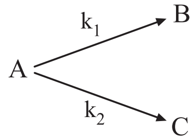
ADVANCED KINETICS Section - 7

1. Parallel / Side Reactions (Elementary Reactions) :



Rate of consumption of 'A' in $A \longrightarrow B : \left.\frac{d[A]}{dt}\right|_1 = -k_1[A]$ $\left[\because \text{Rate of Reaction} = k_1[A] = -\left.\frac{d[A]}{dt}\right|_1\right]$

Similarly, Rate of consumption of 'A' in $A \longrightarrow C : \left.\frac{d[A]}{dt}\right|_2 = -k_2[A]$

$\Rightarrow$ Overall (net) rate of consumption of 'A' = $\frac{d[A]}{dt} = \left.\frac{d[A]}{dt}\right|_1 + \left.\frac{d[A]}{dt}\right|_2$

$$= -k_1[A] - k_2[A]$$

$$\Rightarrow \quad \frac{d[A]}{dt} = -(k_1 + k_2)[A] = -k_{overall}[A] \quad \quad \text{....(i)}$$

$\Rightarrow$ The Overall reaction is also of the same order (here, I^{st} order) with $k_{overall} = k_1 + k_2$

Check yourself that solution of (i) is :

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

Also, from the rate equation : $\frac{d[B]}{dt} = +k_1[A]$ and $\frac{d[C]}{dt} = +k_2[A]$

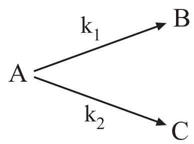
Substituting the value of [A] at (t) in the differential equation for [B] and [C] and integrating, we get :

$$[B] = [B]_o + \int_0^t k_1[A]_0 e^{-(k_1+k_2)t}\, dt = [B]_0 + \frac{k_1[A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

and $$[C] = [C]_o + \int_0^t k_2[A]_0 e^{-(k_1+k_2)t}\, dt = [C]_0 + \frac{k_2[A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

Also, if $[B]_0$ and $[C]_0 = 0$, we get : $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

Illustrating the concept :



$k_1 = 10^{-3} s^{-1}$ and $k_2 = 2 \times 10^{-3} s^{-1}$. Find the overall half life of the reaction.

SOLUTION :

$k_{overall} = k_1 + k_2 = 3 \times 10^{-3} s^{-1}$

$t_{1/2} = \dfrac{0.693}{k_{overall}} = \dfrac{0.693}{3 \times 10^{-3}} s = 231\, sec.$ [Note : Reactions are of first order].

2. Consecutive Reactions (Elementary Reactions) :

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

$$\frac{d[A]}{dt} = -k_1[A] \quad \text{....(i)}$$

$$\frac{d[B]}{dt} = +k_1[A] - k_2[B] \quad \text{....(ii)}$$

$$\frac{d[C]}{dt} = +k_2[B] \quad \text{....(iii)}$$

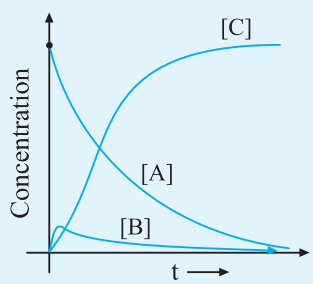
On solving the above differential equations, we get :

$$[A] = [A]_0\, e^{-k_1 t} \quad \text{....(iv)}$$

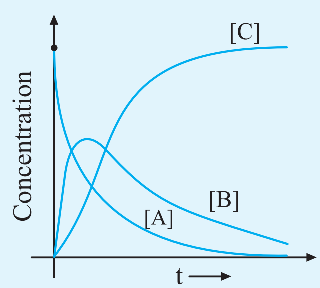
$$[B] = [A]_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad \text{....(v)}$$

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

Note : ➤ $[A] + [B] + [C] = [A]_0$ [Assuming $[B]_0 = [C]_0 = 0$]



$k_2/k_1 = 10$



$k_2/k_1 = 0.5$

➤ [B] is maximum when $\dfrac{d[B]}{dt} = 0$

$\Rightarrow \quad k_1[A] = k_2[B]_{max.} \quad$ ....(vii)

Using (v), $\dfrac{d[B]}{dt} = -k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0 \quad \Rightarrow \quad k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$

$\Rightarrow \quad t = \dfrac{1}{k_2 - k_1} \ell n \dfrac{k_2}{k_1}$

Thus, at $t = \dfrac{1}{k_2 - k_1} \ell n \dfrac{k_2}{k_1}$, [B] is maximum.

Illustration - 16 $A \xrightarrow{k_1 = 0.1 s^{-1}} B \xrightarrow{k_2 = 1/30 s^{-1}} C$

Find the time at which concentration of B is maximum. Also, find the concentration of A, B, and C at this instant. Take $[A]_0 = 1M$

SOLUTION :

$$[B] \text{ is maximum at } t = \frac{1}{k_2 - k_1} \ell n \frac{k_2}{k_1} = \frac{1}{0.1 - 1/30} \ell n \frac{0.1}{1/30} = 15 \ell n 3 \text{ sec.}$$

$$[A]_{t = 15 \ell n3} = [A]_0 e^{-k_1 t}$$

$$= 1 \times e^{-0.1 \times 15 \ell n 3} = e^{\ell n(3^{-1.5})} = 3^{-1.5} = \frac{1}{3\sqrt{3}} M$$

When [B] is max : $k_1[A] = k_2[B]_{max.} \left(\frac{d[B]}{dt} = 0\right)$

$$\Rightarrow \quad \frac{1}{10} \times \frac{1}{3\sqrt{3}} = \frac{1}{30}[B]_{max.} \quad \Rightarrow \quad [B]_{max.} = \frac{1}{\sqrt{3}} M$$

Also, $[A] + [B] + [C] = [A]_0$

$$[C] = 1 - \frac{1}{3\sqrt{3}} - \frac{1}{\sqrt{3}} = 1 - \frac{4}{3\sqrt{3}} M$$

3. Reversible Reaction (Elementary Reactions) :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Net rate of consumption of 'A' $= \frac{d[A]}{dt} = -k_1[A] + k_2[B]$

Also, $[A] + [B] = [A]_0 \quad \Rightarrow \quad [B] = [A]_0 - [A]$

$$\Rightarrow \quad \frac{d[A]}{dt} = -k_1[A] + k_2([A]_0 - [A])$$

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] + k_2[A]_0$$

At equilibrium, $\frac{d[A]}{dt} = 0 \quad \Rightarrow \quad k_1[A]_{eq} = k_2[B]_{eq}$

$$\Rightarrow \quad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_2}$$

Try yourself : Find $[A]_t$ = ? and $[B]_t$ = ?