Chapter # 9

Chemical Kinetics

"Branch of chemistry which deals with the study of the rate of reaction, mechanism of reaction and factor which affect the rate of reaction is called Chemical kinetics."

Rate of Reaction

OR

Velocity of Reaction

Denoted by:-

$$\frac{dx}{dt}$$

⊙ When the reaction Take place concentration of reactant decreases with Time and concentration of product increases with Time.

⊙ Rate of reaction may be define in different ways:

(i)

"Decrease in concentration of

reactant per unit time is called rate of reaction."

(ii)

"Increase in the concentration of product per unit time is called rate of reaction."

(iii)

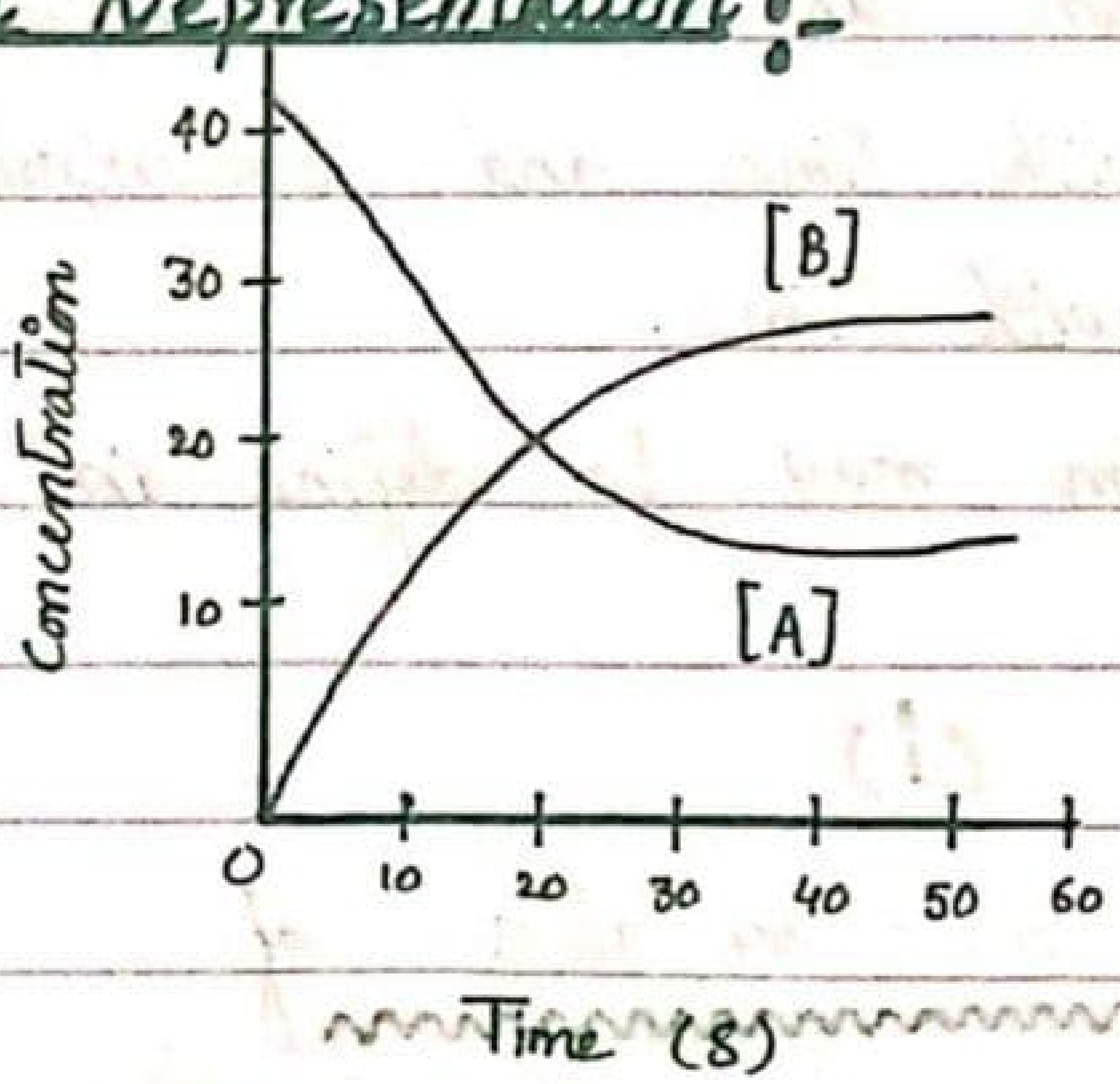
"Change in the concentration of reactant & product per unit time is called rate of reaction."

For general reaction

$$A \longrightarrow B$$

$$\boxed{\text{Rate of reaction} = \frac{\text{Change in concentration of substance}}{\text{Time taken for the change}}}$$

Graphical Representation:-



⊙ In the begining the slope of graph is steep for both reactant and product that shows that:

★ Increase in the concentration of reactant.

★ Decrease in the concentration of product.

⊙ As the reaction proceed slope of graph is less steep shows that:

★ Decrease in concentration of reactant.

★ Increase in concentration of product.

⊙ Therefore rate of reaction also decrease.

Rate of reaction with respect to reactant:-

$$\boxed{\frac{dx}{dt} = -\frac{d[A]}{dt}}$$

-ive sign indicate that the concentration of reactant decrease with time.

Rate of reaction with respect to Product

$$\boxed{\frac{dx}{dt} = +\frac{d[B]}{dt}}$$

+ive sign indicate that the concentration of product increase with time.

Unit of Rate of Reaction:-

Rate of reaction = $\frac{\text{Change in concentration}}{\text{Time taken for the reaction}}$

$$= \frac{mol \cdot dm^{-3}}{s}$$

$$\boxed{= mol \cdot dm^{-3} s^{-1}}$$ as dm^{-3} = liter (L)

$$= mol \cdot L^{-1} s^{-1}$$

Types:-

There are two types or rate of reaction.

(i) Average rate of reaction.

(ii) Instaneous rate of reaction.

Average Rate of Reaction:-

"Rate of reaction b/w two specific time interval is called average rate of reaction."

Formula:-

$$\boxed{\text{Average rate of reaction} = \frac{\text{Total change in concentration}}{\text{Total time taken for the change}}}$$

Instaneous Rate of Reaction:-

"Rate of reaction at any instant is called instaneous rate of reaction."

Formula:-

$$\text{Instaneous rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken for change}}$$

Relation b/w Average rate of reaction & Instaneous Rate of Reaction

- Instantaneous rate of reaction and average rate of reaction are equal for just a short period of time.
- Mostly both are different to each other.
- Initially the instantaneous rate of reaction is greater than average rate of rate of reaction.
- In the mid of reaction both are equal for short Period of time.
- At the end of reaction average rate of reaction is greater than instantaneous rate of reaction.

Determination of Initial Rates

"Initial rate is the instantaneous rate at the moment when reactants are mixed. (i.e at t = 0)."

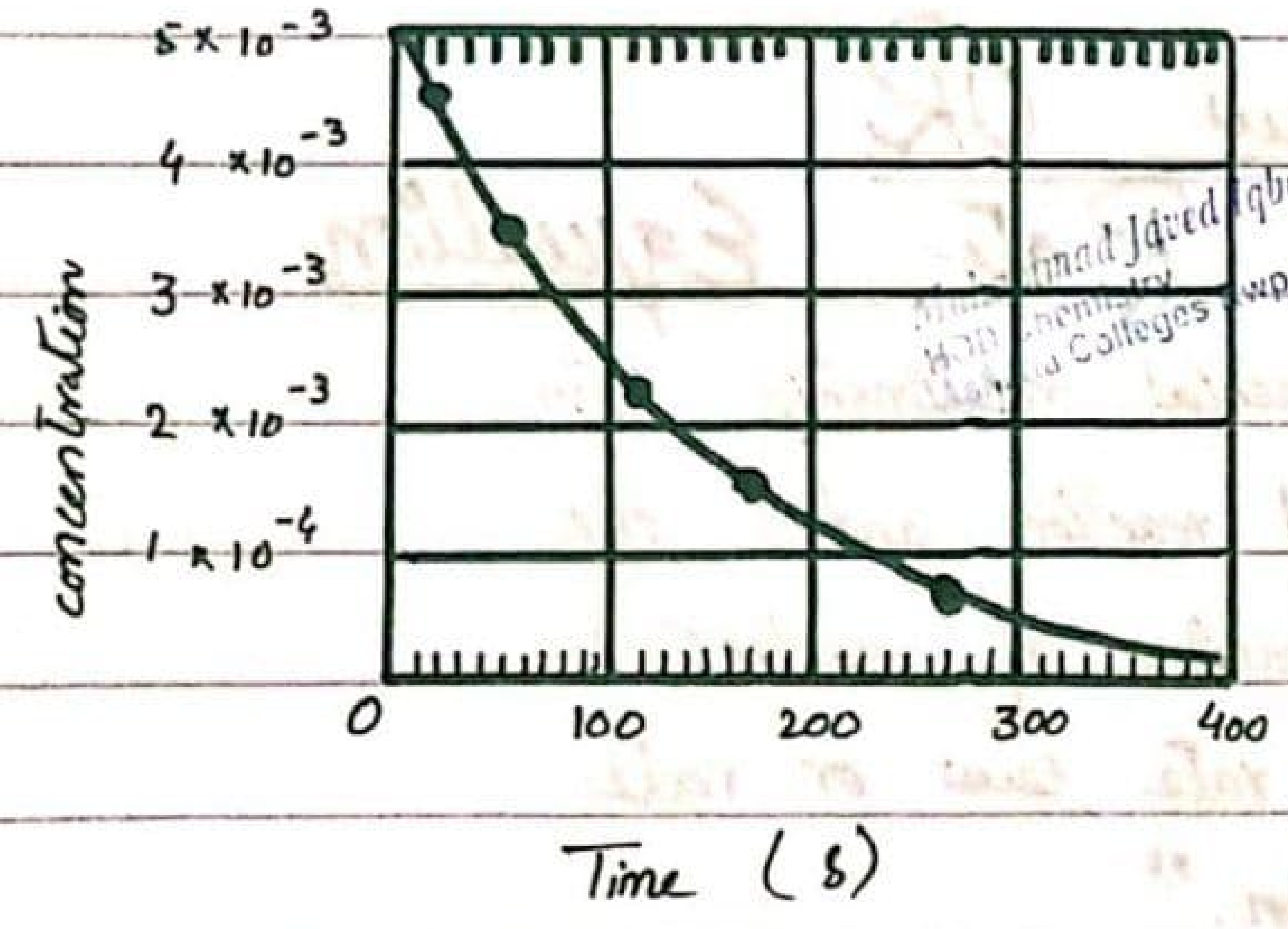
- The intial rate depend upon the initial concentration.
- This is because as the reaction proceeds, the concentration of reactant is decrease.
- In this way reaction rate is decrease.
- The initial rate is measured by determining the slope of line tangent to the curve at Zero.

