

Chemical Kinetics.

The branch of physical chemistry that deals with rate of rxns is called chemical kinetics. It involves:

- Rate of rxn & rate laws.
- Factors affecting rate (T, P, conc., catalyst).
- Mechanism or sequence of steps.

Rxn Rate:- The rate of rxn is defined as the change in conc. of any reactant or product per unit time.

for $A \rightarrow B$.

$$\text{rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt} \quad [\text{mol lit}^{-1}\text{s}^{-1}]$$

Average Rate:

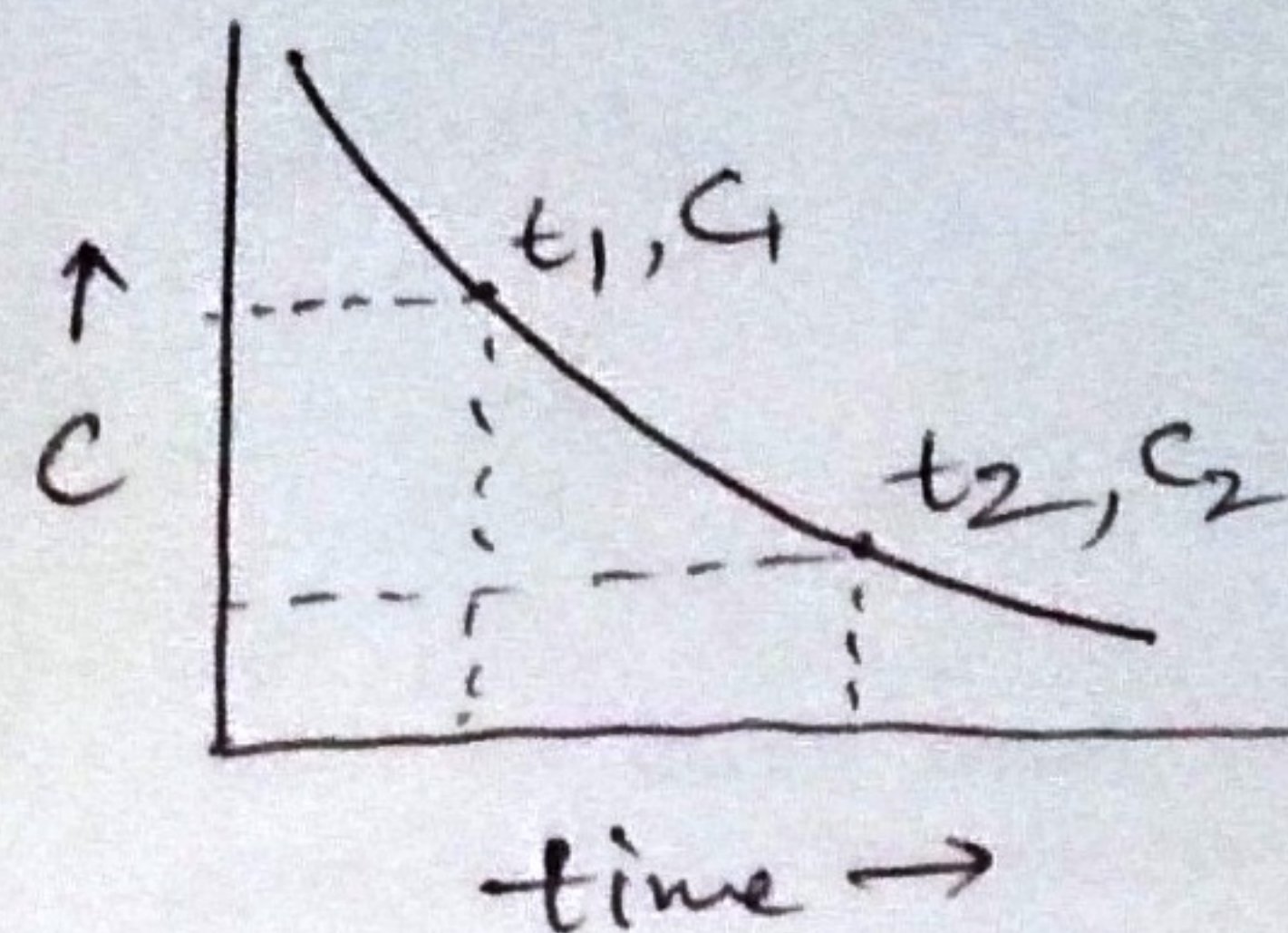
$$r = -\frac{[A]_{t_2} - [A]_{t_1}}{(t_2 - t_1)} \quad A \rightarrow B$$

} changes for different intervals.
Not always useful.

Instantaneous Rate: "At any time the instantaneous rate is equal to the slope of the tangent drawn to the curve at that time."

$$r = \frac{d[A]_t}{dt}$$

(1)



$$\text{Average rate} = \frac{C_2 - C_1}{t_2 - t_1}$$



Instantaneous rate = slope

Rate Law: Rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

$$\text{rate} \propto [A]^n$$

$$r = k[A]^n$$

for $2A + B \rightarrow P$. (Reaction)

$$r = k[A]^2[B]^1 \quad (\text{Rate Law})$$

An expression which shows how the reaction rate is related to concentrations is called the rate law.

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Rate Constant:-

for $A + B \rightarrow P$.

$$\frac{dx}{dt} = k[A][B]$$

when $[A] = 1$; $[B] = 1$, $k = \frac{dx}{dt}$.

⇒ Rate of rxn when the molar conc. of each reactant is unity.

Order of Rxn:

The order of rxn is given by the number of concentration terms of atoms or molecules, which determine the rate law.

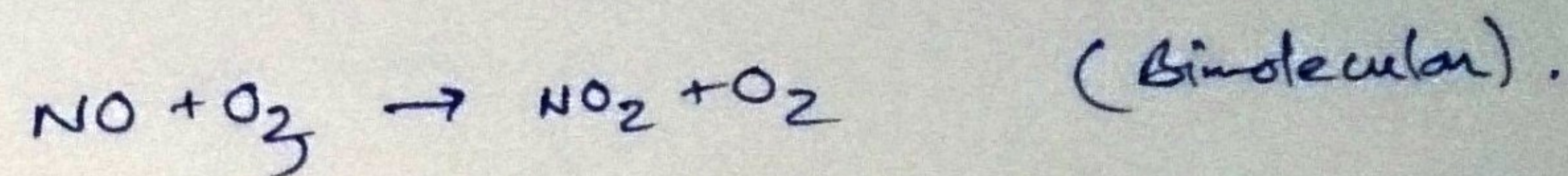
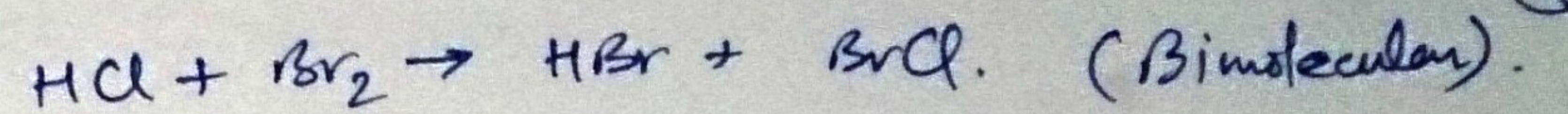
$$\therefore r = \frac{dx}{dt} = k[A] \quad \text{for I order.}$$

$$r = \frac{dx}{dt} = k[A][B] \quad \text{or } k[A]^2 \quad \left. \vphantom{\frac{dx}{dt}} \right\} \text{II order.}$$

$$\frac{dx}{dt} = k[A]^3 \quad \left. \vphantom{\frac{dx}{dt}} \right\} \text{III order.}$$

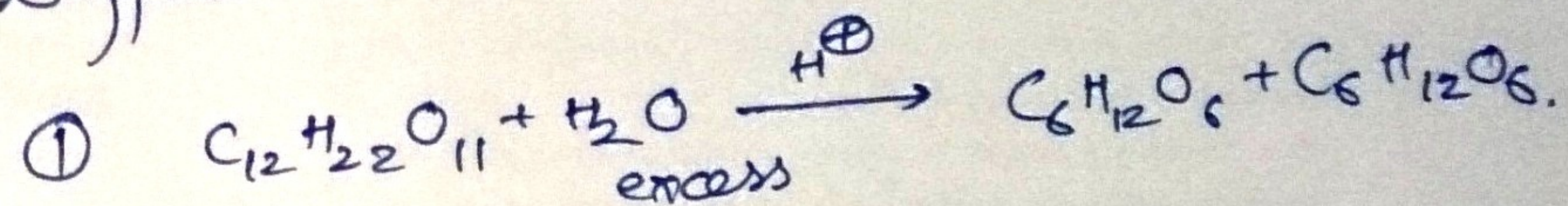
Molecularity: The number of molecules of reactants that are used to form the activated complex.

③



all unimolecular rxns are I order rxns.
(reverse is not true!)

Differences:



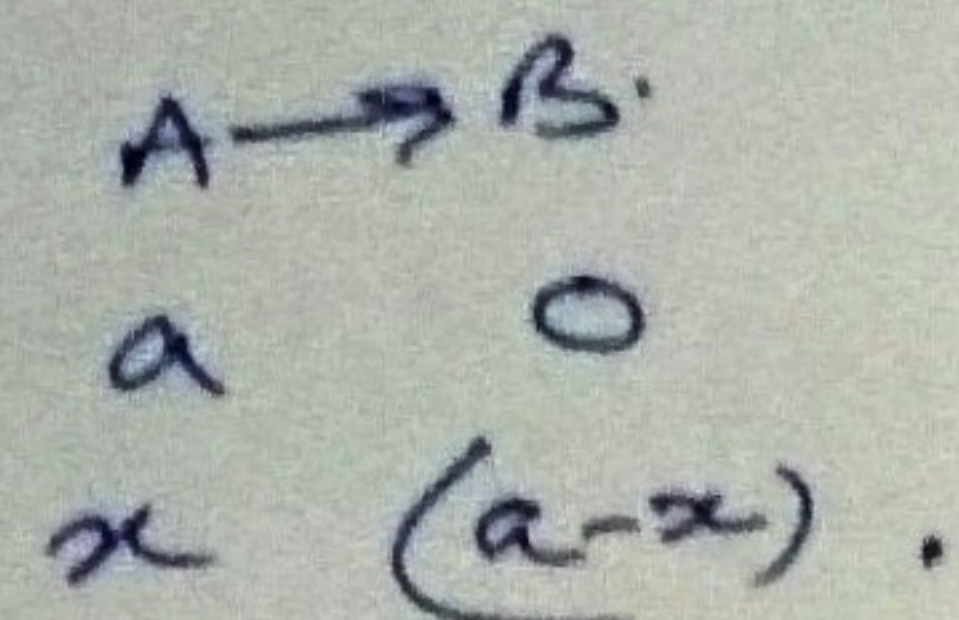
Order 1, molecularity 2.

② { Molecularity is theoretical.
Order is experimental.

③ { Molecularity is whole number.
Order can be zero or fractional.

④ { m. Obtained from single ^{step} balanced rxn.
Order can't be obtained from balanced chemical equations.

Zero Order rxn:-



rate r , $\frac{dx}{dt} = k (\text{constant})$

$$dx = k dt$$

on int.

$$x = kt + I$$

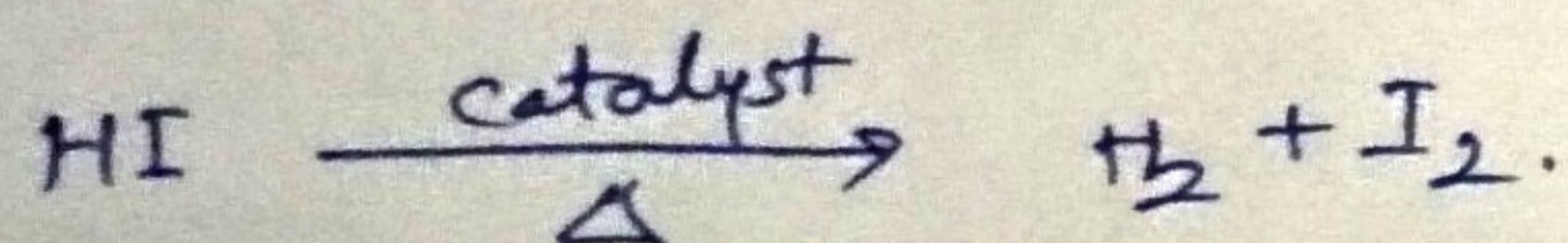
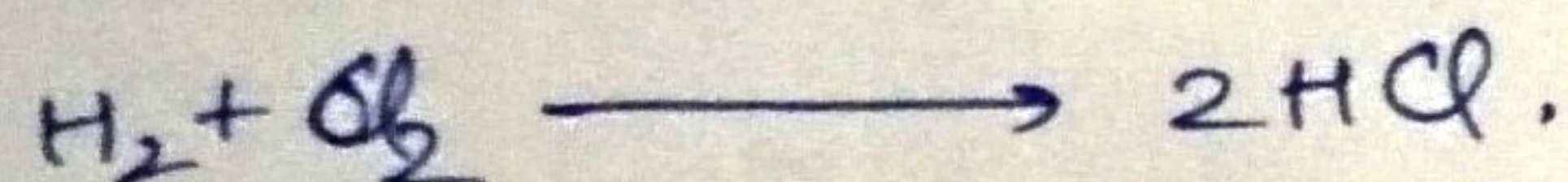
at $t=0$, $x=0$

$$\Rightarrow I=0$$

$$\Rightarrow \boxed{x = kt}$$

unit of $k = \text{mol lit}^{-1} \text{time}^{-1}$.

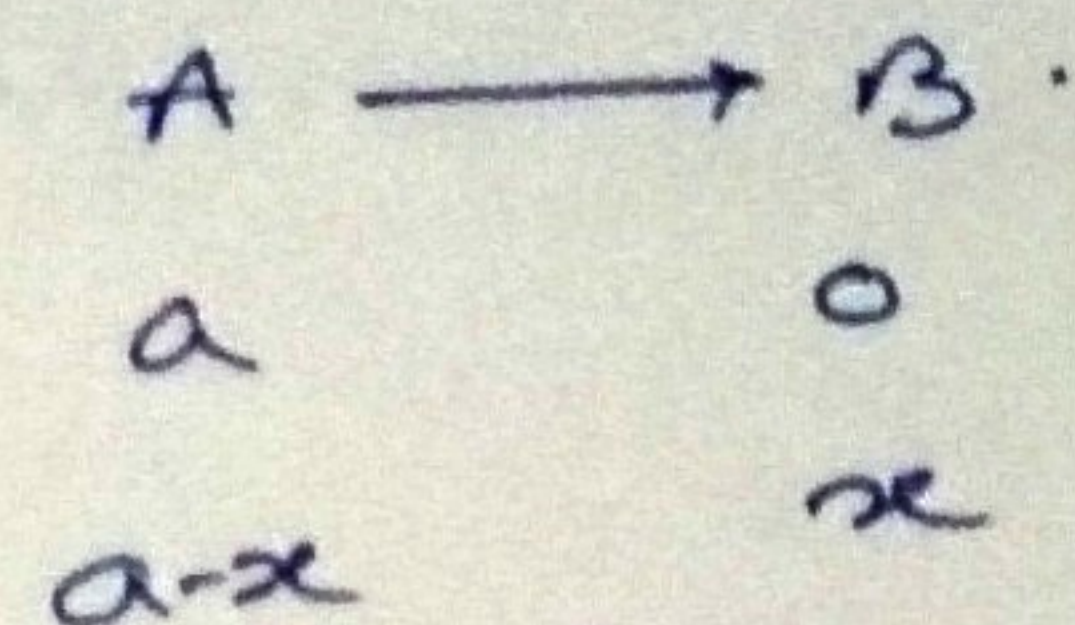
examples:-



⑤

first Order rxn:-

⑥



$$\frac{dx}{dt} = k [A]$$

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

$$\frac{dx}{a-x} = k dt$$

————— ⑦

on int.

$$-\ln(a-x) = kt + I$$

at $t=0$, $x=0$

$$\Rightarrow I = -\ln a$$

$$\Rightarrow -\ln(a-x) = kt - \ln a$$

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\boxed{k = \frac{2.303}{t} \log \frac{a}{a-x}}$$

int. eq. ① between limits t_1 & t_2 .

$$\boxed{-k = \frac{2.303}{(t_2 - t_1)} \log \frac{a-x_2}{a-x_1}}$$

unit of $k = \text{time}^{-1}$.

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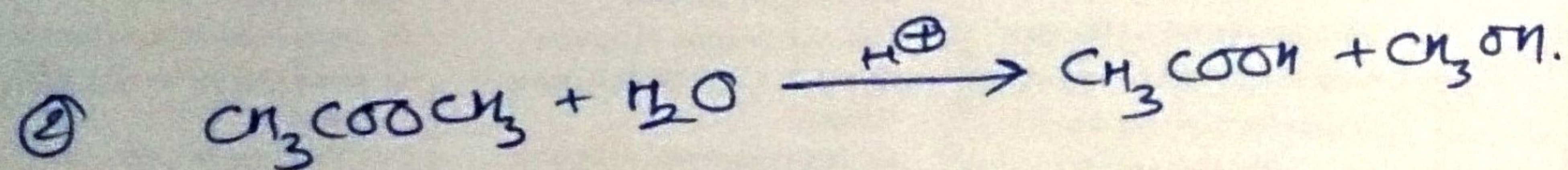
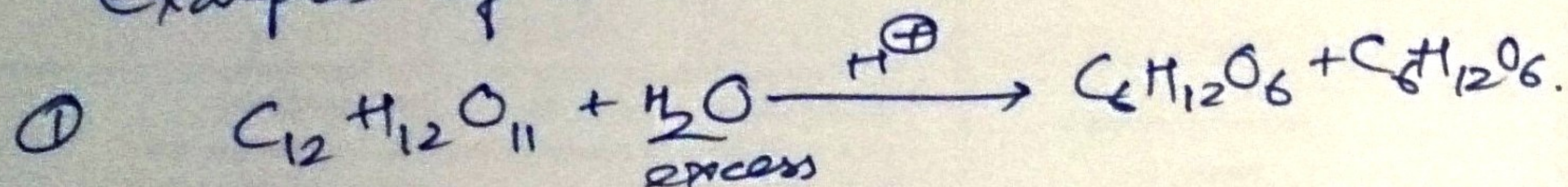
$$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x}$$

at $t = t_{1/2}$, $x = \frac{a}{2}$

$$\Rightarrow k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$$

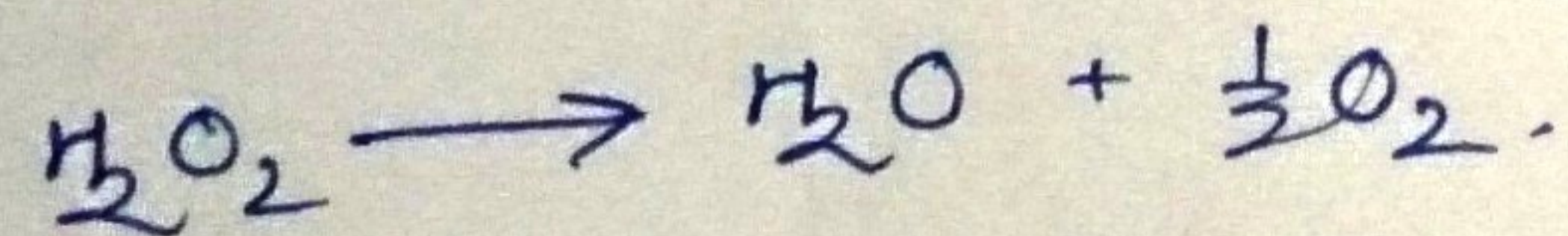
$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

examples of I order rxn:-



③ Radioactive decay:-

④ Decomposition of H_2O_2 in water.



⑤ Decomposition of ammonium nitrite in aqueous solⁿ.



