Opposing Reaction :-

Both forward and backward reactions are 1st order.

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

As time goes concn of 'A' decrease and concn of 'B' ~~concn of~~ increase i.e rate of forward reaction decrease and backward reaction increase. Now overall rate will be -

$$\frac{d[A]}{dt} = -k[A] + k'[B] \quad \text{— (i)}$$

Let the initial concentration of 'A' is $[A]_0$ and $[B]$ is zero. But at any given time $[A] + [B] = [A]_0$

or $[B] = [A]_0 - [A]$

Now from equn (i)

$$\frac{d[A]}{dt} = -k[A] + k'\{[A]_0 - [A]\}$$

or $$\frac{d[A]}{dt} = +k'[A]_0 - (k+k')[A]$$

or $$\frac{d[A]}{k'[A]_0 - (k+k')[A]} = dt.$$

Now integrating, $t = -\frac{1}{k+k'} \ln\{k'[A]_0 - (k+k')[A]\} + z$

When $t=0$, $[A] = [A]_0$

i.e $z = +\frac{1}{k+k'} \ln\{-k[A]_0\}$

$\therefore$ $$t = \frac{1}{k+k'} \ln \frac{k[A]_0}{(k+k')[A] - k'[A]_0} \quad \text{—(ii)}$$

or $$\ln \frac{k[A]_0}{(k+k')[A] - k'[A]_0} = (k+k')t.$$

or $$\frac{k[A]_0}{(k+k')[A] - k'[A]_0} = e^{(k+k')t}$$

or $$\frac{(k+k')[A] - k'[A]_0}{k[A]_0} = e^{-(k+k')t}$$

$$\frac{k+k'}{k}\frac{[B]}{[A]_0} - \frac{k'}{k} = e^{-(k+k')t}$$

or $$\frac{k+k'}{k}\frac{[B]}{[A]_0} = \frac{k'}{k} + e^{-(k+k')t}$$

or $$\frac{[A]}{[B]_0} = \frac{k}{k+k'}\left\{\frac{k'}{k} + e^{-(k+k')t}\right\}$$

or $$\frac{[A]}{[A]_0} = \frac{k}{k+k'} \times \frac{k'}{k} + \frac{k}{k+k'} e^{-(k+k')t}$$

$$= \frac{k'}{k+k'} + \frac{k}{k+k'} e^{-(k+k')t}$$

$$\frac{[A]}{[A]_0} = \frac{k' + k e^{-(k+k')t}}{k+k'}$$

when $t = \infty$; equilibrium condition attain, then concentration of 'A' + 'B', suppose $[A]_\infty$ & $[B]_\infty$ at $t \to \infty$.

$$\frac{[A]_\infty}{[A]_0} = \frac{k' + k e^{-(k+k')\infty}}{k+k'}$$

$$= \frac{k' + 0}{k+k'}$$

$$\frac{[A]_\infty}{[A]_0} = \frac{k'}{k+k'}$$

and $$\frac{[B]_\infty}{[A]_0} = 1 - \frac{[A]_\infty}{[A]} = 1 - \frac{k'}{k+k'} = \frac{k+k'-k'}{k+k'}$$

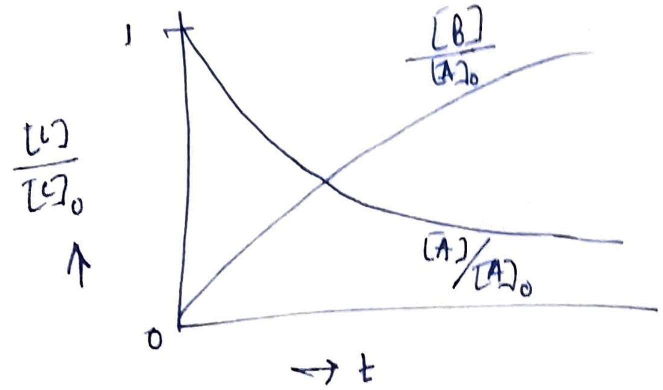
$$\therefore \frac{[B]_\infty}{[A]_0} = \frac{k}{k+k'}$$

now $$\frac{[B]_\infty}{[A]_\infty} = \frac{k}{k+k'} \times \frac{k+k'}{k'} = \frac{k}{k'} = K$$

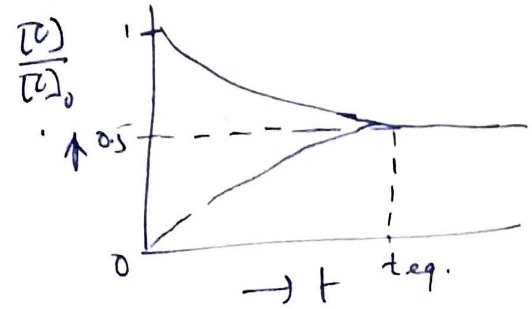
ie, at equilibrium for a opposing reaction, rate of foward reaction and back reaction is constant.

