

11/8/23

## CHAPTER-3

## CHEMICAL KINETICS

"The branch of chemistry which deals with the reaction rates is called chemical kinetics."

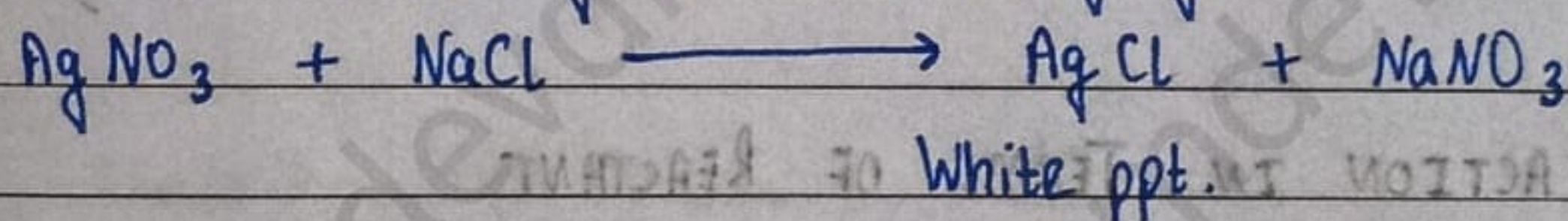


## TYPES OF REACTIONS BASED ON REACTION RATES

- VERY FAST REACTION

The chemical reaction which are completed the <sup>moment</sup> ~~movement~~ at the reactants are mixed.

Example: Generally, the reactions in ionic compound taking place in aqueous solution belong to this category.



- VERY SLOW REACTION

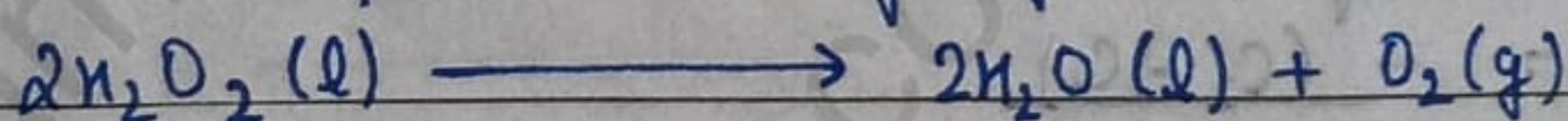
Certain many reactions are very slow.

Example: Rusting of iron, fermentation of sugar in the presence of yeast

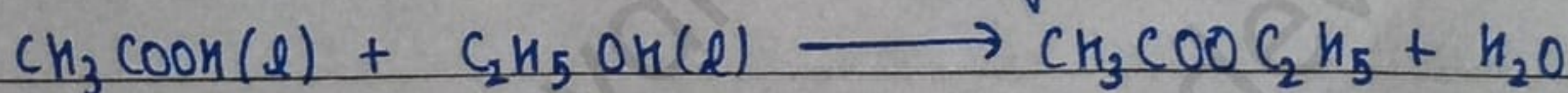
- MODERATE REACTION [REACTION <sup>PROCEEDING</sup> ~~PRODUCING~~ AT MEASURABLE RATE]

These reactions proceed at a limited speed.

Example: (i) Decomposition of Hydrogen peroxide



(ii) Reaction between acetic acid and ethyl alcohol



(Ester) Fruity smell like perfume

- ★ RATE OF A CHEMICAL REACTION

The rate of a chemical reaction is the change in molar

concentration of the species taking part in a reaction per unit time.

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

NOTE → Rate of reaction can be written in terms of change in concentration of reactants as well as product.

### • TYPES OF RATE

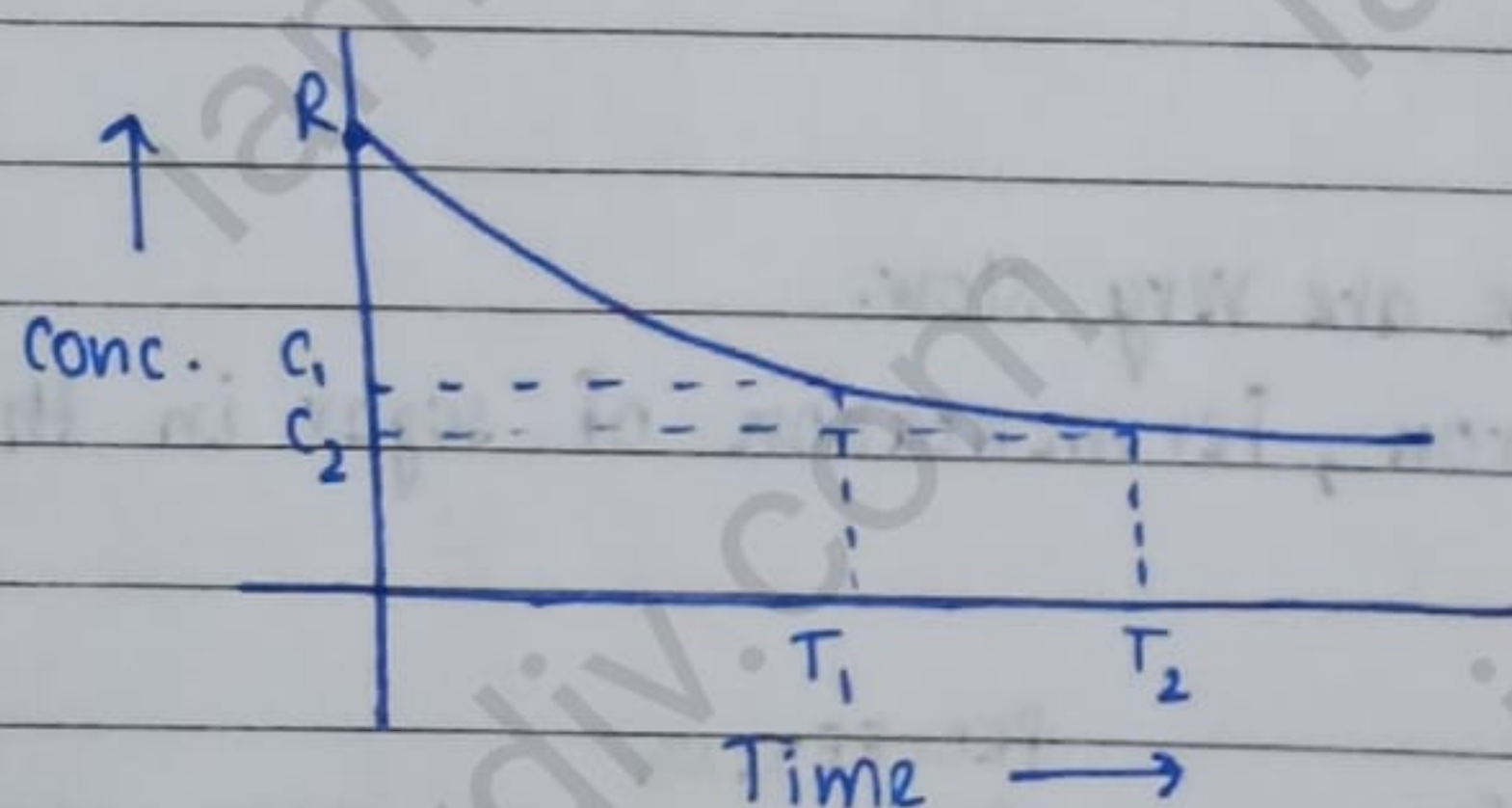
#### 1. AVERAGE RATE ( $v_{\text{avg}}$ )

Rate of reaction measured over a time interval is called  $v_{\text{avg}}$

$$v_{\text{avg}} = \frac{\text{change in conc.}}{\text{Time interval}} = \pm \frac{\Delta C}{\Delta T}$$

Product (Rate of appearance) (ROA)  
Reactant (Rate of disappearance) (ROD)

