General catalytic mechanisms

- The reaction scheme is

$$1. \qquad C + S \rightleftharpoons X + Y$$

$$2. \qquad \mathrm{X} + W \longrightarrow P + Z$$

- Here C represents the catalyst and S represents the substrate.
- X and Y are the intermediates, the first of which undergoes a second reaction with a species W to give the final product or products P together with a side product Z.
- Y and Z don't have any effect on kinetic behaviour.

Arrhenius Intermediates

- In the equation for above reaction

$$\frac{[X][Y]}{[C][S]} = \frac{k_1}{k_{-1}} = K$$

- Since concentrations C and S do not corresponds to the initial concentrations $[C]_o$ and $[S]_o$ since some amount of them has been used to form the intermediate X.

- These initial concentrations may be expressed as:

$$[C]_O = [C] + [S]$$

$$[S]_O = [S] + [X]$$

And the equation becomes,

$$\frac{[X][Y]}{(C_O - [X])(S_O - [X])} = K$$

- This is a quadratic in [X] and can be solved for [X].
- Then an expression for the rate, equal to $k_2[X][W]$, can be written down.

Let us consider two cases,

1. If the initial concentration of the substrate is much greater than that of the catalyst, that is, if $[S]_o >> [C]_o$. It follows that $[S]_o - [X]$ is very close to $[S]_o$, since [X] cannot exceed $[C]_o$. Thus the equation reduces to

$$\frac{[X][Y]}{([C]_o - [X][S]_o)} = K$$

$$[X] = \frac{K[C]_o[S]_o}{K[S]_o + [Y]}$$

- The rate of reaction is therefore,

$$v = k_2[X][W] = \frac{k_2 C_o S_o [W]}{K[S]_o + [Y]}$$

- This rate equation corresponds to a variation of rate of the type represented in figure below: