5.60 Thermodynamics & Kinetics
Spring 2008

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:

$$\left.\begin{aligned} A + B &\rightarrow F \\ F + C &\rightarrow G + D \\ G + C &\rightarrow E \end{aligned}\right\} \text{Elementary Single Step Reactions}$$

F and G are <u>reaction intermediates</u>

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

For <u>single step elementary</u> reactions, <u>Molecularity = Order</u>

$A \rightarrow$ products	1st order	rate = $k[A]$	Unimolecular
$A \rightarrow$ products	2nd order	rate = $k[A]^2$	Bimolecular
$A + B \rightarrow$ prod.	2nd order	rate = $k[A][B]$	Bimolecular
$A + B + C \rightarrow$ prod.	3rd order	rate = $k[A][B][C]$	Termolecular

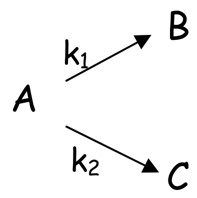
Etc…

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

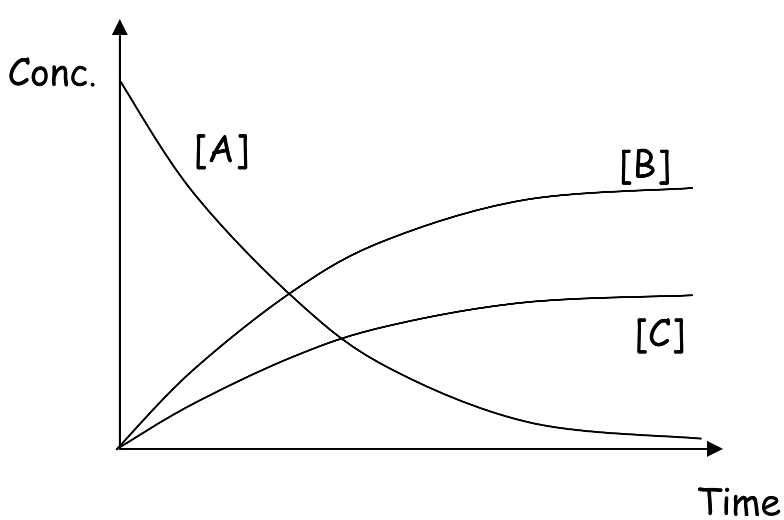


$$\frac{-d[A]}{dt} = k_1[A] + k_2[A]$$

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

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

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



b) Parallel 1st and 2nd order reactions

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

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

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

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

Limiting cases:

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

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

c) <u>Consecutive or Series Reactions</u> (1st order)

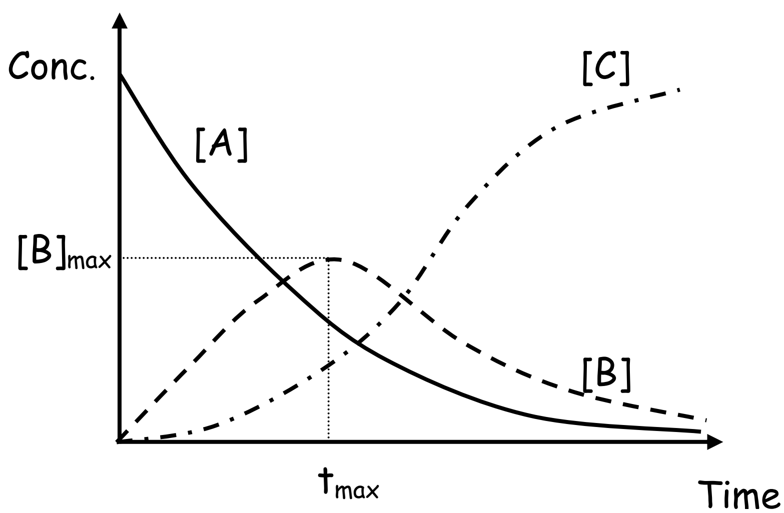
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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

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

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

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



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

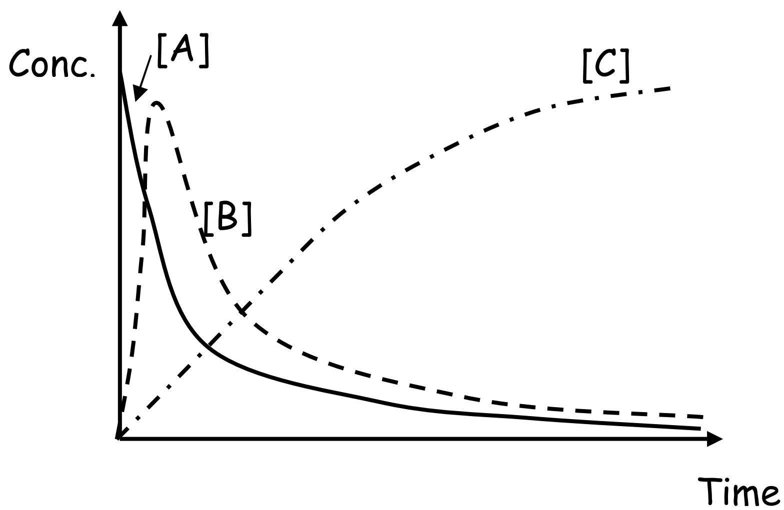
Limiting cases:

i) $k_1 = k_2$ (homework)

ii) $k_1 \gg k_2$

$$[A] = [A]_o e^{-k_1 t} \qquad [B] \approx [A]_o e^{-k_2 t}$$

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

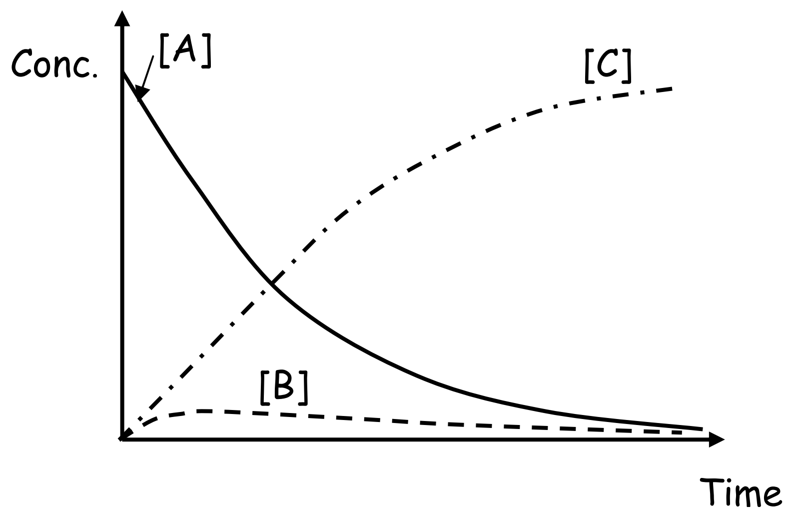


$B \xrightarrow{k_2} C$ is the rate determining step

iii) $k_1 << k_2$

$$[A] = [A]_o e^{-k_1 t} \qquad [B] \approx \frac{k_1}{k_2}[A]$$

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



$A \xrightarrow{k_1} B$ is the <u>rate limiting</u> step