Q. 1 What is zero order reaction? cite some examples. What is the molecularity of this type of reaction? Plot the decay and decay rate vs time for this kind of reaction.

Ans: Zero order reaction means rate of these reactions does not depend on the conc. of the reactants. Let us take the reaction represented as

$$A \longrightarrow \text{Product}$$

Rate equation is $-\frac{dC_A}{dt} = K_0 \cdot C_A^{\,0}$

ie $-\frac{dC_A}{dt} = K_0$

2nd part Examples of zero order reaction

i) The enzyme catalysed reaction is found zero order reaction w.r.t substrate ie the rate equation for the reaction $\text{substrate} \xrightarrow[\text{Enzyme}]{} \text{Product}$ is

$$\text{rate} = K \cdot C_{\text{enzyme}}^{\,1} \cdot C_{\text{substrate}}^{\,0}$$

ii) Heterogeneous catalysed reaction, like decomposition of HI on gold surface; NH$_3$ on tungsten surface.

3rd part

$$A \longrightarrow \text{Product}$$

initial conc	a	0
after time interval t,	(a−x)	x

The rate equation in term of product,

$$\frac{dx}{dt} = K_0$$

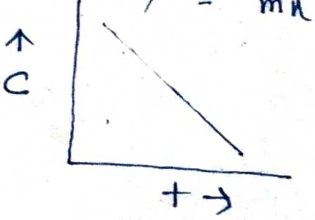
or, $\int_0^x dx = K_0 \int_0^t dt$

or, $x = K_0 t$

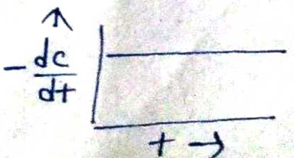
or, $C_0 - C = K_0 t$

or, $C = -K_0 t + C_0$

$y = mx + c$



$$-\frac{dc}{dt} = K_0$$



Q2 Write the differential rate law for the following reaction $A + 2B \longrightarrow P$ and turn it into a pseudo 1st order and pseudo 2nd order rate law.

$$A + 2B \longrightarrow P$$

	A	2B	P
initial Time	a	b	0
at a time t	$(a-x)$	$(b-2x)$	x

The rate equation in turms of product

$$\frac{dx}{dt} = K \cdot (a-x)(b-2x)^2$$

Q5 For a first order process: $A \rightarrow$ products, show that the No. of molecules at a time t is given by $N_t = N_0 \cdot \left(\frac{1}{2}\right)^{t/t_{1/2}}$ where N_0 is the No. of molecules at $t=0$ and $t_{1/2}$ is the time for half decomposition.

Ans :-

$$A \longrightarrow \text{product} \quad (\text{1st order reaction})$$

	A	product
Initial conc.	a	0
conc. at time t	$(a-x)$	x

The rate equation $\quad \frac{dx}{dt} = K\cdot(a-x)$

Now separating the variable and integrating, we get.

$$\int \frac{dx}{(a-x)} = \int K\cdot dt$$

$$\text{or,} \quad -\ln|a-x| = Kt + I_c$$

When $t=0$, $x=0$ so, $I_c = -\ln|a|$

putting the value, we get

$$\ln\left|\frac{a}{a-x}\right| = Kt$$

Here, $a = C_0$ = Initial conc.

$(a-x) = C_t$ = conc. at time t.

$$\circledast \ \text{so,} \quad \ln\left|\frac{C_0}{C_t}\right| = Kt = \frac{\ln 2}{t_{1/2}}\cdot t$$

$$\text{or,} \quad \ln\left|\frac{C_t}{C_0}\right| = \frac{t}{t_{1/2}} \times \ln\left|\frac{1}{2}\right|$$

or, $\ln\left|\frac{N_t}{N_0}\right| = \ln\left|\frac{1}{2}\right|^{t/t_{1/2}}$

or, $\frac{N_t}{N_0} = \left|\frac{1}{2}\right|^{t/t_{1/2}}$

or, $N_t = N_0 \times \left|\frac{1}{2}\right|^{t/t_{1/2}}$

(proved)

Q6 A first order reaction takes 30 min. for 50% completion. calculate the time when the conc reduces to $\left(\frac{1}{e}\right)$ of the initial conc.

Ans:

Given $t_{1/2} = 30$ min

$C = \frac{1}{e}\cdot C_0$

or, $\frac{C_0}{C} = e$

We have integrated rate equation

$\ln\left|\frac{C_0}{C}\right| = Kt$

But $t_{1/2} = \frac{0.693}{K_1}$

or, $K_1 = \frac{0.693}{30}$ min^{-1}

or, $t = \frac{1}{K_1} \times \ln\left|\frac{C_0}{C}\right|$

$= \frac{30}{0.693} \times \ln e$ min

$= 43.3$ min. (Ans)

So, 43.3 min, time requires for reduction of conc. to $\left(\frac{1}{e}\right)$ of the initial conc.