#### a) RATE OF REACTION IN TERMS OF REACTANT

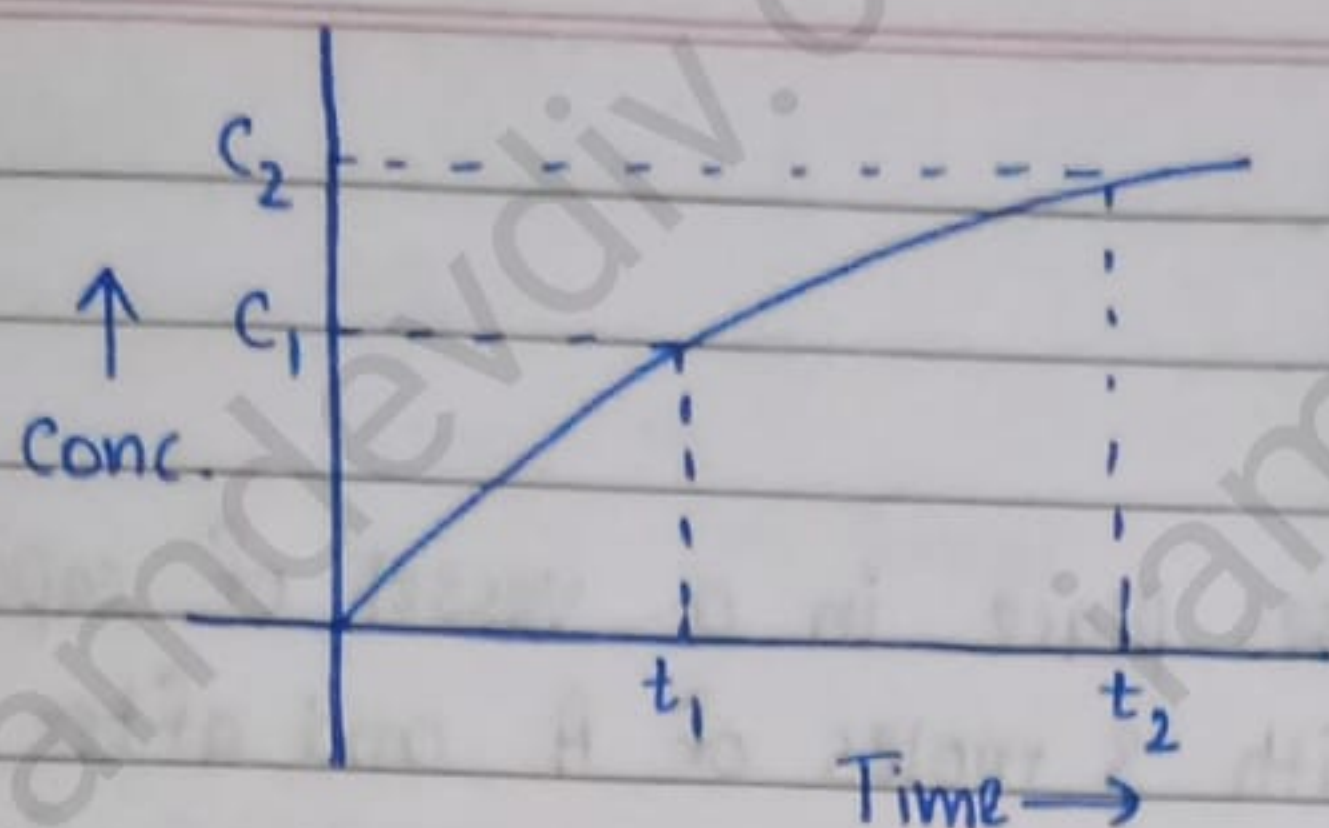


In this graph  $C_2 < C_1$  and the rate calculated have -ve sign which is not according to IUPAC convention.

$$\text{Rate} = - \frac{(C_2 - C_1)}{T_2 - T_1}$$

#### b) RATE OF REACTIONS IN TERMS OF PRODUCT

Next page →



$$r_{\text{avg}} = \frac{\text{Change in concentration}}{\text{Time interval}}$$

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

No need to put - sign because  $C_2 - C_1 > 0$

## 2. INSTANTANEOUS RATE OF REACTION [AT A POINT]

Rate of reaction at any instant during the reaction is called

$r_{\text{inst}}$

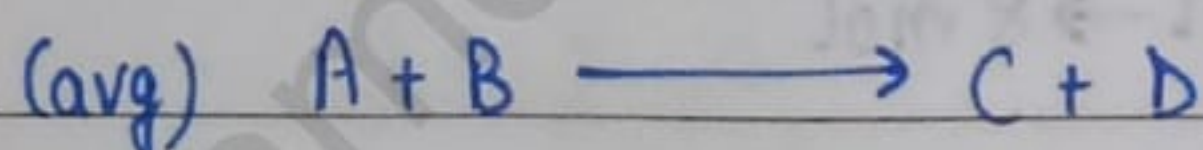
$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \pm \frac{\Delta C}{\Delta t} = \pm \frac{dC}{dt}$$

$$\text{(ROD)} \quad r_{\text{inst}} = - \frac{dC}{dt}$$

$$\text{(ROA)} \quad r_{\text{inst}} = + \frac{dC}{dt}$$

### Example

Let us consider a reaction



$$\text{ROD of A} = - \frac{[\Delta A]}{\Delta t}$$

$$\text{ROD of B} = - \frac{[\Delta B]}{\Delta t}$$

$$\text{ROA of C} = + \frac{\Delta C}{\Delta t}$$

$$\text{ROA of D} = + \frac{\Delta D}{\Delta t}$$

- Q The reaction  $A \rightarrow B$  takes place in a vessel of capacity 1L, the reaction is started with 3 moles of A and after 1M of A remains in the reaction vessel. which takes time of 3 seconds to disappear. Find (a) ROD of A  
(b) ROA of B

Sol. (a)  $\text{ROD of A} = - \frac{[\Delta A]}{\Delta t}$

$$= - \frac{[1-3]}{10-0} = \frac{2}{10} = \frac{1}{5}$$

$$= 0.2 \text{ mol L}^{-1} \text{ sec}^{-1}$$

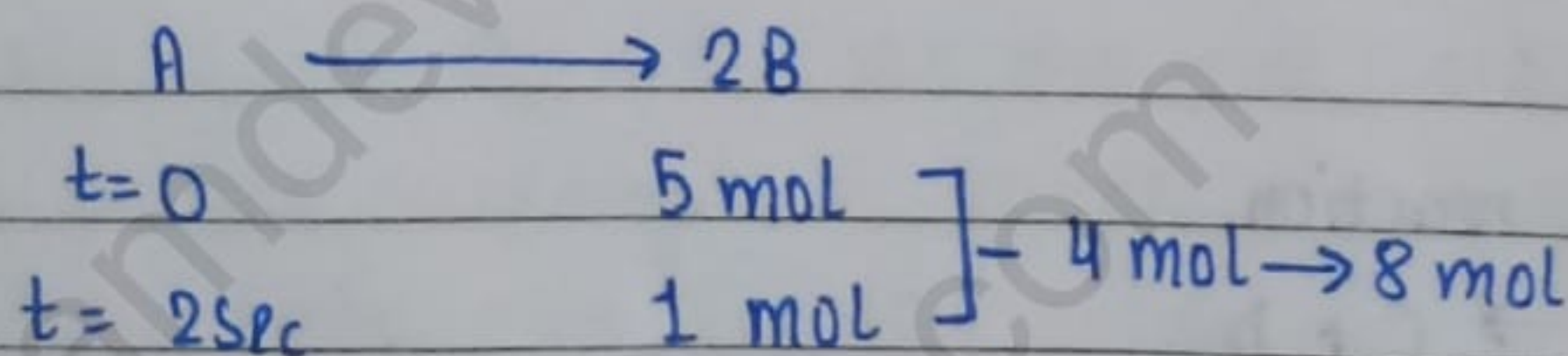
(b)  $\text{ROA of B} = + \frac{\Delta B}{\Delta t}$

$$= + \frac{[2-0]}{10-0} = \frac{2}{10} = \frac{1}{5}$$

$$= 0.2 \text{ mol L}^{-1} \text{ sec}^{-1}$$

### ★ RATE OF REACTION

#### • CONCEPT No. 1

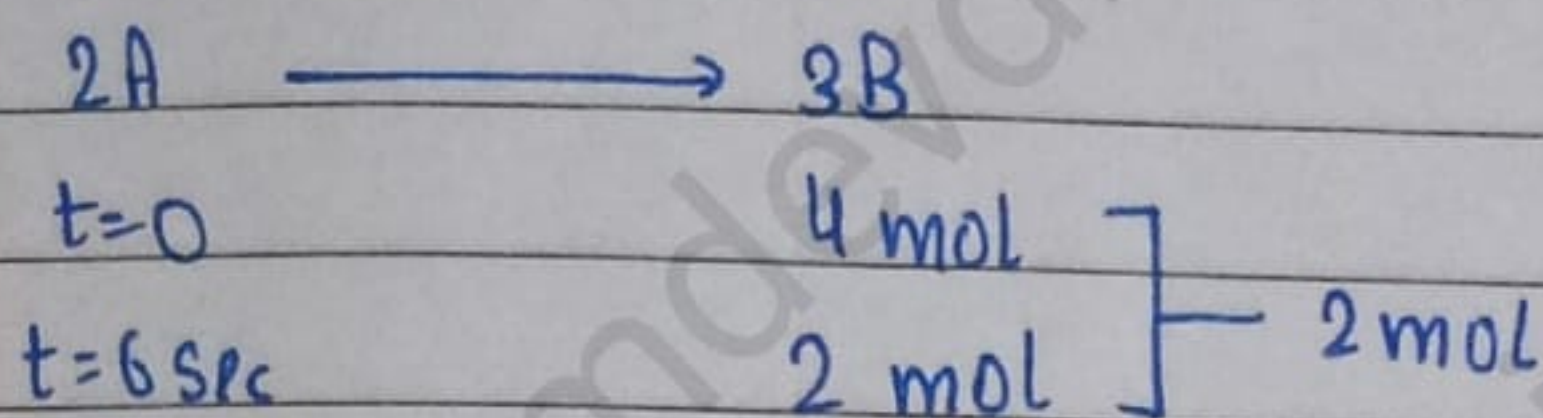


$$(\text{ROD})_A = - \frac{[1-5]}{2-0} = \frac{4}{2} = 2 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(\text{ROA})_B = \frac{8-0}{2-0} = 4$$

$$\text{ROR} = \frac{1}{2} \frac{[\Delta B]}{[\Delta t]} = \frac{1}{2} \times 4 = 2 \text{ mol L}^{-1} \text{ s}^{-1}$$

• CONCEPT No. 2

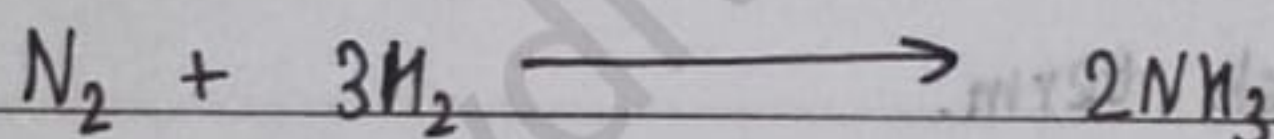


$$\text{ROD} = \frac{-[2-4]}{6-0} = \frac{1}{3} \times \frac{1}{2} = \frac{1}{6} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{ROA} = \frac{3-0}{6-0} = \frac{1}{2} \times \frac{1}{3} = \frac{1}{6} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{ROR} = \frac{-[\Delta A]}{\Delta t} \times \frac{1}{2} = \frac{[\Delta B]}{[\Delta t]} \times \frac{1}{3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Q Write down the equations for rate of reaction for the following equation



