Simple MM

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

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

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

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

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

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

MM with intermediate

For the less simple case with an intermediate we have

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} EI \xrightarrow{k_3} E + P$$

So we can write down the following kinetic equations:

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

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

$$0 = k_2[ES] - k_3[EI]$$
$$0 = k_2\frac{[S]([E]_0 - [EI])}{K_M + [S]} - k_3[EI]$$
$$0 = k_2\frac{[S][E]_0}{K_M + [S]} - k_2\frac{[S][EI]}{K_M + [S]} - k_3[EI]$$
$$k_2\frac{[S][E]_0}{K_M + [S]} = (k_2\frac{[S]}{K_M + [S]} + k_3)[EI]$$
$$[EI] = k_2\frac{[S][E]_0}{(K_M + [S])(k_2\frac{[S]}{K_M+[S]} + k_3)}$$
$$[EI] = k_2\frac{[S][E]_0}{k_2[S] + k_3(K_M + [S])}$$

$$\frac{d[P]}{dt} = v_0 = k_3[EI] = k_3k_2\frac{[E]_0[S]}{k_3K_M + [S](k_2 + k_3)}$$
$$\frac{d[P]}{dt} = \underbrace{\frac{k_3k_2}{k_2 + k_3}}_{k_{cat}} \cdot \frac{[E]_0[S]}{\underbrace{\frac{k_3}{k_2 + k_3}K_M}_{K'_M} + [S]}$$
$$v_0 = k_{cat}\frac{[S][E]_0}{K'_M + [S]}$$

MM with intermediate and backreaction

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

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} EI \xrightarrow{k_3} E + P$$

and we write down

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

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

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

$$\begin{aligned}
\frac{d[P]}{dt} &= v_0 = k_3[EI] \\
v_0 &= k_3k_2[E]_0 \cdot \frac{[S]}{K_M(k_{-2} + k_3) + [S](k_2 + k_{-2} + k_3) + k_2\frac{k_{-2}}{k_1}}
\end{aligned}$$

We can try to simplify

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

$$v_0 = k_{cat} \frac{[E]_0 [S]}{K'_M + [S] + \gamma}$$

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