Q7. Calculate the half-life for the decomposition of N_2O_5 at 25 °C and the fraction decomposed after 8 hrs.

given $K_1 = 3.38 \times 10^{-5}\ sec^{-1}$

1st part → $t_{1/2} = \frac{\ln 2}{K_1}$

$= \frac{0.693}{3.38 \times 10^{-5}}\ sec$

$= 20500\ sec$

2nd part

the integrated rate equation is

$$\ln\left|\frac{a}{a-x}\right| = K_1 t$$

$$\text{or, } \left(\frac{a-x}{a}\right) = e^{-K_1 t}$$

$$\text{or, } \frac{x}{a} = 1 - e^{-K_1 t}$$

$$= 1 - e^{-3.38 \times 10^{-5} \times 8 \times 60 \times 60}$$

$$= 0.622$$

So, the fraction decomposed after 8 hrs is 0.622.

Q.8 The isotope K^{42} has a $t_{1/2}$ of 12 hrs. what fraction of the initial conc. of K^{42} remains after 60 hrs.

Ans. We know
$$\frac{N_t}{N_0} = \left(\frac{1}{2}\right)^{t/t_{1/2}}$$
$$= \left(\frac{1}{2}\right)^{\frac{60}{12}}$$
$$= \left(\frac{1}{2}\right)^{5} = \frac{1}{32}$$

So, the fraction remains after 60 hrs is $\frac{1}{32}$.

Ans.

Q.9 The first order rate const of the reaction $A \rightarrow B$ is K sec^{-1}. Calculate the average life of A molecules.

t_a = Average life of 1st order reaction
$$= \frac{1}{N_0}\int_0^{\alpha} N_t \cdot dt$$
$$= \frac{1}{N_0}\int_0^{\alpha} N_0 e^{-K_1 t} dt$$
$$= \int_0^{\alpha} e^{-K_1 t} \cdot dt$$
$$= \left[\frac{e^{-K_1 t}}{-K_1}\right]_0^{\alpha}$$
$$= \left[\frac{e^{-K_1 t}}{K_1}\right]_{\alpha}^{0} = \frac{1}{K_1}$$

q.10 obtain the integrated rate equation for the elementary reaction $A + B \longrightarrow$ Product, when the initial conc. of A and B, respectively 'a' and b are (i) different $(b \neq a)$ & (ii) same $(b = a)$. Show also that the 2nd result may be directly obtained from the 1st form under the limit $b \rightarrow a$, given that $\ln(1+x) = x$ as $x \rightarrow 0$

(i) Ans:

$$A + B \longrightarrow P$$

	A	B	P
Initial conc at t = 0	a	b	0
conc at time T = t	(a−x)	(b−x)	x

The initial conc. of A and B are a and b respectively. Let x conc. of product is formed after time t. Thus the conc. of A and B after time t are (a−x) and (b−x) respectively. The differential rate equation is

$$\frac{dx}{dt} = K_2 \cdot C_A \cdot C_B = K_2 (a-x) \cdot (b-x)$$

Separating the variable and integrating, we get.

$$\frac{1}{(a-b)} \ln \left| \frac{b(a-x)}{a(b-x)} \right| = K_2 t$$

(ii)

$$A + B \longrightarrow P$$

Initial conc at time t=0 $\quad a \quad b \longrightarrow x$

conc. at time t $\quad (a-x) \quad (b-x) \quad x$

The differential rate equation

$$\frac{dx}{dt} = k_2(a-x)(b-x)$$

but $a = b$, so we can write

$$\frac{dx}{dt} = k_2 \times (a-x)^2$$

Separating the variable and integrating, we get

$$\frac{x}{a(a-x)} = k_2 t$$

Part — 2

The first result is

$$\frac{1}{(a-b)} \times \ln \left| \frac{b(a-x)}{a(b-x)} \right| = k_2 t$$

or, $\frac{1}{(a-b)} \times \ln \left[1 + \frac{(a-b)x}{a(b-x)} \right] = k_2 t$

since $b \to a$, hence $\frac{(a-b)x}{a(b-x)} \to 0$

so taking approximation, $\ln(1+x) = x$
$\quad\quad x \to 0$

we get $\frac{1}{\cancel{(a-b)}} \times \frac{\cancel{(a-b)}x}{a(b-x)} = k_2 t$

or, $\frac{x}{a(b-x)} = k_2 t$ or $\frac{x}{a(a-x)} = k_2 t$ (since $b \to a$)

finally we get the 2nd result from 1st result

Q 11 Show that the ratio $t_{1/2} : t_{3/4}$ of the nth order reaction can be written as a function of n alone. What is the utility of this ratio? calculate it's value for 2nd order reaction.