Activity:-

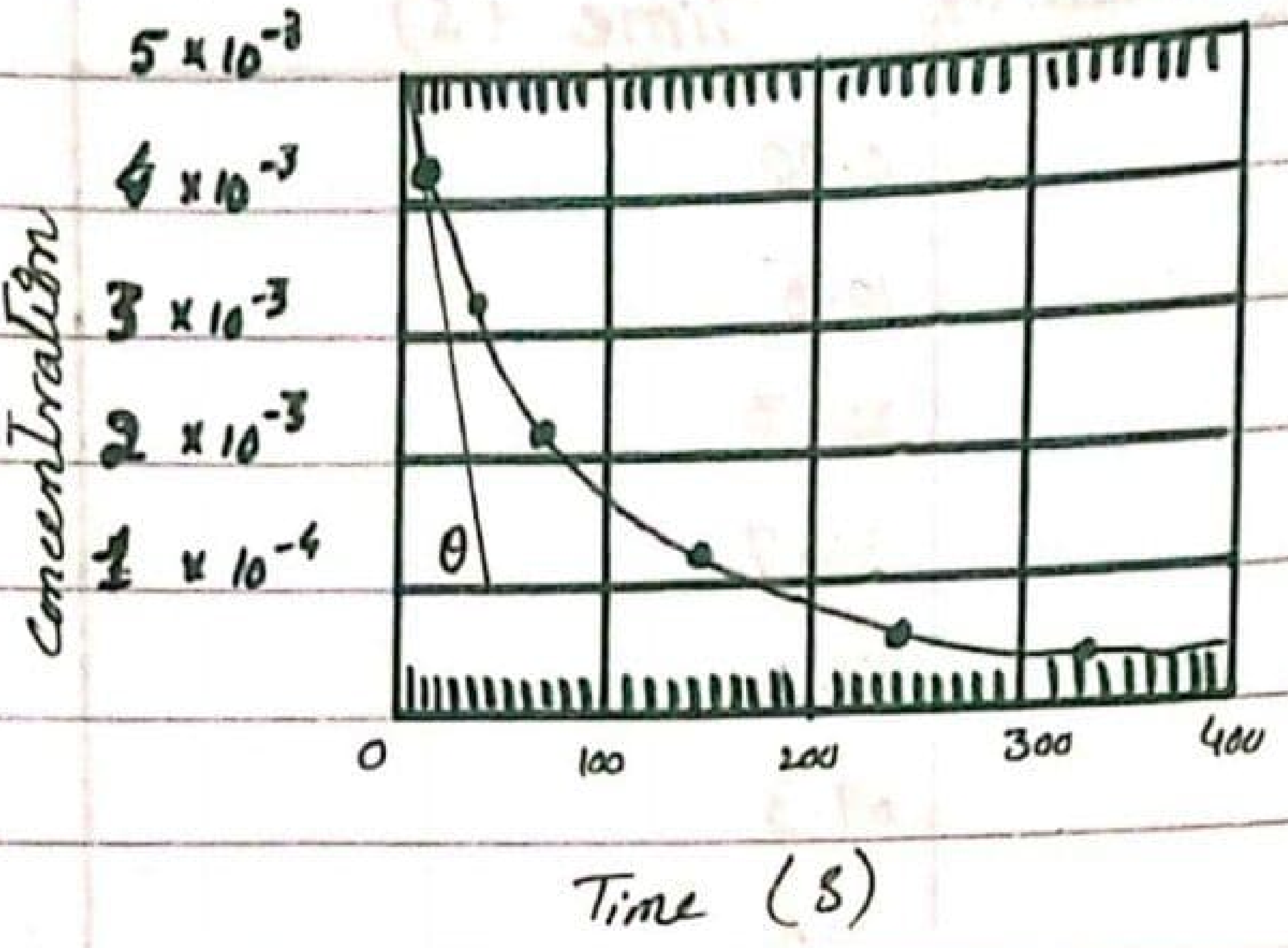
The table shows the concentration of phenolpathaline in a solution that was initially 0.005 M in phenolpathalein and 0.6 M in OH^- ions. When a solution that contain phenolpathaleion in the presence excess base is allowed to stand for few minute, The solution that has initially a pink colour, it graguelly Turns colourless as phenolphthalein react with OH^- ions in solution. Use this data to determine initial rate?

Conc. of Phenolpathalein (M)	Time (s)
0.0050	0.00
0.0045	10.5
0.0040	22.3
0.0035	35.7
0.0030	51.1
0.0025	69.3
0.0020	91.6
0.0015	120.4
0.0010	160.9
0.00050	230.3

Solution:-



Draw tangent to the curve at t = 0.



$$\text{Slop} = \frac{dn}{d_t}$$

$$= \frac{4 \times 10^{-3}}{60}$$

$$\boxed{= 6.67 \times 10^{-5}\ \text{mol dm}^{-3}.\ s^{-1}}$$

Rate Law OR Rate Equation

"Experimental relationship b/w rate of reaction and the concentration of reactant is called **rate law or rate Equation.**"

Note:-

It can only be noted on experimental bases.

Rate equation and chemical equation may be same or different.

e.g:-

(i) Rate eq. and chemical eq. are different

$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$

Rate = k $[NO_2][O_3]$

(ii) Rate eq. and chemical eq are same.

$NO + O_3 \longrightarrow NO_2 + O_2$

Rate = k $[NO][O_3]$

Rate Constant (k)
OR Specific rate Constant:-

Rate constant is define as "Rate of reaction when the molar concentration of reactant is unity is called **rate constant.**"

Denoted by "k"

e.g:-

$NO + O_3 \longrightarrow NO_2 + O_2$

Rate = k $[NO][O_3]$

Where

k = specific rate constant

Order of Reaction:-

Order of reaction may be define as:

"The no. of molecules participate in rate determining process is called **order of reaction**."

OR

"It is the sum of the exponent of the concentration of reactant involve in rate equation is called **order of reaction**."

Consider the general reaction

$$aA + bB \longrightarrow cC + dD$$

$$Rate \propto [A]^x [B]^y$$

$$Rate = k [A]^x [B]^y$$

Where

X = order of reaction with respect to "A"

Y = order of reaction with respect to "B"

k = rate constant

Types of order of Reaction:-

There are six Types of order of reaction:

(i) Zero order reaction

(ii) First order reaction

(iii) 2nd order reaction

(iv) 3rd order reaction

(v) Fractional order reaction

(vi) Pseudo First order reaction

Zero Order Reaction:

"A reaction that is indepandant of the concentration of reactant molecule is called **zero order reaction.**"

e.g:- 1) Photochemical reactions are zero order
$H_2 + Cl_2 \xrightarrow{Sunlight} 2HCl$

2) The decomposition of ammonia

$$2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

Rate $= k\,[NH_3]^0$ order of reaction $= 0$

1^{st} Order Reaction:-

"The reaction in which rate of reaction is directly proportional to the exponent of concentration of single reactant molecule is called **1^{st} order reaction.**"

Examples:-

$$\boxed{Rate = k\,[A]^{01}}$$

(i) Thermal decomposition of N_2O_5

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

Rate $= k\,[N_2O_5]^1$

(ii) Decomposition of NH_4NO_2 in aquaous solution.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$Rate = k\,[NH_4NO_2]^1$$

2nd Order Reaction:

"A reaction for which sum of exponents of rate equation is equal to Two is called 2nd order Reaction."

Expression:-

$$Rate = k\,[A]^2 \quad or$$

$$Rate = k\,[A]^1\,[B]^1$$

Example:-

(i) Decomposition of NO_2

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

$$Rate = k\,[NO_2]^1[O_3]^1$$

(ii) Decomposition of NO_2

$$2NO_2 \longrightarrow 2NO + O_2$$

$$Rate = k\,[NO_2]^2$$

(iii) $NO + O_3 \longrightarrow NO_2 + O_2$

$$Rate = k\,[NO]^1[O_3]^1$$

order of reaction = 1 + 1 = 2.

3rd Order Reaction:-

"A reaction for which the sum of exponents of rate equation is **Three** is called 3rd order reaction."

Expression:-

$$Rate = k[A]^3$$

$$Rate = k[A]^2[B]^1$$

$$Rate = k[A]^1[B]^1[C]^1$$

Example:-

(i) $2NO + O_2 \longrightarrow 2NO_2$

$Rate = k[NO_2]^2[O_2]^1$

∥ order of reaction = 2 + 1 = 3

(ii) $2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$

$Rate = k[FeCl_2]^1[KI]^2$

order of reaction = 1 + 2 = 3

Fractional Order Reaction:-

"A reaction for which the sum of exponents of the rate law of reaction is in fraction is called fractional order reaction."

Expression:-

$$\text{Rate} = K\,[A]^{1/2}$$

Example 1:-

$$H_2 + Br_2 \longrightarrow 2HBr$$

$$\text{Rate} = K\,[H_2]^1[Br_2]^{1/2}$$

Order of reaction = 1 + 0.5 = 1.5

Example: 2

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

$$\text{Rate} = K[CHCl_3][Cl_2]^{1/2}$$

$$\text{Order} = 1 + \frac{1}{2} = 1.5$$

Pseudo First order reaction:-

A bimolecular reaction for which Solvent is in excess and it's concentration remains constant and does not take part in rate determining step is called pseudo First order reaction

$$(CH_3)_3C-Br + \underset{(\text{excess})}{H_2O} \longrightarrow (CH_3)_3C-OH + HBr$$

$$\text{Rate} = K_1\,[(CH_3)_3CBr]$$

$$\text{Order} = 1$$

Determination of Reaction Order & Rate Law:-

⊙ The affect of change in concentration of reactant on reaction rates cannot be determine from chemical equation.