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Second Order rxn:
 $2A \longrightarrow P$

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

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

on int: $\frac{1}{(a-x)} = kt + I$

at $t=0$, $x=0 \Rightarrow I = \frac{1}{a}$

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$k = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$

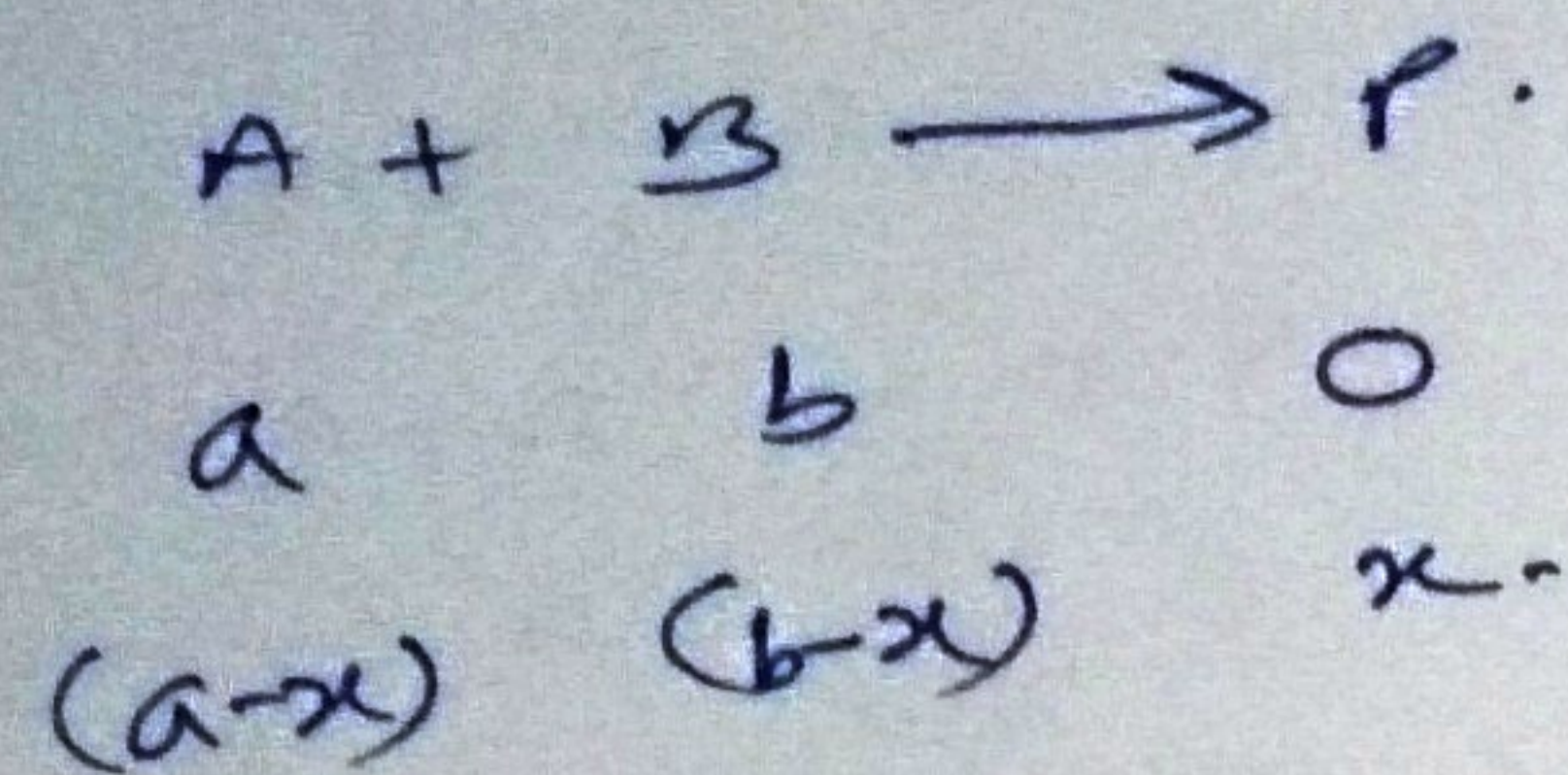
$$\boxed{k = \frac{1}{t} \cdot \frac{x}{a(a-x)}}$$

$$\frac{1}{\text{time}} \frac{\text{conc.}}{\text{conc.} \cdot \text{conc.}}$$

unit: $= \text{mol}^{-1} \text{lit} \cdot \text{time}^{-1}$

Second Order:-

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

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

partial fraction:-

$$\frac{1}{(a-b)} \left\{ \frac{dx}{(b-x)} - \frac{dx}{(a-x)} \right\} = k dt$$

On int:-

$$\frac{1}{a-b} \left\{ -\ln(b-x) + \ln(a-x) \right\} = kt + I$$

$$\text{at } t=0, x=0 \Rightarrow$$

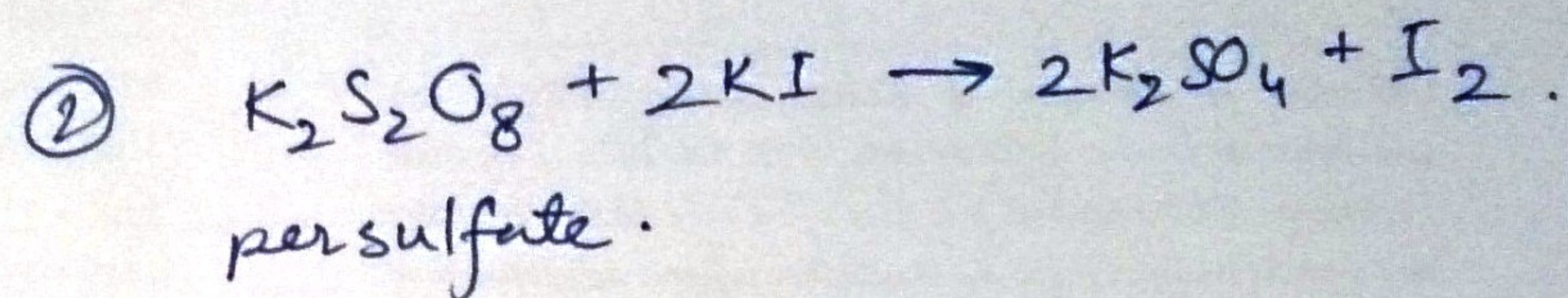
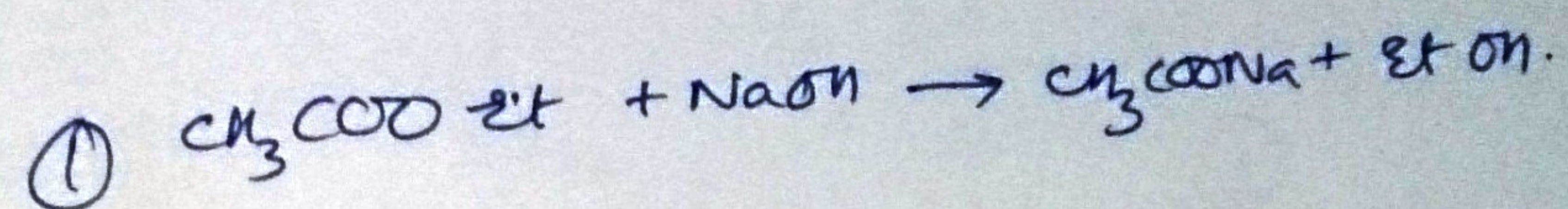
$$\frac{1}{a-b} \ln \frac{a}{b} = I.$$

$$\Rightarrow kt = \frac{1}{a-b} \left[-\ln \frac{a}{b} + \ln \frac{a-x}{b-x} \right]$$

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

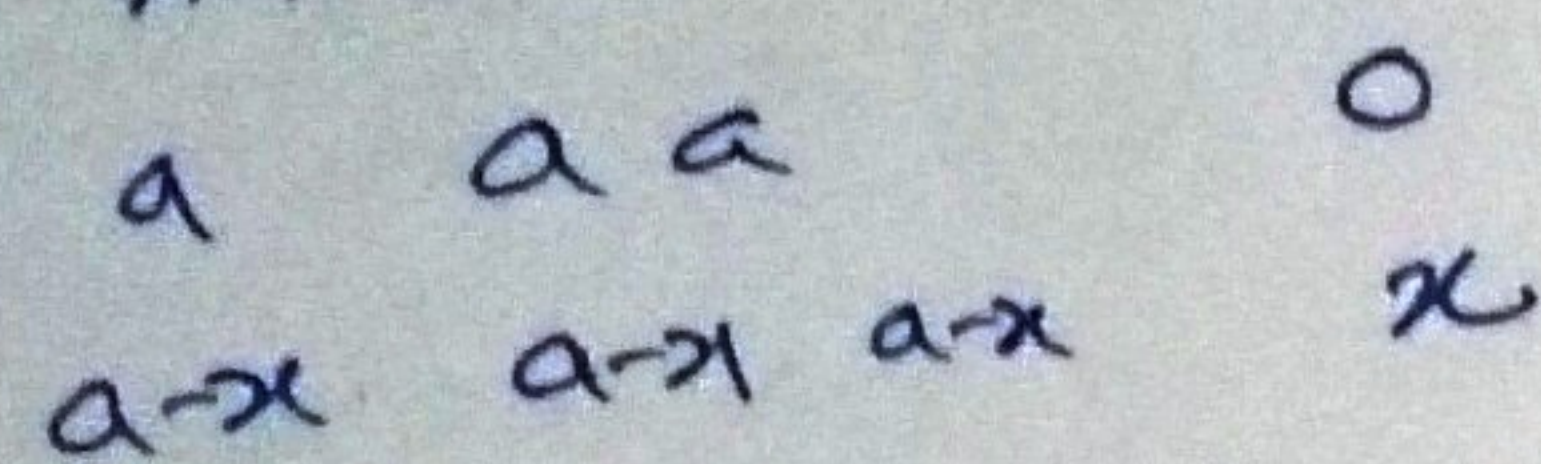
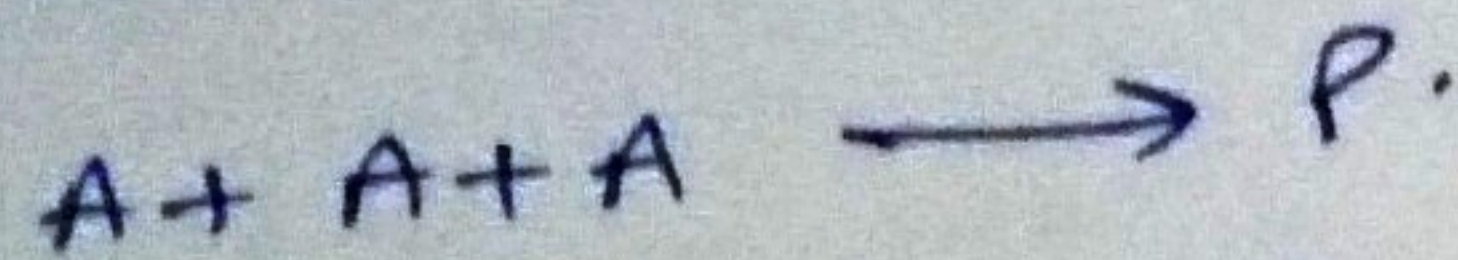
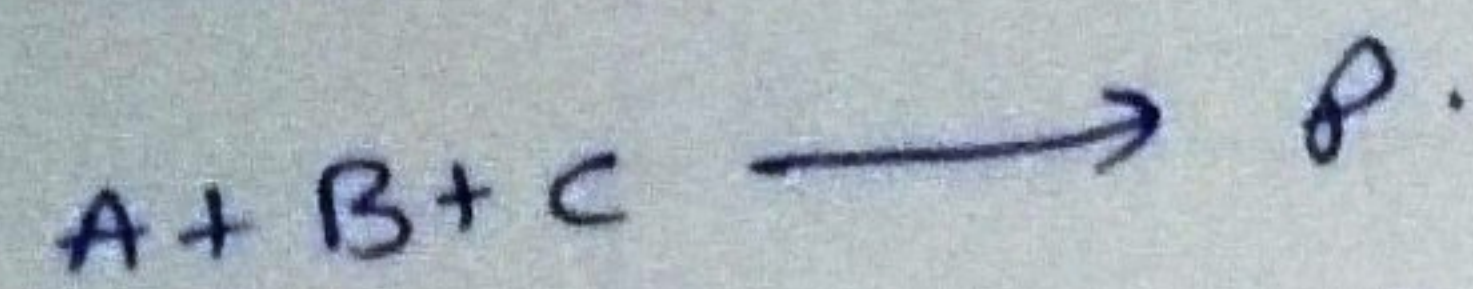
Examples of II order:-

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Third Order Rxn:-

(11)



$$\frac{dx}{dt} = k [a-x]^3$$

$$\frac{dx}{(a-x)^3} = k dt$$

on int:

$$\frac{1}{2(a-x)^2} = kt + I.$$

$$\text{at } t=0, I = \frac{1}{2a^2}$$

$$\Rightarrow kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

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

$$kt = \frac{1}{2} \frac{x(2a-x)}{a^2(a-x)^2}$$

$$k = \frac{1}{2t} \frac{x(2a-x)}{a^2(a-x)^2}$$

$$\text{unit :- } \frac{1}{\text{time}} \frac{\text{conc. conc.}}{\text{conc}^2 \cdot \text{conc}^2} \equiv \text{mol}^{-2} \text{ lit}^2 \text{ time}^{-1}.$$

$t_{1/2}$ for III order rxn:-

(12)

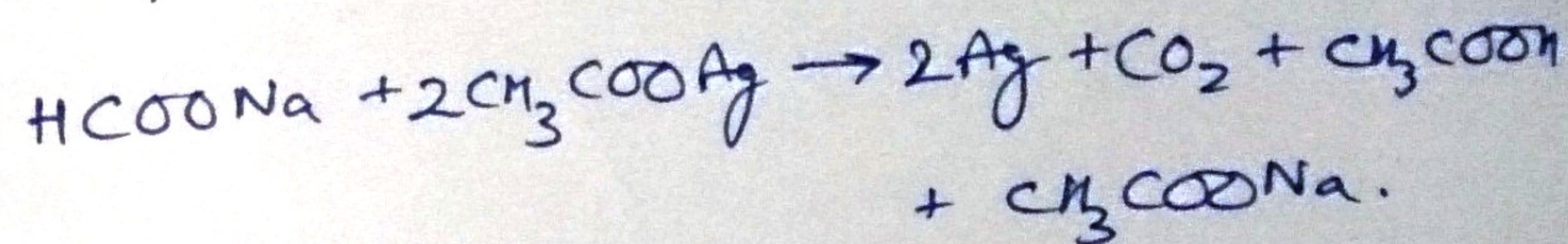
$$k = \frac{1}{2t_{1/2}} \frac{a/2(2a-a/2)}{a^2(a-a/2)^2}$$

$$k = \frac{1}{2t_{1/2}} \frac{3}{a^2}.$$

$$t_{1/2} = \frac{1}{k} \cdot \frac{3}{2} \cdot \frac{1}{a^2}$$

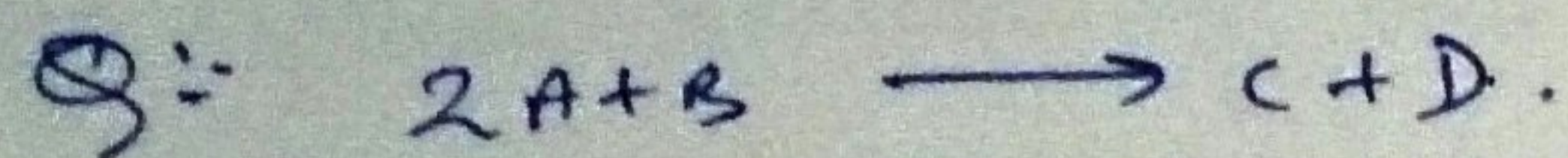
$$t_{1/2} \propto \frac{1}{a^2}$$

Example:-



$t_{1/2}$ for n^{th} order reaction (except I) is proportional to $(n-1)^{\text{th}}$ power of initial conc.

For more than one reactants, half life is always decided by the reactant which is taken in smallest amount.



above rxn follows the rate law :-

$$\frac{dx}{dt} = k[A]^2[B]$$

fill the gaps left in following data set:

$[A]_0 \times 10^5 \text{ mole dm}^{-3}$ $[B]_0 \times 10^5 \text{ mole dm}^{-3}$ $t_{0.5}$

1	300	40	62.6
2	300	60	—
3	5	300	625
4	10	300	—

Ans:-

for set ① & ② conc. of B is small
so, half life is for B.

rate law says rxn is 1st order wrt. B,

so $t_{1/2}$ is independent of initial

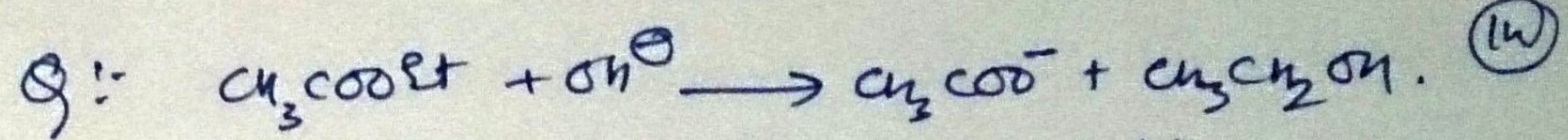
conc. hence 1st gap value is 62.6.

for set ③ & ④ $t_{1/2}$ is for A. which is
second order.

$$\Rightarrow t_{1/2}^{\text{set 3}} \propto \frac{1}{\text{conc.}^{\text{set 3}}} \quad \& \quad t_{1/2}^{\text{set 4}} \propto \frac{1}{\text{conc.}^{\text{set 4}}}$$

by dividing:-

$$t_{1/2}^{\text{IV}} = t_{1/2}^{\text{III}} \times \frac{5}{10} = 625 \times \frac{5}{10} = \underline{\underline{312.5}}$$



follows second order kinetics.

at 25°C, $k = 6.21 \times 10^{-3} \text{ lit mol}^{-1} \text{ sec}^{-1}$.

calculate time for 90% hydrolysis of ester.

initial initial conc. are:

0.05 M ester, & 0.1 M NaOH.

Ans:-

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

$$t = \frac{2.303}{k(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

$$= \frac{2.303}{6.21 \times 10^{-3} (0.1 - 0.05)} \log \frac{0.05 (0.1 - 0.045)}{0.1 (0.05 - 0.045)}$$

$$t = 5.5 \times 10^3 \text{ sec.}$$

$$x = 0.05 \times \frac{90}{100} = \underline{\underline{0.045 \text{ M.}}}$$

Q: Optical rotation of sucrose in presence of dil. HCl at various intervals is as follows: (15)

$t(\text{min})$	0	10	20	40	90	100	∞
rot. (deg)	32.4	28.8	25.5	19.6	10.3	6.1	-14.1

Find order & find when the solution is optically inactive?

Ans: $a \propto r_0 - r_\infty$
 $a-x \propto r_t - r_\infty$

$$k_{10} = \frac{2.303}{10} \log_{10} \frac{32.4 - (-14.1)}{28.8 - (-14.1)}$$

$$k_{10} = \frac{2.303}{10} \log_{10} \frac{46.5}{42.9} = 0.00807 \text{ min}^{-1}$$

$$k_{20} = \frac{2.303}{20} \log_{10} \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = \frac{0.00805 \text{ min}^{-1}}{0.008137 \text{ min}^{-1}}$$

$$k_{40} = \frac{2.303}{40} \log_{10} \frac{32.4 - (-14.1)}{19.6 - (-14.1)} = 0.00805 \text{ min}^{-1}$$

$$k_{90} = 0.007167 \text{ min}^{-1}, \quad k_{100} = 0.008040 \text{ min}^{-1}$$

Average $k = 0.007890 \text{ min}^{-1}$.
 for optical inactivity:

$$k = \frac{2.303}{t} \log_{10} \frac{32.4 - (-14.1)}{+14.1}$$

$$\Rightarrow t = 150.8 \text{ min.}$$

Radioactive Decay follows the following first-order rate law: (16)

$$A = A_0 e^{-kt}$$

A = activity at time t .

A_0 = initial activity (at $t=0$).

k = decay constant (usually written as λ).

t = time.

$$\Rightarrow \frac{A}{A_0} = e^{-kt}$$

$$\ln A - \ln A_0 = -kt$$

$$\ln A = -kt + \ln A_0$$

This equation is equivalent to as "the integrated form of the first-order rate law".
 $-\ln(a-x) = kt - \ln a$. (at page 6).

$$\text{so } k = -\frac{1}{t} \ln \frac{A}{A_0}$$

$$\text{or } \boxed{k = \frac{1}{t} \ln \frac{A_0}{A}}$$

1 order rxn form. for radioactive decay.

Q: A 7.85×10^{-5} mol sample of Cu-61 emits 1.47×10^{19} positrons in 90 min. what is decay const.?