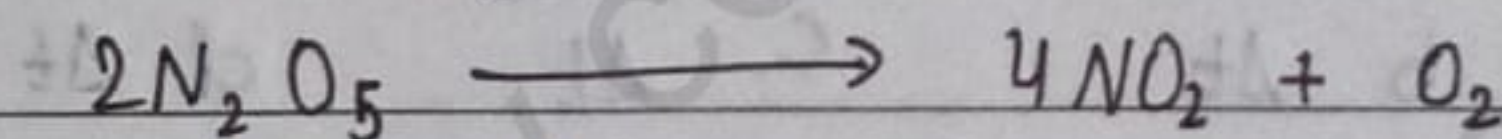
~~$$\frac{[\Delta N_2]}{\Delta t}$$~~

~~$$\frac{1}{2} \frac{[\Delta NH_3]}{\Delta t}$$~~

~~$$\frac{1}{3} \frac{[\Delta H_2]}{\Delta t}$$~~

~~$$\frac{-1}{2} \frac{[\Delta NH_3]}{\Delta t}$$~~

Q Write down the equations for ROR for the following -



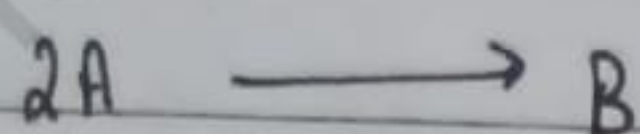
Sol. 
$$\text{ROD} = \frac{-1}{2} \frac{[\Delta N_2O_5]}{[\Delta t]}$$

$$\text{ROA} = \frac{[\Delta O_2]}{[\Delta t]}$$

$$\text{ROR} = \frac{1}{4} \frac{[\Delta NO_2]}{[\Delta t]}$$

Q For a reaction  $2A \longrightarrow B$  is conducted in the closed vessel of 1L and the following data has been given

P.T.O.



$$t = 0 \quad 6 \text{ mol}$$

$$t = 6 \text{ sec} \quad 2 \text{ mol}$$

(a) Find ROD of A

(b) Find ROD of B

(c) Find ROR

Sol. (a)  $\text{ROD} = - \frac{[\Delta A]}{\Delta t} = \frac{4}{6} = \frac{2}{3} \text{ mol l}^{-1} \text{ sec}^{-1}$

(b)  $\text{ROD} = + \frac{[\Delta B]}{\Delta t} = \frac{2}{6} = \frac{1}{3} \text{ mol l}^{-1} \text{ sec}^{-1}$

(c)  $\text{ROR} = - \frac{[\Delta A]}{\Delta t} \times \frac{1}{2} = \left[ \frac{2}{3} \right] \times \frac{1}{2} = \frac{1}{3} \text{ mol l}^{-1} \text{ s}^{-1}$

Q For a reaction  $aA + bB \longrightarrow cC + dD$ , determine ROD, ROA and ROR with respect to each term.

Sol.  $\text{ROD} = - \frac{[\Delta A]}{\Delta t} = - \frac{[\Delta B]}{\Delta t}$

$$\text{ROA} = + \frac{[\Delta C]}{\Delta t} = \frac{[\Delta D]}{\Delta t}$$

$$\text{ROR} = - \frac{1}{a} \frac{[\Delta A]}{\Delta t} = - \frac{1}{b} \frac{[\Delta B]}{\Delta t} = + \frac{1}{c} \frac{[\Delta C]}{\Delta t} = + \frac{1}{d} \frac{[\Delta D]}{\Delta t}$$

Q In a reaction  $A + 2B \longrightarrow 3C + 2D$ , the  $(\text{ROD})_B$  is  $10^{-2} \text{ mol l}^{-1} \text{ sec}^{-1}$ , what will be the ROR?

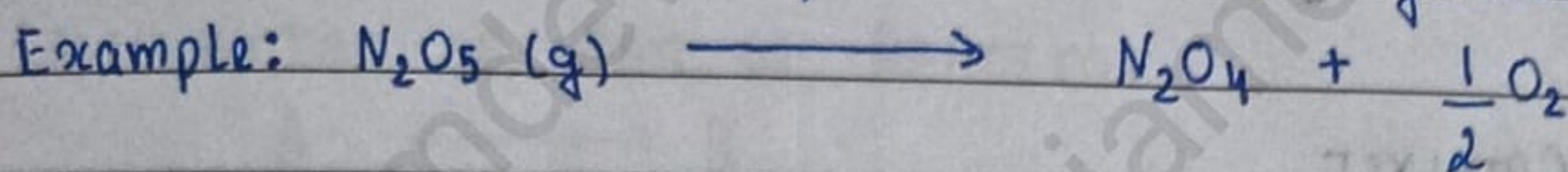
Sol.  $(\text{ROD})_B = 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$

$$\text{ROR} = \frac{1}{2} \frac{[\Delta B]}{\Delta t}$$

$$= \frac{1}{2} \times 10^{-2}$$

- CONCEPT No. 3

If the reactants and products are in gaseous state.



According to ideal gas equation,

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$P = CRT$$

$$P \propto C$$

[If T and R are constant]

NOTE → Rate with respect to reactant or product which has stoichiometric coefficient 1 is always called rate of reaction.

- ★ FACTORS AFFECTING RATE OF REACTION

- CONCENTRATION OF REACTANT

The rate of chemical reaction is directly proportional to concentration of reacting species due to increment in no. of collision per unit time.

- TEMPERATURE

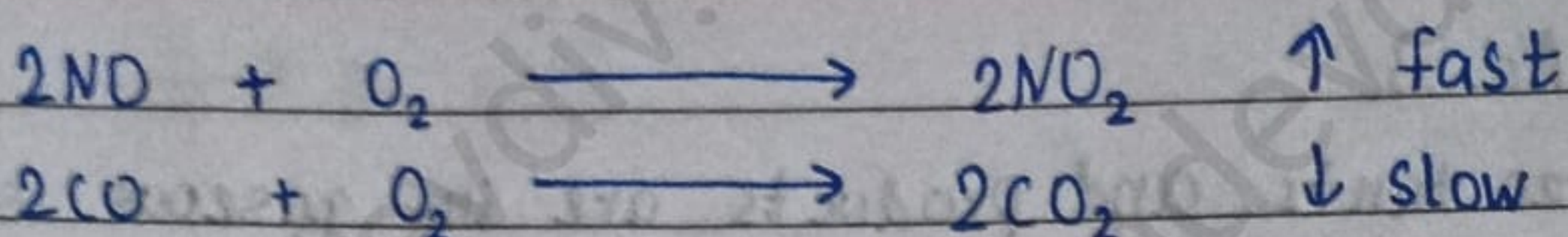
Rate of reaction increases on increasing the temp<sup>r</sup> due to increment per unit time (there are few exceptions as well).

- SURFACE AREA

On increasing the surface area, the rate of reaction increases because it provides more opportunity for the reactants.

- NATURE OF REACTANT

This can also affect the rate of reaction. For example: combustion of nitric oxide is faster ~~that~~ than that of carbon monoxide.

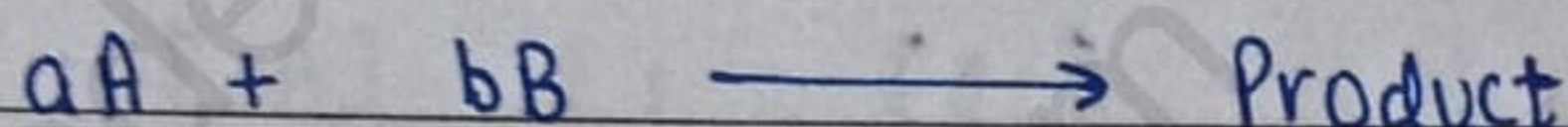


### • EFFECT OF CATALYST

Catalyst may alter the rate of reaction, that is, increases or decreases the substance which inhibit the rate of reaction are called negative catalyst.

### ★ DEPENDENCE OF RATE OF REACTION ON CONCENTRATION

Let us consider a reaction



On applying law of mass action

$$\text{Rate} \propto [\text{A}]^a [\text{B}]^b$$

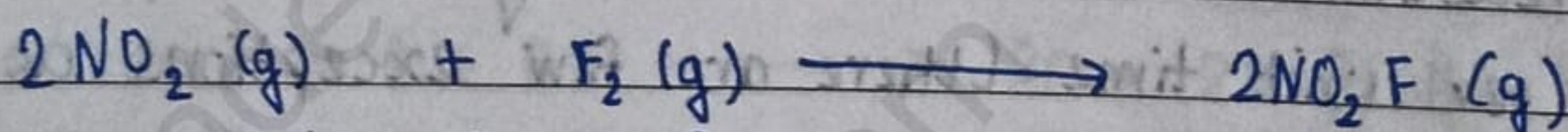
$$\text{Rate} = k[\text{A}]^a [\text{B}]^b$$

↳ rate constant

### \* DRAWBACKS OF MASS ACTION

1. This is not an universal reaction i.e. it doesn't apply to each and every reaction.
2. This is pure theoretical law, no experimental data was found to support.

### REASON

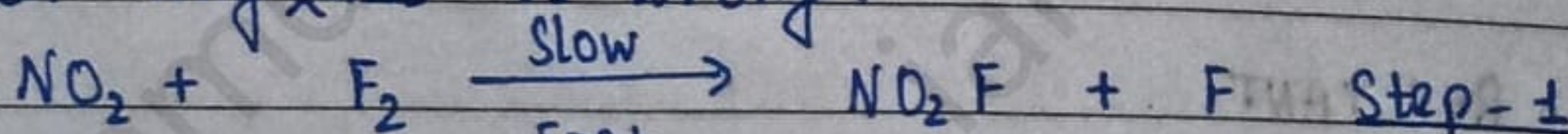


On applying law of mass action,

$$\text{Rate} = k[\text{NO}_2]^2 [\text{F}_2] \quad \times$$

$$\text{But the rate} = k[\text{NO}_2][\text{F}_2] \quad \checkmark$$

Reason why <sup>former</sup> ~~this~~ is wrong:

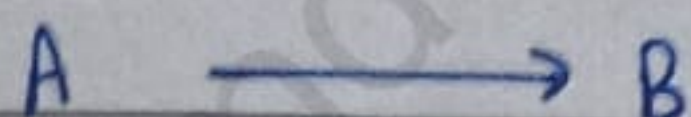


In this reaction, step-1 is a slow reaction which is a rate



determining step

### • CALCULATION OF RATE OF REACTION



Rate law

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

$$[A] = 1M$$

$$r_1 = 2 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$[A] = 2M$$

$$r_2 = 4 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$k[1]^n = 2$$

$$k[2]^n = 4$$

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

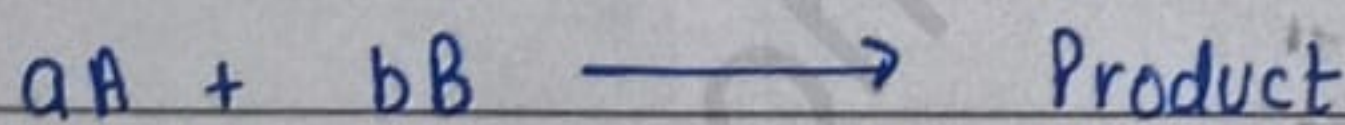
$$\boxed{n = 1}$$

### • ORDER OF REACTION

The exponent of concentration of any reactant in rate law is called order of reaction with respect to that reactant.