For nth order reaction

$$t = \frac{1}{(n-1)K_n}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

For $t = t_{1/2}$, $x = a/2$ and thus

$$t_{1/2} = \frac{1}{(n-1)K_n}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

For $t = t_{3/4}$, $x = \frac{3a}{4}$ and thus

$$t_{3/4} = \frac{1}{(n-1)K_n}\left[\frac{4^{n-1}-1}{a^{n-1}}\right]$$

$$= \frac{1}{(n-1)K_n}\left[\frac{(2^{n-1}-1)(2^{n-1}+1)}{a^{n-1}}\right]$$

Therefore, the ratio

$$t_{1/2} : t_{3/4} = \frac{1}{2^{n-1}+1}$$

The ratio is thus a function of n.

2nd part: Knowing the ratio, we can determine the order (n) of the reaction.

3rd part :

For 2nd order reaction, $n = 2$

thus the ratio,

$$t_{1/2}/t_{3/4} = \frac{1}{2^{n-1}+1} = \frac{1}{2^{2-1}+1}$$

$$= \frac{1}{3}.$$

Q. 12 Discuss the principle of any one method for the determination of the order of a chemical reaction.

Ans : Method of Half-life period

Half-life ($t_{1/2}$) is defined as the time for half decomposition of the reactants. It is seen also that $t_{1/2} \propto \frac{1}{a^{n-1}}$

where, a = Initial conc. of the reactant for n order reaction.

Let us carry two sets of a reaction with different initial conc. a and a' of the reactant. Thus for the reaction

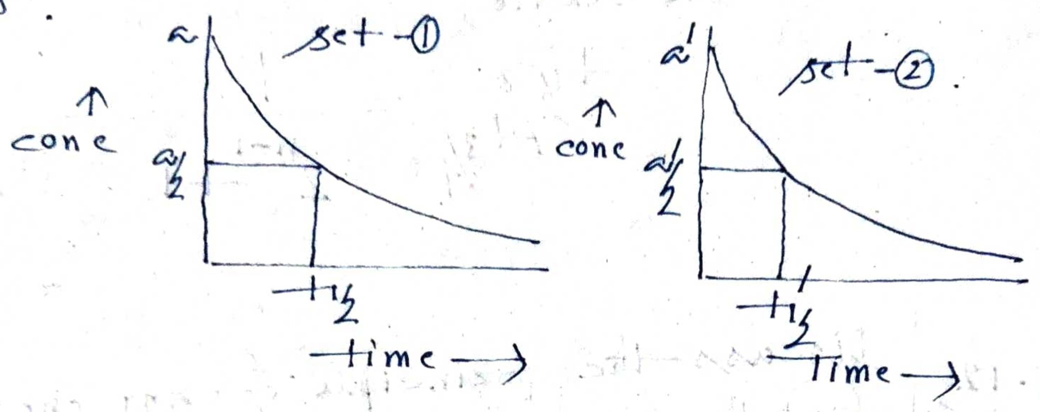
$$t_{1/2}/t'_{1/2} = \left(\frac{a'}{a}\right)^{n-1}$$

Where, $t_{1/2}$ and $t'_{1/2}$ are the half-life periods of the reaction at the initial conc. a and a' of the reactant.

Taking Log and rearranging, we have

$$n = 1 + \frac{\log(t_{1/2}/t'_{1/2})}{\log(a'/a)}$$

using this relation, n can be evaluated provided half-life periods of the reaction are determined at the two sets.



Q.13 Decomposition of a subst A is studied at two different initial conc. a_1 and a_2, where $a_1 = 3a_2$. If the observed half-lifes t_1 and t_2 follow the ratio $t_2 : t_1 = 2:1$. Find the order of the decomposition process.

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

$$\text{or, } \frac{2}{1} = \left(\frac{3a_2}{a_2}\right)^{n-1}$$

$$\text{or, } 3^{n-1} = 2$$

$$\text{or, } (n-1) = \frac{\ln 2}{\ln 3}$$

$$\text{or, } n = 1 + \frac{\ln 2}{\ln 3}$$

$$= 1 + \frac{.693}{1.098}$$

$$= 1 + .63$$

$$= 1.63.$$

Q.14. consider the simplest consecutive reaction involving first order steps: $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, where only A is present initially. If a_t, b_t and c_t are the respective conc. of A, B and C at time t, show schematically the variation of these quantities with time.

Ans:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

~~at~~ a time t $\quad a_t \quad b_t \quad c_t$

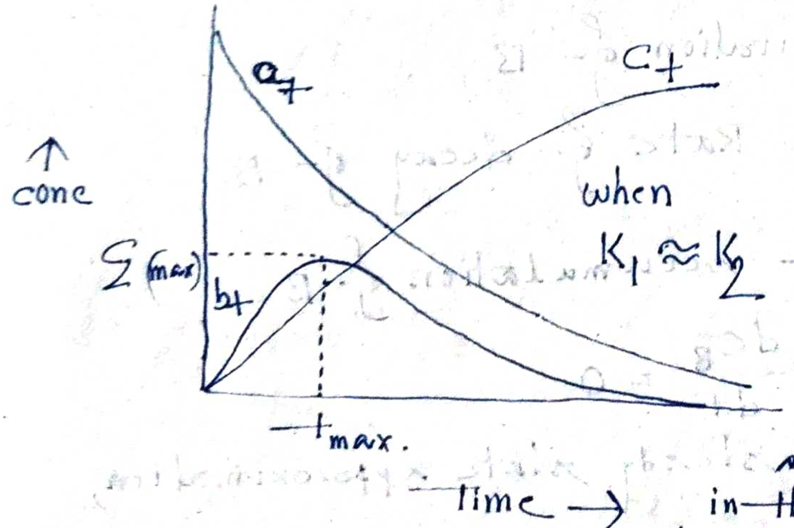
The initial conc. of A is C_0. We can write the ~~ex~~ (determine) the conc. of a_t, b_t and c_t as bellow

