

Rate Constants and the Arrhenius Equation

$$k = \kappa T/h \exp\{-E_a/RT\}$$

$$R = 1.987 \text{ cal mol}^{-1}\text{K}^{-1}$$

$h = 6.626075 \times 10^{-34} \text{ J S}$, which is Planck's constant

$\kappa = 1.38066 \times 10^{-23} \text{ J K}^{-1}$, which is the Boltzmann constant

T is in Kelvin

E_a is activation energy in Kcal/mol (or KJ/mol)

more commonly seen as:

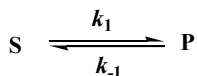
$$k = A \exp\{-E_a/RT\}$$

where A is called the Arrhenius prefactor

or

$$1/k = 1/A \exp\{E_a/RT\}$$

First Order Kinetics



$$\text{velocity or } v = d[P]/dt = -d[S]/dt$$

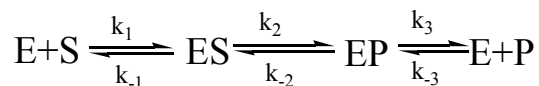
$$v = k_1 [S], \text{ where the first order rate constant } k \text{ has units of } \text{sec}^{-1}$$

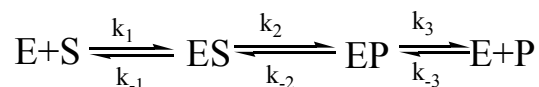
Second Order Kinetics

$$= k [S_1][S_2]$$

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

Simplest Enzyme Mechanism





Steady State Assumption

1) Steady State Conditions $d[ES]/dt = 0$

2) Initial velocity $= V_0 = V_{\max} [S]/(K_M + [S])$, this is the Michaelis-Menton Equation

at saturating conditions and under initial velocity conditions, $[S] > 10 \times K_M$
 $V_{\max} = k_2 [ES]$ 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_{cat} , which is corrected for $[\text{enzyme}]$, is called the pseudo first order rate constant. This rate constant has units of sec^{-1} .