Ans:

Total number of atoms before decay

$$A_0 = 7.85 \times 10^{-5} \text{ mol} \times 6.022 \times 10^{23} \text{ atoms/mol}$$

$$= 4.73 \times 10^{19} \text{ atoms}$$

$$\equiv 100\% \equiv 1$$

$$\text{No of atoms decayed} = 1.47 \times 10^{19}$$

$$\Rightarrow \frac{1.47 \times 10^{19}}{4.73 \times 10^{19}} \times 100 = 31.1\% \equiv 0.311$$

$$\therefore \text{No. of undecayed atoms} \equiv 1 - 0.311 = 0.689$$

$$\text{Now: } \ln A = -kt + \ln A_0$$

$$\Rightarrow \ln 0.689 = -(k)(90.0) + \ln 1$$

$$k = 0.00414 \text{ min}^{-1}$$

Q: Pu-239 has a decay constant of $2.88 \times 10^{-5} \text{ yr}^{-1}$ what % of a sample of Pu-239 remains after 1400 years?

$$\text{Ans: } \ln A = -kt + \ln A_0$$

$$\ln A = -(2.88 \times 10^{-5} \text{ yr}^{-1})(1400 \text{ yr}) + \ln 1$$

$$\ln A = -0.04032$$

$$A = 96.05\% \text{ remaining}$$

$$\frac{2.6108 - 2.7182}{-0.1074}$$

Q: What is the decay constant of Ga-67, half life is given as 78.25 h.

$$\text{Ans: } k = \frac{\ln 2}{t_{1/2}}$$

$$k = \frac{\ln 2}{78.25}$$

$$k = 8.858 \times 10^{-3} \text{ h}^{-1}$$

Q: F-21 had an initial mass of 80 mg. 20 mg of sample remained unchanged after 8.32 s. calculate half life of F-21.

Ans:

$$\ln \frac{20}{80} = -k(8.32)$$

$$\Rightarrow k = 0.167$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.167} = 4.16 \text{ s.}$$

Q: A first order reaction is 15% complete in 20 min. How long will it take to be 60% complete?

Ans:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$k = \frac{2.303}{20} \log_{10} \frac{a}{a - \frac{15}{100}a} \quad \text{--- (1)}$$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - \frac{60}{100}a} \quad \text{--- (2)}$$

by (1) & (2):

$$t = \frac{20 \log \frac{100}{40}}{\log \frac{100}{85}} = 112.7 \text{ sec.}$$

min.

(12)

Q: A solution of H_2O_2 titrated against KMnO_4 solution at different time intervals gave the following results:

t (min.)	0	10	20
vol. of KMnO_4 used.	23.8 ml	14.7 ml	9.1 ml.

show the decomposition of H_2O_2 is a first order rxn.

$$\text{Ans: } k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$a \equiv 23.8.$$

for $t = 10 \text{ sec. min.}$

$$k = \frac{2.303}{10} \log \frac{23.8}{23.8 - 14.7} = 0.04820$$

for $t = 20,$

$$k = \frac{2.303}{20} \log \frac{23.8}{9.1} = 0.042398$$

values of k are fairly constant, hence it is a first order rxn.

(20)

Determination of Order of Reaction.

① Integration method:



Initial conc. of each reactant is determined.

Conc. at various time is determined, Thus, different values of a & x are determined & the data fitted in several rate law expressions.

② Half life method:

$$t_{0.5} \propto \frac{1}{a^{n-1}}$$

~~$t_{1/2}$~~ Start with two ~~ide~~ independent reactions with initial conc. a_1 & a_2 .

$$\therefore t_1 \propto \frac{1}{a_1^{n-1}}$$

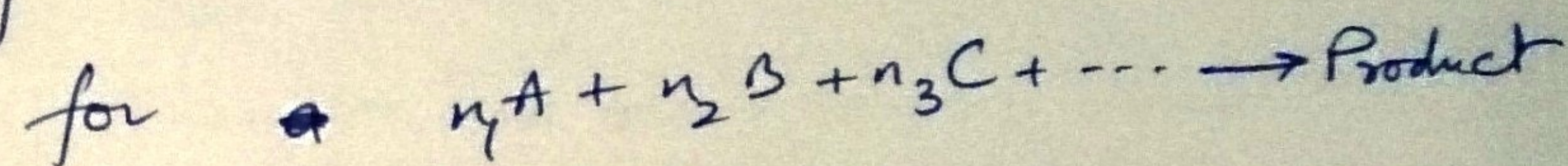
$$t_2 \propto \frac{1}{a_2^{n-1}}$$

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

$$\Rightarrow \boxed{n = 1 + \frac{\log(t_1/t_2)}{\log(a_2/a_1)}}$$

(21)

③ isolation method: conc. of all but one reactant is taken in excess & order of rxn is determined by any method.



$$r = \frac{dx}{dt} = k [A]^{n_1} [B]^{n_2} [C]^{n_3}.$$

$$\therefore \text{order of overall rxn} = n_1 + n_2 + n_3 + \dots$$

④ van't Hoff differential Equation method:

$$\frac{dx}{dt} = k [A]^x [B]^y$$

initial rate of rxn is measured while conc. of one reactant is ~~kept const.~~ varied & others kept const.

$$\frac{dx}{dt} = k' [A]^x \quad \text{if } [B] \text{ is const.}$$

$$\text{or } \ln \frac{dx}{dt} = \ln k' + x \cdot \ln [A]$$

$$\equiv y = c + m \cdot x.$$

value of slope for plot between $\ln[A]$ vs $\ln \frac{dx}{dt}$ gives order of rxn.

(22)

⑤ Graphical method:

for n^{th} order reaction.

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

$\Rightarrow \frac{dx}{dt}$ vs $(a-x)^n$ gives a straight line.

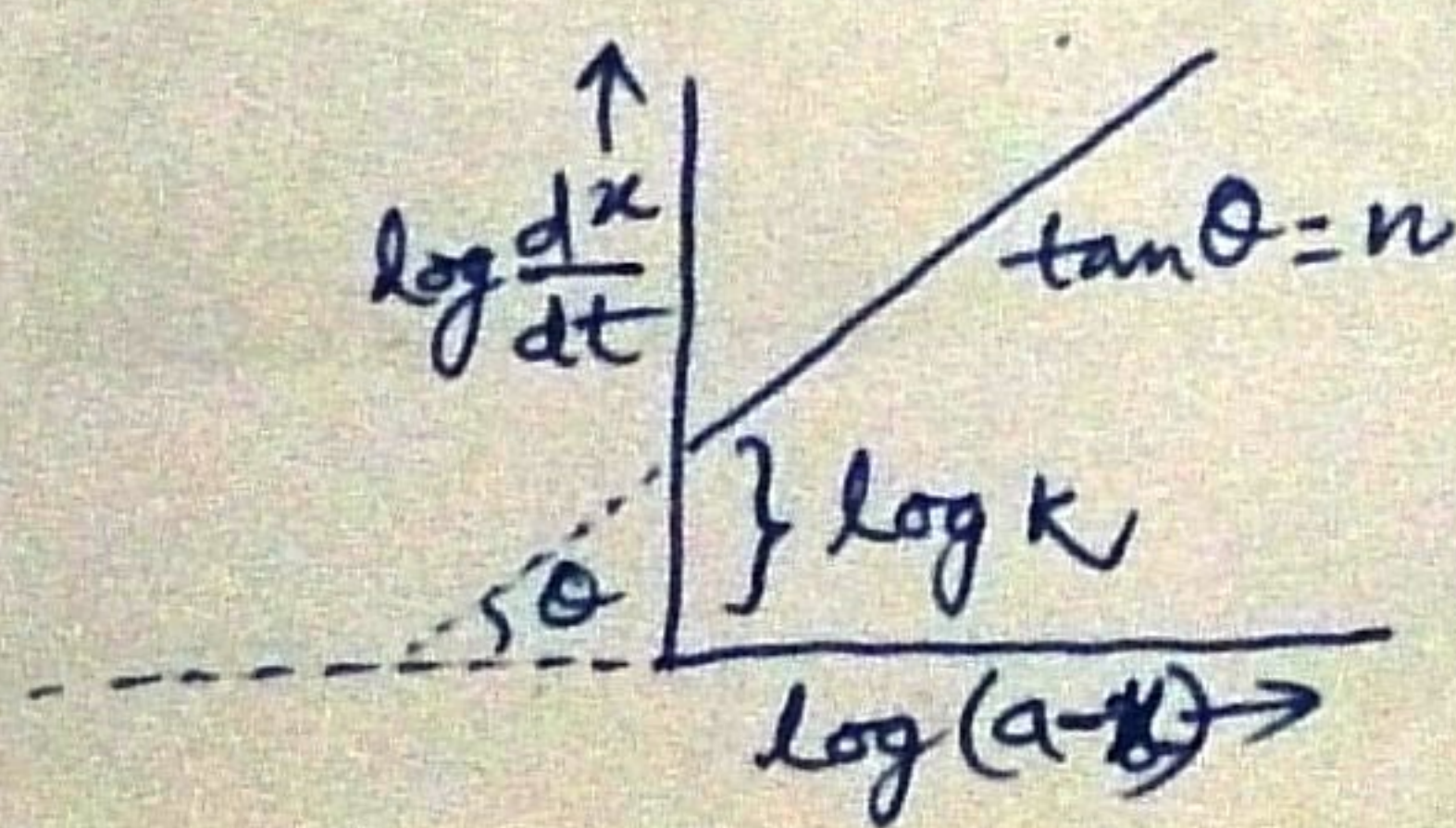
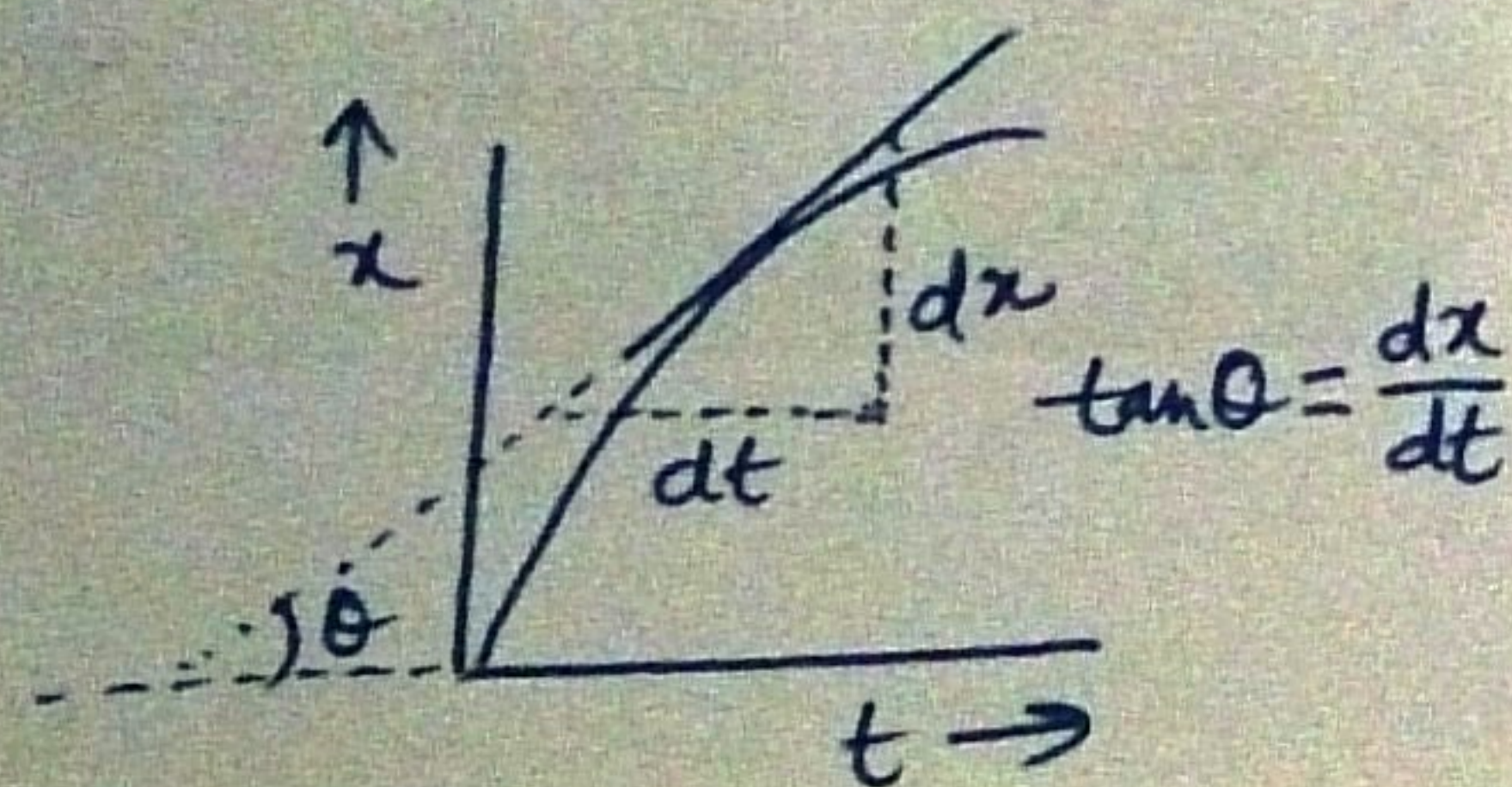
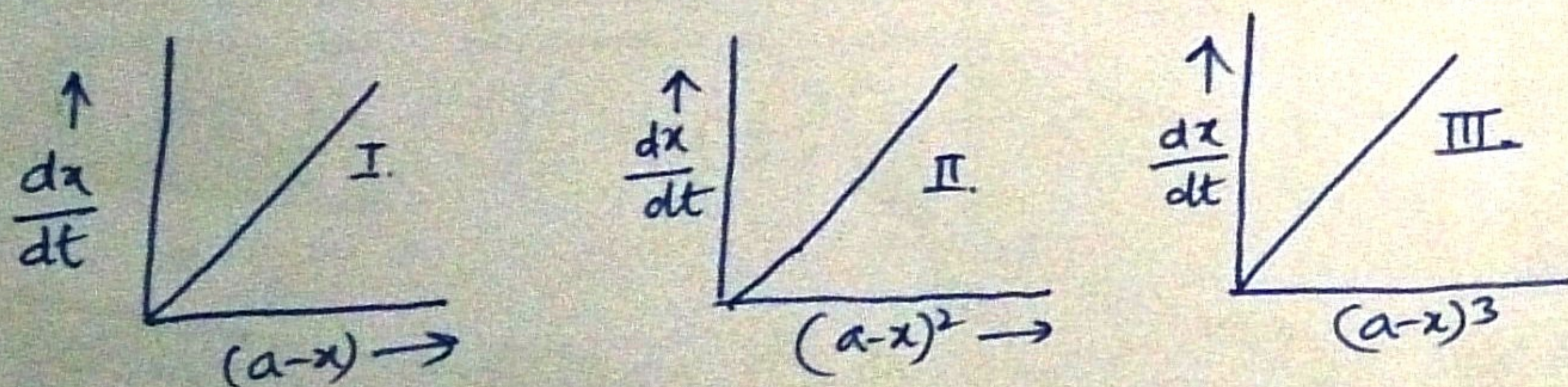
for zero order: x vs t — straight line.

I order: $\frac{dx}{dt}$ vs $(a-x)$ — straight line.

II order: $\frac{dx}{dt}$ vs $(a-x)^2$ — straight line.

III Order: $\frac{dx}{dt}$ vs $(a-x)^3$ — straight line.

or $\log \frac{dx}{dt}$ vs $n \log(a-x)$ gives straight line.



Q:- In the reaction $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, a molecular mixture of gases at 336 mm Hg initial pressure, was half changed in 108 sec. & when the initial pressure was 288 mm Hg, it was half changed in 147 sec. Order? Calculate order of the reaction.

Ans:

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$a_1 \propto 336/2 \text{ mm Hg};$$

$$a_2 \propto 288/2 \text{ mm Hg};$$

$$\frac{108}{147} = \left(\frac{144}{168}\right)^{n-1}$$

$$(n-1) = \frac{\log\left(\frac{108}{147}\right)}{\log\left(\frac{144}{168}\right)} = 2$$

$$\Rightarrow n = 2+1 = 3$$

⑤ Graphical method:

Rate law expressions for reaction of different orders may be rearranged in form of equations of straight line; i.e.,

$y = mx + c$; where, x & y are variables & m is slope of st. line & c is intercept to the y axis.

Therefore:

Rxn.
Zero order

Standard Rate law.