For example:

For a reaction,



Rate according to mass action,

$$R = \cancel{[A]^a} \cancel{[B]^b} [A]^a [B]^b$$

$$\text{Order} = \cancel{a} + \cancel{b}$$

Rate according to rate law,

$$R = [A]^x [B]^y$$

$$\text{Order} = x + y$$

Order is an experimental quantity, its value may be positive, negative, integer, fraction, etc.

Order with respect to any reactant may or may not be equal to its stoichiometry coefficient.

## • RATE CONSTANT (k)

It is the proportionality constant in a rate law of any chemical reaction

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

where,  $k$  = rate constant

$n$  = order

\* Rate constant is also called velocity constant or specific reaction constant.

\* Rate constant depends upon the following "factors":

1. Nature of reaction

2. Temp<sup>r</sup>

## \* UNIT OF RATE CONSTANT

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

$$k = \frac{r}{[A]^n} \text{ (unit)}$$

$$= \frac{\text{mol L}^{-1} \text{ time}^{-1}}{[\text{mol L}^{-1}]^n}$$

$$= \frac{\text{mol L}^{-1} \text{ time}^{-1}}{\text{mol}^n \text{ L}^{-n}}$$

$$\boxed{\text{Unit of } k = \text{mol}^{(1-n)} \text{ L}^{(n-1)} \text{ time}^{-1}}$$

For example: unit for 0 order reaction  
( $n=0$ )

$$\text{Unit of } k = \text{mol}^{(1-0)} \text{ L}^{(0-1)} \text{ time}^{-1}$$

$$= \text{mol}^{(1-0)} \text{ L}^{(0-1)} \text{ time}^{-1}$$

$$\text{Zero order } (k) = \text{mol L}^{-1} \text{ T}^{-1}$$

(which is equal to unit of rate of reaction)

unit for 1 order reaction

$$n = 1$$

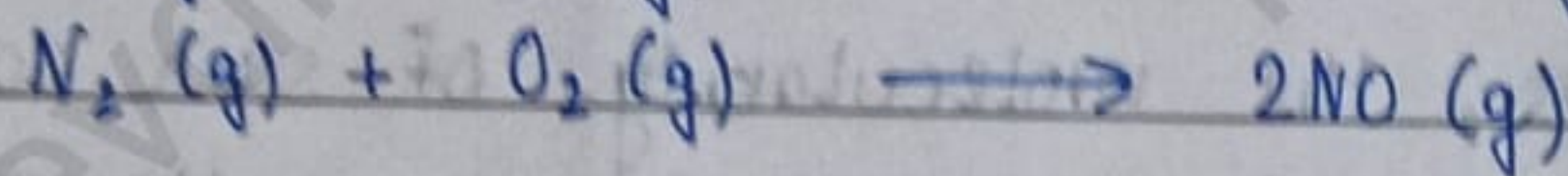
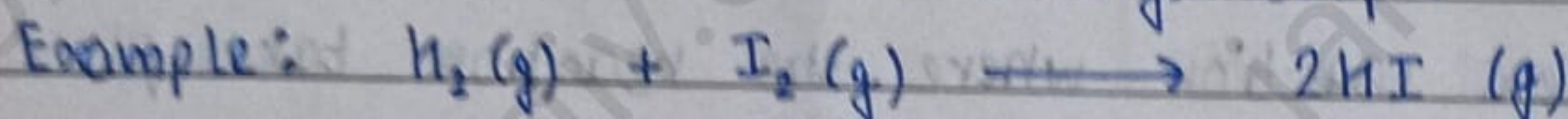
$$\text{mol}^{(1-1)} \text{ l}^{(1-1)} \text{ s}^{-1}$$

First order  $(k) = \text{s}^{-1}$

## \* TYPES OF REACTION

### • ELEMENTARY

Reactants combine to form a single step.

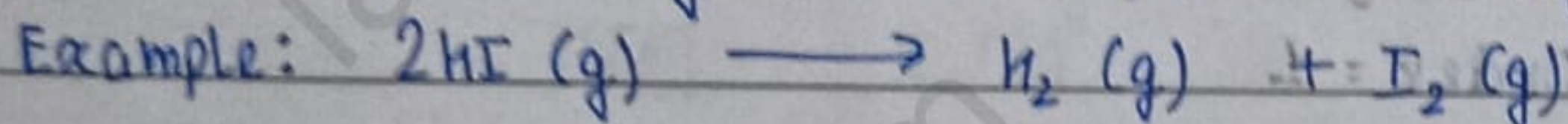


### • COMPLEX

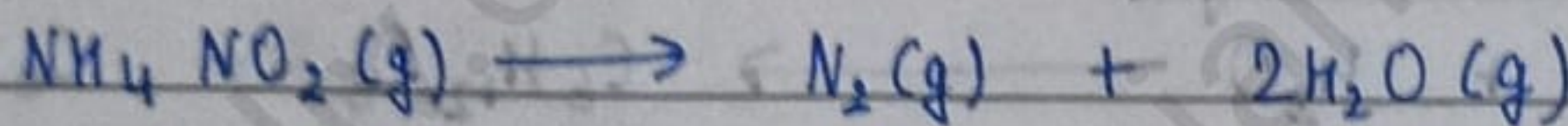
These are the reactions which take place in more than one step to form final product.

## \* MOLECULARITY

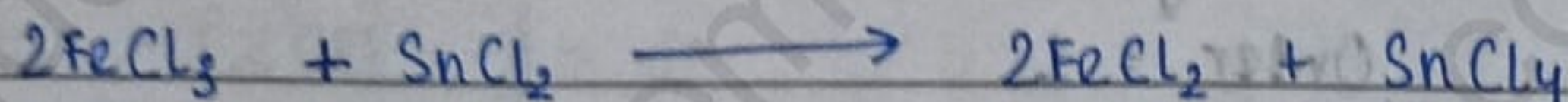
The number of molecules or atoms of reactants that take part in elementary chemical reaction (single-step reaction)



Molecularity = 2



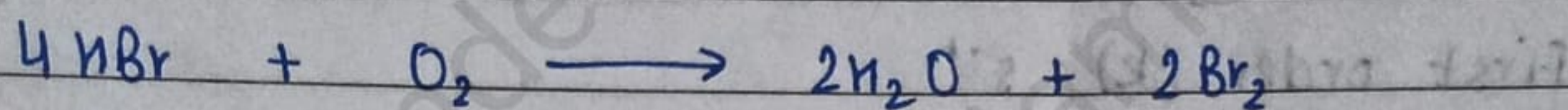
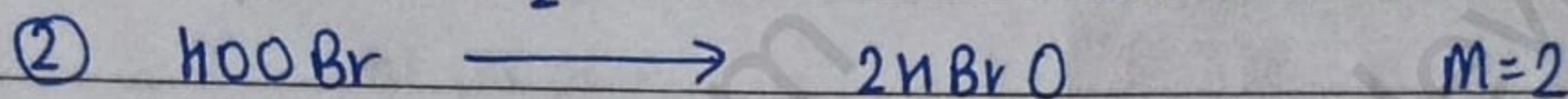
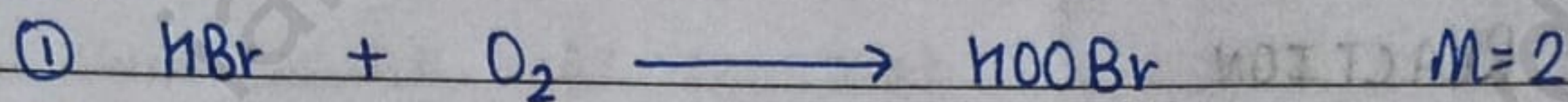
Molecularity = 1



Molecularity = 3

The no. of atoms or molecules of reactants that must collide simultaneously and effectively to give product in an elementary reaction.

## \* EXAMPLE OF COMPLEX REACTION

Steps

NOTE → For a complex reaction where the reaction takes place in multiple steps, the molecularity of such each step can be determined ~~in~~ individually but overall molecularity cannot be determined.

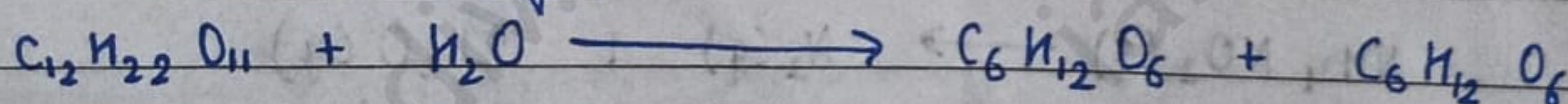
Hydrolysis of ester

Molecularity = 2

Rate law of this reaction,

$$\text{rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

Order = 2

Inversion of cane sugar

(excess)

Molecularity = 2

Order = 1

## \* DIFFERENCE BETWEEN ORDER AND MOLECULARITY

ORDER

1. Order is experimental quantity.
2. It is derived from the rate law.

MOLECULARITY

1. It is theoretical.
2. It is derived from the mechanism of reaction.

- |   |  |
|---|--|
| 3. Order can be fractional.   | 3. It can't be fractional, it is always a whole number.                              |
| 4. Order of reaction may be zero.   | 4. It can never be zero.   |
| 5. In a multistep reaction, order is determined for the slowest step only.  | 5. In a multi-step reaction, molecularity of each individual step can be calculated. |
| 6. The overall order of the multi-step reaction is given by slow-step only. | 6. A multistep reaction has no overall molecularity, only steps have molecularity.   |

NOTE → IF the molecularity of any reactants is found to be greater than 3, the reaction will definitely be a complex reaction.

