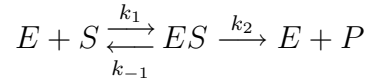


## Simple MM

The enzymatic reaction is assumed to be irreversible, and the product does not bind to the enzyme.



$$\frac{d[ES]}{dt} = k_1[E][S] - [ES](k_{-1} + k_2) \stackrel{!}{=} 0 \quad (1)$$

$$\frac{d[P]}{dt} = k_2[ES]$$

$$[E]_0 = [E] + [ES] \stackrel{!}{=} \text{const}$$

$$0 = k_1[S]([E]_0 - [ES]) - [ES](k_{-1} + k_2)$$

$$k_1[S][E]_0 = k_1[S][ES] + [ES](k_{-1} + k_2)$$

$$[S][E]_0 = [S][ES] + [ES] \underbrace{\frac{(k_{-1} + k_2)}{k_{-1}}}_{K_M}$$

$$[S][E]_0 = (K_M + [S])[ES]$$

$$[ES] = \frac{[S][E]_0}{K_M + [S]}$$

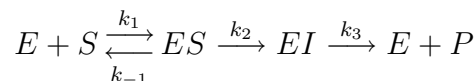
$$\frac{d[P]}{dt} = v_0 = k_2[ES] = \underbrace{k_2[E]_0}_{v_{max}} \frac{[S]}{K_M + [S]}$$

$$v_0 = \frac{v_{max}[S]}{K_M + [S]}$$

$$\frac{1}{v_0} = \frac{K_M}{v_{max}} \cdot \frac{1}{[S]} + \frac{1}{v_{max}}$$

## MM with intermediate

For the less simple case with an intermediate we have



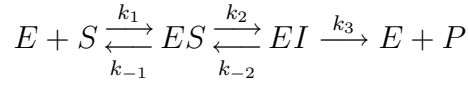
So we can write down the following kinetic equations:

$$\begin{aligned} \frac{d[P]}{dt} &= k_3[EI] \\ \frac{d[EI]}{dt} &= k_2[ES] - k_3[EI] \stackrel{!}{=} 0 \\ \frac{d[ES]}{dt} &= k_1[E][S] - [ES](k_{-1} + k_2) \stackrel{!}{=} 0 \\ [E]_0 &= [E] + [ES] + [EI] \stackrel{!}{=} \text{const} \\ \\ 0 &= k_1[S]([E]_0 - [ES] - [EI]) - [ES](k_{-1} + k_2) \\ k_1[S]([E]_0 - [EI]) &= k_1[S][ES] + [ES](k_{-1} + k_2) \\ [S]([E]_0 - [EI]) &= [S][ES] + [ES] \underbrace{\frac{(k_{-1} + k_2)}{k_{-1}}}_{K_M} \\ [S]([E]_0 - [EI]) &= (K_M + [S])[ES] \\ [ES] &= \frac{[S]([E]_0 - [EI])}{K_M + [S]} \\ \\ 0 &= k_2[ES] - k_3[EI] \\ 0 &= k_2 \frac{[S]([E]_0 - [EI])}{K_M + [S]} - k_3[EI] \\ 0 &= k_2 \frac{[S][E]_0}{K_M + [S]} - k_2 \frac{[S][EI]}{K_M + [S]} - k_3[EI] \\ k_2 \frac{[S][E]_0}{K_M + [S]} &= (k_2 \frac{[S]}{K_M + [S]} + k_3)[EI] \\ [EI] &= k_2 \frac{[S][E]_0}{(K_M + [S])(k_2 \frac{[S]}{K_M + [S]} + k_3)} \\ [EI] &= k_2 \frac{[S][E]_0}{k_2[S] + k_3(K_M + [S])} \\ \\ \frac{d[P]}{dt} &= v_0 = k_3[EI] = k_3 k_2 \frac{[E]_0[S]}{k_3 K_M + [S](k_2 + k_3)} \\ \frac{d[P]}{dt} &= \underbrace{\frac{k_3 k_2}{k_2 + k_3}}_{k_{cat}} \cdot \frac{[E]_0[S]}{\underbrace{\frac{k_3}{k_2 + k_3} K_M + [S]}_{K'_M}} \\ v_0 &= k_{cat} \frac{[S][E]_0}{K'_M + [S]} \end{aligned}$$


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## MM with intermediate and backreaction

For the more general simple case with an intermediate and reverse reaction we have



and we write down

$$\begin{aligned} \frac{d[P]}{dt} &= k_3[EI] \\ \frac{d[EI]}{dt} &= k_2[ES] - k_{-2}[EI] - k_3[EI] \stackrel{!}{=} 0 \\ \frac{d[ES]}{dt} &= k_1[E][S] + k_{-2}[EI] - [ES](k_{-1} + k_2) \stackrel{!}{=} 0 \\ [E]_0 &= [E] + [ES] + [EI] \stackrel{!}{=} \text{const} \end{aligned}$$

$$\begin{aligned} 0 &= k_1[S]([E]_0 - [ES] - [EI]) + k_{-2}[EI] - [ES](k_{-1} + k_2) \\ k_1[S]([E]_0 - [EI]) + k_{-2}[EI] &= k_1[S][ES] + [ES](k_{-1} + k_2) \\ [S]([E]_0 - [EI]) + \frac{k_{-2}}{k_1}[EI] &= [S][ES] + [ES] \underbrace{\frac{(k_{-1} + k_2)}{k_{-1}}}_{K_M} \end{aligned}$$

$$\begin{aligned} [S]([E]_0 - [EI]) + \frac{k_{-2}}{k_1}[EI] &= (K_M + [S])[ES] \\ [ES] &= \frac{[S]([E]_0 - [EI])}{K_M + [S]} + \frac{k_{-2}}{k_1} \frac{[EI]}{K_M + [S]} \end{aligned}$$

$$\begin{aligned} 0 &= k_2[ES] - k_{-2}[EI] - k_3[EI] \\ 0 &= k_2 \frac{[S][E]_0}{K_M + [S]} - k_2 \frac{[S][EI]}{K_M + [S]} + k_2 \frac{k_{-2}}{k_1} \frac{[EI]}{K_M + [S]} - k_{-2}[EI] - k_3[EI] \\ k_2 \frac{[S][E]_0}{K_M + [S]} &= (k_2 \frac{[S]}{K_M + [S]} + k_2 \frac{k_{-2}}{k_1} \frac{1}{K_M + [S]} + k_{-2} + k_3)[EI] \\ [EI] &= k_2[S][E]_0 \frac{1}{k_2[S] + k_2 \frac{k_{-2}}{k_1} + K_M(k_{-2} + k_3) + [S](k_{-2} + k_3)} \end{aligned}$$

$$\begin{aligned} \frac{d[P]}{dt} &= v_0 = k_3[EI] \\ v_0 &= k_3 k_2 [E]_0 \cdot \frac{[S]}{K_M(k_{-2} + k_3) + [S](k_2 + k_{-2} + k_3) + k_2 \frac{k_{-2}}{k_1}} \end{aligned}$$

We can try to simplify

$$v_0 = \frac{k_3 k_2}{\underbrace{k_2 + k_{-2} + k_3}_{k_{cat}}} [E]_0 \cdot \frac{[S]}{\underbrace{K_M \frac{k_{-2} + k_3}{k_2 + k_{-2} + k_3}}_{K'_M} + [S] + \underbrace{k_2 \frac{k_{-2}}{k_1(k_2 + k_{-2} + k_3)}}_{\gamma}}$$
$$v_0 = k_{cat} \frac{[E]_0 [S]}{K'_M + [S] + \gamma}$$

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