$$a_t = C_0 \cdot e^{-K_1 t}$$

$$b_t = \frac{K_1 C_0}{K_2 - K_1} \cdot \left[e^{-K_1 t} - e^{-K_2 t} \right]$$

$$c_t = C_0 \left[1 - \frac{K_2}{K_2 - K_1} \cdot e^{-K_1 t} - \frac{K_1}{K_1 - K_2} \cdot e^{-K_2 t} \right]$$

The conc. of A, B and C when plotted against t, ~~the~~ following type of curve are obtained.



The conc of A (a_t) decreases exponentially with time t. The conc. of intermediate B (b_t) rises from zero to a max^m and then drops back to zero and finally C (c_t) dominates in the mixture, reaching to the value of C_0.

Q 15. Assume now a steady state approximation for the above problem to obtain expressions for b_t and c_t. Explain clearly when the approximation is valid.

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

When the intermediate (B) is highly reactive, the situation becomes as $K_2 \gg K_1$

ie the intermediate B immediately breaks into product C as soon as it forms from A.

The conc. of B becomes as

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

but $K_2 \gg K_1$, hence $K_2 - K_1 = K_2$

$e^{-K_2 t} = 0$

since K_2 = Large.

Thus,
$$C_2 = \frac{K_1 C_0}{K_2} \cdot e^{-K_1 t}$$

since $C_1 = C_0 \cdot e^{-K_1 t}$

or, $K_2 C_2 = K_1 C_1$

ie Rate of formation of B

= Rate of decay of B

Thus, Rate of accumulation of B

ie
$$\frac{dC_B}{dt} = 0$$

This is known as steady state approximation,

$$\frac{dC_{\text{intermediate}}}{dt} = 0$$

The steady state approximation helps to simplify the Kinetic calculation of multistep reaction.

$$\frac{dC_B}{dt} = K_1 C_A - K_2 C_B$$

But steady state approximation state that $\frac{dC_B}{dt} = 0$, since B is highly reactive.

$$0 = K_1 C_A - K_2 \cdot C_B$$

or, $$C_B = \frac{K_1}{K_2} \cdot C_A$$

or, $$C_B = \frac{K_1}{K_2} \cdot C_0 \cdot e^{-K_1 t}$$

or, $$\boxed{b_t = \frac{K_1}{K_2} \cdot C_0 \cdot e^{-K_1 t}}$$

Again,
$$\frac{dC_c}{dt} = K_2 \cdot C_B = K_2 \cdot b_t$$

or, $$\frac{dC_c}{dt} = K_2 \times \frac{K_1}{K_2} \times C_0 \cdot e^{-K_1 t}$$

or, $$\frac{dC_c}{dt} = K_1 \cdot C_0 \cdot e^{-K_1 t}$$

or, $$\int dC_c = K_1 C_0 \int e^{-K_1 t} \cdot dt$$

or, $$C_t = K_1 \cdot C_0 \cdot \left(\frac{1}{-K_1}\right) \cdot e^{-K_1 t} + I_c$$

When $t = 0$, $C_t = 0$, so, $I_c = C_0$

Hence, $$\boxed{C_t = C_0\left[1 - e^{-K_1 t}\right]}$$

Q. 16 Slowest step in a multistep reaction is the rate determining step. Discuss giving one example.

$$A \xrightarrow[\text{Slow}]{K_1} B \xrightarrow[\text{Fast}]{K_1'} C$$

The formulation of the kinetics of the consecutive reaction illustrate the above. Let the rate const. (K_1') is much greater than the rate const. (K_1).

The expression of conc of the product

$$C_3 = C_0\left[1 - \frac{K_1}{K_1 - K_1'} \cdot e^{-K_1't} - \frac{K_1'}{K_1' - K_1} \cdot e^{-K_1t}\right]$$

But, $K_1' \gg K_1$, hence $K_1' - K_1 \approx K_1'$

$K_1 - K_1' \approx -K_1'$

and $e^{-K_1't} = 0$

since $K_1' = \text{Large}$.

Thus, $C_3 = C_0\left[1 - e^{-K_1t}\right]$

This shows that the formation of C depends only on the smaller rate const (K_1).

For this reason, the step with the slowest rate is called the rate-determining step of the reaction.