⊙ They can be determine experimently by determining the order of reaction.

⊙ For this reason the concentration of one reactant is change while other are kept constant.

⊙ In this way the initial rate of reaction on every change is determine.

Factor Affecting the rate of Reaction:-

Collosion Theory:-

"The rate of reaction is proportional to the no. of collosion among the reactant molecule."

⊙ Any factor that change the no. of affective collosion per second, affect the rate of chemical reaction.

⊙ Some factors that affect that the rate of reaction are follow:

(i) Nature of reactant
(ii) Concentration of reactant
(iii) Surface area
(iv) Temperature
(v) Catalyst

Nature of Reactant:-

⊙ Nature of reactant can affect the rate of chemical reaction.

⊙ Chemical reactivity of matel depends upon their electronic configuration.

Alkali Matels:-

★ Alkali matels contain one electron in their outer most shell.

★ They are highly electropositive.

★ They react violently.

Alkaline Earth Matels:-

★ They contain two e^- in their outer most shell.

★ They are less electropositive than alkali matels.

Ionic Compound:-

★ Reactant containing ionic compound undergo faster reaction.

★ Because they involve in combination of opposite charge.

★ They are not involve in rearrangement of electronic cloud.

Covalent Compound:-

★ Reactant contain covalent bonds are slower in reaction.

★ They are involve in rearrangement of e^- cloud.

Concentration of Reactant:-

⇒ As the concentration of reactant increase reaction rate increase.

rate of reaction ∝ concentration of reactant

Law of Mass of Action:-

"The rate of reaction
is directly proportional
to the concentration
of reactant."

⇒ When the concentration is increase, no. of affective collision is increase. So, the rate of reaction is increase.

Example:-

(i) When the pressure on H_2 and Cl_2 is increase for making HCl, their concentration increase. Therefore rate of reaction is increase.

(ii) Combustion reaction occur rapidly in pure O than in air (21%).

(iii) $CaCO_3$ react at different rate at different concentration of HCl.

Surface Area:-

Rate of reaction ∝ Surface area.

⇒ As the surface area is increase, the possibility of contact b/w their particle increase, the no. of affective collision increase. So reaction rate increase.

Example:-

(ii)

Powder Zn react <u>rapidly</u> with HCl as compare large piece of Zn.

Because in Powder shap surface area is increase.

$$\underset{(s)}{Zn} + \underset{(aq)}{2HCl} \longrightarrow \underset{(aq)}{ZnCl_2} + \underset{(g)}{H_2}$$

(ii) The foil of AL react with NaOH at normal rate although it is warm.

- ★ Powder AL react rapidly with NaOH.

$$2AL + 2NaOH + 6H_2O \rightarrow 2Na[AL(OH)_4] + 3H_2$$

Temperature:-

Temperature ∝ Rate of Reaction

⇒ When temperature increase:

- ★ kinetic energy of molecule increase.
- ★ No. of affective collision increase
- ★ So, rate of reaction is increase.

Activation Energy:-

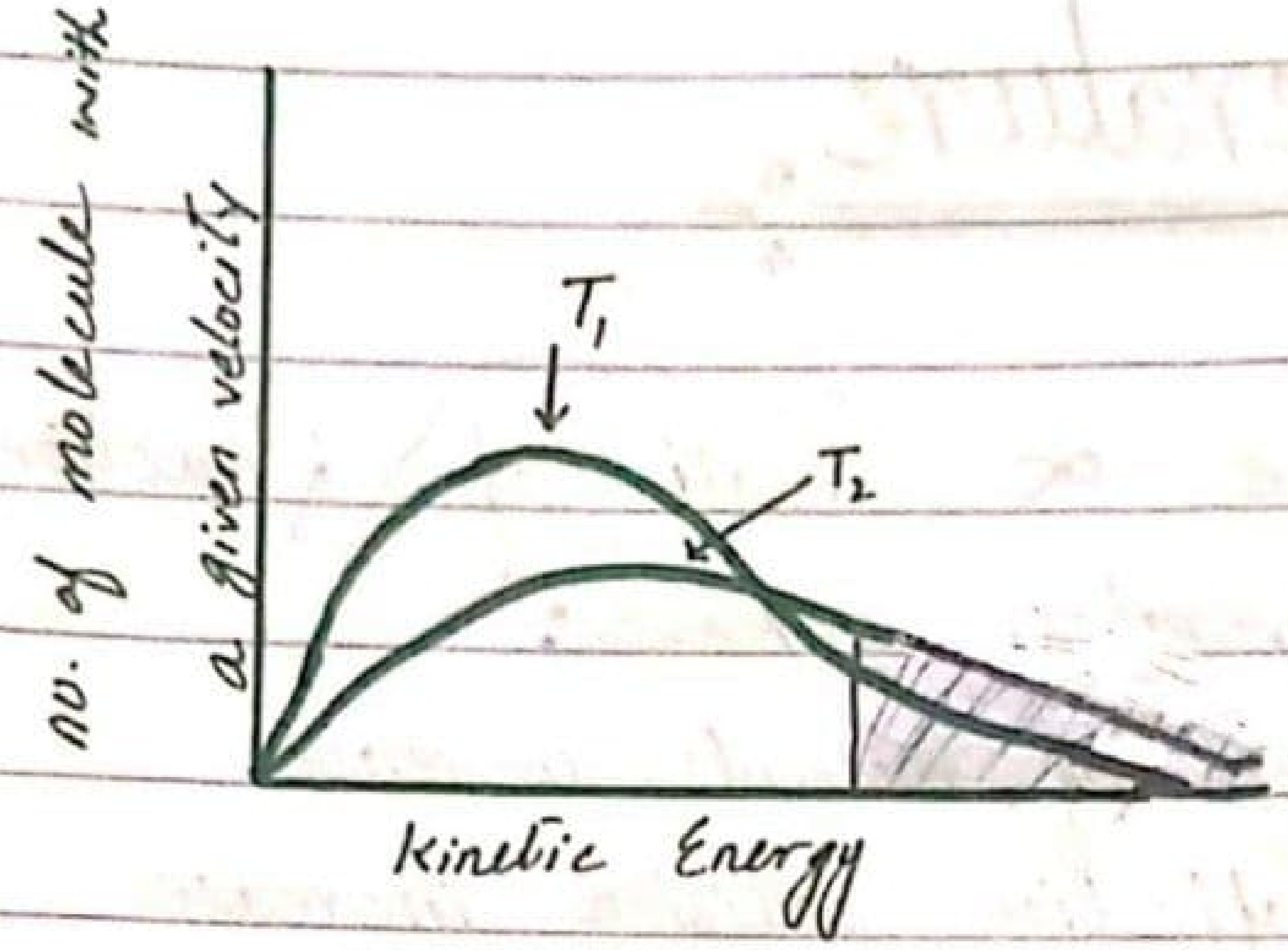
"The minimum amount of energy required to convert reactant into product is called activation Energy."

⇒ When molecule prosess E_a (activation energy) they are converted into product.

⇒ At minimum temp. small amount of molecule get E_a and small amount of reactant converted into product. So reaction rate is slow.

⇒ At maximum temp. large amount of molecule are get E_a and large amount of reactant are converted into product. So the reaction rate is maximum.

Graphical Representation:-



Energy needed for effective collision.

⇒ Shaded area in "Manwell Boltzmann Curve" of K.E shows no. affective collision.

⇒ When Temperature is increase:

- K.E energy become greater than E_a
- No. of affective collision increase
- Shaded area is increase
- Rate of reaction is increase.

Arheneous Equation:-

⇒ In 1889 Arheneous study the affect of change in Temperature on reaction rate.

He found the affect of temperature on reaction is given by:

$$\boxed{K = Ae^{-E_a/RT}}$$

Where

K = rate Constant
A = Arrheneous constant
E_a = Activation Energy
R = Ideal gas constant ($R = 8.3143\ JK^{-1}\ mole^{-1}$)
T = Absolute temperature

Uses of Arrheneous Equation:-
OR
Application of Arrheneous Equation:-

It can be used

(i) To understand the role of **K** (rate constant) in theoratical determination of reaction rate.
(ii) To calculate K at different temperature.
(iii) $K \propto T$
(iv) To calculate the energy of activation.

Catalyst:-

"The substance that increase the rate of reaction without themself being usedup."

⇒ It can increase the rate of reaction by lowering the activation energy.

⇒ Once the reaction reached to the equilibrium it does not affect on the position of equilibrium.

RATE DETERMINING STEP :-

" When the reaction Take place in single step then the same step of reaction is **rate determining step.**

When the reaction Take place in more than one step then **slow step** of the reaction is **rate determing** step."

Example :-

$$NO_2 + CO \longrightarrow NO + CO_2$$

$$Rate = k\,[NO_2]^2$$

Mechanism:-

Step - 1:-

$$NO_2 + NO_2 \xrightarrow[\text{Rate determining step}]{\text{slow step}} NO_3 + NO$$

