Enzyme Kinetics I

An enzyme-catalyzed reaction of substrate S to product P, can be written

$$S \xrightarrow{E} P$$

actually, the enzyme and substrate must combine and E recycled after the reaction is finished, just like any catalyst.

Because the enzyme actually binds the substrate the reaction can be written as:

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

The simplest reaction is a single substrate going to a single product.

Rate or velocity of the reaction depends on the formation of the ES

- The P -> ES is ignored
- The equilibrium constant Keq is based on the idea that the reaction is limited to the formation of the ES complex and that only K1 and K-1 are involved because the thermodynamics of the reversal of K2 cause it to be minimal

$$Keq = \frac{k_1}{K_{-1}}$$

How fast an enzyme catalyzes a reaction is it's rate. The rate of the reaction is in the number of moles of product produced per second

$$\text{rate } (v) = \frac{d[P]}{dt} = k_2 [ES]$$

The relationship between the concentration of a substrate and the rate of an enzymatic reaction is described by looking at the concentration of S and v

- When the reaction is first order - the rate is dependent on [S]
- When the reaction is zero order, there is no relationship between v and S
- A second order is between 1st and 0 order, where the relationship between V and [S] is not proportional to [S]

To study enzymes, first order kinetics must be followed!

Think of the graph of [S] vs. v in this way:

- The velocity increases as the substrate concentration is increased is increased up to a point where the enzyme is "saturated" with substrate.
- At this point the rate of the reaction (v) reaches a maximal value and is unaffected by further increases in substrate because all of the enzyme active site is bound to substrate

For the most part enzyme reactions are treated as if there is only one substrate and one produce. If there are two substrates, one of them is held at a high concentration (0 order) and the other substrate is studied at a lower concentration so that for that substrate, it is a first order reaction. This leads us to the M and M equation.

Conditions for Michaelis -Menten

Two assumptions must be met for the Michaelis-Menten equation

- Equilibrium -the association and dissociation of the substrate and enzyme is assumed to be a rapid equilibrium and Ks is the enzyme:substrate dissociation constant.
- Steady state - the enzyme substrate complex ES is at a constant value. That is the ES is formed as fast as the enzyme releases the product. For this to happen the concentration of substrate has to be much higher than the enzyme concentration. That is why we only study the initial velocity. Later in the reaction the substrate concentration is relatively lower and the rate of product starts to be limited by diffusion and not the mechanism of the enzyme.