Q. 17

consider the following transuramic transformation with half lives as indicated

$$^{239}_{92}U \xrightarrow[23.5\,min\ (K_1)]{\beta} {}^{239}_{93}Np \xrightarrow[235\,days\ (K_1')]{\beta} {}^{239}_{94}Pu$$

If one starts with 10^{16} molecule number of uranium atoms initially, approximately How many Pu atoms will be created after 400 days? Derive the relation that you employ in solving the problem.

Ans: $A \xrightarrow{K_1} B \xrightarrow{K_1'} C$

$$^{239}_{92}U \xrightarrow{K_1} {}^{239}_{93}Np \xrightarrow{K_1'} {}^{239}_{94}Pu$$

initial conc	C_0	0	0
at a time t	c_1	c_2	c_3

so, we can write $C_0 = c_1 + c_2 + c_3$

The rate law decomposition of $^{239}_{92}U$ is

$$-\frac{dc_1}{dt} = K_1 \cdot c_1$$

separating the variable and integrating we get $c_1 = c_0 \cdot e^{-K_1 t}$

Rate of accumulation of B is

$$\frac{dc_2}{dt} = K_1 c_1 - K_1' c_2$$

or, $$\frac{dc_2}{dt} + K_1' c_2 = K_1 c_1$$

or, $$\frac{dc_2}{dt} \times e^{K_1' t} + K_1' c_2 e^{K_1' t} = K_1 c_1 \cdot e^{K_1' t}$$

or, $\frac{d}{dt}(c_2 \cdot e^{K_1' t}) = K_1 (c_0 \cdot e^{-K_1 t}) \cdot e^{K_1' t}$

separating the variables and integrating,

or, $\int d(c_2 \cdot e^{K_1' t}) = \int K_1 \cdot c_0 \cdot e^{(K_1' - K_1)t} dt$

or, $c_2 \cdot e^{K_1' t} = \frac{K_1 \cdot c_0}{K_1' - K_1} \cdot e^{(K_1' - K_1)t} + I_c$

when $t = 0$, $c_2 = 0$ and $I_c = -\frac{K_1 \cdot c_0}{K_1' - K_1}$

putting the integration const I_c, we get

$$c_2 = \frac{K_1 c_0}{(K_1' - K_1)} \cdot \left[e^{-(K_1 t)} - e^{-K_1' t}\right]$$

Now the conc of the product c is obtained as, $c_3 = c_0 - c_1 - c_2$

$$c_3 = c_0 - c_0 \cdot e^{-K_1 t} - \frac{K_1 c_0}{K_1' - K_1}\left(e^{-K_1 t} - e^{-K_1' t}\right)$$

or, $c_3 = c_0 \left[1 - e^{-K_1 t} - \frac{K_1}{K_1' - K_1} \cdot e^{-K_1 t} + \frac{K_1}{K_1' - K_1} \cdot e^{-K_1' t}\right]$

or, $c_3 = c_0 \left[1 - \frac{K_1'}{K_1' - K_1} \cdot e^{-K_1 t} - \frac{K_1}{K_1 - K_1'} \cdot e^{-K_1' t}\right]$

This is the required relation for this problem.

$K_1 = \frac{0.693}{23.5}\ \text{min}^{-1}$, $K_1' = \frac{0.693}{235}\ \text{day}^{-1}$

so, $K_1 >> K_1'$

using the approximation, $(K_1 >> K_1')$

we get $C_3 = C_0\left[1 - e^{-K_1' t}\right]$

or $N_3 = N_0\left[1 - e^{-K_1' t}\right]$

$= 10^6 \times \left[1 - e^{-\frac{0.693}{235} \times 400}\right]$

$= 6.9 \times 10^{15}$

so, the No. of Pu atoms created after 400 days $= 6.9 \times 10^{15}$.

Q.18 consider the consecutive reaction involving 1st order steps, $A \xrightarrow{K_1} B \xrightarrow{K_2} C$. The conc. of C at any time t is given by

$$C(C) = C(A_0)\left[1 - \frac{K_2}{K_2 - K_1} \cdot e^{-K_1 t} - \frac{K_1}{K_1 - K_2} \cdot e^{-K_2 t}\right]$$

Explain the significance of the result when $K_1 << K_2$.

Ans :

$$C(c) = C(A_0)\left[1 - \frac{K_2}{K_2 - K_1}\cdot e^{-K_1 t} + \frac{K_1}{K_2 - K_1}\cdot e^{-K_2 t}\right]$$