$$x = kt$$

Rearranged form

$$x = kt$$

First order

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\ln(a-x) = \ln a - kt$$

Second order

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

$$\frac{1}{(a-x)} = \frac{1}{a} + kt$$

Third order

$$k = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right]$$

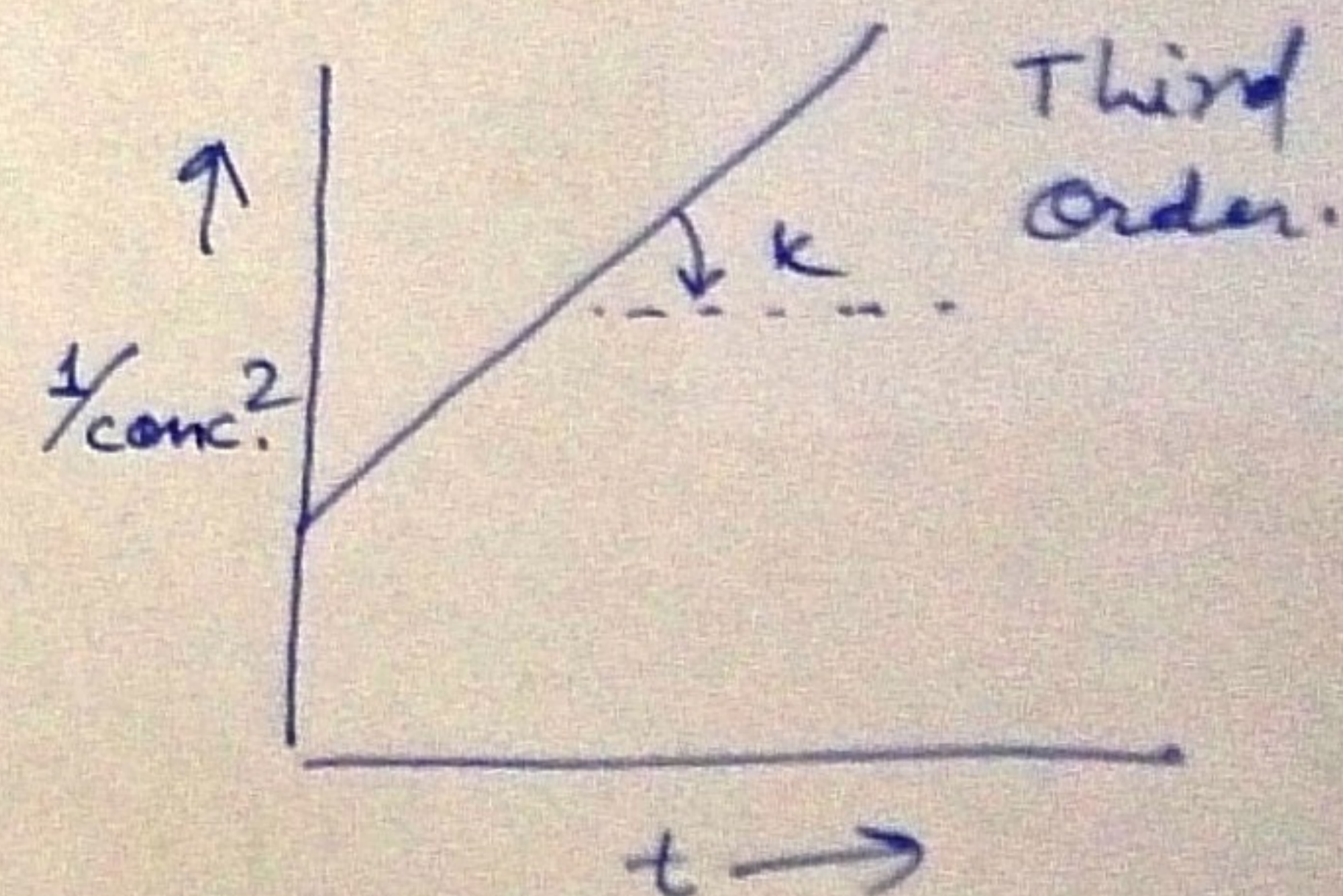
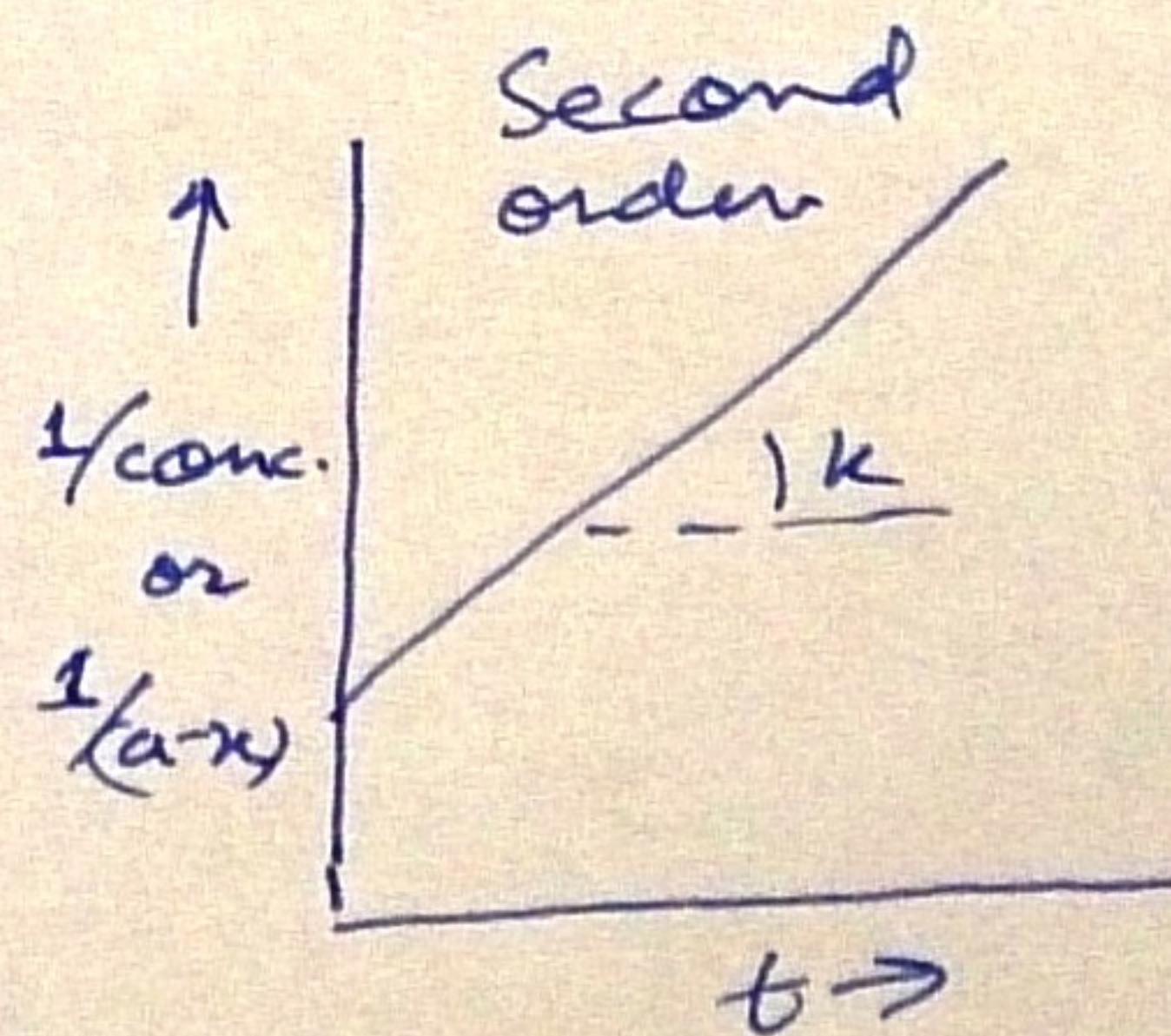
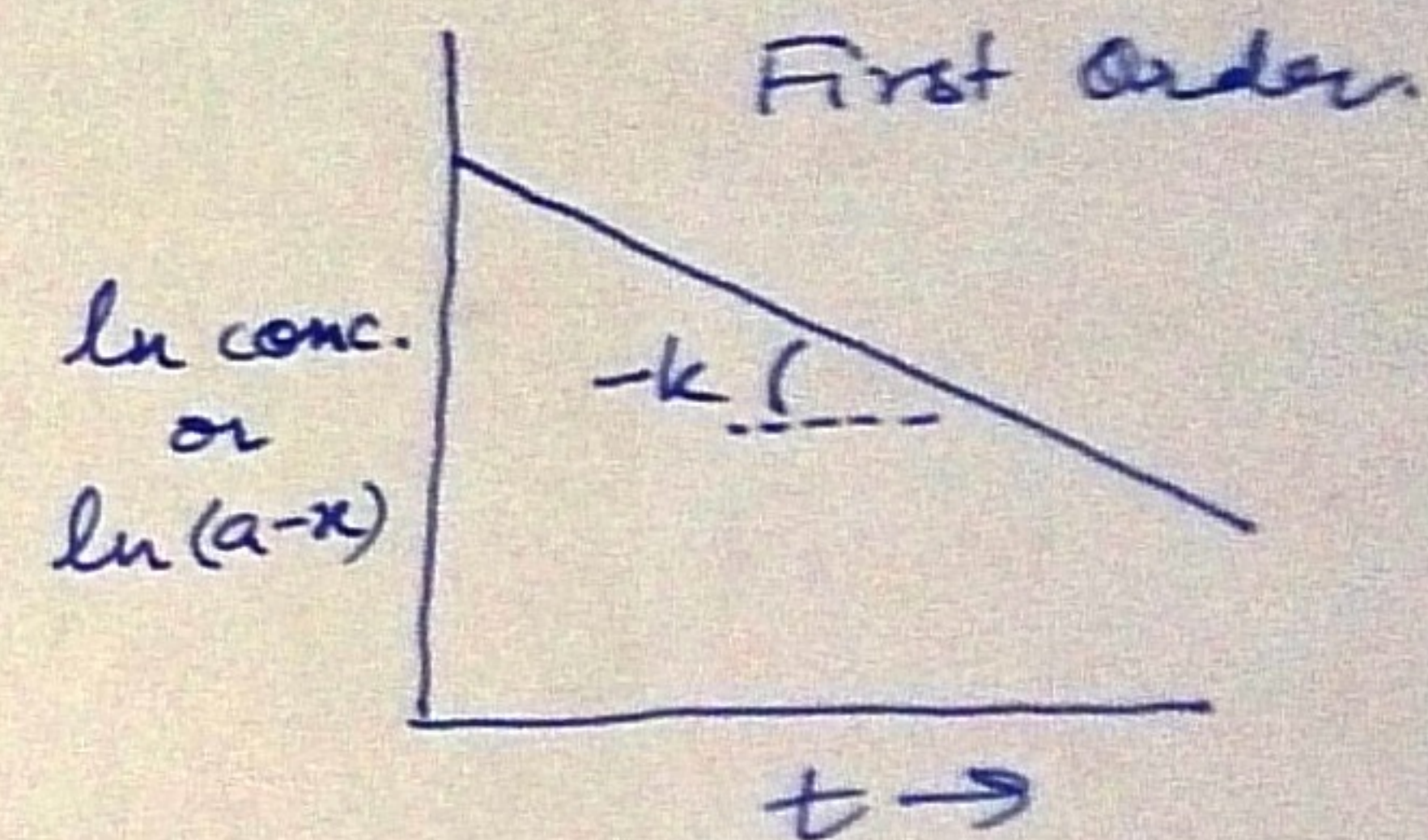
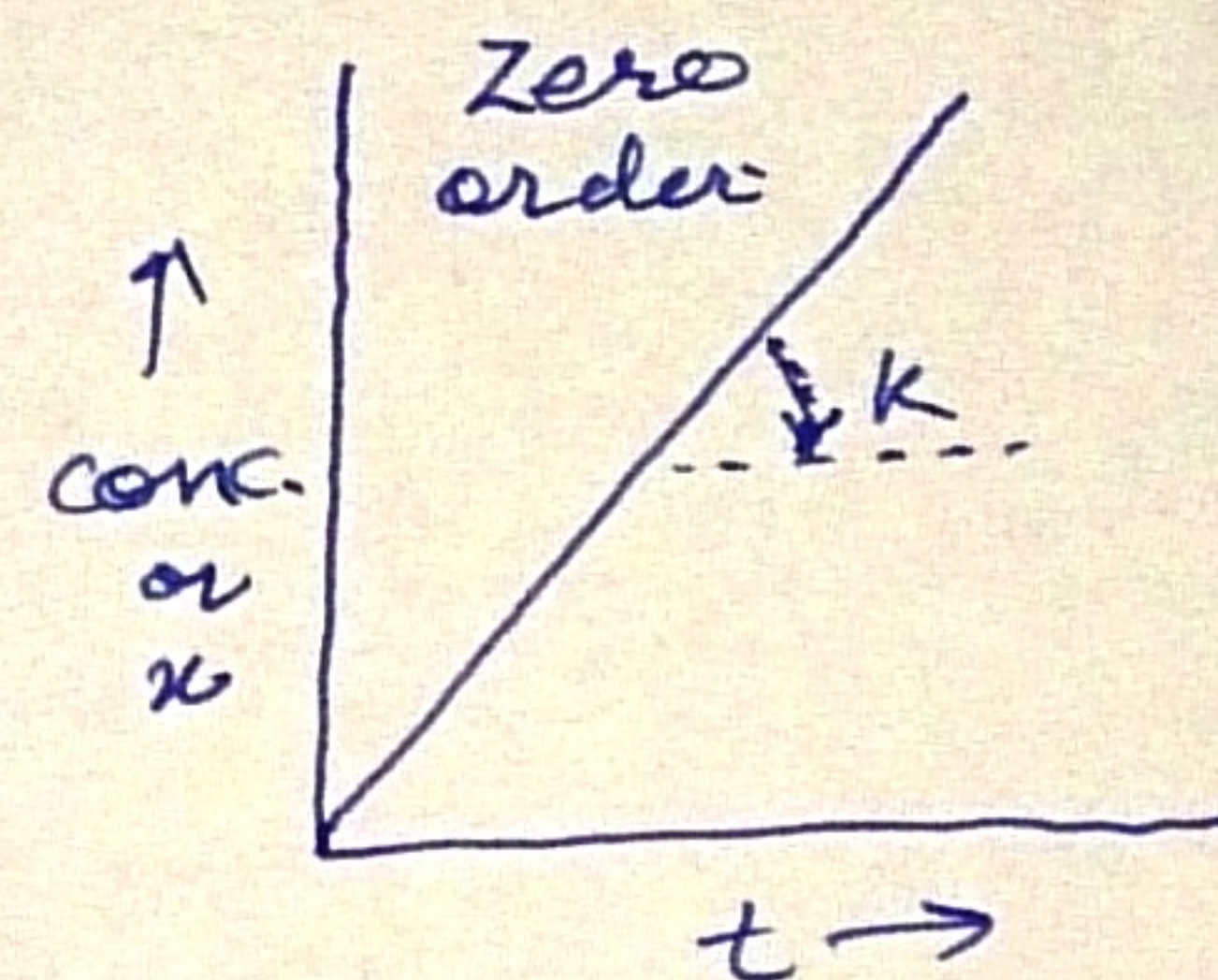
$$\frac{1}{2(a-x)^2} = \frac{1}{2a^2} + kt$$

or

$$\frac{1}{(a-x)^2} = \frac{1}{a^2} + 2kt$$

would give straight line, confirming the respective order of the reaction.

Thus:



Thus, plotting t vs concentration ~~den~~ terms expressed in rearranged form of rate law

Q: From the following data of initial conc. & rate, calculate the order & k for $aA \rightarrow P$.

[A]	0.1	0.2	0.4
r	9×10^{-5}	36×10^{-5}	144×10^{-5}

Ans: let the order be n & rate constant as k.

$$\therefore r = k[A]^n$$

from data $r_1 = 9 \times 10^{-5} = k[0.1]^n$ — (1)

$r_2 = 36 \times 10^{-5} = k[0.2]^n$ — (2)

$r_3 = 144 \times 10^{-5} = k[0.4]^n$ — (3)

dividing (1) & (2).

$$\frac{r_1}{r_2} = \frac{9 \times 10^{-5}}{36 \times 10^{-5}} = \frac{k[0.1]^n}{k[0.2]^n}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{0.1}{0.2}\right)^n$$

$$\Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$$

$$\Rightarrow n = 2. \text{ (order of rxn)}$$

Placing value of n in eq (1) or (2), (3) [for example in (3)]

$$144 \times 10^{-5} = k(0.4)^2$$

$$k = 9 \times 10^{-3}$$

Ans.

(25)

Q: At 298K, the specific rate constant for hydrolysis of ethyl acetate by NaOH is $6.36 \text{ lit mol}^{-1} \text{ min}^{-1}$. Starting with conc. of base & ester of $0.01 \text{ mol lit}^{-1}$, what proportion of ester will be hydrolysed in 20 min.

Ans: $a = 0.01 \text{ mol lit}^{-1}$
 $t = 20 \text{ min}$

$$k = 6.36 \text{ lit mol}^{-1} \text{ min}^{-1}$$

Second order rate law is given by:-

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

$$6.36 = \frac{1}{20} \frac{x}{0.01(0.01-x)}$$

$$x = 0.0056$$

let conc. $0.01 \equiv 100\%$

$$\Rightarrow \text{conc. } 0.0056 \equiv \frac{100}{0.01} \times 0.0056$$

$$= 56\%$$

Therefore 56% ester will be hydrolyzed in 20 min.

$$1.272 \times 0.01 - 1.272x = x$$

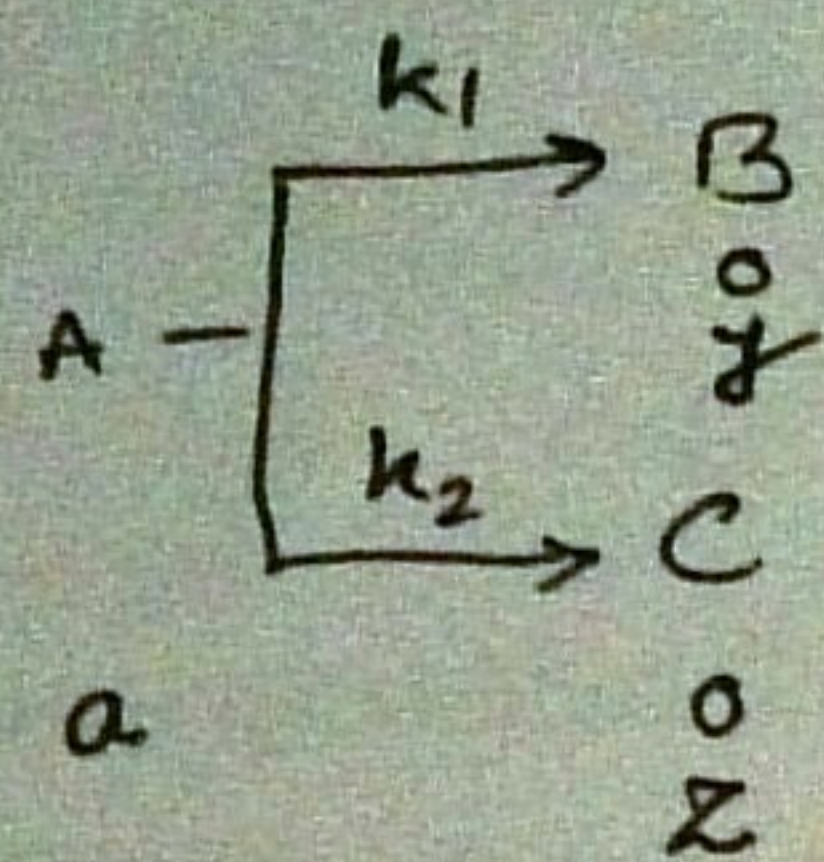
$$x + 1.272x = 0.01272$$

$$x = \frac{0.01272}{2.272}$$

$$x = 0.0056$$

(26)

① Side reactions (Parallel reactions).



$$\frac{dx}{dt} = k_1(a-x)$$

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

since both B & C are formed from A, thus,

$$\frac{dx}{dt} = \frac{dx}{dt} + \frac{dz}{dt}$$

$$= k_1(a-x) + k_2(a-x)$$

$$\text{or } \frac{dx}{dt} = (k_1 + k_2)(a-x)$$

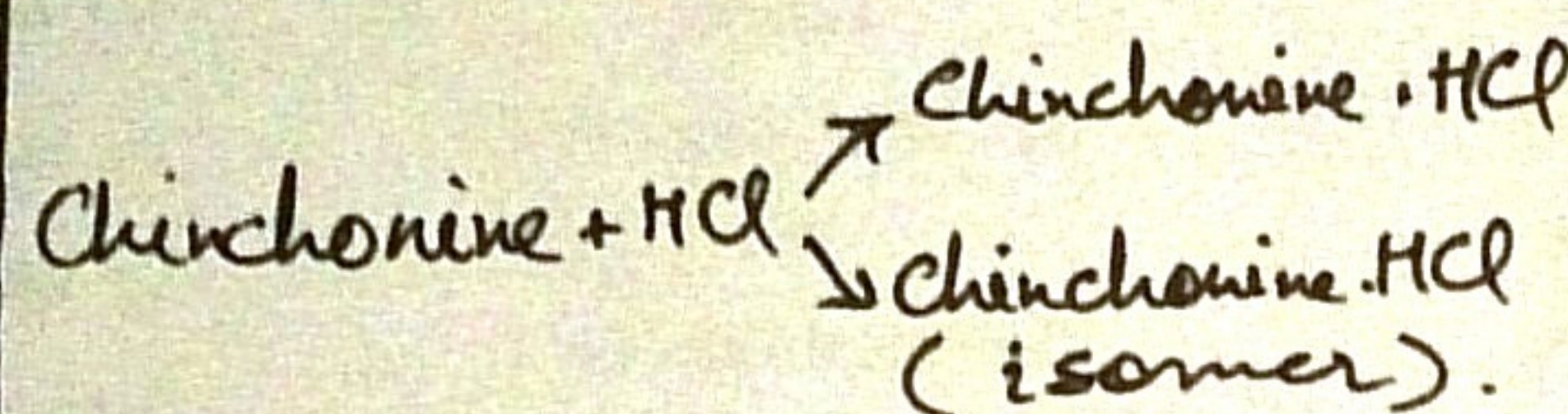
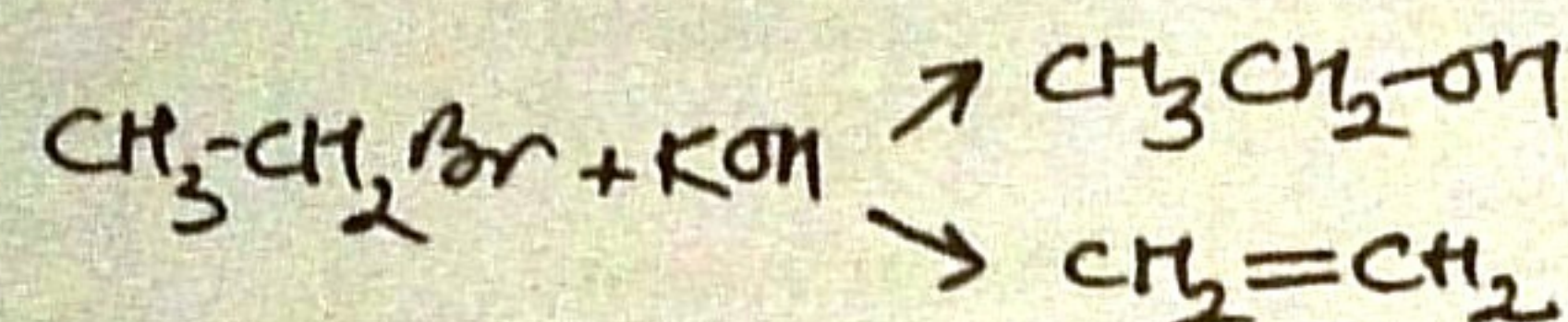
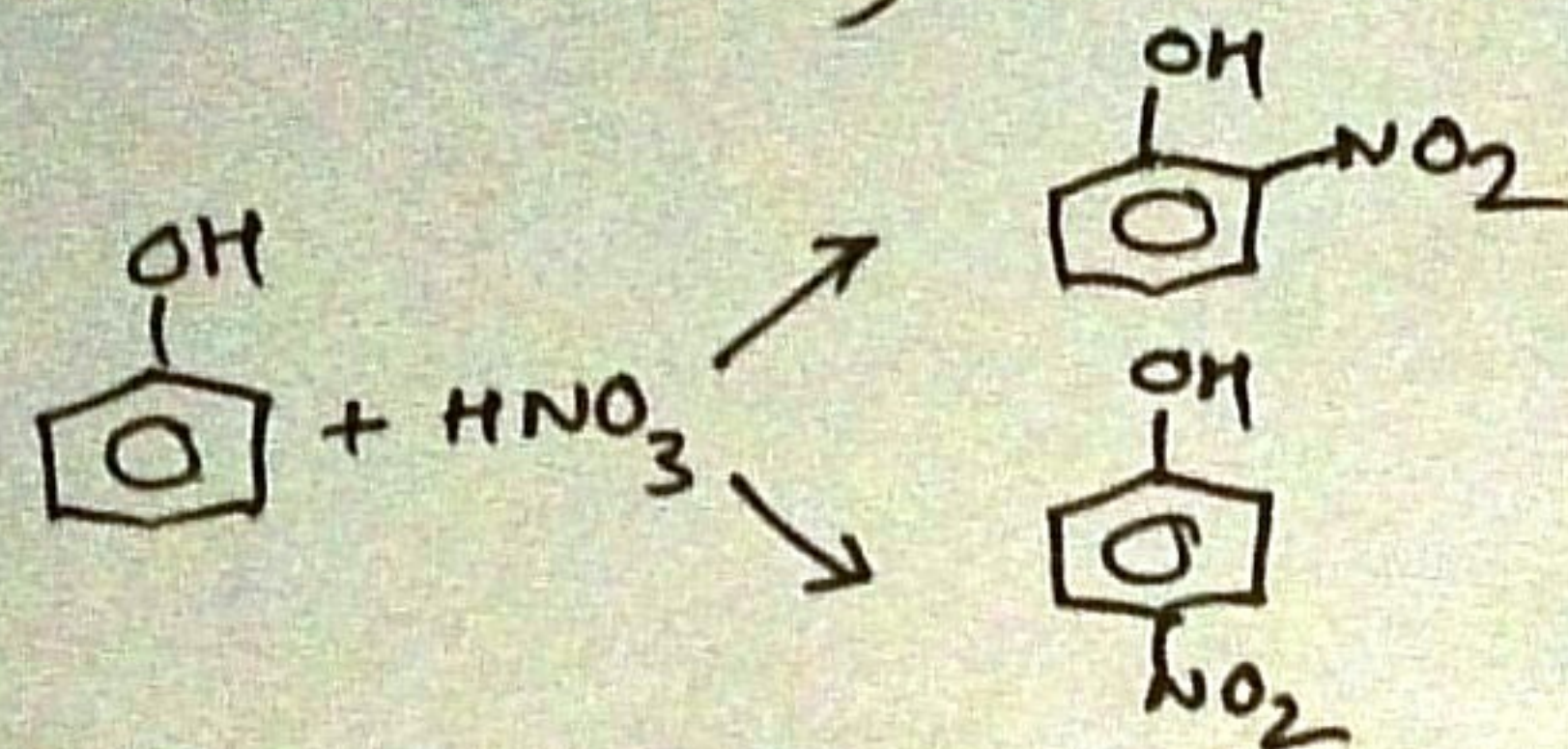
$$\frac{dx}{a-x} = (k_1 + k_2) dt$$

