❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment

In 1901, a French Chemist, Victor Henri, proposed that enzyme reactions are actually initiated by a bond formed between the substrate and the enzyme. The concept was further developed by German researches Leonor Michaelis and Canadian scientist Maud Menten, who examined the kinetics of an enzymatic reaction mechanism of invertase. The final model of Michaelis and Menten's treatment was published in 1913 and gained immediate popularity among the scientific community.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\longrightarrow} P \tag{247}$$

Where E is the enzyme that binds to a substrate S, and forms a complex ES. This enzyme-substrate complex then turns into product P. The overall rate of product formation should be

$$+\frac{d[P]}{dt} = r = k_2[ES] \tag{248}$$

Since $[ES]$ is intermediate, the steady-state approximation can be applied i.e.

$$Rate\ of\ formation\ of\ [ES] = Rate\ of\ decomposition\ of\ [ES] \tag{249}$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \tag{250}$$

$$k_1[E][S] = (k_{-1} + k_2)[ES] \tag{251}$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \tag{252}$$

Now, defining a new parameter named as Michaelis- Menten constant (K_m) with the following expression,

$$K_m = \frac{k_{-1} + k_2}{k_1} \tag{253}$$

equation (252) takes the form

$$[ES] = \frac{[E][S]}{K_m} \tag{254}$$

Now, if we put the $[ES]$ concentration given above into equation (248), we will get the rate of enzyme-catalyzed reaction in terms of substrate concentration and enzyme left unused i.e. $[E]$. This is again a problem that can be solved if we obtain the rate expression in terms of total enzyme concentration i.e. $[E_0]$; which would make the calculation of catalytic efficiency much easier. In order to do so, recall the total enzyme concentration mathematically i.e.

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$$[E_0] = [E] + [ES] \tag{255}$$

Where $[E]$ is the enzyme concentration left unused whereas $[ES]$ represents the enzyme concentration that is bound with the substrate. Rearranging equation (253), we get

$$[E] = [E_0] - [ES] \tag{256}$$

After using the value of $[E]$ from equation (256) in equation (254), we have

$$[ES] = \frac{\{[E_0] - [ES]\}[S]}{K_m} \tag{257}$$

$$[ES] = \frac{[E_0][S] - [ES][S]}{K_m} \tag{258}$$

Rearranging for $[ES]$ again

$$K_m[ES] = [E_0][S] - [ES][S] \tag{259}$$

$$K_m[ES] + [ES][S] = [E_0][S] \tag{260}$$

$$[ES] = \frac{[E_0][S]}{K_m + [S]} \tag{261}$$

After putting the value of $[ES]$ from above equation into equation (248), we get

$$r = \frac{k_2[E_0][S]}{K_m + [S]} \tag{262}$$

If the rate of the enzyme-catalyzed reaction is recorded in the very initial stage, the substrate concentration can also be replaced by the initial substrate concentration i.e. $[S_0]$. Therefore, the initial enzyme-catalyzed rate (r_0) should be

$$r_0 = \frac{k_2[E_0][S_0]}{K_m + [S_0]} \tag{263}$$

Which is the well-known Michaelis-Menten equation.

Although the equation (263) is the complete form of the Michaelis-Menten equation that has measurable quantities like $[E_0]$ and $[S_0]$, the more popular form of the same includes the maximum initial rate. At very large initial substrate concentration, the K_m can simply be neglected in comparison to $[S_0]$ in the denominator, which makes the equation (263) to take the form

$$r_{max} = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \tag{264}$$

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After using the $k_2[E_0] = r_{max}$ in equation (263), we have

$$r_0 = \frac{r_{max}[S_0]}{K_m + [S_0]}$$

(265)

Which is the most popular form of the Michaelis-Menten equation. The plot of the initial reaction rate for the enzyme-catalyzed reaction is given below.
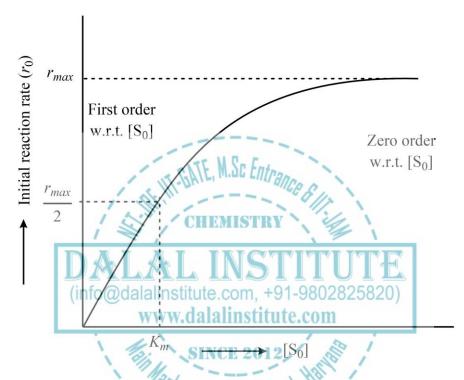

Figure 2. The variation of initial reaction rate as a function of substrate concentration for an enzyme-catalyzed reaction.

> ➤ *Order of Enzyme Catalysed Reactions*

The reaction kinetics of the enzyme-catalyzed reactions can be well understood by looking at the general form of Michaelis-Menten equation.

i) At high [S_0]: When initial substrate concentration is very high, K_m can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0]$$

(266)

Hence, the reaction will be zero-order w.r.t. substrate concentration and first order w.r.t the total enzyme concertation.

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ii) At low [S$_0$]: When initial substrate concentration is low, [S$_0$] can be neglected, and the equation (263) takes the form

$$r_0 = \frac{k_2}{K_m}[E_0][S_0] \tag{267}$$

Hence, the reaction will be the first-order w.r.t. substrate concentration and first order w.r.t the total enzyme concertation as well.

> ➤ *Calculation of Catalytic Efficiency*

The catalytic efficiency of enzyme-catalyzed reactions is simply the maximum overall reaction rate per unit of enzyme concentration. When initial substrate concentration is very high, K_m can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \tag{268}$$

$$k_2 = \frac{r_{max}}{[E_0]} \tag{269}$$

Hence, k_2 is simply equal to the catalytic efficiency of enzyme-catalyzed reactions.

> ➤ *Calculation of Michaelis-Menten Constant*

The Michaelis-Menten constant of enzyme-catalyzed reactions can simply be calculated once the maximum initial reaction rate is known. When initial substrate concentration is very high, K_m can be neglected, and the equation (263) takes the form

$$r_{max} = \frac{k_2[E_0][S_0]}{[S_0]} = k_2[E_0] \tag{270}$$

After using the $k_2[E_0] = r_{max}$ in equation (263), we have

$$r_0 = \frac{r_{max}[S_0]}{K_m + [S_0]} \tag{271}$$

When the initial reaction rate is half of the maximum initial rate i.e. $r_0 = r_{max}/2$, we have

$$\frac{r_{max}}{2} = \frac{r_{max}[S_0]}{K_m + [S_0]} \tag{272}$$

$$K_m + [S_0] = 2[S_0] \tag{273}$$

$$K_m = [S_0] \tag{274}$$

Hence, the concentration at which the initial rate in half of the maximum initial rate, will be equal to K_m.

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Volume I

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