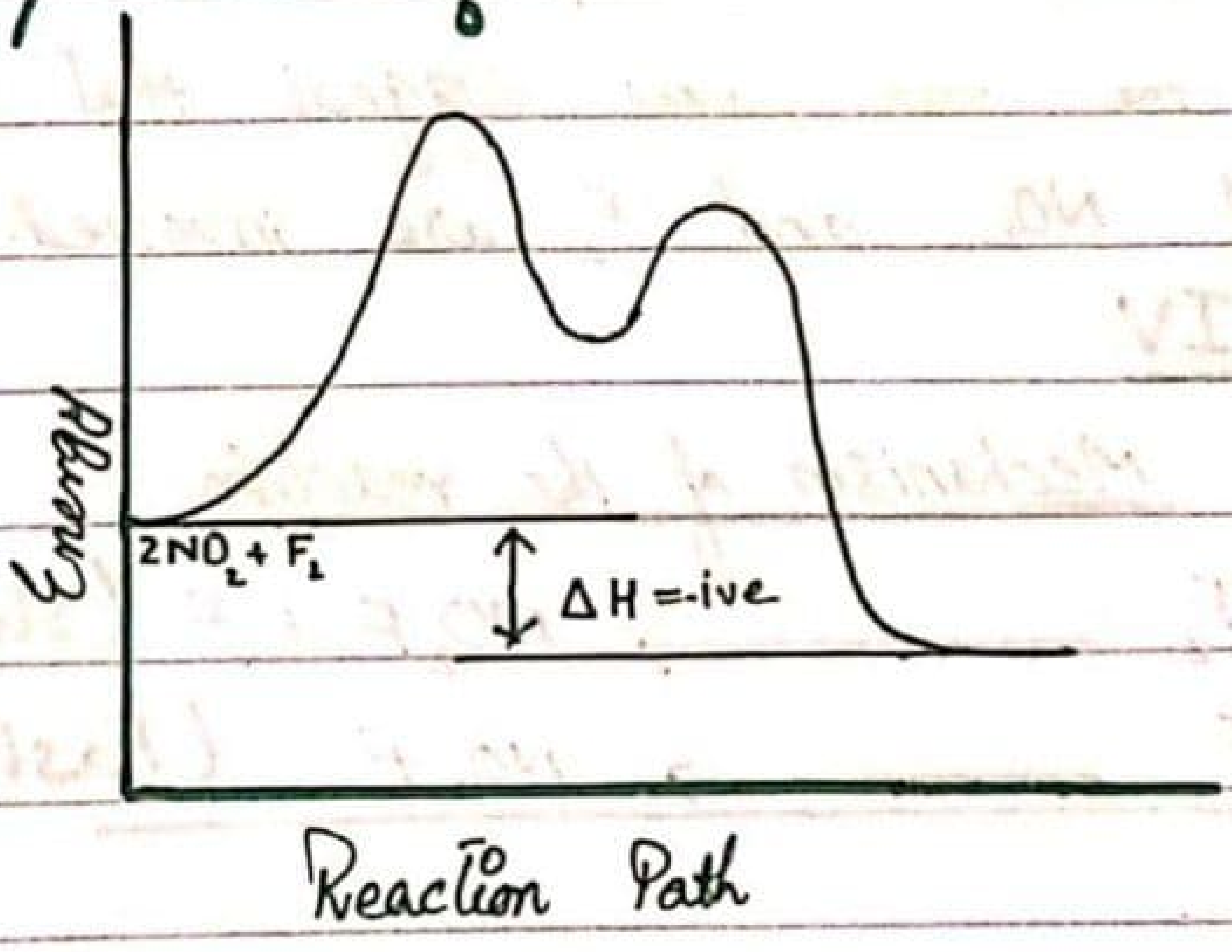
$$NO_3 + CO \xrightarrow{\text{Fast step}} NO_2 + CO_2$$

Note:-

Slow step of reaction is rate determining step.

POTENTIAL ENERGY DIAGRAM AND REACTION MECHANISM

Example 9.7:-



Potential energy diagram for reaction b/w NO_2 and F_2 is shown in figure. The experimental rate law for this reaction is given below:

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

$$Rate = k[NO_2][F_2]$$

Solution:-

Step - 1:- Determine no. of element by no. of peaks.

Step - II Identify rate determining step.

As the P.E diagram show 2 peaks so two reactants are present. And Activation energy of step 1 is higher than 2. So step 1 is rate determining step.

Step - III:-

Use rate law to determine no. of molecules involved in rate determining step.

Here the rate law suggest that only one molecule of NO_2 and F_2 are involved.

Step - IV

Mechanism of the reaction

$$NO_2 + F_2 \longrightarrow NO_2F + F \text{ (Slow step)}$$

$$NO_2 + F \longrightarrow NO_2F \text{ (Fast)}$$

$$NO_2 + F_2 \longrightarrow NO_2F + F$$

$$NO_2 + F \longrightarrow NO_2F$$

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

COLLISION THEORY, TRANSITION STATE & ACTIVATION ENERGY

ACTIVATION ENERGY:-

“Minimum amount of energy which is required to convert reactant into product is called **Activation Energy**.”

OR

“Amount of Energy to form activated complex is called **Activation Energy**.”

Denoted by:-

It is denoted by “E_a”

Relationship b/w Activation Energy & Rate of Reaction:-

$\Rightarrow$ Activation Energy $\propto \frac{1}{\text{rate of reaction}}$

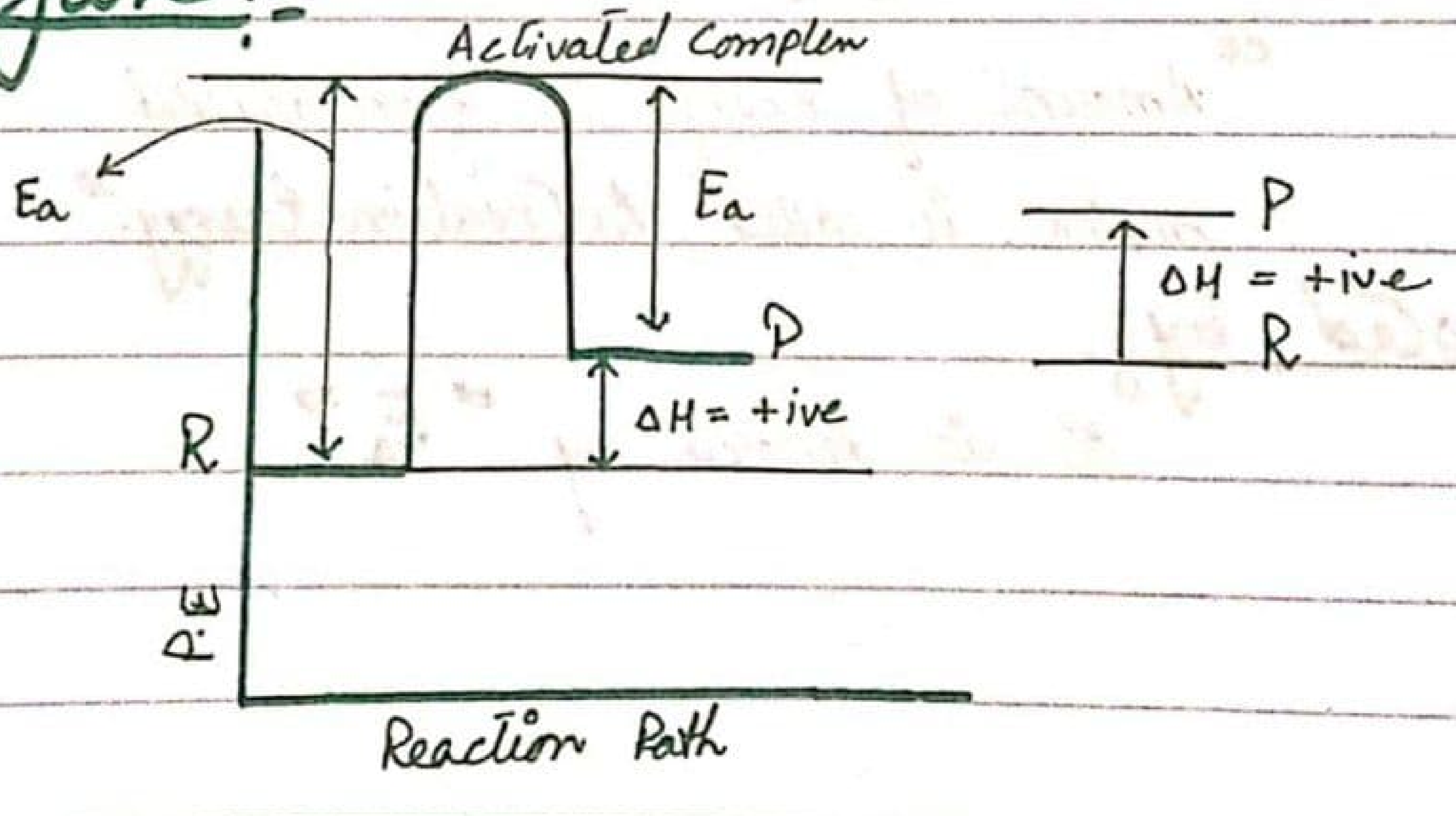
$\Rightarrow$ When the activation energy is increase, the rate of reaction decrease because small amount of reactant molecule posses the A.C. energy and converted into product.

$\Rightarrow$ When the A.C. energy decrease, the reaction rate is increase because large amount of molecule posess activation energy and converted into product.

Note:-

The rate of reaction will not occur when the energy of reacting molecule is less than A.C. energy.

Figure:-



COLLISION THEORY:-

Collision theory is define as:

"The rate of reaction is directly proportional to the no. of collision among the reactant molecule."

Postulates of Collision Theory:-

(i) Chemical reaction:-

For a chemical reaction to occur, atoms of reactant must collide with each other.

(ii) TYPE OF COLLISION:-

The collision may be **affective** or **Inaffective** depending upon the the energy and orientation of colliding particles.

(iii) AFFCTIVE COLLISION:-

"when the atoms or molecule collide with each other to form activated complex. It has higher energy than reactant and the product. And the product is form. Such collision is called **Affective Collision**."

INAFFECTIVE COLLISION:-

"When the atoms and molecules collide with each other and does not form activated Complen and also product are not formed. Such Collision is calle al In- Inaffactive collision."

(iv) Proper Orientation:-

Proper orientation means at the Time of collision, the atoms which are required to make a bond must collide with each other.

(v) Energy of Reactant:-

The reaction will not occur when the energy of reactant is less than activation Energy.

TRNSITION STATE:-

Activated Complen:-

"During affective collision the molecules form and unstable species which is called **Activated Complen**."

TRANSITION STATE:-

"Activated Complex is also called Transition state."

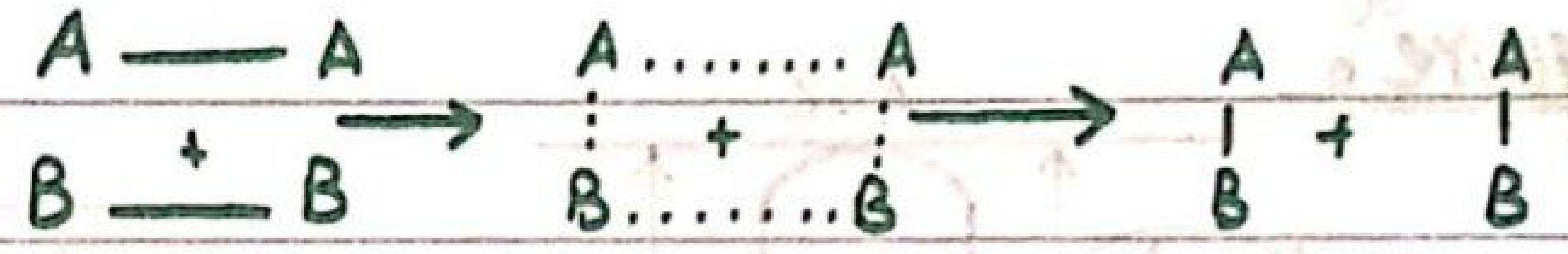
Note:-

Since it is high energy species, it is short lived and quickly breaks down to the products.

