Enzyme Kinetics Notes for Chem 527

\[ S \xrightarrow{k_1} P \xleftarrow{k_{-1}} \]

**First Order Kinetics**

velocity or \( \nu = \frac{d[P]}{dt} = -\frac{d[S]}{dt} \)

\( \nu = k_1 [S] \), where \( k_1 \) has units of sec\(^{-1}\)

**Second Order Kinetics**

\( \nu = k [S_1][S_2] \)

where \( k \) has 2\(^{nd}\) order units of M\(^{-1}\)sec\(^{-1}\)

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**Rate Constant**

\[ k = \frac{K_T}{h} \exp\{-E_a/RT\} \]

\( R = 1.987 \) cal mol\(^{-1}\)K\(^{-1}\)

\( h = 6.626075 \times 10^{-34} \) J S, which is Planck’s constant

\( K = 1.38066 \times 10^{-23} \) J K\(^{-1}\), which is the Boltzmann constant

\( T \) is in Kelvin

\( E_a \) is activation energy in cal mol\(^{-1}\)
Steady State Assumption

1) Steady State Conditions  \[ \frac{d[ES]}{dt} = 0 \]
2) Initial velocity  \[ v_0 = \frac{V_{\text{max}}}{[S]}/(K_M + [S]), \] this is the Michaelis-Menton Equation

at saturating conditions and under initial velocity conditions,  \[ [S] > 10 \times K_M \]

\[ V_{\text{max}} = k_2 [ES] \] and the units are \( \mu\text{mol L}^{-1} \text{ sec}^{-1} \)

For simple mechanisms  \[ k_2 = k_{\text{cat}} \] (assuming \( k_3 \gg k_2 \))

\( k_{\text{cat}} \), which is corrected for [enzyme], is called the pseudo first order rate constant (units of sec\(^{-1}\)).

The enzyme activity is proportional to the [enzyme]
For ADH this will be [NADH]

Follow reaction by appearance of NADH $\epsilon_{340} = 6,220 \text{ M}^{-1} \text{ cm}^{-1}$

The enzyme saturation curve

Michaelis-Menten Equation

$$v = \frac{V_{\text{max}} [S]}{K_m + [S]}$$
Lineweaver-Burk Replot of Saturation Curve

Lineweaver-Burk equation:

\[
\frac{1}{v_0} = \frac{K_m}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}
\]
Competitive Inhibition

(a) $E + S \xrightleftharpoons[k_{-1}]{k_1} ES \xrightarrow{k_{cat}} E + P$

(b) Graph showing Michaelis-Menten kinetics with inhibition.

$K_i$