this is the expression of conc of the product. When $K_1 << K_2$

$$K_2 - K_1 \approx K_2$$

and $e^{-K_2 t} \approx 0$

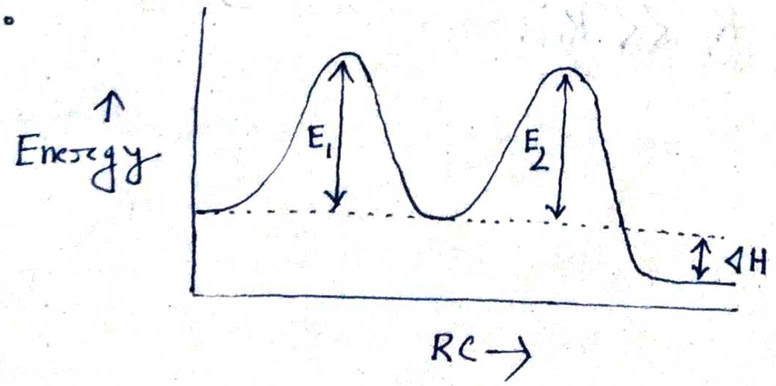
so, the equation reduced to

$$C(c) = C(A_0)\left[1 - e^{-K_1 t}\right]$$

This shows that the formation of c depends only on the smaller rate const (K_1). For this reason, the step with slowest step is called the rate-determining step of the reaction.

Q 19. Draw a typical diagram showing energy as a function of reaction coordinate. Indicate in the diagram the following.
The consecutive reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ with $K_1 \approx K_2$ and overall $A \rightarrow C$ exothermic.

Ans :



Q.20 consider the opposing reaction

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

$t=0$, a $\quad 0$

$t=t$, $(a-x)$ $\quad x$

both the forward and backward reaction are 1st order. Write the rate equation and integrate. Show that the expression may be written as

$$\ln\left|\frac{x_e}{x_e - x}\right| = (K_1 + K_{-1})t$$

where x_e is the equil^m value of x. ~~Discu~~ Discuss the case where $K_1 \gg K_{-1}$.

Ans:

In case of opposing reaction

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

initial conc
$T=0$ $\quad a \quad 0$

at time
$T=t$ $\quad (a-x) \quad x$

so, $$\frac{dx}{dt} = \text{Rate of formation of } B - \text{Rate of decomposition of } B$$

$$= K_1(a-x) - K_{-1}\cdot x$$

or, $$\frac{dx}{dt} = K_1 a - (K_1 + K_{-1})x$$

Separating the variable and integrating we get,

$$\int \frac{dx}{K_1 a - (K_1 + K_{-1})x} = \int dt \quad \text{---} ①$$

Let $K_1 a - (K_1 + K_{-1}) x = Z$

or, $dZ = -(K_1 + K_{-1})\, dx$

or, $dx = -\frac{1}{(K_1 + K_{-1})} \times dZ$

putting the value of Z and dx in the equation ①, we get

$$-\frac{1}{(K_1 + K_{-1})} \int \frac{dZ}{Z} = \int dt$$

or, $-\frac{1}{(K_1 + K_{-1})} \times \ln Z = t + I_c$

putting the value of Z, we get

or, $-\frac{1}{(K_1 + K_{-1})} \times \ln \left| K_1 a - (K_1 + K_{-1}) x \right| = t + I_c$

When $t = 0$, $x = 0$, so $I_c = -\frac{1}{(K_1 + K_{-1})} \times \ln K_1 a$

Now putting the value of I_c and we get

or, $$\frac{1}{(K_1 + K_{-1})} \ln \left| \frac{K_1 a}{K_1 a - (K_1 + K_{-1}) x} \right| = t$$

or, $$\ln \left| \frac{K_1 a}{K_1 a - (K_1 + K_{-1}) x} \right| = (K_1 + K_{-1}) t \quad \text{—— ②}$$

At equilibrium, $\left[\frac{dx}{dt}\right]_e = 0$

so, $\left(\frac{dx}{dt}\right)_e = K_1 (a - x_e) - K_{-1} x_e = 0$

$= K_1 a - (K_1 + K_{-1}) x_e = 0$

so, $K_1 a = (K_1 + K_{-1}) x_e$

putting this value in the equation 2, we get

$$\ln\left|\frac{(K_1+K_{-1})x_e}{(K_1+K_{-1})x_e-(K_1+K_{-1})x}\right| = (K_1+K_{-1})t$$

or, $$\ln\left|\frac{x_e}{x_e-x}\right| = (K_1+K_{-1})t$$

(proved a.)

2nd part.

When $K_1 \gg K_{-1}$

then, $K_1 a - (K_1+K_{-1})x = K_1 a - K_1 x$

$K_1 + K_{-1} = K_1$

neglecting the value of K_{-1}

Now, the equation ② changes to

$$\ln\left|\frac{K_1 a}{K_1 a - K_1 x}\right| = K_1 \cdot t$$

or, $$\ln\left|\frac{a}{a-x}\right| = K_1 t$$

Thus, we see that when the reverse reaction rate is very slow compare to forward reaction ($K_1 \gg K_{-1}$), the integrated rate equation becomes that of simple 1st order reaction.

a.