on integrating

$$-\ln(a-x) = (k_1 + k_2)t + I$$

$$\text{at } t=0, x=0 \Rightarrow I = -\ln a$$

Putting in eqn ①



$$k_1 + k_2 = \frac{1}{t} + \ln \frac{a}{a-x}$$

$$\text{let } k_1 + k_2 = K.$$

$$\Rightarrow \boxed{K = \frac{1}{t} \ln \frac{a}{a-x}} \quad \text{--- ②}$$

We can measure K directly; not k_1 & k_2 .
 To calculate k_1 & k_2 , a relation between them is needed.

The amounts of B & C at any time depend on the rate of reactions.

$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at any stage}} = \frac{dx/dt}{dz/dt} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} = K' \quad \text{--- ③}$$

At the end of reactions we can measure the amounts of B & C, thus can calculate K' .

$$\text{Now } k_1 + k_2 = K \quad \text{--- ④}$$

$$\& \quad k_1/k_2 = K' \quad \text{--- ⑤}$$

$$\text{from ④ \& ⑤ } \Rightarrow k_1 = K' k_2 \quad \& \quad k_2 = k_1/K'$$

$$K' k_2 + k_2 = K$$

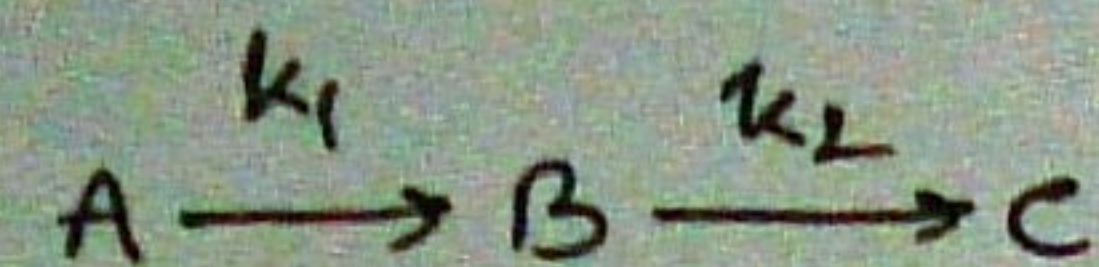
$$\boxed{k_2 = \frac{K}{1 + K'}}$$

$$k_1(1 + \frac{1}{K'}) = K$$

$$\boxed{k_1 = \frac{KK'}{1 + K'}}$$

★ "The ratio between the amounts of the substances formed in two side reactions is independent of time."
 (Wegscheider's Principle).

Consecutive Reactions:



at $t=0$ a 0 0

at t x y z

Suppose we start with a moles of A & after t time, x moles of A are left behind. & y & z moles of B & C were formed respectively.

$$\Rightarrow a = x + y + z \quad \text{--- (i)}$$

rate of disappearance of A ,

$$-\frac{dx}{dt} = k_1 x \quad \text{--- (ii)}$$

rate of formation of C ,

$$+\frac{dz}{dt} = k_2 y \quad \text{--- (iii)}$$

rate at which B accumulates,

$$\frac{dy}{dt} = \left(-\frac{dx}{dt}\right) - \left(+\frac{dz}{dt}\right)$$

or $\frac{dy}{dt} = -k_1 x - k_2 y$

$$\frac{dy}{dt} = k_1 x - k_2 y \quad \text{--- (iv)}$$

(29)

Integrating (ii)

$$-\int \frac{dx}{x} = \int k_1 dt$$

$$-\log x = k_1 t + I$$

$$\text{at } t=0, x=a \Rightarrow I = -\log a$$

$$\text{or } -\log x = k_1 t - \log a$$

$$\Rightarrow \frac{x}{a} = e^{-k_1 t}$$

$$x = a e^{-k_1 t} \quad \text{--- (v)}$$

Eq (v) shows conc. of A decreases exponentially.

Substituting value of x in eq (iv)

$$\frac{dy}{dt} = k_1 a e^{-k_1 t} - k_2 y$$

$$y = e^{-k_2 t} \left[\frac{k_1 a \cdot e^{(k_1 - k_2)t}}{(k_2 - k_1)} + C \right]$$

when $t=0$, $y=0$, so $C = -k_1 a / (k_2 - k_1)$

$$\therefore y = e^{-k_2 t} \left[\frac{k_1 a e^{(k_1 - k_2)t}}{(k_2 - k_1)} - \frac{k_1 a}{(k_2 - k_1)} \right]$$

$$\text{or } y = \frac{a k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) \quad \text{--- (vi)}$$

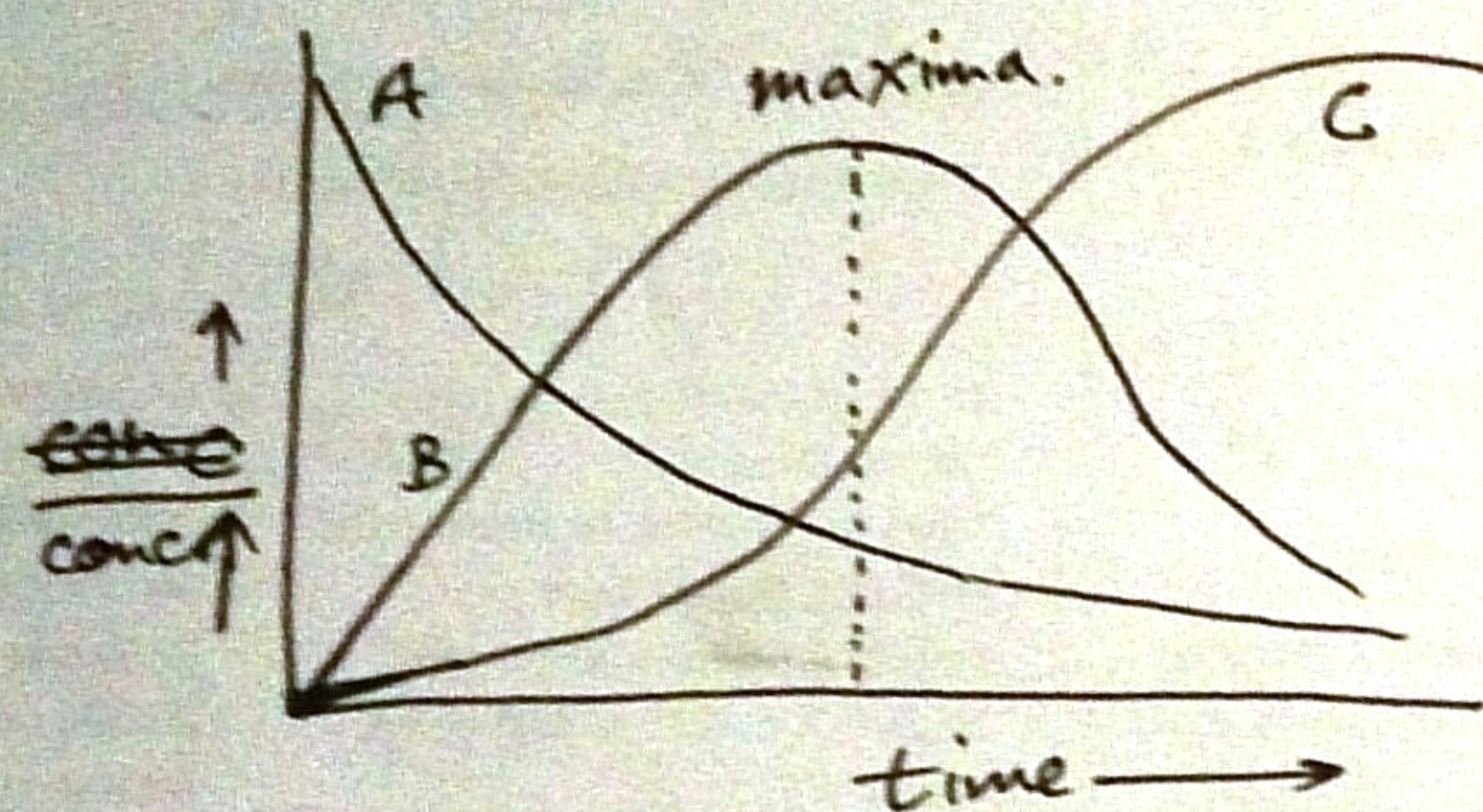
(30)

Substituting the value of x & y in eq (1),

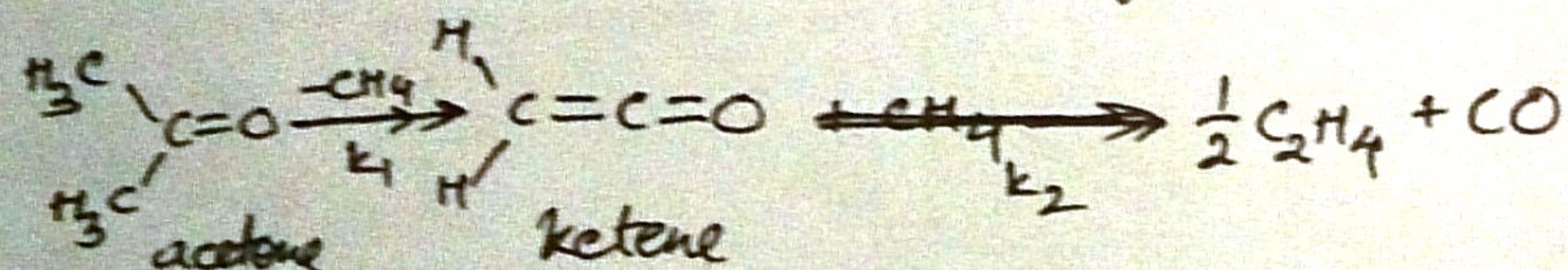
$$Z = a - x - y$$

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

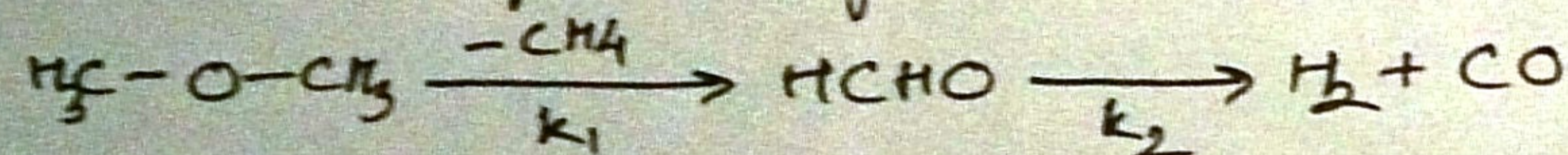
$$\text{or } Z = a \left\{ 1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right\} \quad \text{--- (7)}$$



Example : ① Thermal decomposition of acetone,

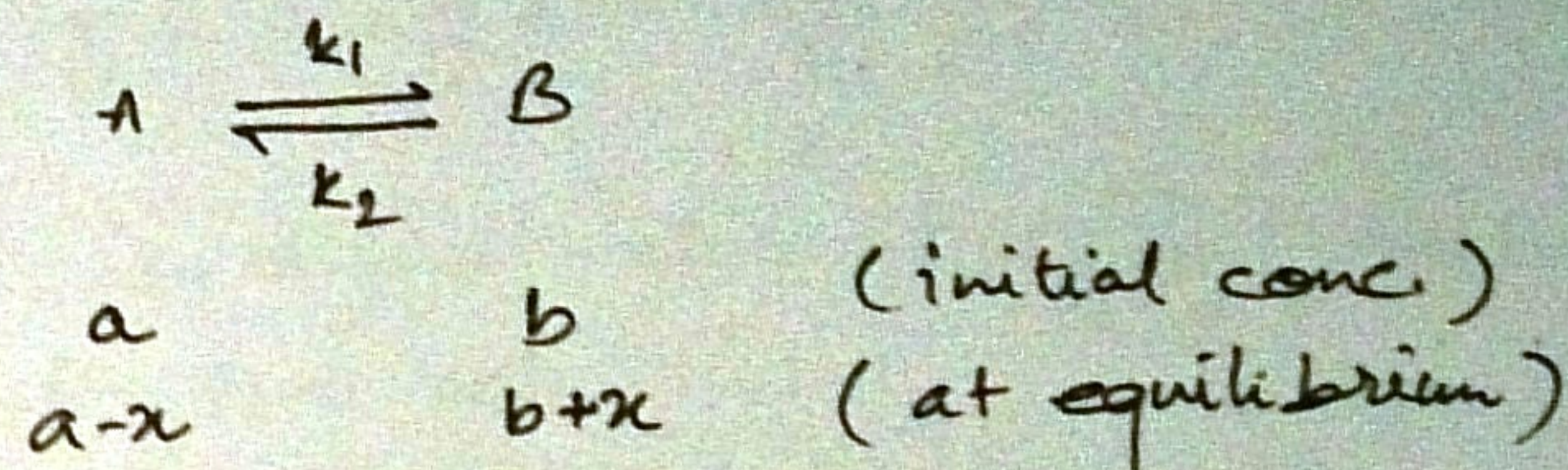


② Decomposition of dimethyl ether.



Opposing Rxns or Reversible Reactions

case: I order rxn opposed by I order rxn.



$$\frac{dx}{dt} = k_1(a-x) - k_2(b+x) \quad \text{--- (1)}$$

$$\text{at eq. } \frac{dx}{dt} = 0 \Rightarrow k_1(a-x_e) = k_2(b+x_e) \quad \text{--- (2)}$$

$$\Rightarrow b+x_e = \frac{k_1}{k_2}(a-x_e)$$

$$b = \frac{k_1}{k_2}(a-x_e) - x_e$$

Placing value of b in eq (1):

$$\begin{aligned} \frac{dx}{dt} &= k_1(a-x) - k_2 \left\{ \left[\frac{k_1}{k_2}(a-x_e) - x_e \right] + x \right\} \\ &= k_1(a-x) - k_1(a-x_e) + k_2 x_e - k_2 x \\ &= k_1(a-x-a+x_e) + k_2(x_e-x) \end{aligned}$$

$$\frac{dx}{dt} = k_1 + k_2(x_e - x)$$

$$\frac{dx}{x_e - x} = (k_1 + k_2) dt$$

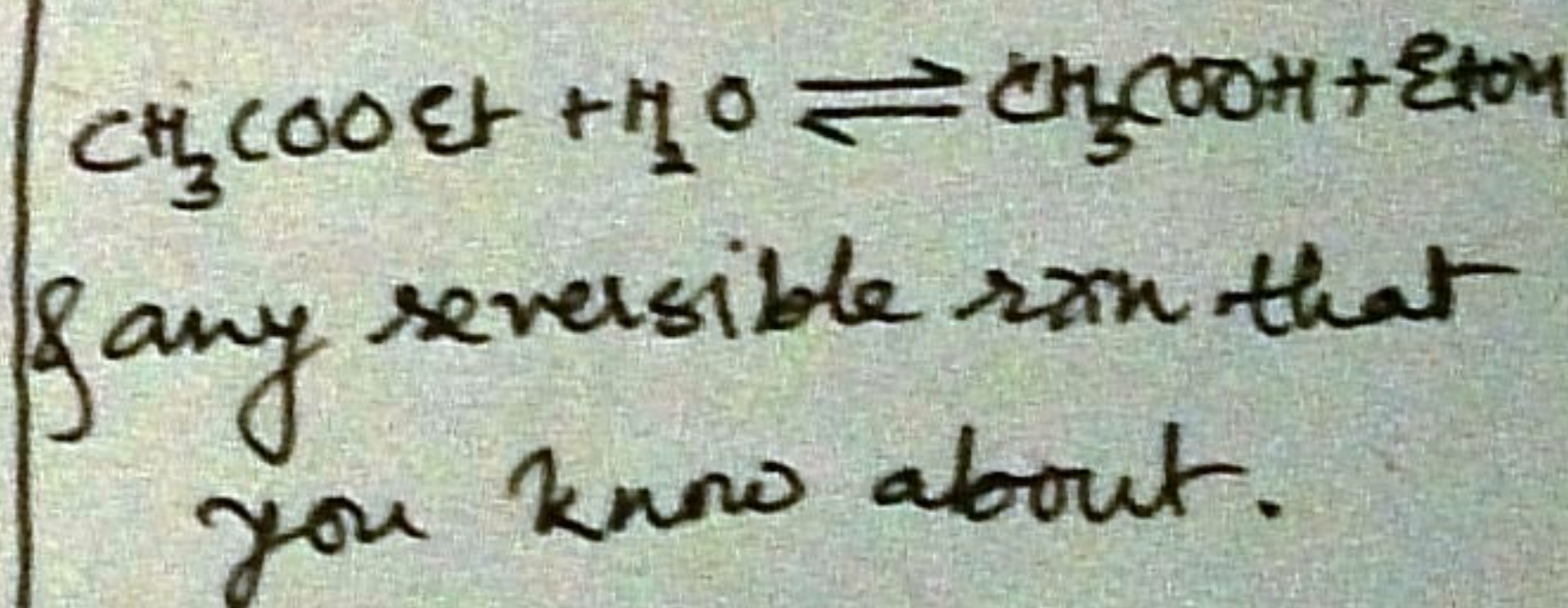
$$\int_{x_0}^x \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2) dt$$

$$\ln \frac{x_e - x_0}{x_e - x} = (k_1 + k_2) t$$

$$(k_1 + k_2) = \frac{1}{t} \ln \frac{x_e - x_0}{x_e - x} \quad \text{--- (3)}$$

eq. (3) is similar to I order rate expression.

Examples :



Arrhenius eqⁿs

Passive molecules become active due to the absorption of heat energy.

$$k = A e^{-E_a/RT}$$

* A is constant called frequency factor (or collision no.).

* $e^{-E_a/RT}$ factor is responsible for the effect of temp. on reaction rate.

Determination of Activation Energy.