### ★ ZERO ORDER REACTION

A zero order reaction is the reaction in which the reaction rate is proportional to zero power of concentration of reactants.

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

The instantaneous rate for zero order reaction,

$$-\frac{d[A]}{dt} = k[A]^0$$

$$\Rightarrow -\frac{d[A]}{dt} = k$$

$$\Rightarrow -d[A] = k dt$$

Integrating both sides

$$\Rightarrow -\int d[A] = \int k \cdot dt$$

$$\Rightarrow A = -k \cdot t + I$$

Here,  $I$  is the integrating constant and its value can be calculated from initial conditions

$$\text{When, } t = 0$$

$$A = [A]_0$$

$$A = -k \cdot t + I \quad \text{①}$$

Put this  $[A]_0 = I$  in ①

$$\Rightarrow A = -k \cdot t + [A]_0$$

$$\Rightarrow k \cdot t = [A]_0 - A$$

OR

$$\Rightarrow k = \frac{[A]_0 - [A]}{t}$$

This equation is called integrated rate equation for zero-order reaction.

### • HALF LIFE PERIOD FOR ZERO ORDER REACTION

(i) Half life period of a reaction is the time taken to complete half of the reaction.

(ii) It is denoted by  $t_{1/2}$

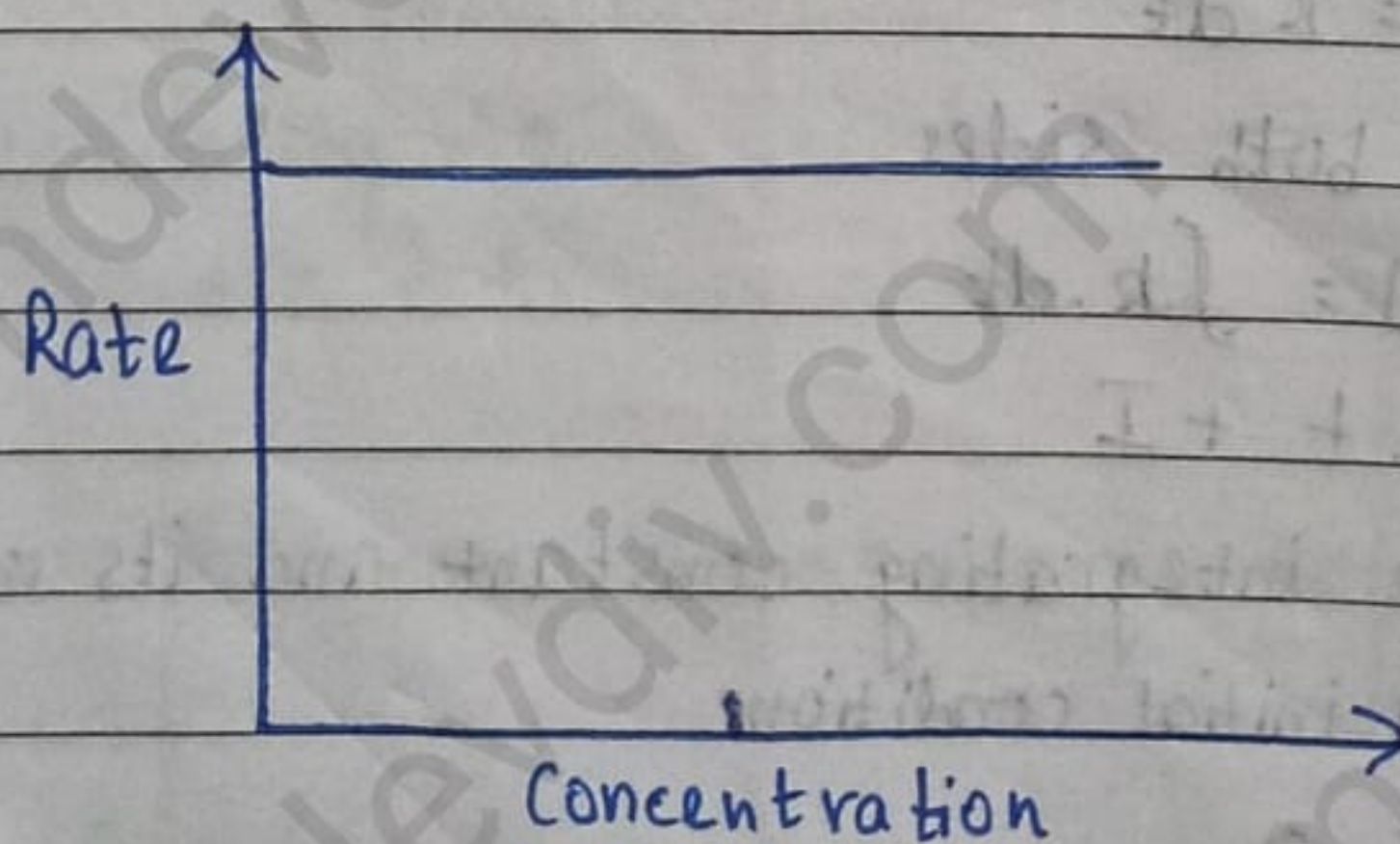
$$\text{If } t = t_{1/2} \Rightarrow S_0 [A] = [A]_0 / 2$$

$$k = \frac{[A]_0 - [A]_0 / 2}{t_{1/2}}$$

$$\Rightarrow k = \frac{[A]_0}{2 t_{1/2}}$$

$$\Rightarrow t_{1/2} = \frac{[A]_0}{2k}$$

(iii) In zero order reaction, half life period is inversely proportional to the rate constant.



Example: Thermal decomposition of gases like ammonia on catalyst surface is an example of zero order reaction.

## ★ FIRST ORDER REACTION

In a first order reaction, the rate of reaction is directly proportional to concentration of reactants.

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

$$r = -k[A]$$

$$\text{Instantaneous } r = -\frac{d[A]}{dt}$$

$$-\frac{d[A]}{dt} = -k[A] \quad \text{--- (1)}$$

$$\Rightarrow \frac{d[A]}{[A]} = -kt$$

$$\Rightarrow \int \frac{d[A]}{[A]} = -\int k dt$$

$$\Rightarrow \ln[A] = -kt + I \quad \text{--- (2)}$$

For integration constant,  
 $t = 0$

$$[A] = [A]_0$$

$$\Rightarrow -\ln[A]_0 = -k \times 0 + I$$

$$\Rightarrow -\ln[A]_0 = I$$

$$-\ln[A] = -kt - \ln[A]_0$$

$$\Rightarrow -\ln[A]_0 + \ln[A]_0 = kt$$

$$\Rightarrow \ln \frac{[A]}{[A]_0} = kt$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

$$\Rightarrow k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]}$$

This equation is called integrated rate equation for first order reaction.

## • HALF LIFE PERIOD FOR FIRST ORDER REACTION

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]}$$

$$\Rightarrow t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]}$$

$$\text{When } t = t/2, [A] = [A]_0/2$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \log_{10} \frac{[A]_0 \times 2}{[A]}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \times \log_{10} 2$$