Q:21 | Specific rate const. of a reaction has the unit litre^2. mole^{-2}. Sec^{-1}. What is the order ?

$$\underset{(a-x)}{A} \longrightarrow \underset{x}{P}$$

For nth order reaction the rate equation is

$$\frac{dx}{dt} = K\cdot(a-x)^n$$

$$\text{or, } K = \frac{dx}{(a-x)^n} \times \frac{1}{dt}$$

so, the unit of $K = \frac{\text{conc}}{(\text{conc})^n} \times \frac{1}{\text{Time}}$

$$= (\text{conc})^{1-n} \times \text{Time}^{-1}$$

$$= \left(\frac{\text{mole}}{\text{Litre}}\right)^{1-n} \times \text{Sec}^{-1}$$

$$= \text{mole}^{1-n} \times \text{Litre}^{n-1} \times \text{Sec}^{-1}$$

so, we can write

$$\text{Litre}^{n-1} \times \text{mole}^{1-n} \times \text{Sec}^{-1} = \text{Litre}^{2} \times \text{mole}^{-2} \times \text{Sec}^{-1}$$

Hence, from this equation, we get

$$n-1 = 2$$

$$\text{or, } n = 3$$

so, the order is 3.

Q.22 While it is expected that larger amount of subst would take a ~~ta~~ longer time to decompose, the dependence of half life on the initial conc do not indicate so in general.

Ans: Decomposition rate is not usually const except for zero order reaction. According to mass action law, larger amt of subst, larger the decomposition rate and smaller time is required for its half-decomposition ie smaller will be the half-life. only for the case of zero order reaction, rate = K and thus larger amt. of subst, longer time requires to decompose and so half-life ($t_{1/2}$) $\propto$ initial conc.

Q.㉓ The decomposition of a gas at an initial pressure of 600 mm Hg was studied in a closed vessel at a certain tempr. the gas was found to be 50% decomposed in 30 min and 75% decomposed in 90 min. Show that the reaction is 2nd order, and calculate the rate const.

Ans: given $t_{1/2} = 30$ min and $t_{3/4} = 90$ min.

The ratio $t_{1/2} : t_{3/4} = 30 : 90 = \frac{1}{3}$

we have, ratio $= \frac{1}{2^{n-1}+1} = \frac{1}{3}$

$2^{n-1}+1 = 3$

$2^{n-1} = 2 = 2^1$

$n-1 = 1$

$n = 2$

$\therefore 2^{n-1}+1 = 3$ (~~$\therefore 2^{n-1} = 14 = 2^2$~~

~~$\therefore n-1 = 2 \therefore n = 3$~~)

Show the reaction is 2nd order reaction.

again,

$$k_2 = \frac{1}{at} \times \frac{x}{a-x}$$

$$= \frac{1}{600 \times 30} \times \frac{300}{600-300} (mm\,Hg)^{-1} min^{-1}$$

$$= 5{\cdot}5 \times 10^{5}\ mmHg^{-1} \times min^{-1}$$

Q ㉔ For a reaction A → B + C It is found that the rate increases by a factor 2·25 when the conc. of A is increased by a factor of 1·5 at the same tempr. what is the order w.r.t to A ?

Ans: we have,

$$\frac{R_1}{R_2} = \left(\frac{C_1}{C_2}\right)^n$$

$$or,\ 2{\cdot}25 = (1{\cdot}5)^n$$

$$or,\ (1{\cdot}5)^2 = (1{\cdot}5)^n \quad or,\ n = 2$$

Q. 25 Rate of a reaction, A + B → Product is given below as a function of different initial conc. of A and B.

[A] mole lit⁻¹	[B] mole lit⁻¹	Initial rate mole. lit⁻¹. min⁻¹
0·01	0·01	0·005
0·02	0·01	0·010
0·01	0·02	0·005

Determine the order of the reaction w.r.t A and w.r.t B. what is the half life of A in the reaction.

Q.26 comment on the statements:
i) Order of a reaction is always integral.
ii) Stoichiometry of the reaction indicates its order.

Ans:- The given statements are wrong. order is not always an Integer. It may be fraction, Zero or even negative. Furthermore It is an experimentally determinable quantity. So It can not be known from stoichiometry.

Q.27 For a given reaction rate is independent of conc, will it go to completion?

Ans: if the rate of a reaction does not depend on concentration of reactant, then it is a zero order reaction. we know zero order reactions go to completion.

Q.28 Are all reactions characterized by some order?

Ans: All reactions are not characterized by some order. chain reactions follow some complicated mechanism. Expression for rate for such reactions consists of reactant term in both numerator and denominator, product terms are also found in rate expressions. So they ~~are~~ can not be characterized by order.

q.29 | A certain reactant A gives two products B and C; how can you know that the path is (i) parallel (ii) consecutive ?

Ans: When a reactant A gives two products B and C the path may be parallel $\left[A \begin{cases} \to B \\ \to C \end{cases}\right]$ or consecutive $(A \to B \to C)$. In first case the concentration ratio C_B/C_C will remain same at any time, in the second case the ratio C_B/C_C will varry with time.

q.30 | What is the significance of $E_1 - E_2$ (E = activation energy) for a reversible reaction.