Example:-

★ Consider the reaction b/w A_2 and B_2 molecules to form a new molecule AB.

★ If the energy of reactant molecules is equal or more than activation energy, then old bonds are break and new bonds are formed.



Effective Collision a molecule

Mechanism:-

⇒ In an affective collision colliding molecules come closer to each other.

⇒ Their K.E decrease and P.E energy increase.

⇒ Activation energy appears as a hill b/w reactant and product.

⇒ Only the molecules that have proper activation energy are converted into product by crossing hill.

=> On the other hand, the molecules that have no proper activation energy cannot cross the hill. So they are not converted into product.

Potential Energy Diagram:-

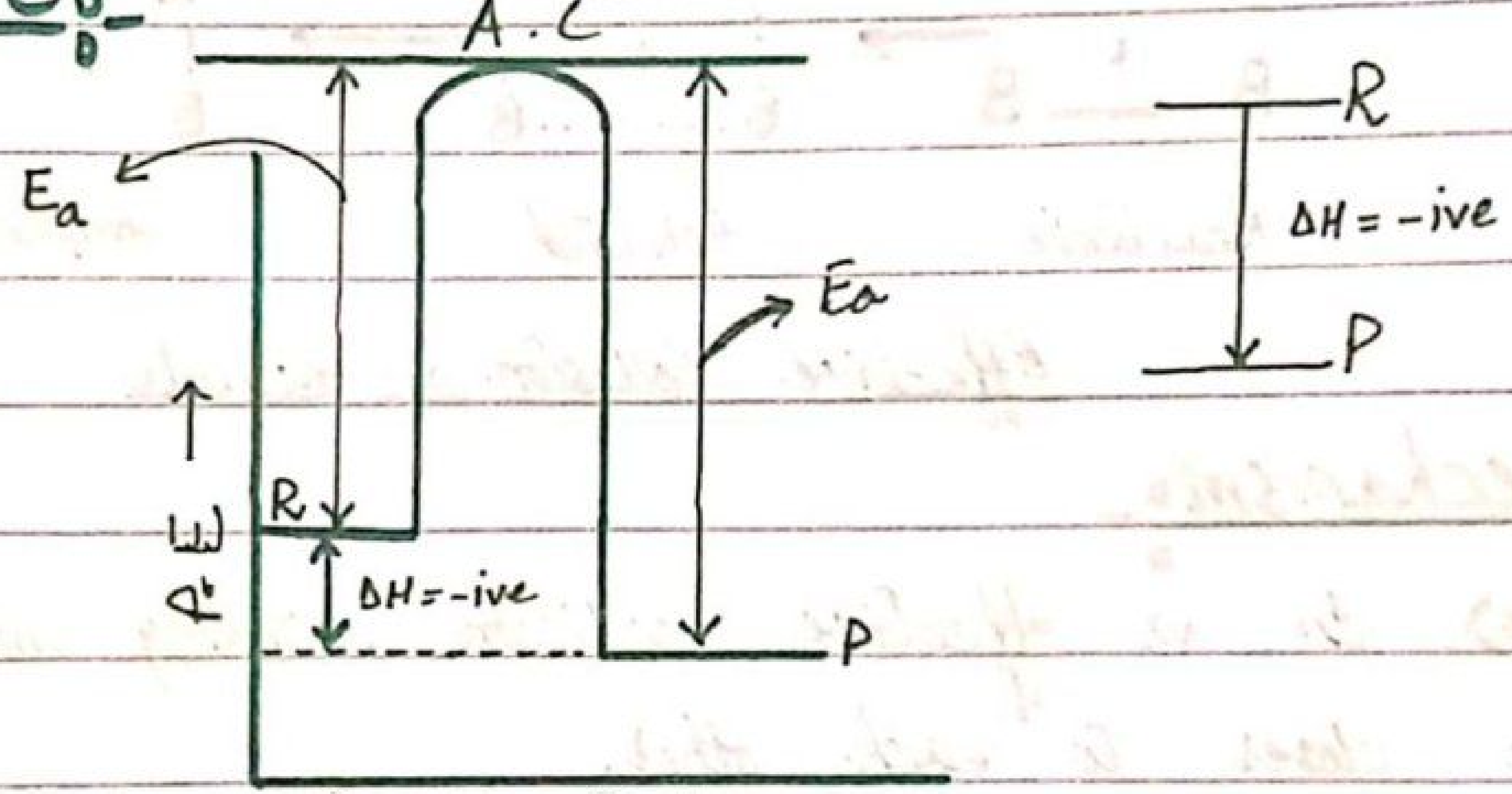
=> Potential energy diagram helps in understanding the enthalpy change in chemical reaction.

=> The heat of reaction is equal to energy difference b/w reactant and product.

Exothermic Reaction:-

In exothermic reaction products are at lower energy level than to reactant

Figure:-



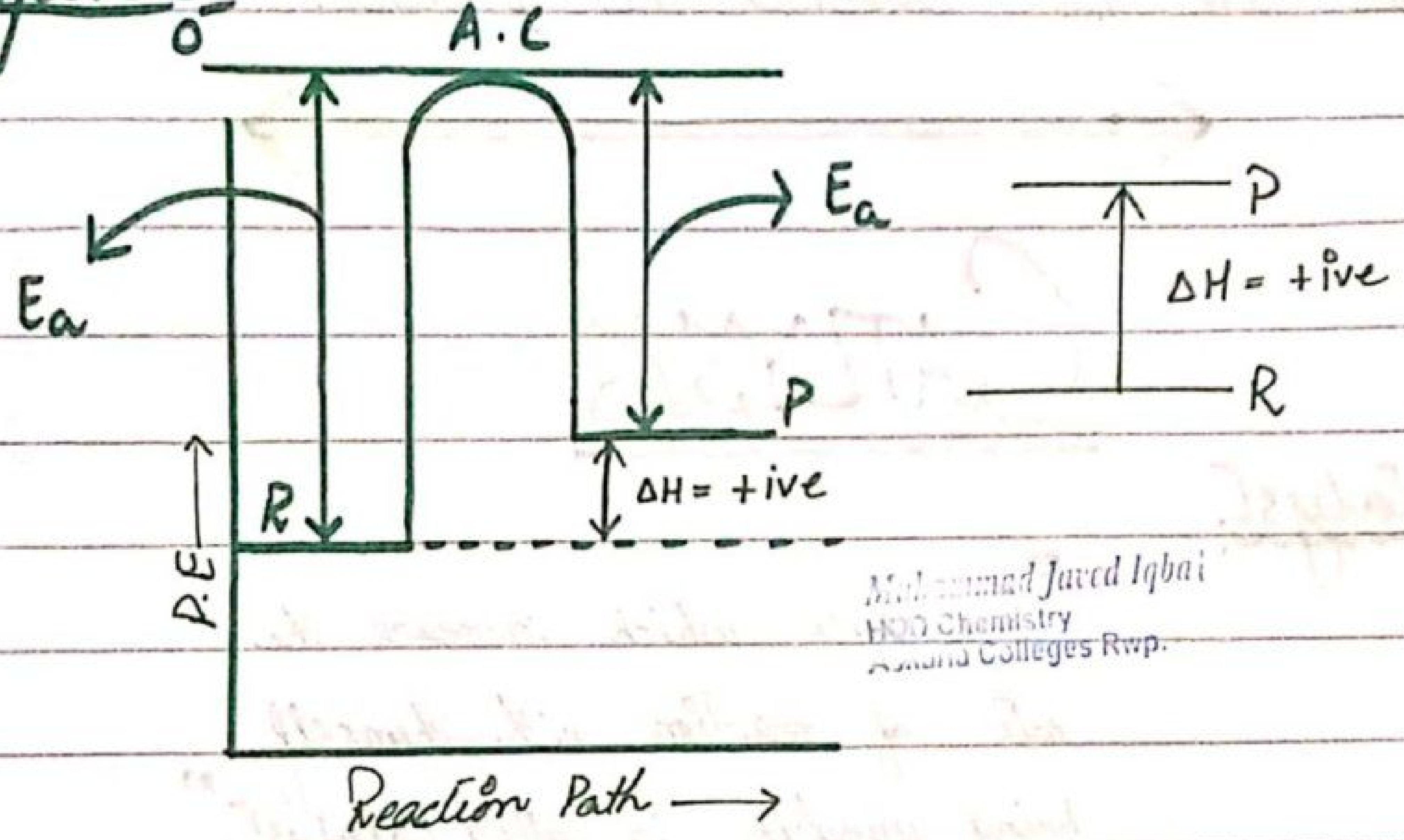
Q:- Why exothermic reations are irreversible?

Ans:- The most exothermic reactions are irreversible because product are at lower energy level than reactant. Reactant are at higher energy, therefore, they are easily converted into product. While product require high energy to convert into reactant. Therefore exothermic reactions are irreversible.

Endothermic Reaction:

In endothermic reactions product are at higher energy level than reactant.

Figure:



Q:

Why endothermic reaction are mostly reversible?

Ans:

Endothermic reactions are mostly reversible because the product at higher energy level so they are easily converted back into reactant. While reactant are at lower energy level so a continuous energy supply is required for the reaction to complete. Therefore endothermic reactions are mostly revesible.

Conclusion:-

★ Activation energy is a barrier b/w reactant and product.

★ The colliding molecule that cross the barrier are converted into product.

★ The colliding molecules that cannot cross the barrier are not converted into product.

CATLYSIS

Catalyst:-

"Substance which increase the rate of reaction withoutthemself being usedup is called **catalyst**."

⇒ They increase the rate of reaction by lowering activation Energy.

CATALYSIS:-

"Reaction in which catalyst is used is called **catalysed reaction**. And the phonemena is called **catalysis**."

