Rate Constants and the Arrhenius Equation

$$k = \text{Ϗ}\, T/\text{ħ} \exp\{-Ea/RT\}$$

R = 1.987 cal $mol^{-1}K^{-1}$
ħ = 6.626075 x 10^{-34} J S, which is Planck's constant
Ϗ = 1.38066 x 10^{-23} 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:

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

where A is called the Arrhenius prefactor

or

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

First Order Kinetics

$$S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$$

velocity or v = d[P]/dt = -d[S]/dt

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

Second Order Kinetics

= k [S1][S2]

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

Simplest Enzyme Mechanism

$$E+S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} E+P$$

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} E + P$$

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 μmol L^{-1} sec^{-1}

For simple mechanisms $k_2 = k_{cat}$ (assuming $k_3 >> k_2$)

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