① Graphical Method:

$$\therefore k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

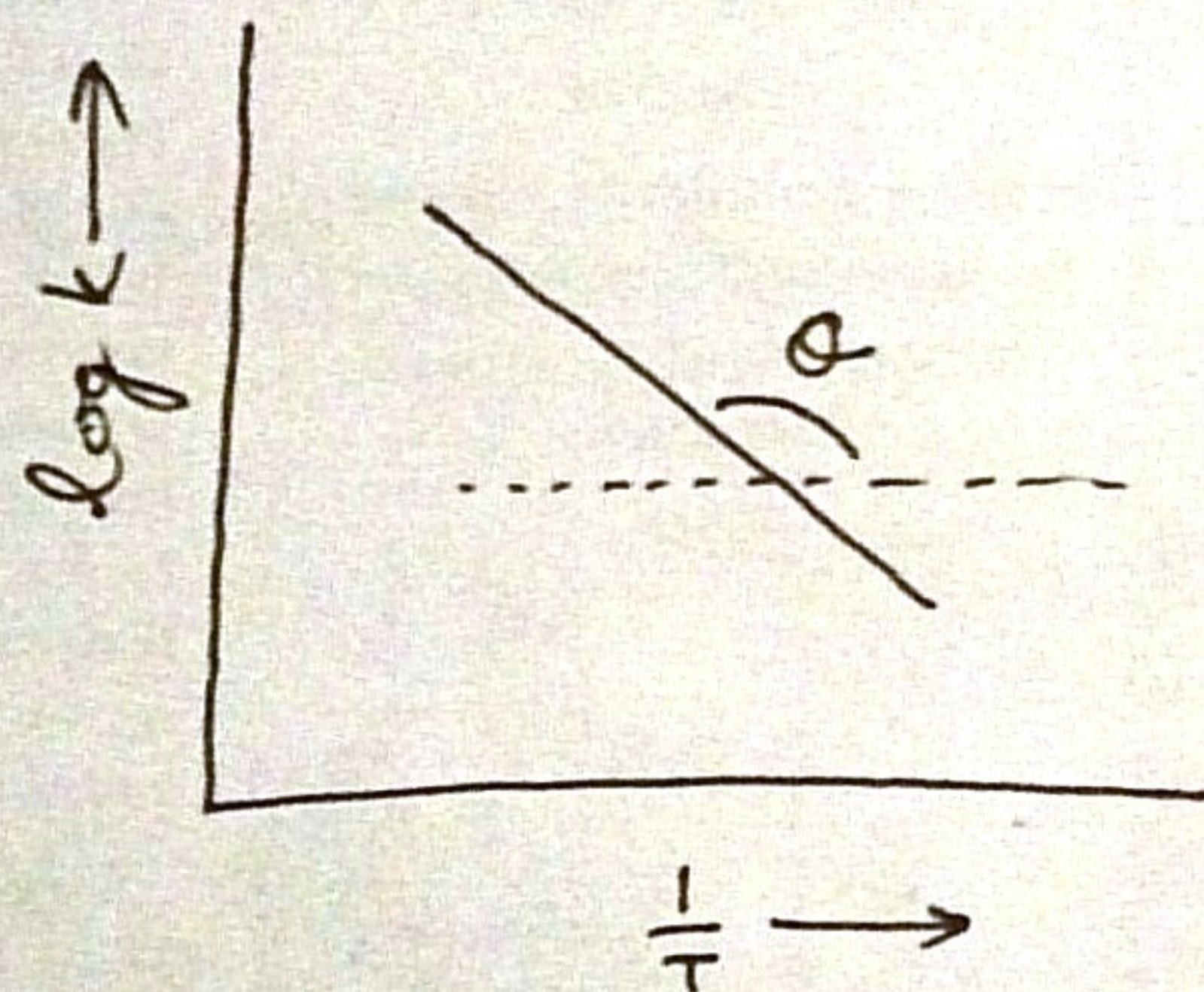
$$\text{or } \log k = \log A - \frac{E_a}{2.303 RT}$$

This equation represents a straight line for a

plot $\frac{1}{T}$ vs. $\log k$.

Slop of plot $\left\{ \tan \theta = -\frac{E_a}{2.303 RT} \right\}$

* intercept of this straight line with y-axis will give the value of $\log A$ (constant).



Second Method:

$$\therefore \log k = \log A - \frac{E_a}{2.303 RT}$$

Since k has different values at different temperatures
Therefore for two sets T_1 & T_2 ,

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1} \quad \text{--- ①}$$

$$\log k_2 = \log A - \frac{E_a}{2.303 RT_2} \quad \text{--- ②}$$

Subtracting ① from ②

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \text{--- ③}$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{--- ④}$$

So eq ③ or ④ can be used to calculate E_a if rate constants at T_1 & T_2 are known.

* for many reactions 10° rise in temperature causes 2.7 time increase in rate constant.

Q1. For a first order reaction, rate constant is found to be 7.0×10^{-7} at 7°C & 9×10^{-4} at 57°C . Calculate E_a & specific reaction rate at 127°C . (35)

Ans:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$T_1 = 7 + 273 = 280\text{K}$$

$$T_2 = 57 + 273 = 330\text{K}$$

$$\therefore \log \frac{9 \times 10^{-4}}{7 \times 10^{-7}} = \frac{E_a}{2.303 \times 1.987} \left[\frac{1}{280} - \frac{1}{330} \right]$$

$$E_a = 26.29 \times 10^3 \text{ cal/mole.}$$

Specific rate (k) at 127°C (i.e. 400K) is given by:

$$\log \frac{k_{400}}{7 \times 10^{-7}} = \frac{26.29 \times 10^3}{2.303 \times 1.987} \left[\frac{1}{280} - \frac{1}{400} \right]$$

$$k_{400} = 0.02032 \text{ min}^{-1}$$

Ans.

Q2. for a reaction at temperature T , the velocity constant k is expressed as (36)

$$k = A e^{-27000 k/T}; \text{ where } k \text{ is Boltzmann constant.}$$

Given, $R = 2 \text{ cal mole}^{-1} \text{K}^{-1}$. Calculate E_a .

Ans:

$$k = A e^{-E_a/RT}$$

$$\text{Given } k = A e^{-27000 k/T}$$

On comparison,

$$\frac{E_a}{RT} = \frac{27000 k}{T} \quad \left(\because k = \frac{R}{N_A} \right)$$

$$E_a = \frac{27000 R^2}{N_A}$$

$$E_a = \frac{27000 \times 4}{6.23 \times 10^{23}} = 18 \times 10^{-20} \text{ cal.}$$

A value of E_a is very small, so rxn would be very fast.

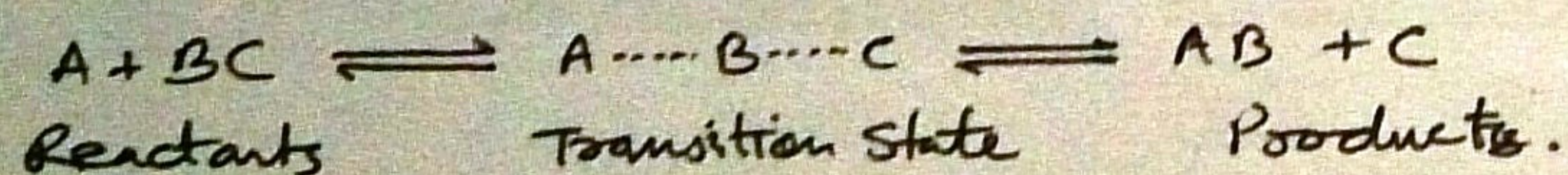
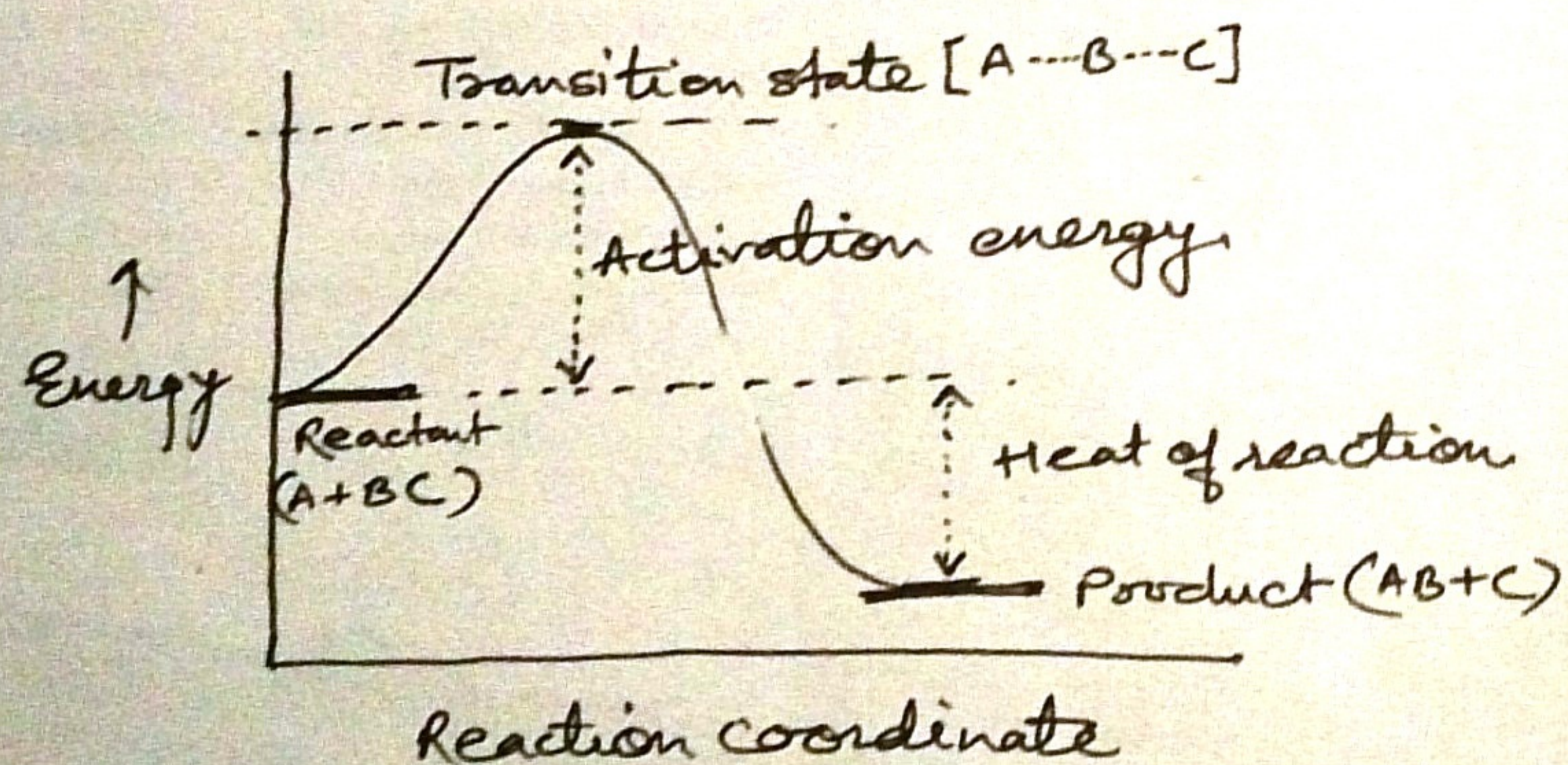
Activation Energy & Chemical Reactions

(37)

The minimum amount of energy which must be associated with molecules so that mutual collision may result in chemical reaction, is termed as threshold energy.

The excess energy that the molecules having energy less than threshold energy must ~~as~~ acquire in order to react to give the final products is known as activation energy.

$$\text{Activation Energy} = \text{Threshold Energy} - \text{Energy of molecule}$$



Theories of Rxn Rates.

Collision Theory (Arrhenius Eqⁿ) & Transition State Theory.

(38)

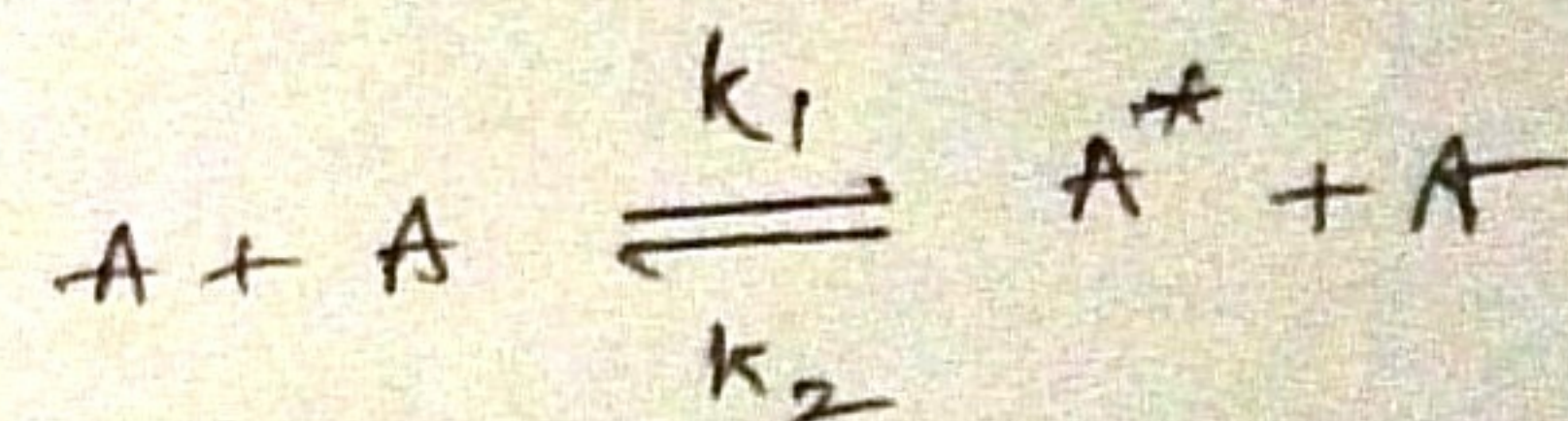
① Collision Theory:

How do molecules in unimolecular reactions attain their energy of activation?

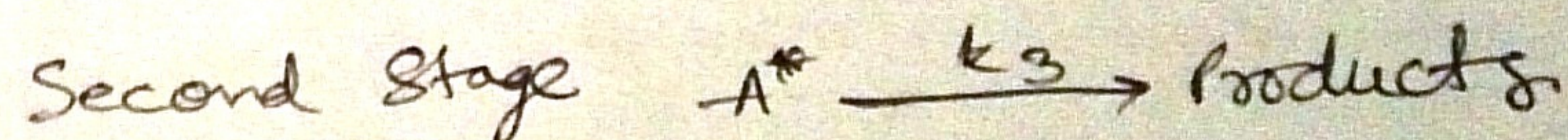
Lindemann Theory of Unimolecular Reaction.

Lindemann explained unimolecular reactions on the basis of bimolecular collisions provided we postulate that a time lag exists between activation and reaction during which activated molecules may either react or get deactivated to ordinary molecules.

First stage



Second stage



$$\text{Rate of activation} = k_1 [A]^2$$

$$\text{Rate of deactivation} = k_2 [A^*] [A]$$

$$\text{Rate of decomposition} = k_3 [A^*]$$

According to s.s.a., whenever a short lived intermediate occurs in a system, its rate of formation can be taken as equal to its rate of disappearance.

thus: $k_1 [A]^2 = k_2 [A^*] [A] + k_3 [A^*]$

$$= [A^*] \{ k_2 [A] + k_3 \}$$

$$[A^*] = \frac{k_1 [A]^2}{k_2 [A] + k_3}$$

Since rate of reaction is proportional to the conc of activated molecules, therefore,

$$\text{Rate of rxn} = -\frac{d[A]}{dt} = k_3 [A^*]$$

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3}$$

At high pressure: $k_2 [A] \gg k_3$

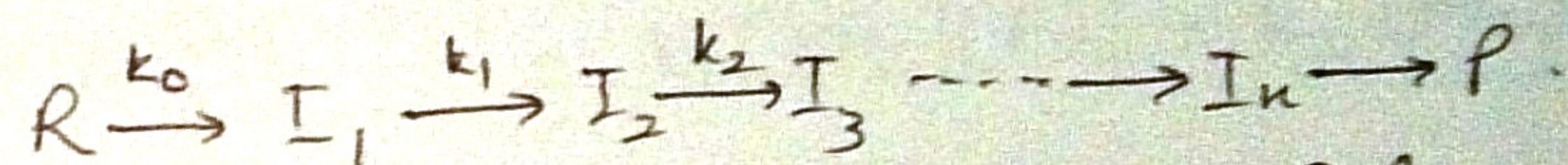
$$\Rightarrow -\frac{d[A]}{dt} = \frac{k_1 k_3}{k_2} [A] = k' [A] \quad (\text{1st order})$$

At low pressure: $k_3 \gg k_2 [A]$

$$-\frac{d[A]}{dt} = \frac{k_1 k_3}{k_3} [A]^2 = k_1 [A]^2 \quad (\text{2nd order})$$

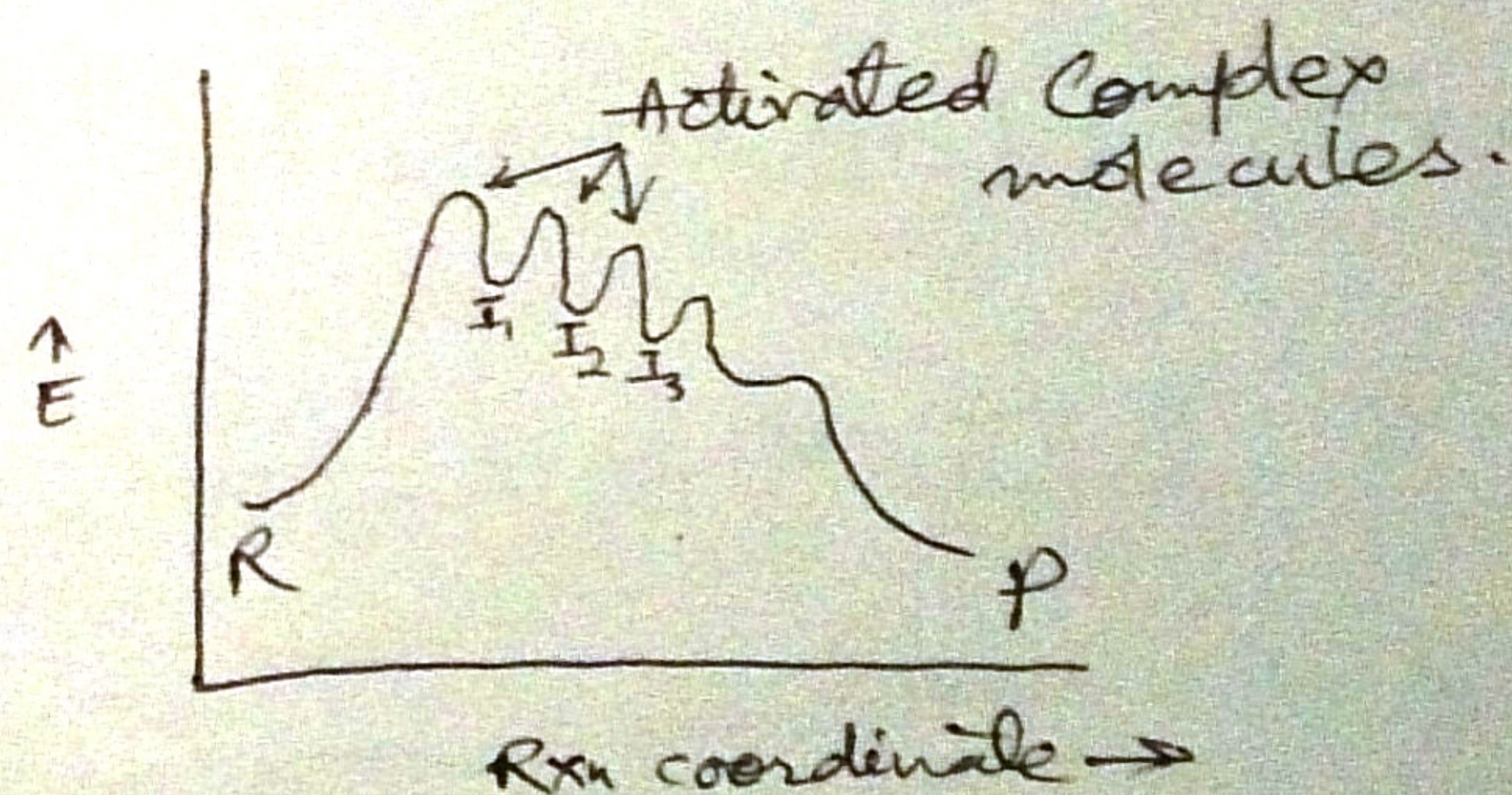
Steady State Approximation

If reactions are investigated under such conditions that the slowest rate determining step does not exist, one assumes the steady state approx. for the transient species.



the rate of formation of ~~the~~ intermediates is equal to the rate of its decomposition:

