Rate Constants and the Arrhenius Equation

\[ k = \frac{K \cdot T}{h} \exp\{-E_a/RT\} \]

\( R = 1.987 \text{ cal mol}^{-1}\text{K}^{-1} \)
\( h = 6.626075 \times 10^{-34} \text{ J S}, \text{ which is Planck's constant} \)
\( K = 1.38066 \times 10^{-23} \text{ J K}^{-1}, \text{ which is the Boltzmann constant} \)
\( T \text{ is in Kelvin} \)
\( E_a \text{ is activation energy in Kcal/mol (or KJ/mol)} \)

more commonly seen as:

\[ k = A \exp\{-E_a/RT\} \]

where \( A \) is called the Arrhenius prefactor

or

\[ 1/k = 1/A \exp\{E_a/RT\} \]

First Order Kinetics

\[
\begin{array}{c}
S \\
\xrightarrow{k_1} \\
\xrightarrow{k_1} \text{P}
\end{array}
\]

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

\[ v = k_1 [S], \text{ where the first order rate constant } k \text{ has units of sec}^{-1} \]

Second Order Kinetics

\[ = k [S1][S2] \]

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

Simplest Enzyme Mechanism

\[
\begin{array}{c}
E+S \\
\xrightarrow{k_1} \\
\xrightarrow{k_2} \text{ES} \\
\xrightarrow{k_2} \text{EP} \\
\xrightarrow{k_3} \text{E+P}
\end{array}
\]
Steady State Assumption

1) Steady State Conditions \( \frac{d[ES]}{dt} = 0 \)

2) Initial velocity \( V_0 = V_{\text{max}} \frac{[S]}{(K_m + [S])} \), 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. This rate constant has units of \( \text{sec}^{-1} \).