⇒ A catalyst has no affect on the enthalpy of reaction.

Example:-

In stratosphere, conversion of ozone molecule by an oxygen in to two O_2 molecule occur. The reaction has higher energy of reaction.

$$O_3 + O_2 \longrightarrow 2O_2 \quad E_a = 17.1\ kJmol^{-1}$$

★ Chloroflorocarbon compound diffuse up into stratosphere. They absorb short wavelength UV radiation and break into Carbon - Chlorine bond and chlorine.

★ Cl atom catalyze the reaction and lower activation energy.

$$O_3 + Cl \longrightarrow O_2 + ClO \quad E_a = 2.1\ kJ/mol$$
$$\underline{ClO + O \longrightarrow O_2 + Cl \quad E_a = 0.4\ kJ/mol}$$
$$O_3 + O \longrightarrow 2O_2 \quad E_a = 2.5\ kJ/mol$$

GRAPHYSICAL REPRESENTATION
(on Page no. 39)

TYPES:-

There are two types of Catalysis.

★ Homogeneous catalysis
★ Heterogeneous catalysis

Homogeneous Catalysis:-

"A reaction in which catalyst and reactant both are in same physical phase is called Homogeneous catalysis."

Example:-

(i) $\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \xrightarrow{NO_2(g)} \underset{(g)}{2SO_3}$

(ii) $\underset{(aq)}{CH_3COOC_2H_5} + \underset{(l)}{H_2O} \xrightarrow{H_2SO_4(aq)} \underset{(l)}{CH_3COOH} + \underset{(l)}{HCl}$

(iii) $\underset{(aq)}{C_{12}H_{22}O_{11}} + \underset{(l)}{H_2O} \xrightarrow{sucrase} \underset{(aq)}{C_6H_{12}O_6} + \underset{(aq)}{C_6H_{12}O_6}$

(iv) $\underset{(g)}{2O_3} \xrightarrow{NO(g)} \underset{(g)}{3O_2}$

Heterogeneous Catalysis:-

"A reaction in which catalyst and reactant are both in different physical phase is called Heterogeneous catalysis."

Examples:

(i) $\underset{(g)}{N_2} + \underset{(g)}{3H_2} \xrightarrow{Fe_2O_3(s)} \underset{(g)}{2NH_3}$

(ii) $\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \xrightarrow{V_2O_5(s)} \underset{(g)}{2SO_3}$

(iii) $\underset{(l)}{HCOOH} \xrightarrow{Al_2O_3(s)} \underset{(l)}{H_2O} + \underset{(g)}{CO}$

(iv) $\underset{(l)}{HCOOH} \xrightarrow{Cu(s)} \underset{(g)}{H_2} + \underset{(g)}{CO_2}$

(v) $\underset{(l)}{\text{Vegetable oil}} + \underset{(g)}{H_2} \xrightarrow{Ni/Pt/Pd(s)} \underset{(s)}{\text{Margarine}}$

ENZYMES

Enzymes are define as:

"They are complex protein molecule."

OR

“The substance that increase the rate of chemical reaction that occur in living organism without themselves being usedup is called **Enzymes**.”

⇒ They increase the rate of reaction by the factor 10^{30}

⇒ A single enzyme catalyze a single reaction.

⇒ Most enzymes are found inside of cell.

⇒ Some enzymes are present in exo cellular fluid such as sliva, gastric juice etc.

Holoenzymes:-

“The complete enzyme is called holoenzyme.”

Apoenzyme:-

“The protein part of enzyme is called **apoenzyme**.

Co-factor or Co-Enzyme:-

“The non-protein part of enzyme is called **Co-enzyme**.”

Mechanism of Enzyme:-

Substrate:-

"A molecule on which neucleofile or electrofile react is called substrate."

Active Site:-

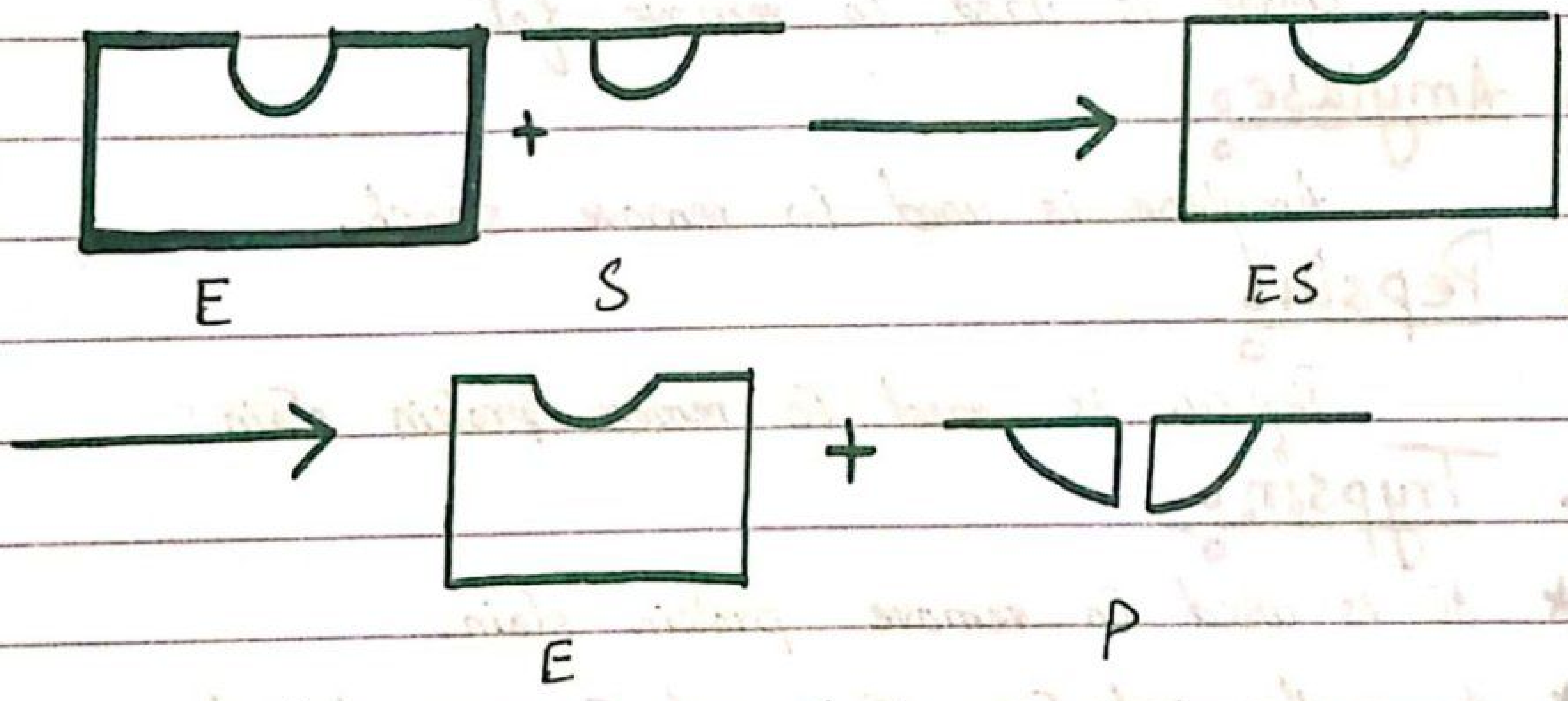
"An enzyme react with it's substrate at specific location is called **active site**."

⇒ Specific enzyme can react with specific substrate to form enzyme-substrate complex.

⇒ It is then converted into product and enzyme is released.

$$E + R \longrightarrow ER \longrightarrow E + P$$

Enzyme reactant Enzyme reactant complex Enzyme Product



Daily Life Application of Enzyme:-

⇒ Daily life application of enzymes are follow:
Enzymes are affective in removing stains from fabrics.

⇒ For this purpose specific enzyme that can act the substance present in stain are used.

⇒ They can decompose the substance present in stain into simple - water soluble compound that can be removed by washing.

⇒ Food removing stains are follow:

- ★ Pepsin
- ★ Trypsin
- ★ Lipase
- ★ Amylase

⇒ **Lipase:-**

Lipase is used to remove fat.

⇒ **Amylase:-**

Amylase is used to remove starch.

⇒ **Pepsin:-**

Pepsin is used to remove protein stain.

⇒ **Trypsin:-**

- ★ It is used to remove protein stain.
- ★ In leather industries it is used to remove hair from animal hide.

★ In pharmaceuticle industries it is used to treat inflamation.

★ It is also used to convert complex insoluble-water compound into simple- soluble water compound.