$$\Rightarrow t_{1/2} = \frac{2.303 \times 0.3010}{k}$$

$$\Rightarrow t_{1/2} = \frac{0.6932}{k}$$

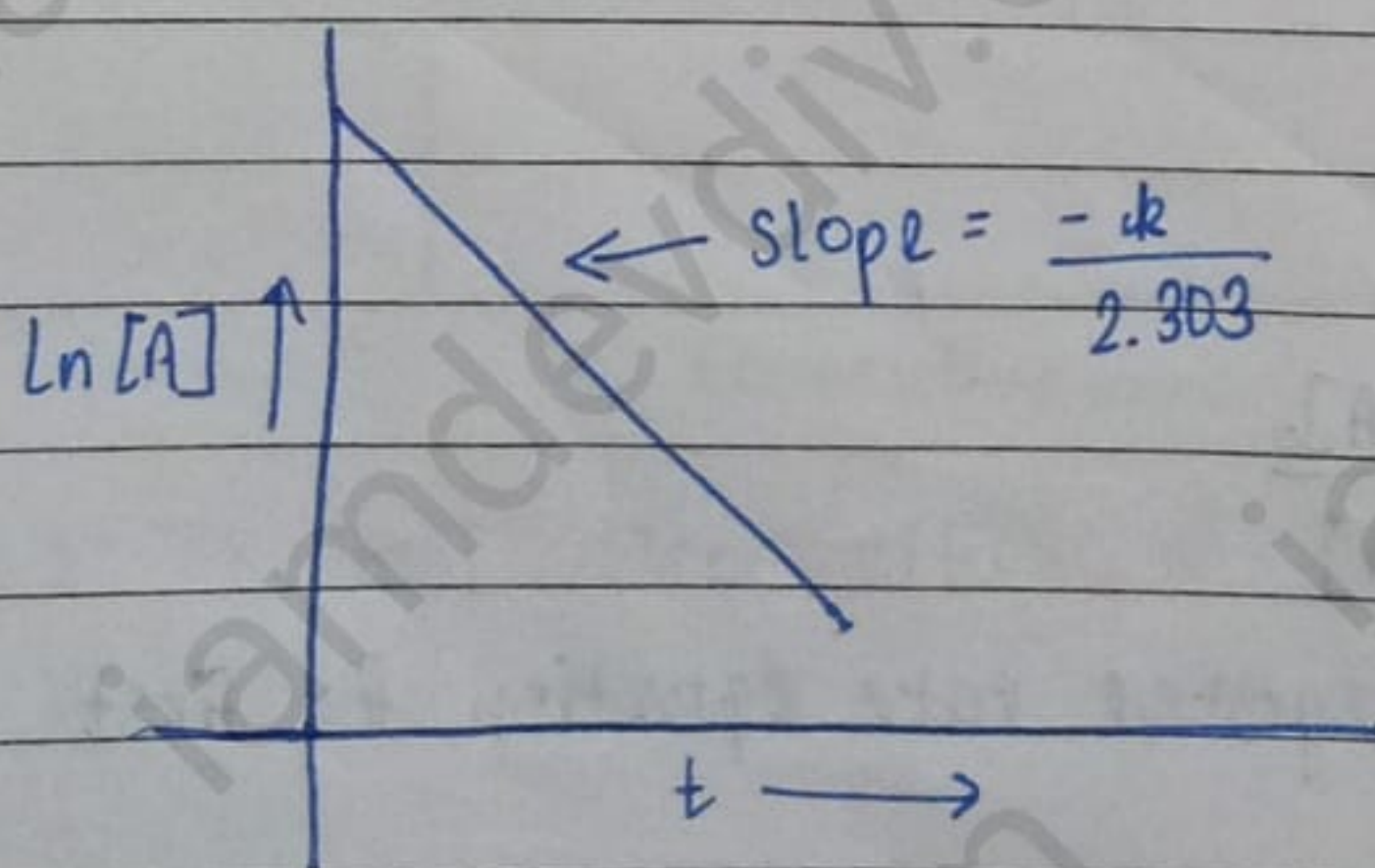
## • SOME IMPORTANT GRAPHS

### 1. GRAPH BETWEEN $\ln[A]$ V/S TIME FOR FIRST ORDER

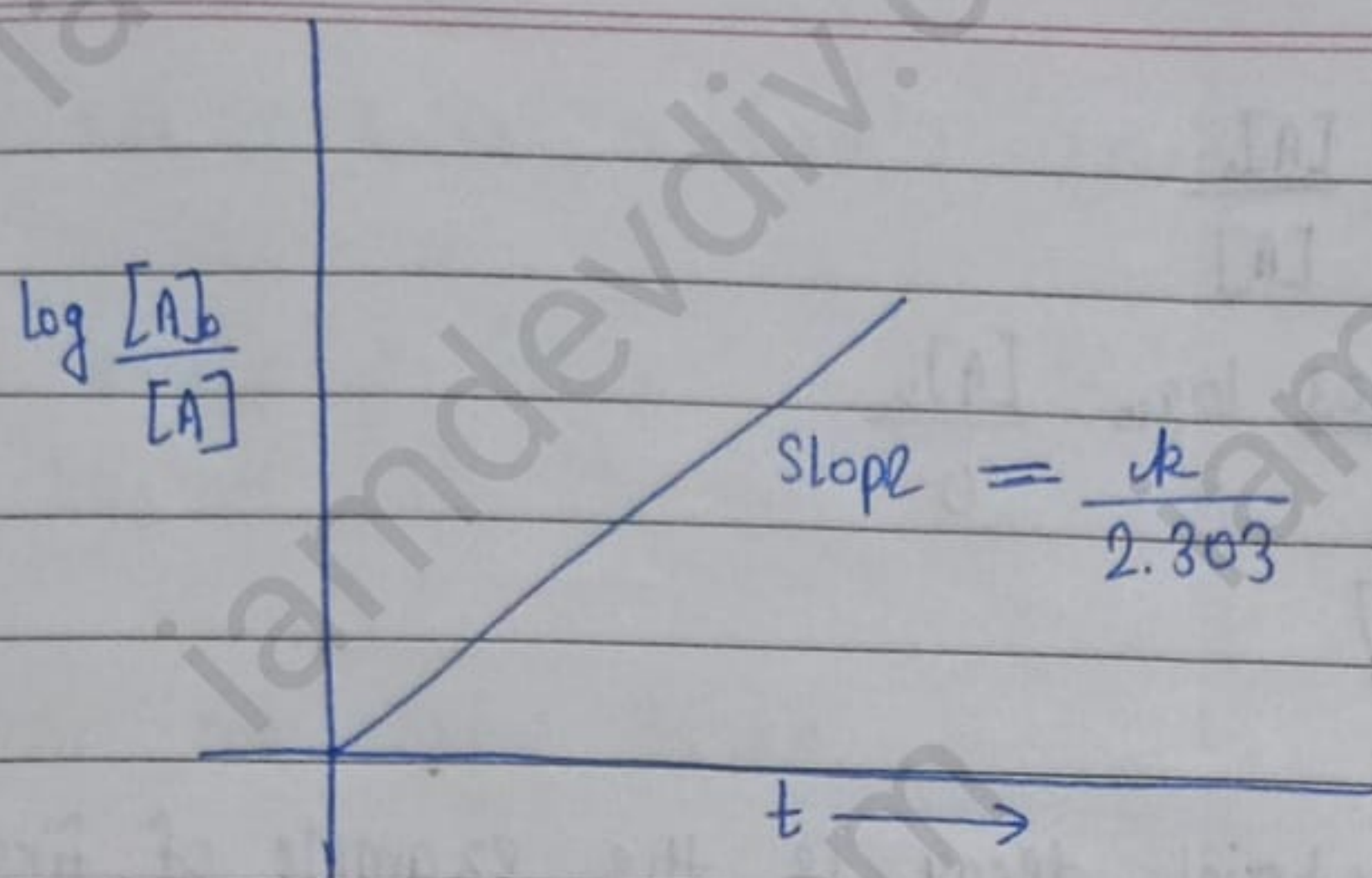
$$\frac{\ln[A]_0}{[A]} = kt \quad (\text{OR}) \quad \log_{10} \frac{[A]_0}{[A]} = \frac{kt}{2.303}$$

$$\log_{10} [A]_0 - \log_{10} [A] = \frac{kt}{2.303}$$

$$\Rightarrow \log [A]_0 = \frac{kt}{2.303} + \log_{10} [A]$$





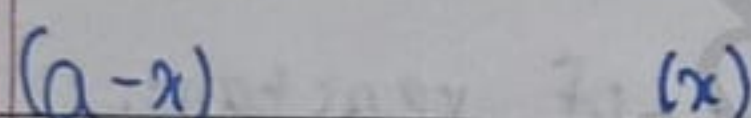
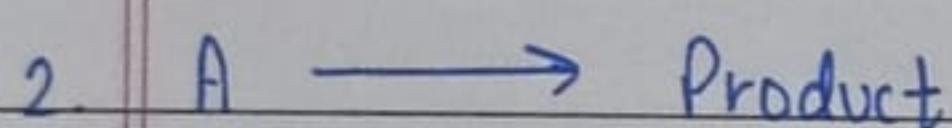
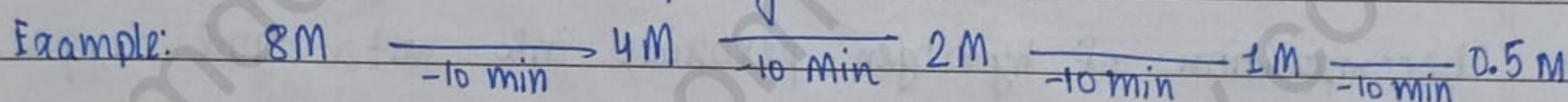


$$\log_{10} \frac{[A]_0}{[A]} = \frac{kt}{2.303}$$

$$\text{Slope} = \frac{k}{2.303}$$

### CHARACTERISTICS OF FIRST ORDER REACTION

- The value of  $t_{1/2}$  is independent of initial concentration which means it takes some time to completely react 50%



$$t=0$$

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

$$\Rightarrow t_{3/4} = \frac{2.303}{k} \log \frac{100}{25}$$

$$\Rightarrow t_{3/4} = \frac{2.303}{k} 2 \log 2$$

$$\Rightarrow t_{3/4} = \frac{2.303}{k} \times 2 \times 0.3010$$

$$\Rightarrow t_{3/4} = 2 \times t_{1/2}$$

### EXAMPLES OF FIRST ORDER REACTION

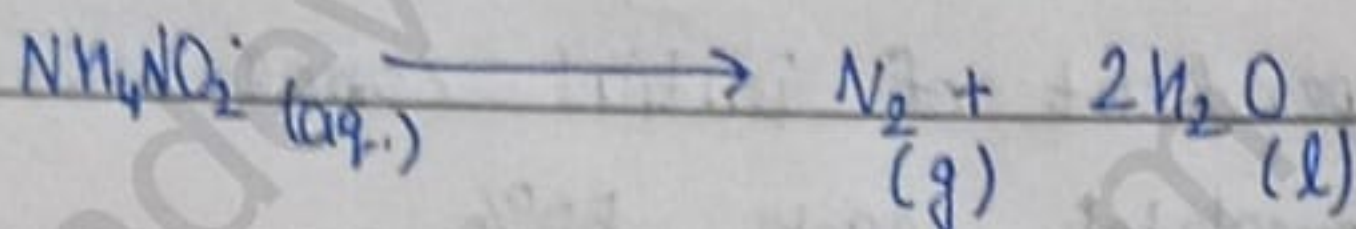
- All the nuclear reactions are of first order.

$$t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]}$$

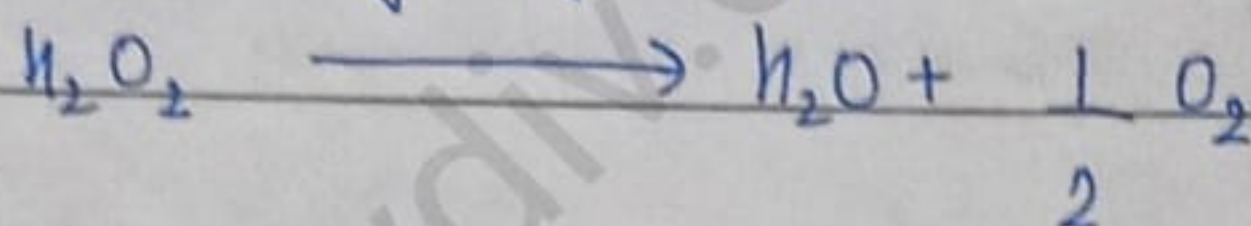
$$t_{100\%} = \frac{2.303}{k} \log_{10} \frac{[A]_0}{0}$$

$$t_{100\%} = \infty$$

- Bacterial growth or bacterial decay is the example of first order reaction.
- Conversion of ammonium nitrite into nitrogen and water.