Ans: During derivation of Arrhenius equation from vant Hoff's equation it can be shown that $E_1 - E_2$ = Heat of reaction (ΔH).

q.31 | A certain reaction takes place in three steps with rate consts K_1, K_2 and K_3 and activation energy E_1, E_2 and E_3. If overall rate const. $K = K_1K_3/K_2$ show that over all activation energy

$$E = E_1 - E_2 + E_3$$

Ans: Over all rate const. (K) is related with stepwise rate constants as –

$$K = \frac{K_1 K_3}{K_2}$$

So, $\ln K = \ln K_1 - \ln K_2 + \ln K_3$

putting the arrhenius equation

$$\ln K = \ln A - \frac{E}{RT}$$

$$\ln A - \frac{E}{RT} = \ln \frac{A_1 A_3}{A_2} - \frac{E_1 - E_2 + E_3}{RT}$$

compairing between like terms,

$$\boxed{E = E_1 - E_2 + E_3}$$

Q. 32 consider the reaction

$$\begin{tikzcd} & B \\ A \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & C \end{tikzcd}$$

Show that activation energy (E_a) for the disappearance of A is $E_a = \frac{K_1 E_1 + K_2 E_2}{K_1 + K_2}$

Where E_1 and E_2 are activation energies for paths with rate consts K_1 and K_2.

Ans: For the reaction

$$\begin{tikzcd} & B \\ A \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & C \end{tikzcd}$$

if K is overall rate const, then $K = (K_1 + K_2)$. Now from Arrhenius equation

$$\frac{d\ln K}{dt} = \frac{E_a}{RT^2} \quad \text{——— ①}$$

or, $$\frac{d\ln (K_1+K_2)}{dt} = \frac{E_a}{RT^2}$$

or, $$\frac{1}{(K_1+K_2)} \times \frac{d}{dt}(K_1+K_2) = \frac{E_a}{RT^2}$$

putting $K_1 = A_1 e^{-E_1/RT}$ and $K_2 = A_2 \cdot e^{-E_2/RT}$

$$\frac{d\ln(K_1+K_2)}{dt} = \frac{1}{(K_1+K_2)} \cdot \frac{d}{dt}(K_1+K_2)$$

$$= \frac{1}{(K_1+K_2)} \left[\frac{d}{dT}\left(A_1 e^{-E_1/RT}\right) + \frac{d}{dT}\left(A_2 \cdot e^{-E_2/RT}\right)\right]$$

$$= \frac{1}{(K_1+K_2)} \cdot \left[A_1 \cdot e^{-E_1/RT} \cdot \frac{E_1}{RT^2} + A_2 e^{-E_2/RT} \cdot \frac{E_2}{RT^2}\right]$$

$$= \frac{1}{RT^2(K_1+K_2)} \left[K_1E_1 + K_2E_2\right]$$

$$= \frac{1}{RT^2} \cdot \left[\frac{K_1E_1 + K_2E_2}{K_1+K_2}\right] \text{———} ②$$

comparing the equation ① and ②, we get

$$E_a = \left(\frac{K_1E_1 + K_2E_2}{K_1+K_2}\right)$$

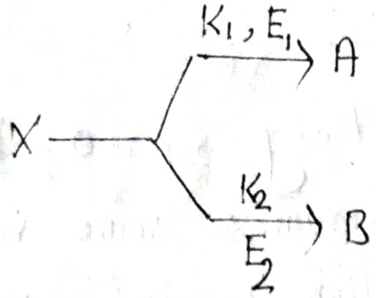
(proved)

Q.33 Substance X undergoes parallel reaction as follows $X \to A\ (K_1, E_1)$; $X \to B\ (K_2, E_2)$

$X \to A + B$ (overall) (K, E)

Show that $\boxed{E = f_1E_1 + f_2E_2}$

[K_i are reat consts, E_i are energies of activation and $f_i = K_i/K$]



The overall activation energy/mole

$$E = \frac{K_1E_1 + K_2E_2}{K_1+K_2}$$

But for parallel reaction overall rate const $K = K_1 + K_2$.

So,
$$E = \frac{K_1E_1 + K_2E_2}{K}$$
$$= \frac{K_1}{K}\cdot E_1 + \frac{K_2}{K}\cdot E_2$$
$$= f_1 E_1 + f_2 E_2$$

Q.34 | Draw conc. vs time for three species A, B, C undergoing first order consecutive reaction —
$A \xrightarrow{K_1} B \xrightarrow{K_2} C$ under the conditions
(i) $K_1 \approx K_2$ (ii) $K_1 \gg K_2$ and $K_1 \ll K_2$

Ans: It can be shown by calculation that for a consecutive reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, the concⁿ of A, B and C after time t are

$$C_A = C_0 \cdot e^{-K_1t}$$

$$C_B = \frac{K_1C_0}{K_2-K_1}\left[e^{-K_1t} - e^{-K_2t}\right]$$

and
$$C_C = C_0\left[1 - \frac{K_2}{K_2-K_1}\cdot e^{-K_1t} - \frac{K_1}{K_1-K_2}\cdot e^{-K_2t}\right]$$