} \frac{dl_a}{dt} = -k l_a \\ l_a(0) = l_0 \end{cases} \Rightarrow l(t) = l_0 \exp(-kdt)$$

l_0

$l_a(0) = l_0$

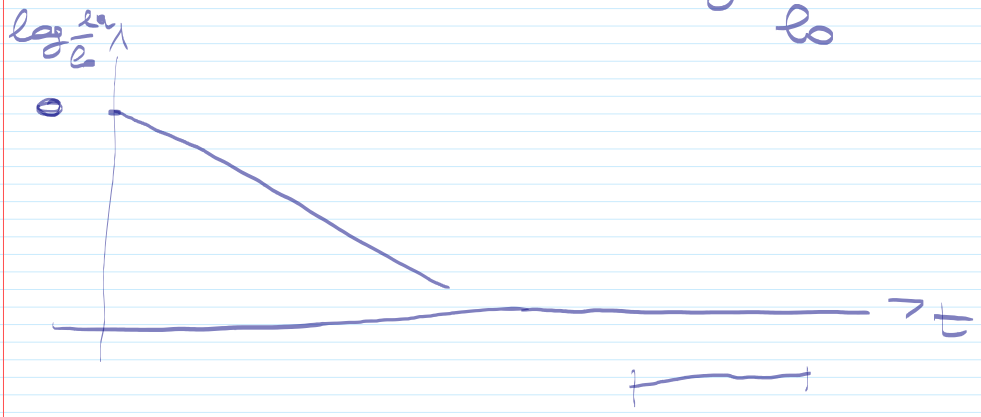
$l(t)$?

$E_a \rightarrow E_i$

$r = k_d [E_a]$

$\frac{d[E_a]}{dt} = -k[E_a]$ $\quad [E_a](0) = [E_a]_0$ $\Rightarrow [E_a](t) = [E_a]_0 \exp(-k_d t)$

$\log \frac{[E_a](t)}{[E_a]_0} = -k_d t$



$E_a \rightarrow E_i$

1) $E_a + S = E_aS$

2) $E_aS \rightarrow E_a + P$

$v = k [E_aS]$

$K_S = \frac{[E_a] \cdot S}{[E_aS]}$ $\quad \nexists \quad [E_aS] = \frac{[E_a] \cdot S}{K_S}$

$[E_a]_{TOT} = [E_a] + [E_aS] =$

$= \frac{K_S}{S} [E_aS] + [E_aS] = [E_aS] \left(\frac{K_S}{S} + 1 \right)$

$\Rightarrow [E_aS] = \frac{[E_a]_{TOT}}{\frac{K_S}{S} + 1}$ $\quad \therefore \quad v = \frac{k [E_a]_{TOT} S}{K_S + S}$

$E_a \rightarrow E_i$

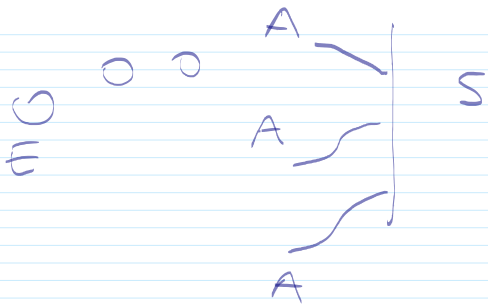
$\frac{d[E_a]_{TOT}}{dt} = -k_d [E_a]$; $\quad [E_a]_{TOT} = [E_a] + [E_aS] =$

$= [E_a] + \frac{[E_a] S}{K_S} = [E_a] \left(1 + \frac{S}{K_S} \right)$

$$[la] = \frac{[la]_{TOT}}{1 + \frac{S}{K_S}}$$

$$\frac{d[la]_{TOT}}{dt} = -\frac{K_d [la]_{TOT}}{1 + S/K_S}$$

Catalisi enzimatica - enzima in fase liquida con adsorbimento su substrato in fase solida



$E + A = EA$

$EA \rightarrow P + E$

$k_a = \frac{l \cdot a}{l_a}$ (*)

$a_0 = a + l_a = \frac{k_a \cdot l_a}{l} + l_a =$

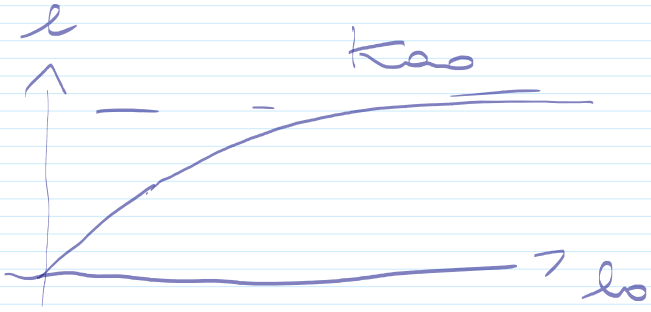
$= l_a \left(\frac{k_a}{l} + 1 \right)$

$l_a = \frac{a_0}{\frac{k_a}{l} + 1}$; $r = k\, l_a = \frac{k\, a_0\, l}{k_a + l}$

$l_0 = l + l_a$

$l_0 \simeq l$

$r = \frac{k a_0 l_0}{k_a + l_0}$



$l_0 << k_a \quad r \simeq k a_0 l_0$

$l_0 \gg k_a \quad r \simeq k a_0$