- Decomposition of hydrogen peroxide into water and oxygen



**NOTE** → In first order reaction, definite percentage takes definite time for completion which is independent of initial conc. of reactant.

Let initial conc. of the reactant =  $[A]_0$

Reactant left after first  $t_{1/2} = \frac{[A]_0}{2}$

→ after second  $t_{1/2} = \frac{[A]_0}{4}$

→ after third  $t_{1/2} = \frac{[A]_0}{2^3}$

→ after  $n$   $t_{1/2} = \frac{[A]_0}{2^n}$

### ★ OTHER GRAPHS

- GRAPH FOR  $t_{1/2}$  V/S CONCENTRATION

$$t_{1/2} = \frac{[A]_0}{2k} \quad [\text{zero}]$$

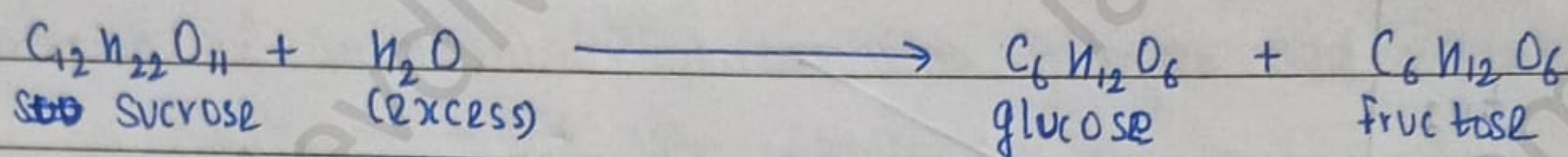


In ester hydrolysis, ester is hydrolysed/ reacted with dil. sol<sup>n</sup> of an acid such as HCl to form an organic acid ( $\text{CH}_3\text{COOH}$ ) and alcohol which is ethyl alcohol. In this reaction, when the order of the reaction is ~~studied~~ studied, it is found to be rate dependent on ester only.

$$r \propto [\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{H}_2\text{O}]^0 \quad \boxed{\text{Order} = 1}$$

Because ester is present in excess

## 2. INVERSION OF CANE SUGAR



This reaction is supposed to be second order by this. But it's pseudo first order reaction because water is present in excess.

## ★ COLLISION THEORY

The reaction species taking part in a chemical reaction can give product only in case they come in contact with each other or they collide with each other. This is called collision theory of reaction rate.

### • COLLISION FREQUENCY

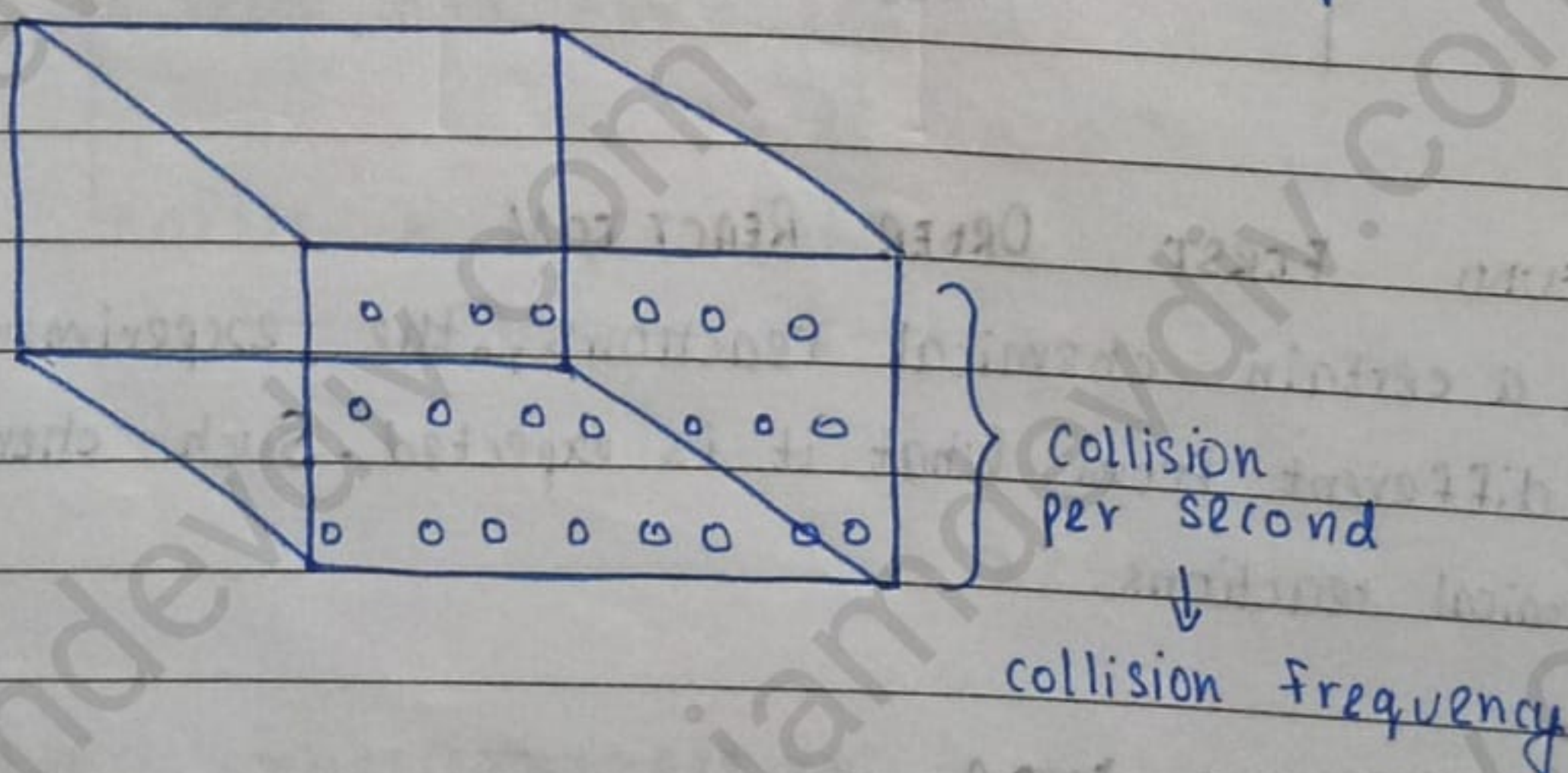
The number of collisions that take place per second per unit volume of reaction mixture is known as collision frequency.

$$L = 1 \text{ cm}$$

$$b = 1 \text{ cm}$$

$$h = 1 \text{ cm}$$

$$V = 1 \text{ cm}^3$$

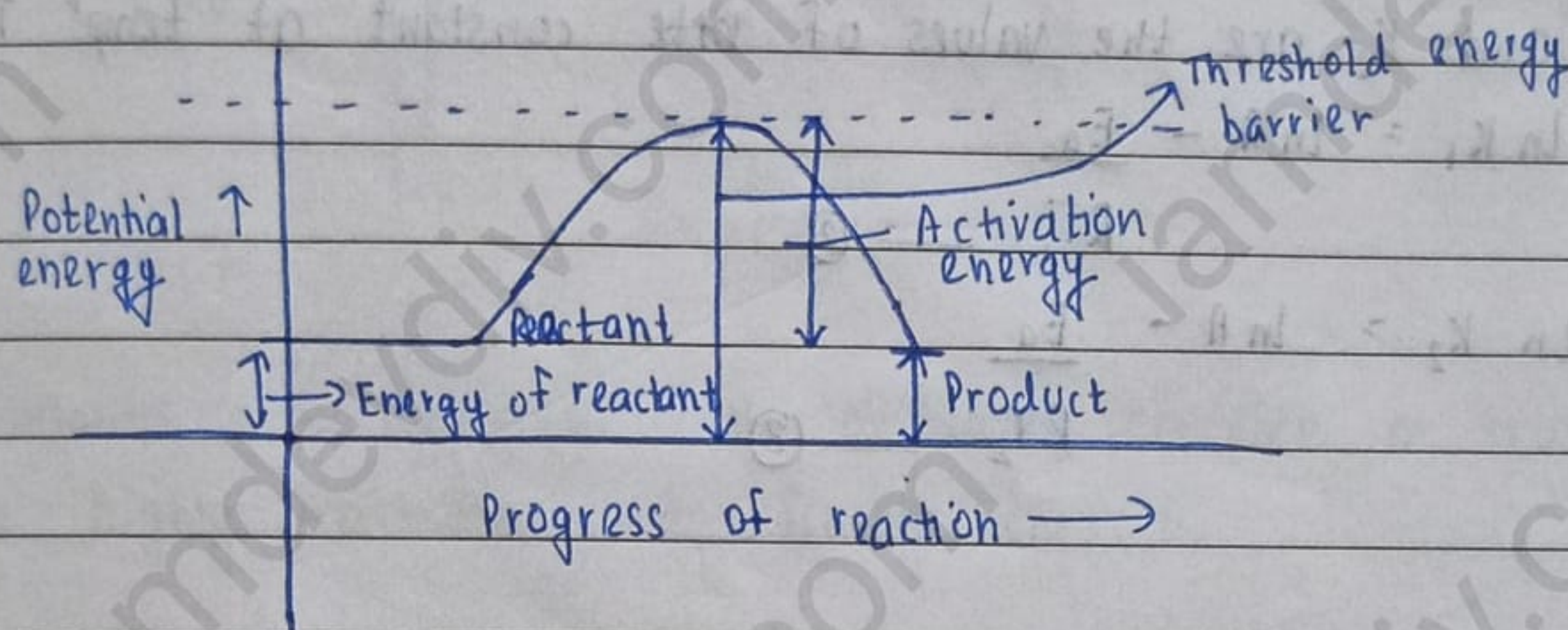


Under ordinary conditions of temp<sup>r</sup> ( $25^\circ\text{C}$ ) and pressure (1 atm), the collision frequency is of the order of  $10^{25}$  to  $10^{28}$ .