Now $\frac{k}{k'} = K$

So $\frac{[A]}{[A]_0} = \frac{1 + K e^{-k'(K+1)t}}{1+K}$



when $k = k'$



Consecutive Reactions :-

	$A \xrightarrow{K_1}$	$B \xrightarrow{K_2}$	C
$t=0$	C_0	0	0
$t=t$	C_1	C_2	C_3

$$C_0 = C_1 + C_2 + C_3$$

K_1 & K_2 are rate constant and suppose the elementary reactions are 1st order reaction.

So, $-\frac{dc_1}{dt} = K_1 C_1$ or $C_1 = C_0 e^{-K_1 t}$

or $\frac{C_1}{C_0} = e^{-K_1 t}$ —— (i)

$$\frac{dc_2}{dt} = K_1 C_1 - K_2 C_2$$

or $\frac{dc_2}{dt} + K_2 C_2 = K_1 C_1 = K_1 C_0 e^{-K_1 t}$

multiplying both side with $e^{K_2 t}$.

$$e^{K_2 t} \frac{dc_2}{dt} + K_2 C_2 e^{K_2 t} = K_1 C_0 e^{(K_2 - K_1)t}$$

Integrating both side

$$C_2 e^{K_2 t} = \frac{K_1}{K_2 - K_1} C_0 e^{(K_2 - K_1)t} + Z$$

Z = Integrating constant.

Now $t=0$; $C_2 = 0$ ∴ $Z = -\frac{K_1}{K_2 - K_1} C_0$

$$\therefore C_2 e^{K_2 t} = \frac{K_1 C_0}{K_2 - K_1} \left[e^{(K_2 - K_1)t} - 1 \right]$$

$$\therefore \frac{C_2}{C_0} = \frac{k_1}{k_2 - k_1}\left[\frac{e^{(k_2-k_1)t} - 1}{e^{k_2 t}}\right]$$

$$\text{or} \quad \frac{C_2}{C_0} = \frac{k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] \qquad \text{—(ii)}$$

Now

$$C_3 = C_0 - C_1 - C_2$$

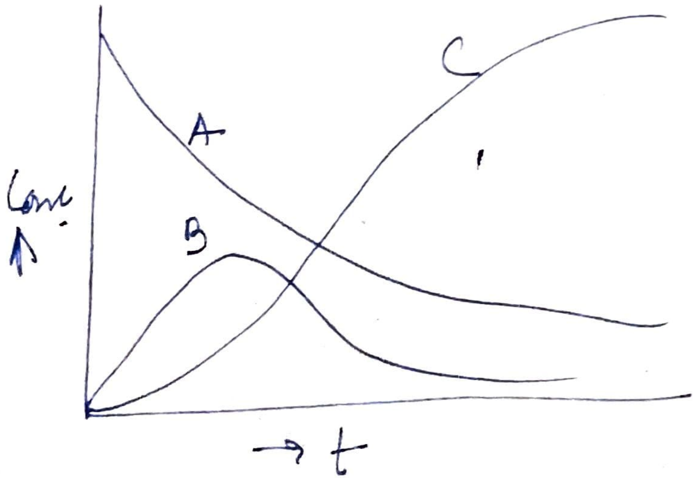
$$= C_0 - C_0 e^{-k_1 t} - \frac{C_0 k_1}{k_2 - k_1} e^{-k_1 t} + \frac{C_0 k_1}{k_2 - k_1} e^{-k_2 t}$$

$$= C_0\left[1 - e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right]$$

$$= C_0\left[1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right]$$

$$= C_0\left[1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right]$$

$$\frac{C_3}{C_0} = 1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \qquad \text{—(iii)}$$



When does concentration of B be maximum?

⇒ for maxima condition –

$$\frac{dc_2}{dt} = 0$$

or $$\frac{k_1 c_0}{k_2 - k_1}\left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right] = 0$$

or $$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

or $$\frac{k_1}{k_1} = e^{(k_1 - k_2)t}$$

or $$t = \frac{\ln k_1 - \ln k_2}{k_1 - k_2}$$