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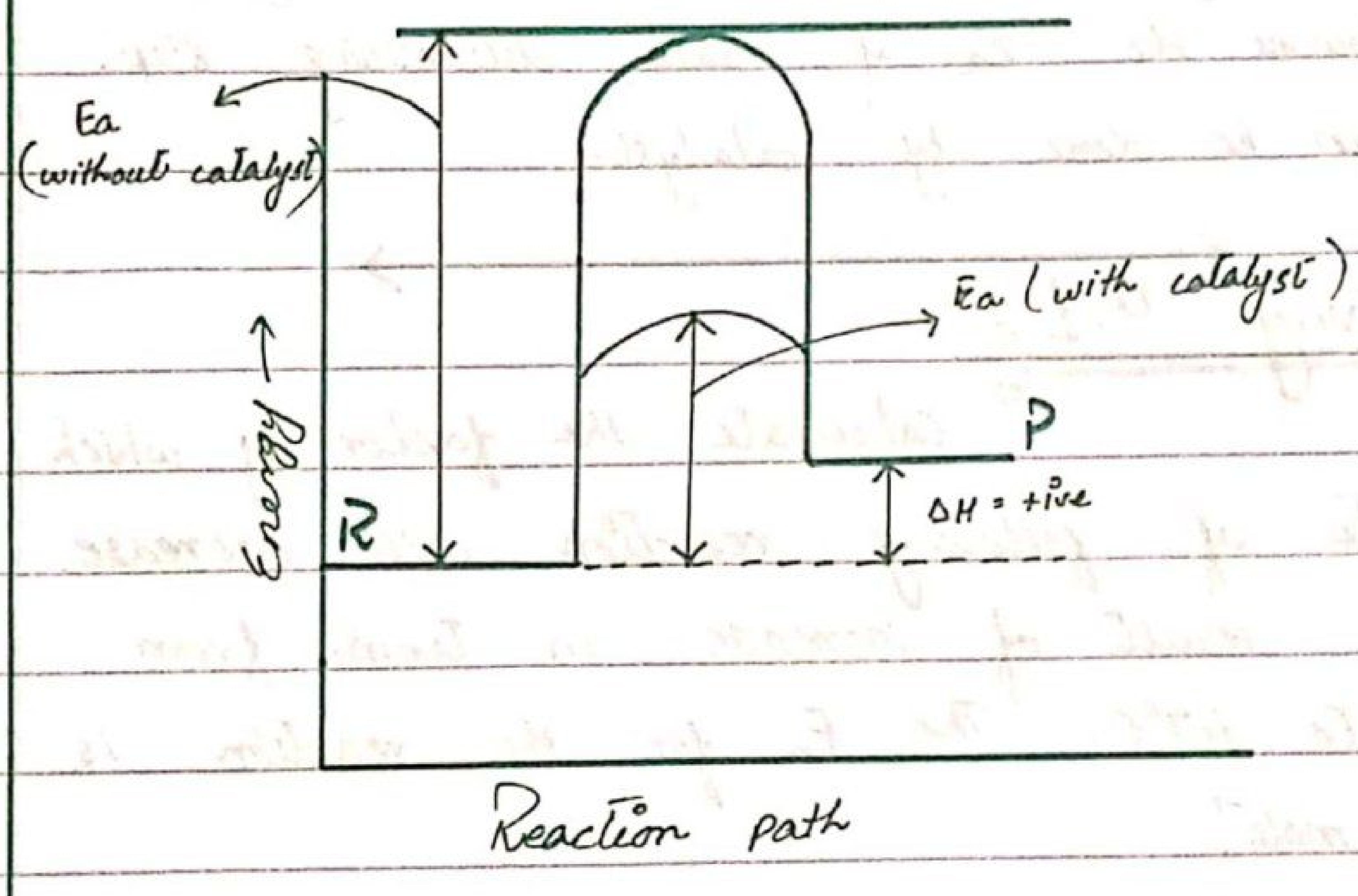
GRAPHYCAL REPRESENTATION OF CATALYST



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Q:-

How we can increase the rate of reaction?

OR

How industrial reactions are catalysed?

Ans:-

Industrial reaction are carried out at high temperature is maximize the amount of product that can be synthesized in a given time. High temperature reactions introduce safely concerns and many chemical species are not stable at high temperature. Thus a different method for increasing the rates of chemical reactions would be useful.

Another way to increase the rate of reaction is to change its mechanism in a way that way lowers the E_a of rate determining step. This can be done by catalyst.

Activity 9.1:

calculate the factor by which the rate of following reaction will increase as a result of increase in Temp. from 37°C to 47°C. The E_a for the reaction is 106 kJ mole^{-1}.

$$C_{12}H_{22}O_{11\,(aq)} + H_2O_{(l)} \longrightarrow C_6H_{12}O_{6\,(aq)} + C_6H_{12}O_{6\,(l)}$$

Solution:

$$k_1 = Ae^{-Ea/RT}$$

$$k_2 = Ae^{-Ea/RT_2} \xrightarrow{\quad} (2)$$

Divide eq (ii) by eq (i)

$$\frac{k_2}{k_1} = \frac{Ae^{-Ea/RT_2}}{Ae^{-Ea/RT_1}}$$

$$\frac{k_2}{k_1} = e^{\frac{-Ea}{RT_2} + \frac{Ea}{RT_1}}$$

$$\frac{k_2}{k_1} = e^{(Ea/RT_1 - Ea/RT_2)}$$

Take the natural lagrathm of both sides.

$$\ln\frac{k_2}{k_1} = \ln(e^{Ea/RT_1 - Ea/RT_2})$$

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

Convert natural log into common log

$\therefore \ln = 2.303\log$

$$2.303\log\frac{k_2}{k_1} = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

$$2.303\log\frac{k_2}{k_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

As Data is

$E_a = 106\ kJ/mol = 106 \times 10^3\ J\ mol^{-1}$

$R = 8.314\ J\ mol^{-1} k^{-1}$

$T_1 = 37^\circ C = 37 + 273 = 310 k$

$T_2 = 47^\circ C = 47 + 273 = 320 k$

So,

$$\log \frac{k_2}{k_1} = \frac{106 \times 10^3}{2.303\,(8.314)} \left(\frac{320 - 310}{(320)(310)} \right)$$

$$\log \frac{k_2}{k_1} = 0.5581$$

$$\frac{k_2}{k_1} = \text{anti log}\,(0.5581)$$

$$\boxed{\frac{k_2}{k_1} = 3.6}$$ Ans

Self Check 9.2

The following reaction is first order in H_2 and 2nd order in NO. Write rate law for the reaction?

$$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$$

Solution:-

Rate $\propto [H_2]$ $\longrightarrow$ (i)

Rate $\propto [NO]^2$ $\longrightarrow$ (ii)

Combining eq (i) and eq (ii)

Rate $\propto [H_2][NO]^2$

$$\boxed{\text{Rate} = k[H_2][NO]^2}$$

Example 9.1:

Solutions:

Data:

Sr. No	Initial (NO)	Initial $[O_3]$	Initial rates (mol dm^{-3} s)
1.	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
2.	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
3.	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}

$$NO + O_3 \longrightarrow NO_2 + O_2$$

with respect to [NO]

$$\frac{1.00 \times 10^{-6}}{1 \times 10^{-6}} : \frac{2 \times 10^{-6}}{1. \times 10^{-6}} \qquad \frac{1.98 \times 10^{-4}}{1.98 \times 10^{-4}} : \frac{3.96 \times 10^{-4}}{1.98 \times 10^{-4}}$$

$$1 : 2 \qquad 1 : 2$$

Rate $= k[NO]^1$

with respect to $[O_3]$

$\frac{9\times10^{-6}}{9\times10^{-6}} : \frac{3\times10^{-6}}{9\times10^{-6}}$ $\qquad$ $\frac{1.98\times10^{-4}}{1.98\times10^{-4}} : \frac{6.60\times10^{-5}}{1.98\times10^{-4}}$

$1 : \frac{1}{3}$ $\qquad$ $1 : \frac{1}{3}$

Rate $\propto [O_3]^1$

Overall rate order

$$\boxed{\begin{array}{l} \text{Rate} = k[NO]^1[O_3]^1 \\ \text{order} = 1+1 = 2 \end{array}}$$ Ans

Example 9.2:-

Solution

$$H_2 + Br_2 \longrightarrow 2HBr$$

Rate $\propto [H_2]$

Rate $\propto [Br_2]^{1/2}$

So,

Rate $\propto [H_2][Br_2]^{1/2}$

Rate $= k[H_2][Br_2]^{1/2}$

Self Check 9.3:-

$CO + Cl_2 \longrightarrow COCl_2$

Sr.No	Initial [CO]	Initial [Cl_2]	Initial rate ($mol\,dm^{-3}\,s^{-1}$)
1.	1.000	0.100	1.29×10^{-29}
2.	0.100	0.100	1.30×10^{-30}
3.	1.000	1.00	1.30×10^{-30}

Rate eq w.r.t [CO]

$$\frac{1.000}{1} : \frac{0.100}{1} \qquad \frac{1.29 \times 10^{-29}}{1.29 \times 10^{-29}} : \frac{1.30 \times 10^{-30}}{1.29 \times 10^{-29}}$$

$$1 : \frac{1}{10} \qquad 1 : \frac{1}{10}$$

$$\text{Rate} = k\,[CO]$$

Rate eq w.r.t [Cl_2]

$$\frac{0.1}{0.1} : \frac{1}{0.1} \qquad \frac{1.29 \times 10^{-29}}{1.29 \times 10^{-29}} , \frac{1.30 \times 10^{-30}}{1.29 \times 10^{-29}}$$

$$1 : 10 \qquad 1 : \frac{1}{10}$$

$$\text{Rate} = k\,[Cl_2]^{-1}$$

$$\boxed{\begin{array}{l} \text{Rate} = k\,[CO]^{1}[Cl_2]^{-1} \\ \text{order} = 1 - 1 = 0 \end{array}}$$

(2)

Solution

$$NO_2 + CO \longrightarrow NO + CO_2$$

Rate $\propto [NO_2]^2$

Rate $\propto [CO]^0$

So rate eq. is

$\boxed{Rate = k[NO_2]^2}$ Ans.

Self Check 9.4:-

For the following reaction with mechanism is correct?

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

Rate $= k[NO_2][F_2]$

Solution

True mechanism is:

$NO_2 + F_2 \longrightarrow NO_2F + F$ (slow step)

$NO_2 + F \longrightarrow NO_2F$ (Fast step)

Self Check 9.5

....

$$2H_2 + 2NO \rightarrow 2H_2O + N_2$$

Solution:-

Sr.No	$[H_2]$	$[NO]$	initial rate (moles $dm^{-3} s^{-1}$)
1.	0.010	0.025	2.4×10^{-6}
2.	0.0050	0.025	1.2×10^{-6}
3.	0.010	0.0125	0.6×10^{-6}

Rate eq w.r.t $[H_2]$

$$\frac{0.010}{0.010} : \frac{0.0050}{0.010} \qquad \frac{2.4 \times 10^{-6}}{2.4 \times 10^{-6}} \quad \frac{1.2 \times 10^{-6}}{2.4 \times 10^{-6}}$$

$$1 : \frac{1}{2} \qquad 1 : \frac{1}{2}$$

$$\text{Rate} \propto [H_2]$$

Rate eq w.r.t [NO]

$$\frac{0.25}{0.25} : \frac{0.0125}{0.25} \qquad \frac{2.4 \times 10^{-6}}{2.4 \times 10^{-6}} : \frac{0.6 \times 10^{-6}}{2.4 \times 10^{-6}}$$

$$1 : \frac{1}{2} \qquad 1 : \frac{1}{4}$$

$$\text{Rate} \propto [NO]^2$$

Overall

$$\boxed{\begin{array}{l} \text{Rate} \propto [NO]^2[H_2] \\ \text{Rate} = k[NO]^2[H_2] \\ \text{order} = 2+1 = 3 \end{array}}$$

(b)

Write mechanism of reaction?

