

Complex Reactions and Mechanisms

Mechanisms: A series of elementary steps that make up a reaction.

e.g. for $A + B + 2C \rightarrow D + E$

Mechanism could be:

| | | |
|---------------------------|---|--|
| $A + B \rightarrow F$ | } | Elementary Single Step Reactions |
| $F + C \rightarrow G + D$ | | |
| $G + C \rightarrow E$ | | |

F and G are reaction intermediates

Molecularity: The number of molecules that come together to react in one elementary step

For single step elementary reactions, Molecularity = Order

$A \rightarrow \text{products}$ 1st order rate = $k[A]$ Unimolecular

$A \rightarrow \text{products}$ 2nd order rate = $k[A]^2$ Bimolecular

$A + B \rightarrow \text{prod.}$ 2nd order rate = $k[A][B]$ Bimolecular

$A + B + C \rightarrow \text{prod.}$ 3rd order rate = $k[A][B][C]$ Termolecular

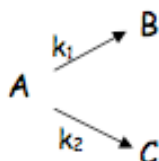
Etc...

Molecularity is the number of molecules that need to collide, and in one step form the products.

Some Simple Mechanisms

I) Parallel Reactions

a) Parallel 1st order reactions



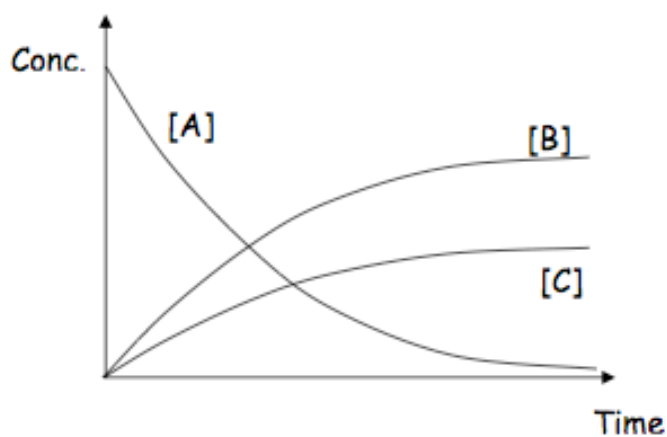
$$-\frac{d[A]}{dt} = k_1[A] + k_2[A]$$

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

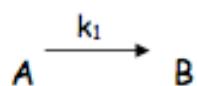
$$[B] = \frac{k_1[A]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t})$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t})$$

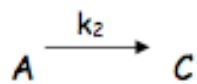
Branching Ratio: $\frac{[B]}{[C]} = \frac{k_1}{k_2}$



b) Parallel 1st and 2nd order reactions



$$\frac{d[B]}{dt} = k_1[A]$$



$$\frac{d[C]}{dt} = k_2[A]^2$$

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A]^2$$

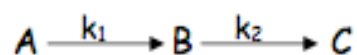
$$[A] = \frac{k_1[A]_0}{e^{k_1 t}(k_1 + k_2[A]_0) - k_2[A]_0}$$

Limiting cases:

i) $k_2[A]_0 \ll k_1 \Rightarrow [A] = [A]_0 e^{-k_1 t}$

ii) $k_2[A]_0 \gg k_1 \Rightarrow \frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$

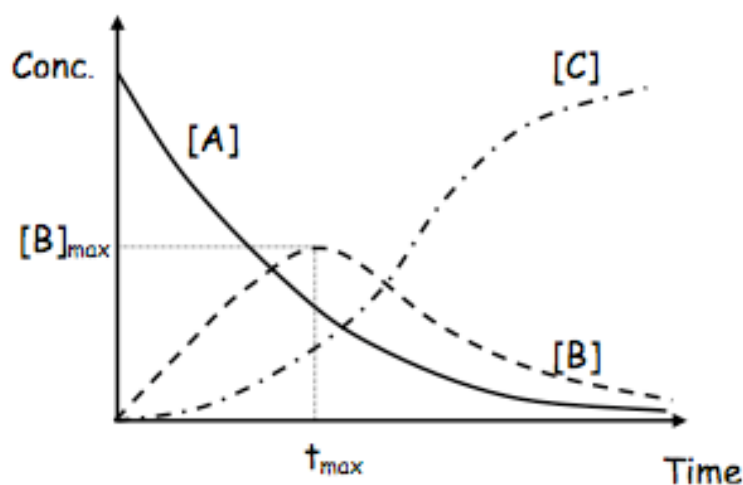
c) Consecutive or Series Reactions (1st order)



$$\begin{array}{l} -\frac{d[A]}{dt} = k_1[A] \qquad \qquad \qquad -\frac{d[C]}{dt} = k_2[B] \\ \frac{d[B]}{dt} = k_1[A] - k_2[B] \end{array}$$

$$[A] = [A]_0 e^{-k_1 t} \qquad [B] = \frac{k_1 [A]_0}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \quad \text{with } k_1 \neq k_2$$

$$[C] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$



$$t_{\max}^B = \frac{\ln(k_1/k_2)}{k_1 - k_2} \quad \text{with } k_1 \neq k_2 \qquad [B]_{\max} = \frac{k_1}{k_2} [A]_0 e^{-k_1 t_{\max}^B}$$

Limiting cases:

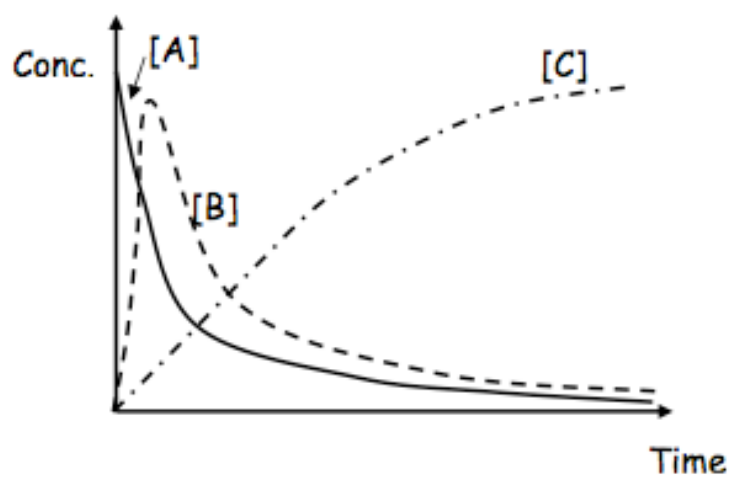
i) $k_1 = k_2$ (homework)

ii) $k_1 \gg k_2$

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] \approx [A]_0 e^{-k_2 t}$$

$$[C] \approx [A]_0 (1 - e^{-k_2 t})$$



$B \xrightarrow{k_2} C$ is the rate determining step

iii) $k_1 \ll k_2$

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] \approx \frac{k_1}{k_2} [A]$$

$$[C] \approx [A]_0 - [A]$$