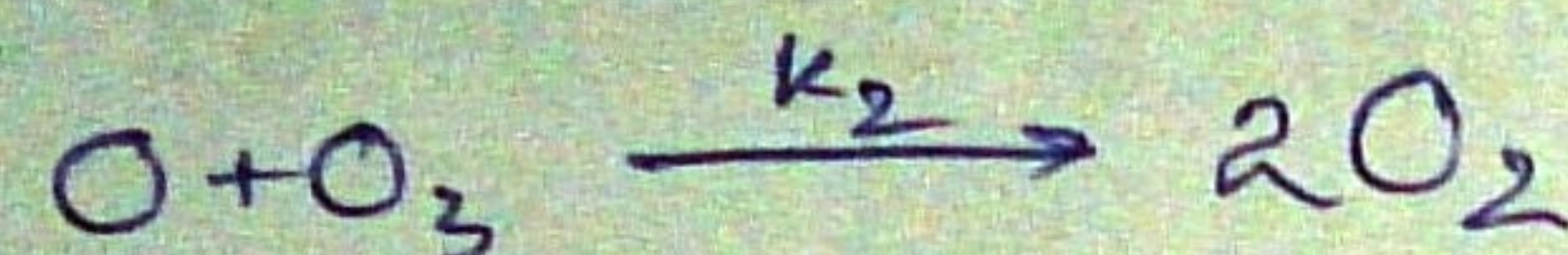
$$\frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} = \frac{d[I_n]}{dt} = 0$$



Example 8
Decomposition of Ozone:



Proposed mechanism:



Total rate of disappearance of O_3 :-

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_2[O_3][O].$$

now: $\frac{d[O]}{dt} = 0 = k_1[O_3] - k_2[O][O_3]$

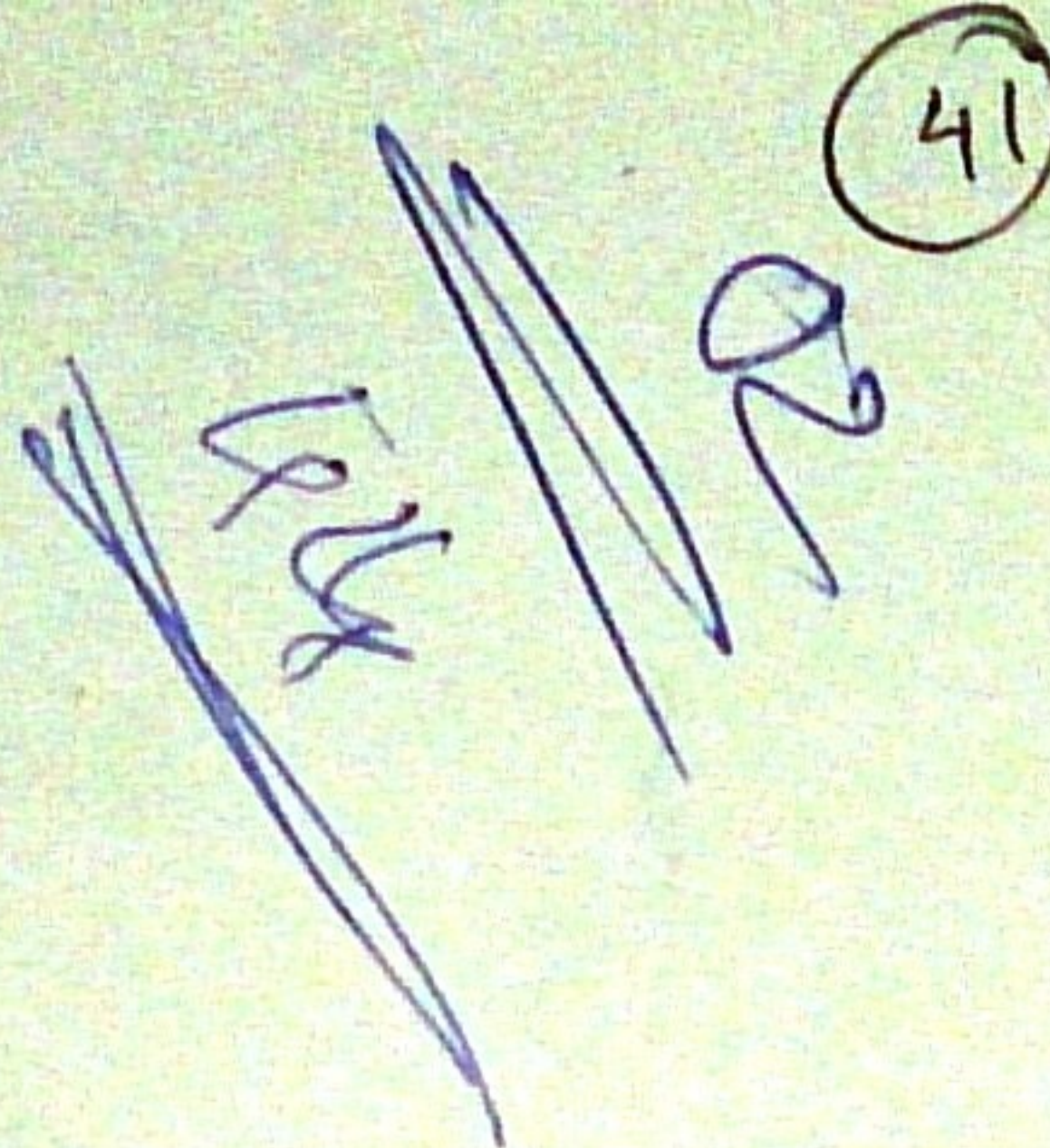
$$\Rightarrow [O] = \frac{k_1}{k_2}$$

Placing value of $[O]$ in eq ①.

$$-\frac{d[O_3]}{dt} = k_1[O_3] + k_1[O_3].$$

$$\text{or } -\frac{1}{2} \frac{d[O_3]}{dt} = k_1[O_3]$$

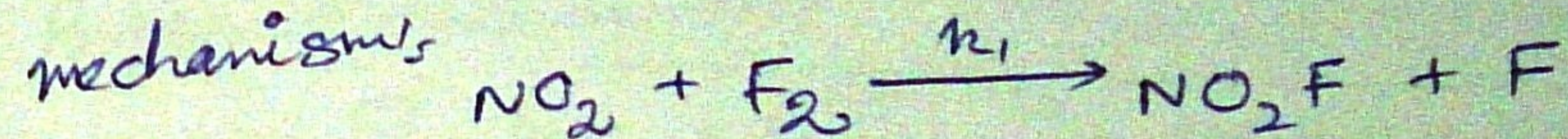
Thus decomposition of O_3 follows 1st order kinetics



Reaction between NO_2 & F_2 :



mechanism:



$$-\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] + k_2[NO_2][F]. \quad \text{--- ①}$$

Now applying SSA for $[F]$:

$$\frac{d[F]}{dt} = 0 = k_1[NO_2][F_2] - k_2[F][NO_2].$$

$$\Rightarrow [F] = \frac{k_1}{k_2}[F_2]$$

Placing the value in eq ①.

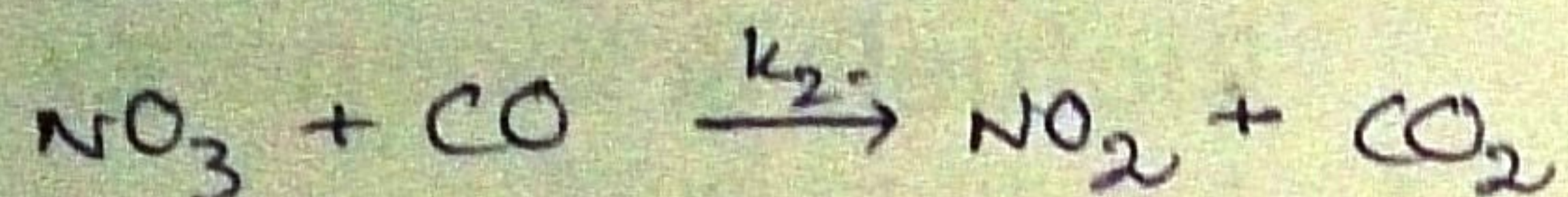
$$-\frac{d[NO_2]}{dt} = k_1[NO_2][F_2] + k_1[NO_2][F_2].$$

$$\text{or } -\frac{1}{2} \frac{d[NO_2]}{dt} = k_1[NO_2][F_2].$$

(second order)



Mechanism:



$$-\frac{d[\text{NO}_2]}{dt} = 2k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}]$$

Applying ssa for $[\text{NO}_3]$.

$$\frac{d[\text{NO}_3]}{dt} = 0 = k_1[\text{NO}_2]^2 - k_2[\text{NO}_3][\text{CO}]$$

$$\Rightarrow [\text{NO}_3] = \frac{k_1}{k_2} \frac{[\text{NO}_2]^2}{[\text{CO}]}$$

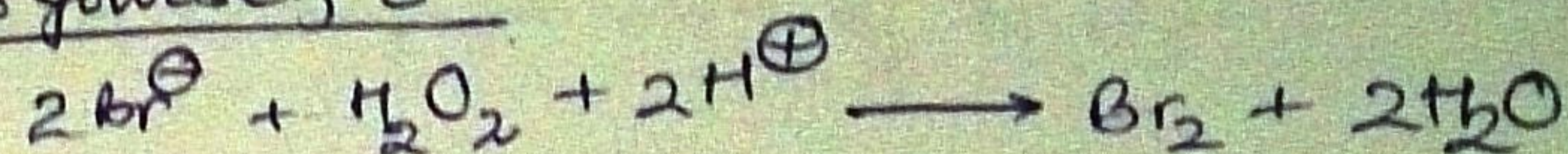
$$\Rightarrow -\frac{d[\text{NO}_2]}{dt} = 2k_1[\text{NO}_2]^2 - k_2 \cdot \frac{k_1}{k_2} \frac{[\text{NO}_2]^2}{[\text{CO}]} [\text{CO}]$$

$$-\frac{d[\text{NO}_2]}{dt} = k_1[\text{NO}_2]^2$$

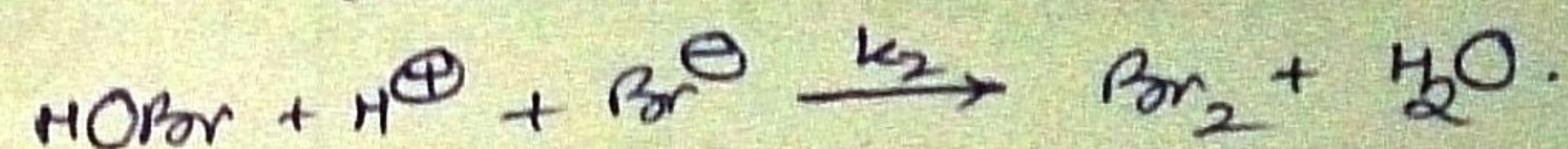
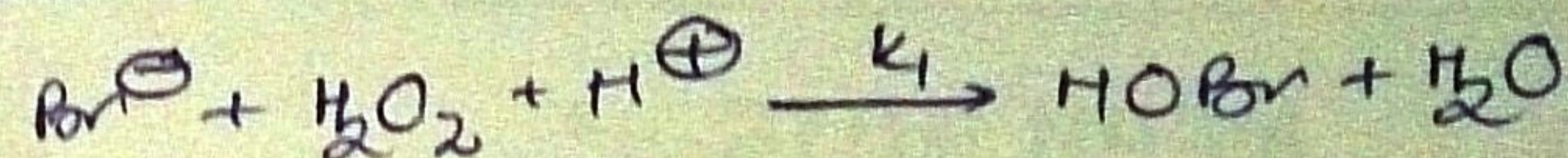
Second Order

(43)

Do yourself 8



Proposed mechanism:

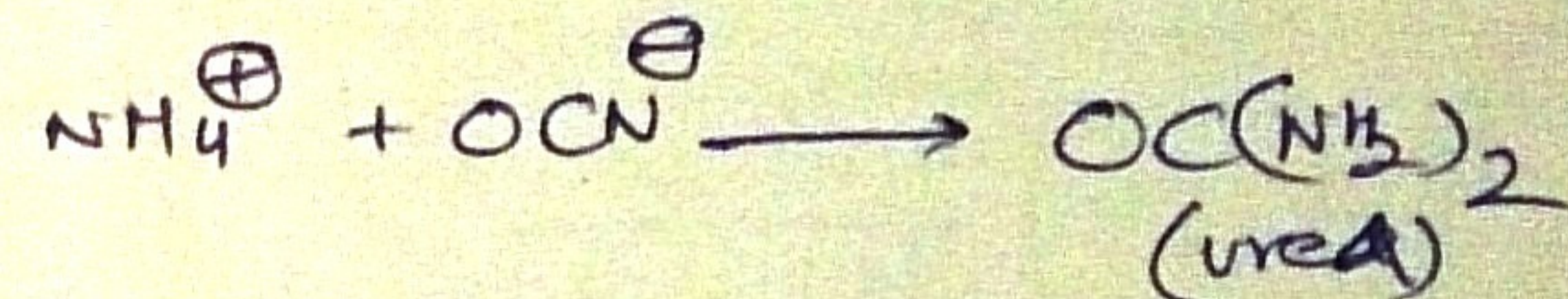


Get the expressions:

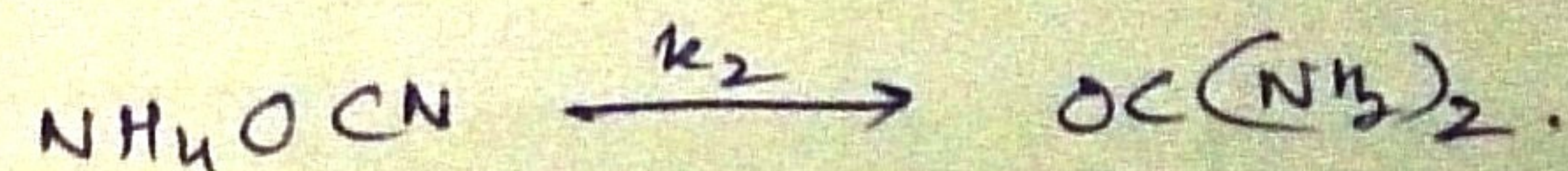
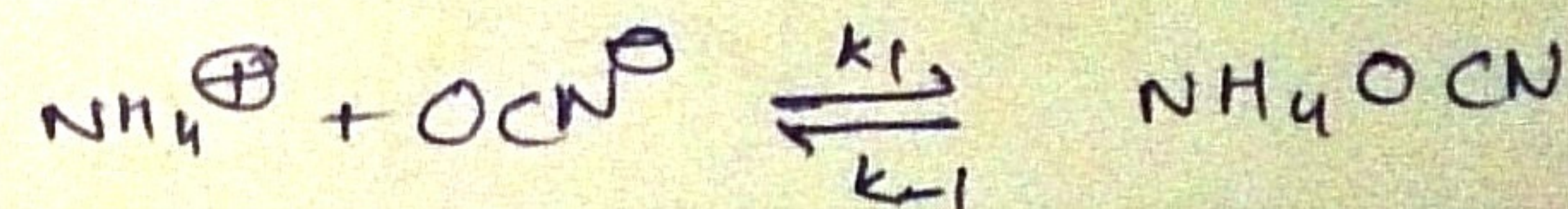
$$\frac{d[\text{Br}_2]}{dt} = k_2[\text{HOBr}][\text{Br}^\ominus]$$

$$\frac{d[\text{Br}_2]}{dt} = k_1[\text{H}_2\text{O}_2][\text{H}^\oplus][\text{Br}^\ominus]$$

Q2:



Proposed mechanism:



Get the expression.

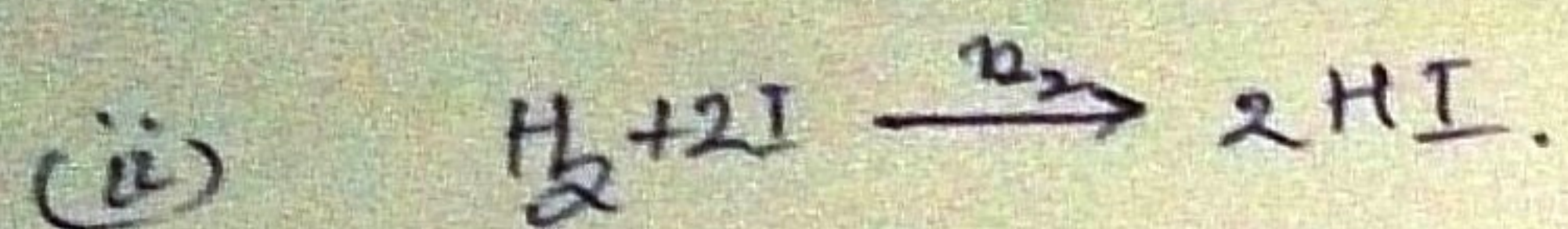
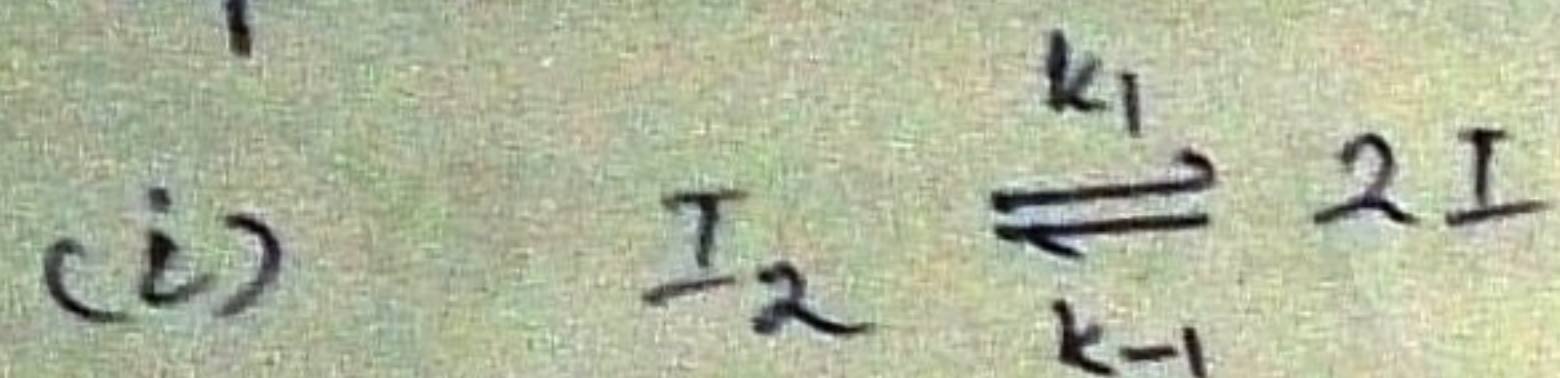
$$\frac{d[\text{urea}]}{dt} = \underbrace{k_2 K_{eq}}_k [\text{NH}_4^\oplus][\text{OCN}^\ominus]$$

(44)

Hydrogen-Iodine Reactions-

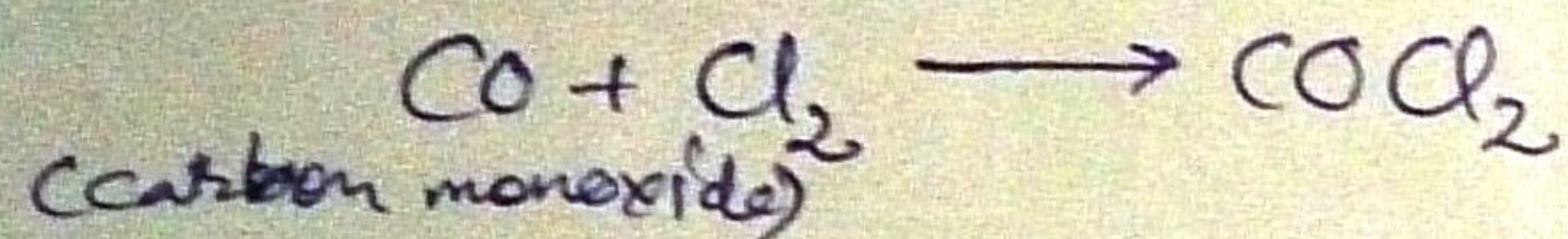


Proposed mech:

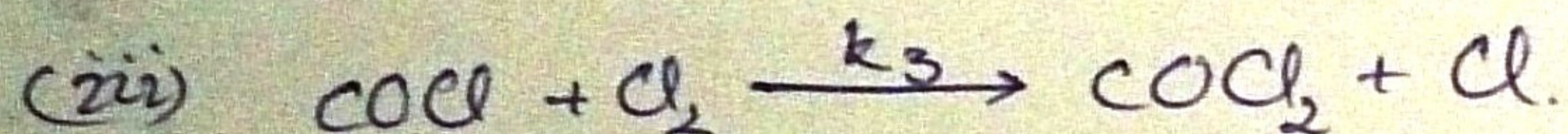
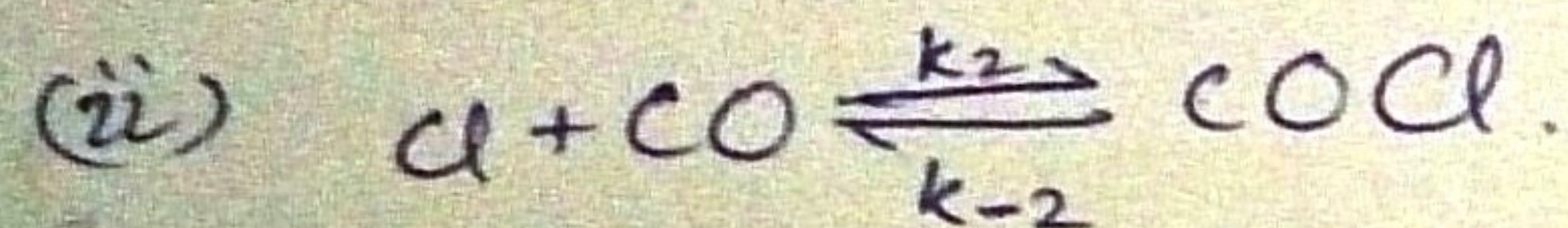
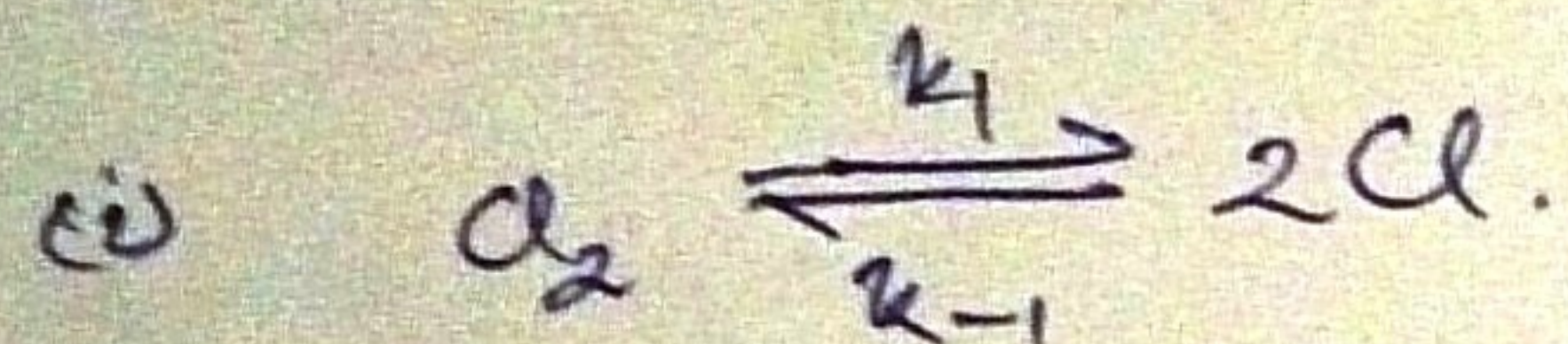


Get: $\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_2 \frac{k_1}{k_{-1}} [\text{H}_2][\text{I}_2]$

Formation of phosgene:



Mech:-



get: $\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$

Hint 3 - $k = k_3 \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}} \right)^{1/2}$

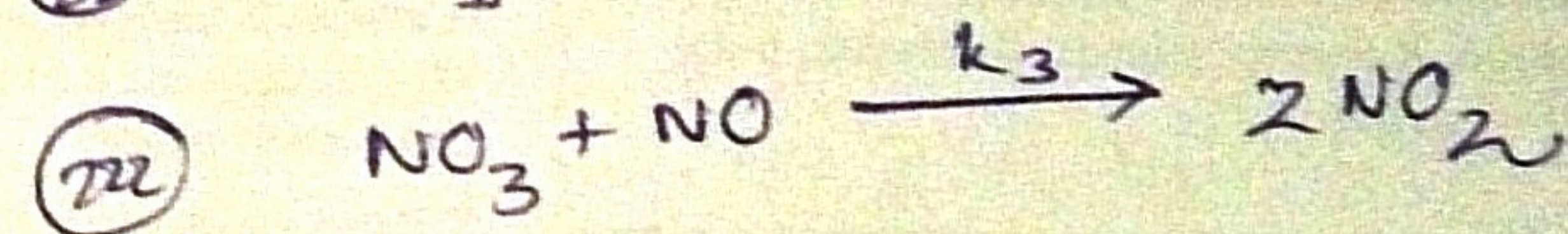
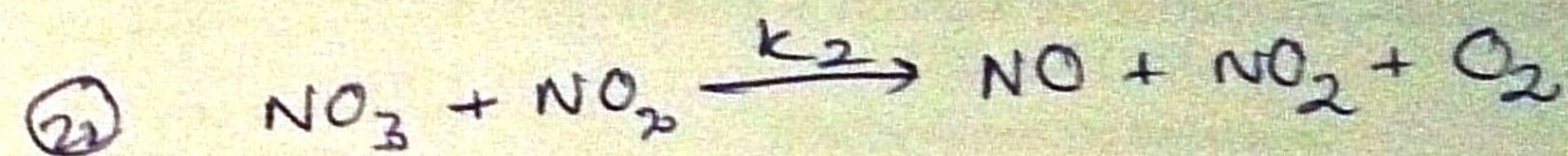
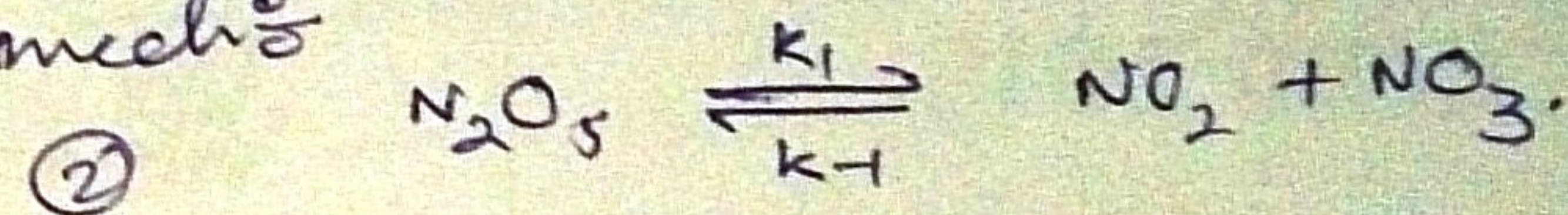
(45)

Decomposition of N_2O_5

(46)



mech:



Get: $\frac{d[\text{O}_2]}{dt} = k_2 \left(\frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + 2k_2)[\text{NO}_2]} \right) [\text{NO}_2]$

$$= \frac{k_2 k_1}{k_{-1} + 2k_2} [\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = k[\text{N}_2\text{O}_5]$$

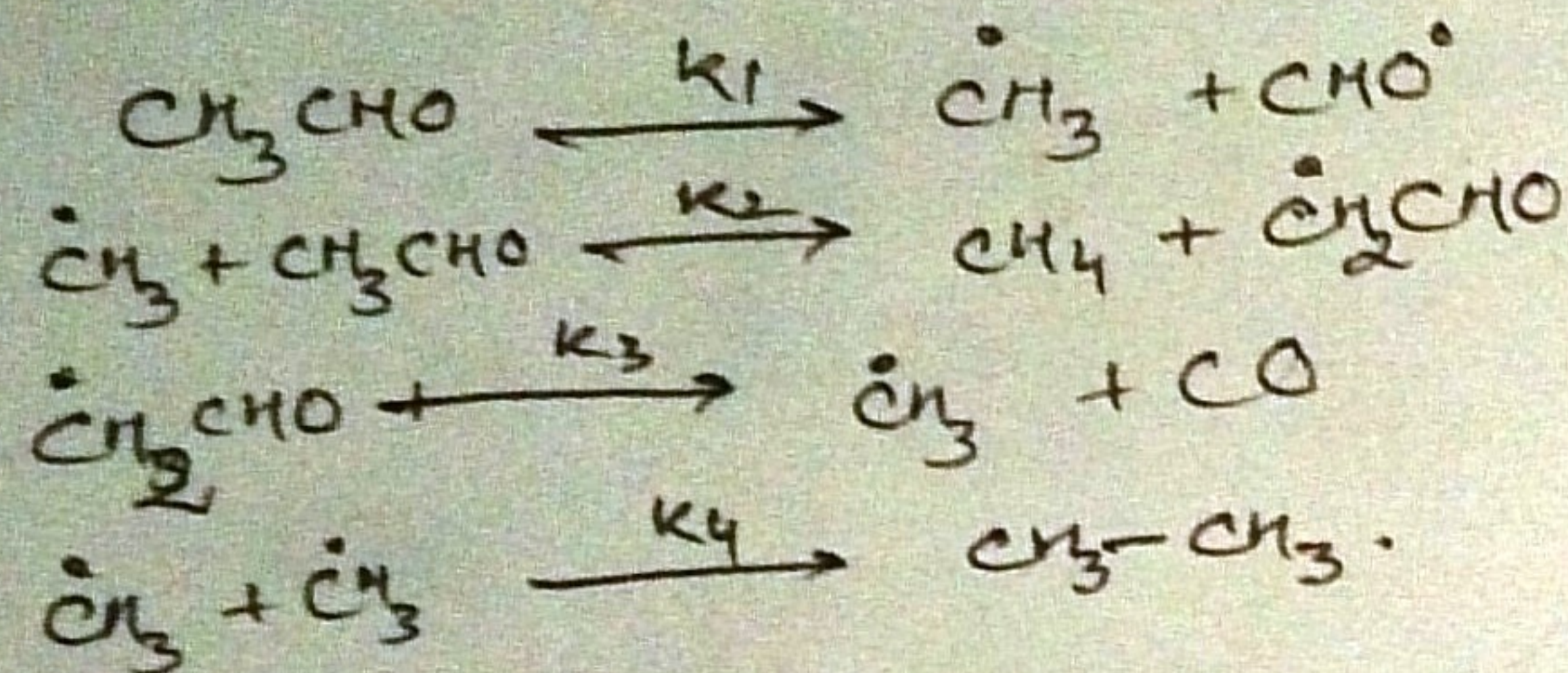
Decomposition of Acetaldehydes



rate law:

$$\frac{d[\text{CH}_4]}{dt} = k [\text{CH}_3\text{CHO}]^{3/2}$$

mechanism:



Solution 8

$$\therefore \frac{d[\text{CH}_4]}{dt} = k_2 [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] \quad \text{--- (1)}$$

applying ssa to $[\dot{\text{C}}\text{H}_3]$.

$$\frac{d[\dot{\text{C}}\text{H}_3]}{dt} = 0 = k_1 [\text{CH}_3\text{CHO}] - k_2 [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] - k_3 [\dot{\text{C}}\text{H}_2\text{CHO}] - 2k_4 [\dot{\text{C}}\text{H}_3]^2 \quad \text{--- (2)}$$

Applying ssa to $[\dot{\text{C}}\text{H}_2\text{CHO}]$.

$$\begin{aligned} \frac{d[\dot{\text{C}}\text{H}_2\text{CHO}]}{dt} &= k_2 [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] - k_3 [\dot{\text{C}}\text{H}_2\text{CHO}] = 0 \\ [\dot{\text{C}}\text{H}_2\text{CHO}] &= \frac{k_2}{k_3} [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] \quad \text{--- (3)} \end{aligned}$$

from (2) & (3):

$$0 = k_1 [\text{CH}_3\text{CHO}] - k_2 [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] - \frac{k_2}{k_3} [\dot{\text{C}}\text{H}_3] [\text{CH}_3\text{CHO}] - 2k_4 [\dot{\text{C}}\text{H}_3]^2$$

$$\Rightarrow [\dot{\text{C}}\text{H}_3] = \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} \quad \text{--- (4)}$$

from (1) & (4):

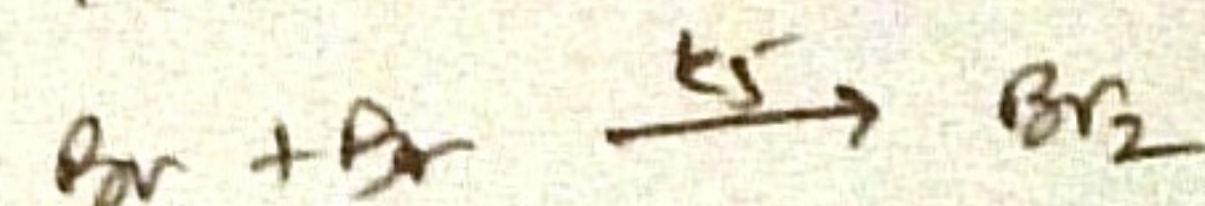
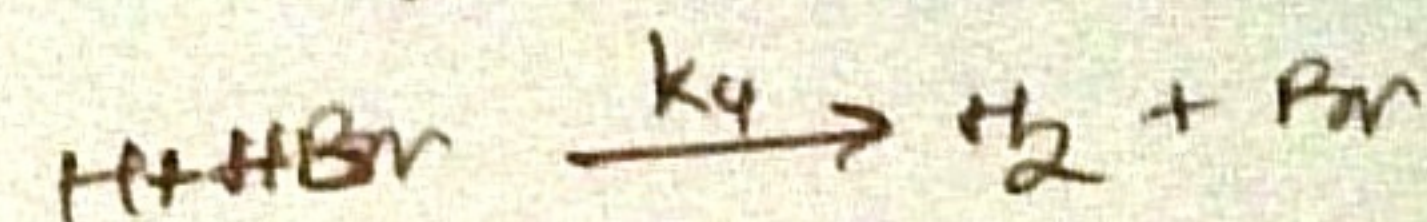
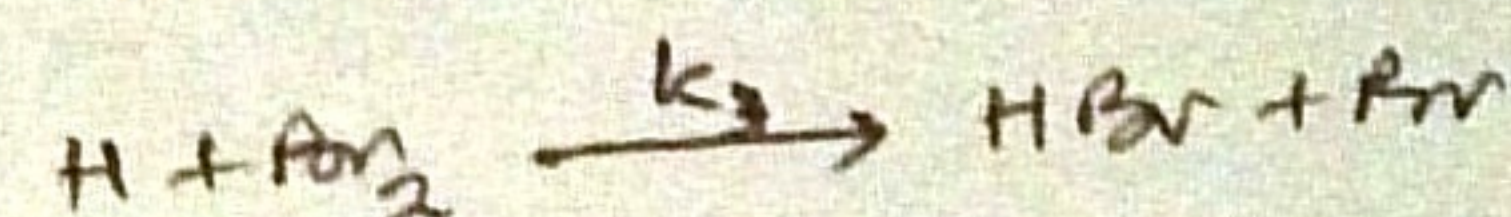
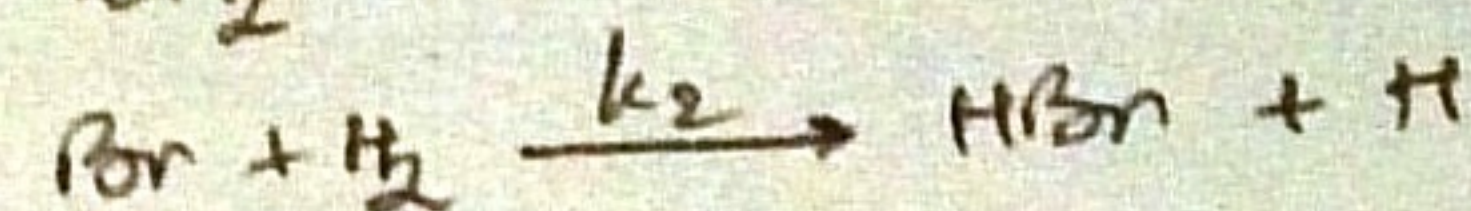
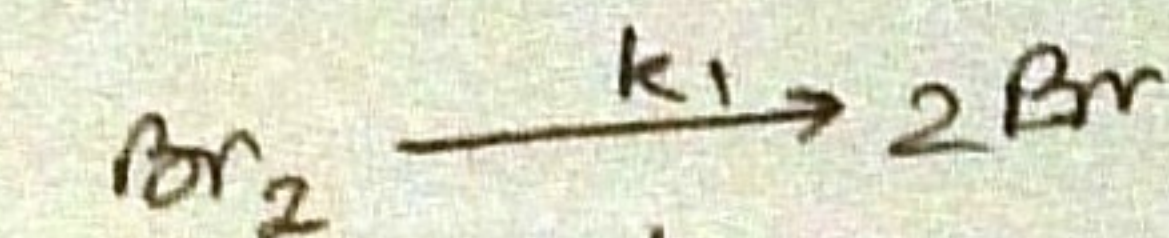
$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Proved

(47)

SSA example: Reaction between hydrogen & bromine.

(48)



$$\left| \frac{d[\text{HBr}]}{dt} = \frac{k [\text{Br}_2]^{3/2} [\text{H}_2]}{[\text{Br}_2] + k' [\text{HBr}]} \right.$$

$$\frac{d[\text{HBr}]}{dt} = k_2 [\text{Br}] [\text{H}_2] + k_3 [\text{H}] [\text{Br}_2] - k_4 [\text{H}] [\text{HBr}] \quad \text{--- (1)}$$

applying ssa to $[\text{H}]$.

$$\frac{d[\text{H}]}{dt} = k_2 [\text{Br}] [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] - k_4 [\text{H}] [\text{HBr}] = 0 \quad \text{--- (2)}$$

applying ssa to $[\text{Br}]$.

$$\begin{aligned} \frac{d[\text{Br}]}{dt} &= 2k_1 [\text{Br}_2] - k_2 [\text{Br}] [\text{H}_2] + k_3 [\text{H}] [\text{Br}_2] \\ &\quad + k_4 [\text{H}] [\text{HBr}] - 2k_5 [\text{Br}]^2 = 0 \quad \text{--- (3)} \end{aligned}$$

from (2) & (3):

$$\begin{aligned} 2k_1 [\text{Br}_2] &= 2k_5 [\text{Br}]^2 \\ \Rightarrow [\text{Br}] &= \left(\frac{k_1}{k_5} \right)^{1/2} [\text{Br}_2]^{1/2} \quad \text{--- (4)} \end{aligned}$$

from eq (2):

$$k_2 [\text{Br}] [\text{H}_2] = [\text{H}] (k_3 [\text{Br}_2] + k_4 [\text{HBr}])$$

$$\Rightarrow [\text{H}] = \frac{k_2 [\text{Br}] [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]}$$

Placing value of $[\text{Br}]$

$$\rightarrow [\text{H}] = \frac{k_2 \left(\frac{k_1}{k_5} \right)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \quad \text{--- (5)}$$

Placing the value of $[H]$ & $[Br]$ in eq (1).

(49)

$$\begin{aligned} \frac{d[HBr]}{dt} &= k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2] \\ &+ k_3 \frac{k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br]^{\frac{1}{2}} [H_2]}{k_3 [Br_2] + k_4 [HBr]} [Br_2] \\ &- \cancel{k_4 \frac{k_2 [Br] [H_2]}{k_3 [Br_2] + k_4 [HBr]} [HBr]} \\ &- k_4 \cdot \frac{k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2]}{k_3 [Br_2] + k_4 [HBr]} [HBr] \end{aligned}$$

~~Eq (2)~~

$$\begin{aligned} &= k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2] \left\{ 1 + \frac{k_3 [Br_2] + k_4 [HBr]}{k_3 [Br_2] + k_4 [HBr]} \right\} \\ &= k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2] \left\{ \frac{k_3 [Br_2] + k_4 [HBr] + k_3 [Br_2] - k_4 [HBr]}{k_3 [Br_2] + k_4 [HBr]} \right\} \\ &= k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2] \left\{ \frac{2 k_3 [Br_2]}{k_3 [Br_2] + k_4 [HBr]} \right\} \\ &= k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}} [H_2] \left\{ \frac{2 [Br_2]}{[Br_2] + \frac{k_4}{k_3} [HBr]} \right\} \\ &= 2 k_2 \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}} \cdot \frac{[Br_2]^{\frac{3}{2}} [H_2]}{[Br_2] + \frac{k_4}{k_3} [HBr]} \end{aligned}$$

$$\frac{d[HBr]}{dt} = \frac{k [Br_2]^{\frac{3}{2}} [H_2]}{[Br_2] + k' [HBr]}$$

Hence the proposed mechanism well explains the observed reaction's rate law expression.