(Hint O is intermidiate)

$$\text{Rate} = k[NO]^2[H_2]$$

Equation obtain

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

Mechanism:-

$$2NO + H_2 \xrightarrow{\text{Slow step}} N_2 + H_2O + [O]$$

$$H_2 + [O] \xrightarrow{\text{Fast step}} H_2O$$

$$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$$

Q: NO = 2, (self check 9.5)

Following the reaction has been proposed and mechanism of reaction

$$H_2O + I^- \longrightarrow H_2O + OI^-$$

$$OI + H_2O_2 \longrightarrow H_2O + O_2 + I^-$$

Choose catalyst, reaction intermidiate and rate determining step?

Solution:-

Catalyst:-

"I^-"

Reaction Intermidiate:-

"OI"

Rate determining step:-

The experimental rate law is needed to suggest the rate determining step. So, it cannot be decided.

Q: NO 3 (Self check 9.5)

The rate law for the following reaction is $k[H_2][NO]^2$

$$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$$

Is following mechanism, is consistant with the rate law?, Argue.

Mechanisom (True)

$$H_2 + 2NO \longrightarrow H_2O + N \quad (slow)$$
$$N + NO \longrightarrow N_2 + O \quad (fast)$$
$$O + H_2 \longrightarrow H_2O \quad (fast)$$

Solution:-

The rate law shows that there must be 2 molecules of NO and 1 molecule of H_2 required. Since above mechanism donot fulfill the demand so it is not correct.

(b)

Q: NO = 4 (Self check 9.5)

The rate law for the reaction,

$$2N_2O \longrightarrow 2N_2 + O_2$$

is rate = $[N_2O]$

write mechanism of reaction take [O] as intermidiate?

Solution:-

Mechanisom:-

$$N_2O \longrightarrow N_2 + [O] \quad \text{(Slow step)}$$

$$N_2O + [O] \longrightarrow N_2 + O_2 \quad \text{(fast step)}$$

$$2N_2O \longrightarrow 2N_2 + O_2$$

Exercise

Choose the Correct answer?

(i)	(b)
(ii)	(d)
(iii)	(a)
(iv)	(d)
(v)	(d)
(vi)	(c)
(vii)	(d) none of these
(viii)	(d)
(ix)	(b)
(x)	(c)

Q: NO = 2.

Define chemical kinetics? How do you differentiate Chemical kinetics from chemical equilibrium?

Ans: **Chemical kinetics:**

"Branch of chemistry which deals with the study of rate of reaction, mechanism of the reaction and factor affecting the rate of reaction is called Chemical kinetics."

Difference b/w Chemical kinetic and Chemical Equilibrium.

Chemical kinetics	Chemical Equilibrium
1. The branch of chemistry which deals with rate of reaction, mechanism of reaction and factor affecting the rate of reaction is called chemical kineti.	1. When the rate of forward reaction is equal to the rate of reverse reaction is called chemical equilibrium.
2. It is aplicable on both reversible and irreversible reaction.	2. It is applicable on only reversible reaction.
3. We can determine the mechanism of reaction.	3. We cannot determine the mechanism of reaction.

<u>Q8 NO</u> : <u>(Practise question)</u>

Explain the significance of rate determining step on overall rate of multiple step reaction?

<u>Ans</u>:

<u>Rate Determining step</u>:

"When the reaction is take place in single step then the same step of a reaction is called rate determing step."

OR

When the reaction take place more than one step then the slow step of a reaction is called rate determining step."

Significance:-

The significance of rate determining step are follow:

1. We can determine rate equation or rate laws
2. E_a is highest for rate determining step.
3. We can determine the mechanism of the reaction.
4. We can determine the no. of molecules take part in rate determining step.

Example:-

$$NO_2 + CO \longrightarrow NO + CO_2 \quad Rate = k[NO_2]^2$$

Mechanism

$$NO_2 + NO_2 \longrightarrow NO_3 + NO \text{ (slow step)}$$
$$NO_3 + CO \longrightarrow NO_2 + CO_2 \text{ (fast step)}$$

Q: NO:-
(See on page no. 16.)

Q: NO= :-

(See on page no. 1, 10, 9, 22, 25, 32, 35)

Q: NO= :-

(See on page no. 25, 29)

Q: NO = :-

(see on page no. 27, 28)

Q: NO = :-

(see on page no. 39)

Q: NO= 6 :-

What is the affect of catalyst on following:

(i) **Rate of reaction:-**

catalyst increase the rate of reaction.

(ii) **The ENERGY OF ACTIVATION:-**

catalyst lower the E_a.

(iii) **The Equilibrium position of a reversible reaction:-**

No affect.

Q: NO = 7 :-

The reaction of an alkyl halide R-X with water as follows:

$$R-X \ H_2O \longrightarrow R-OH + HX$$

If a reaction is single step process, what would you predict the rate law to be?

Ans

$$Rate = k\ [R-x][H_2O]$$

Rate order = 1 + 1 = 2

In this case water is used as solvent. Solvent is present in excess. Rate of reaction does not depend upon excess reactant. Therefore, rate equation is:

$$\boxed{\begin{array}{l} Rate = k\ [R-x] \\ order = 1^{st} \end{array}}$$

It is pseudo-first order reaction because it is appear to be second order but actually it is first order.

Q: NO = 8 :-

The reaction of compound A & B to give C and D was found to be 2nd order in A and second order overall. Write expression for the reaction?

Ans:-

$$Rate \propto [A]^2$$

Equation

$$A + B \longrightarrow C + D$$

$$Rate = k\ [A]^2$$

Rate of reaction does not depend upon reactant B.

Q: NO= 9:

Defend the following statements?

(a)

A very small amount of catalyst may prove sufficient to carryout a reaction?

Ans: Catalyst is a substance that increase the rate of reaction without themselves being usedup.

Therefore, it's concentration does not matter on rate of reaction.

(b)

The reaction rate decrease every moment.

According to law of mass of action

The rate of reaction is
directly proportional to
the concentration of
the reactant.

As the reaction proceed the concentration of reactant decrease. So the reaction rate decrease.

(c)

The unit of rate constant of 2nd order reaction is $dm^3\ mole^{-1}\ s^{-1}$:

$$Rate = k[A][B]$$

$$k = \frac{R}{[A][B]}$$

$$k = \frac{\cancel{mole\ dm^{-3}} \cdot s^{-1}}{[\cancel{mole\ dm^{-3}}][mol \cdot dm^{-3}]}$$

$$\boxed{k = dm^3\ mol^{-1}\ s^{-1}}$$ Ans.

Q: NO = : Practise question

From the equation proposed.....

.... Identify intermidiate and write rate law and stoichemetric equation?

$$NO_2 + NO_2 \longrightarrow NO_3 + NO \quad (slow)$$

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \quad (fast)$$

Solution

Stoicheometric Equation:

$$\cancel{NO_2} + NO_2 \longrightarrow \cancel{NO_3} + NO$$

$$\cancel{NO_3} + CO \longrightarrow \cancel{NO_2} + CO_2$$

$$NO_2 + CO \longrightarrow NO + CO_2$$

Intermidiate:

"The substance that do not appear in intial and final stage of reaction and formed in one step and consumed in other step is called intermidiate."

So NO_3 is intermidiate.

Rate law:

$$\text{Rate} \propto [NO_2]^2$$
$$\text{Rate} = k\,[NO_2]^2$$

Q: NO = 10.

Sr. No	[A]	[B]	Initial rate (mol dm⁻³ s⁻¹)
1.	0.10	0.01	1.00×10^{-5}
2.	0.10	0.02	2.00×10^{-5}
3.	0.20	0.01	2.00×10^{-5}
4.	0.30	0.02	6.00×10^{-5}

Rate equation w.r.t [A]

$$\frac{0.10}{0.10} : \frac{0.20}{0.10} \qquad \frac{1 \times 10^{-5}}{1 \times 10^{-5}} : \frac{2 \times 10^{-5}}{1 \times 10^{-5}}$$

$$1 : 2 \qquad 1 : 2$$

$$\text{Rate} = k\,[A]$$

Rate equation with respect to [B]

$$\frac{0.01}{0.01} : \frac{0.02}{0.01} \qquad \frac{1 \times 10^{-5}}{1 \times 10^{-5}} : \frac{2 \times 10^{-5}}{2. \times 10^{-5}}$$

$$1 : 2 \qquad 1 : 2$$

$$\text{Rate} = k\,[B]$$

Overall Rate equation :-

Rate $\propto [A][B]$

Rate $= k[A][B]$

order $= 1+1 = 2$

Q: NO =

(see on page no.)

Q: NO = :- Practise question

The rate for the reaction is

$$CO + NO_2 \longrightarrow CO_2 + NO$$

rate $= k[NO_2]^2$

Is the following mechanism consistent with this rate law?

$$2NO_2 \longrightarrow N_2 + 2O_2 \quad (slow)$$

$$2CO + O_2 \longrightarrow 2CO_2 \quad (fast)$$

$$N_2 + O_2 \longrightarrow 2NO \quad (fast)$$

Ans :-

$$2NO_2 \longrightarrow N_2 + 2O_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$N_2 + O_2 \longrightarrow 2NO$$

$$2CO + 2NO \longrightarrow 2CO_2 + 2NO$$

The whole eq. is divided by 2.

Then

$$NO_2 + CO \longrightarrow NO + CO_2$$

Q: NO: Practise question

Predict the rate law for the oxidation of Iodine by hypochloride.

$$I^- + ClO \longrightarrow Cl^- + IO^-$$

If the reaction proceed by following mechanism:

$$ClO^- + H_2O \longrightarrow HOCl + OH^- \quad (\text{slow})$$
$$I^- + HOCl \longrightarrow HOI + Cl^- \quad (\text{fast})$$
$$HOI + OH^- \longrightarrow IO + H_2O \quad (\text{fast})$$

Solution:

Rate law:

$$Rate = k\,[ClO^{-1}][H_2O]$$

Final Equation:

$$ClO + \cancel{H_2O} \longrightarrow \cancel{HOCl} + \cancel{OH}$$
$$I^- + \cancel{HOCl} \longrightarrow \cancel{HOI} + Cl^-$$
$$\cancel{HOI} + \cancel{OH} \longrightarrow IO + \cancel{H_2O}$$

$$ClO + I^- \longrightarrow Cl^- + IO$$

The End