All the collisions are not responsible for the formation of product but among reacting species which are responsible or they form product are called effective collisions.

In order to make the collision effective, there are few criterias:

### 1. ENERGY BARRIER



To make the collision effective, the species taking part in a chemical reaction must have certain minimum energy which is called threshold energy (energy required to break the bond of reacting species).

for standard conditions  $T = 25^\circ\text{C}$  and  $T + 10 = 35^\circ\text{C}$

### ★ ARRHENIUS EQUATION

Arrhenius developed a mathematical equation between temp<sup>r</sup> and rate constant which is

$$k \propto e^{-E_a/RT}$$

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

where,

$k$  = rate constant

$A$  = Arrhenius constant / frequency fraction or pre-exponential factor

$E_a$  = Activation energy

$R$  = Gas constant

$T$  = Temp<sup>r</sup>

## • INTEGRATED FORM OF ARRHENIUS EQUATION

Taking log on both sides

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

$$\ln k = \ln A - \frac{E_a}{RT} \cdot \ln e \quad [\ln e = 1]$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{--- (1)}$$

If  $k_1$  and  $k_2$  are the values of rate constant at temp<sup>r</sup>  $T_1$  and  $T_2$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- (2)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- (3)}$$

(3) - (2)

$$\ln k_2 - \ln k_1 = \cancel{\ln A} - \frac{E_a}{RT_2} - \cancel{\ln A} + \frac{E_a}{RT_1}$$

$$\Rightarrow \ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

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

OR

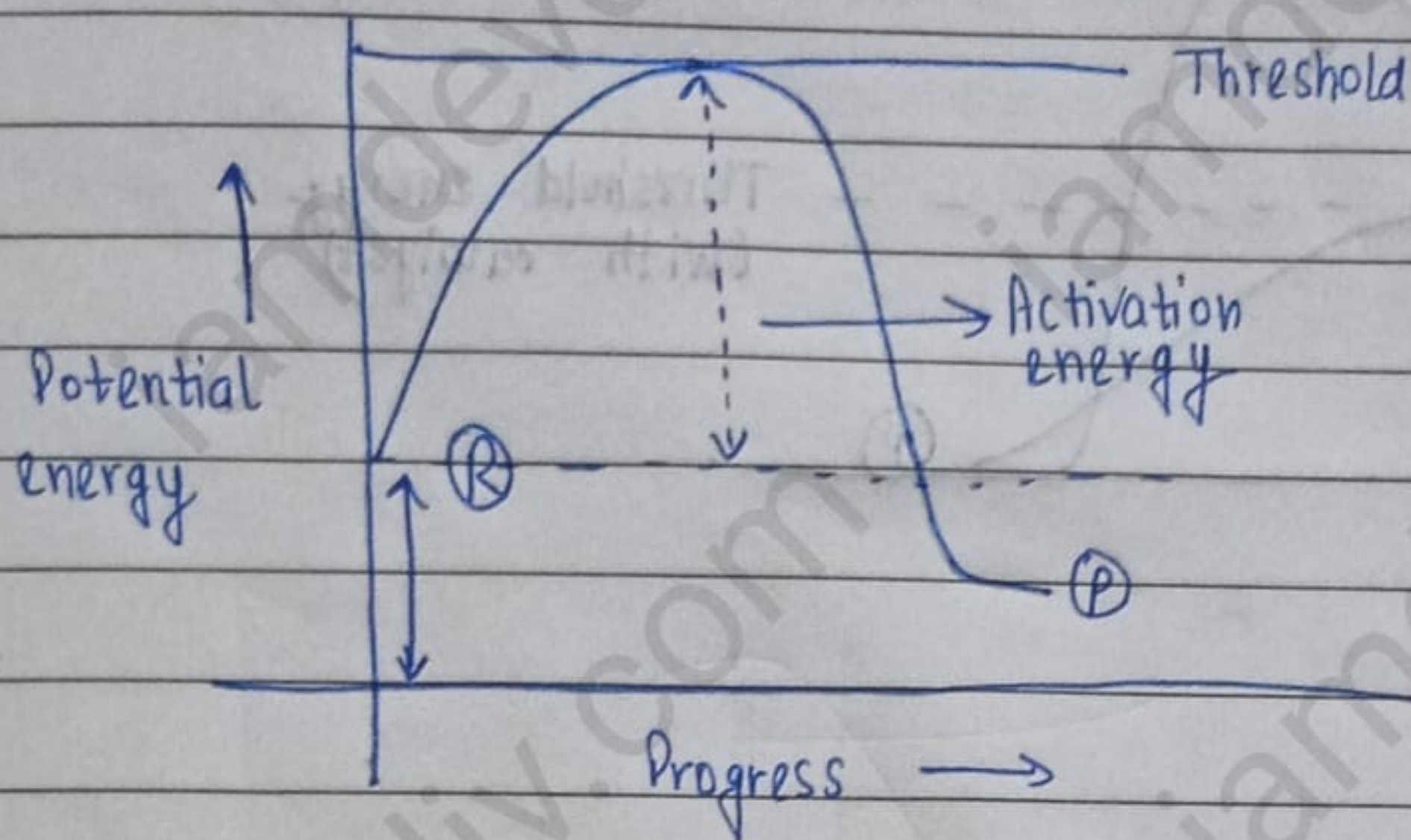
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

This is called Arrhenius equation which gives actual relationship between temp<sup>r</sup> and rate constant

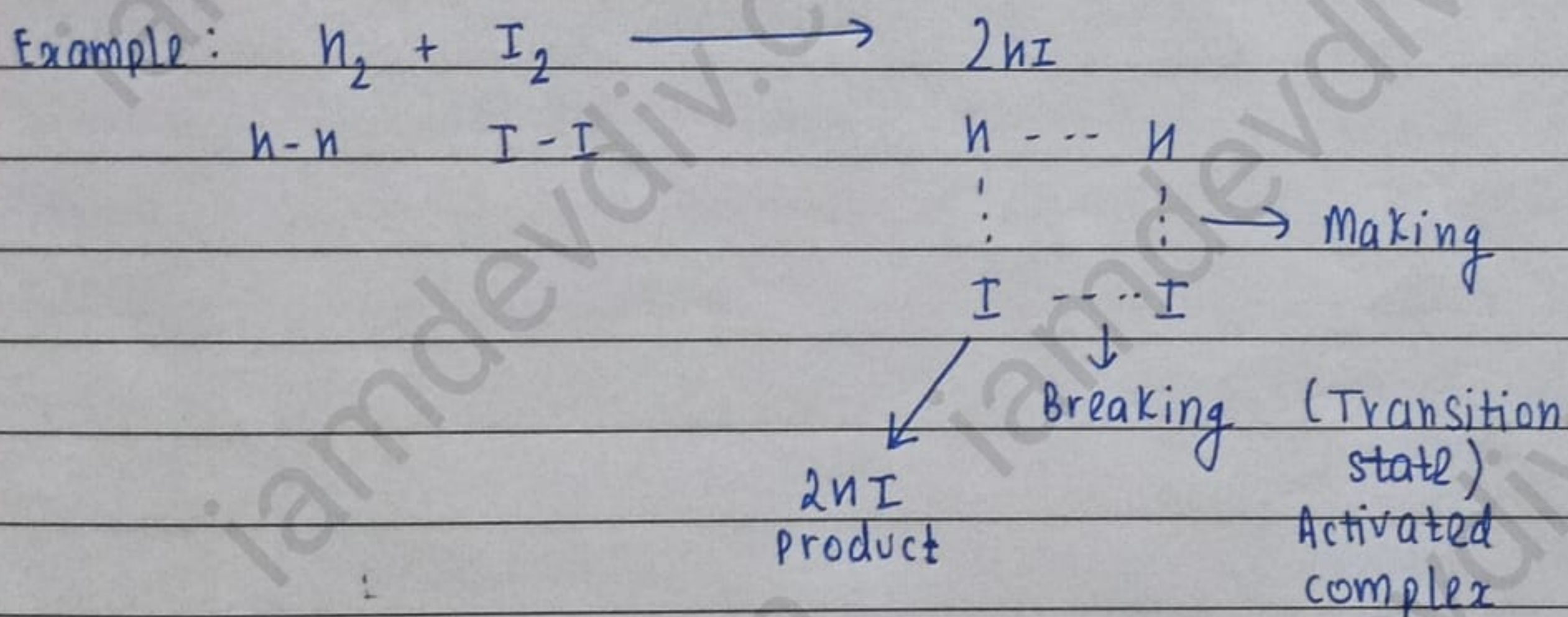
## • ACTIVATION ENERGY

The extra amount of energy which has to be supplied to reacting species in their normal state to make their energy equal to threshold energy

Activation energy = Threshold energy - Normal energy of reactants



Reactants get converted into activation complex or transition state which is highly unstable and finally converts.



Activation energy and reversible reaction ~~for exothermic reactions~~

(A) For exothermic reactions

$$E_a(\text{b}) > E_a(\text{f})$$

backward                      forward

(B) For endothermic reaction, activation energy for forward reaction is that of greater than backward reaction.

### • EFFECT OF CATALYST

Catalyst increases the rate of reaction by providing alternative path way of lower activation energy which means the threshold energy barrier decreases.

