



CHAPTER

11

REACTION KINETICS

CHEMICAL KINETICS

“The study of rate of a chemical reaction, factors affecting the reaction rates and mechanism of the reaction is called **chemical kinetics or reaction kinetics**.”

Mechanism:

“The path of reaction of steps involved in chemical reaction is called **mechanism**.”

Mechanism describes how a chemical reaction occurs. It is a series of steps that defines the order in which bonds are broken and new bonds are formed until the final products are obtained.

On the basis of rate there are three types of reaction, i.e. **rapid, moderate and slow**.

For example, a white precipitate of silver chlorides is formed immediately on addition of silver nitrate solution to sodium chloride solution. Some reactions proceed at a moderate rate e.g. hydrolysis of an ester. Still other reactions take a much longer time e.g. rusting of iron, the chemical weathering of stone work of buildings by acidic gases in the atmosphere and the fermentation of sugars.

Importance of Reaction Kinetics:

The rates of reactions and their control are often important in industry as they might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction and it is important to discover the conditions under which the reaction will proceed most economically.

Rate Determining Step:

“If a reaction consists of several steps, one step will be slowest than all other steps. The slowest step is rate determining step. Other step will not affect the rate.

RATE OF REACTION

“The change in concentration of reactants or products per unit time is called **velocity or rate of chemical reaction**.”

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken for change}} = \frac{\Delta C}{\Delta t}$$

The **unit** of rate of reaction is:



$$\text{Rate of reaction} = \frac{\text{mol dm}^{-3}}{\text{second}} = \text{mole dm}^{-3} \text{ sec}^{-1}$$

For gas phase reactions, the pressure units are used instead of molar concentration.

The concentration of reactant decreases with passage of time and concentration of product increases with time.

Consider a reaction in which reactant A changes to product B.



With the passage of time, concentration of reactant decreases.

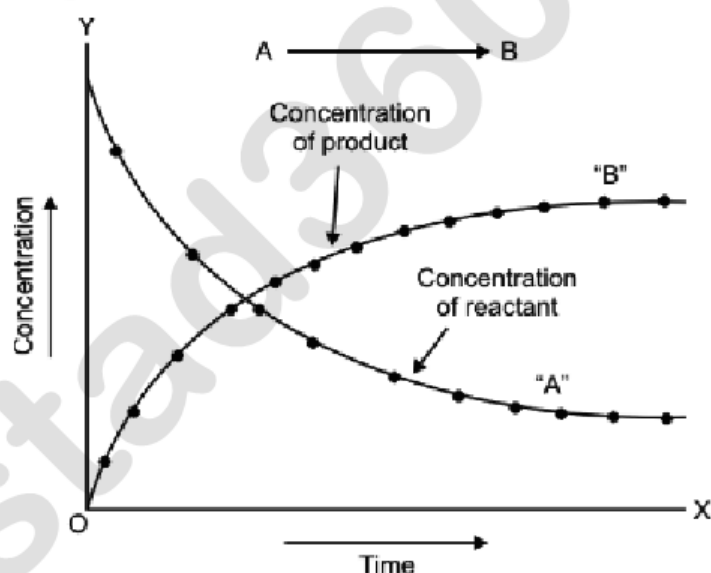
$$\text{Rate} = \frac{-\Delta A}{\Delta t} = \frac{\text{Change in Concentration}}{\text{Time}}$$

Minus sign indicates to the decrease in concentration. On the other hand concentration of product increases. It can be represented as:

$$\text{Rate} = \frac{\Delta B}{\Delta t} = \frac{\text{Change in Concentration}}{\text{Time}}$$

If we plot a graph between the concentration of reactants and products and time following shape is obtained.

The slope of the graph for the reactant or the product is the **steepest at the beginning** showing rapid decrease in the concentration of the reactant and the consequently a rapid increase in the concentration of the product. As the reaction proceeds the slope becomes less steep indicating that the reaction is **slowing down with time**. Where the graph becomes a horizontal straight line, the reaction stops.



Change in the concentration of reactants and products with time for the reaction $A \longrightarrow B$

(Change in the concentration of reactants and products with time for the reaction $A \longrightarrow B$)".



It shows from the above graph that the change in concentration of the reactant A or the product B is much more at the start of reaction and then it decreases gradually. So the reaction rate decreases with time. **It never remains uniform** during different time periods. It decreases continuously till the reaction ceases.

TYPE OF RATES

- (i) Average rate (ii) Instantaneous rate

(i) Average Rate:

“The rate of reaction between two specific times is called **average rate**.”

(ii) Instantaneous Rate:

“The rate at any one instant during a specific interval of time is called **instantaneous rate**.”

The average rate and instantaneous rate are equal for only one instant in any time interval. At first, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate becomes lower than the average rate. As the time interval becomes smaller, the average rate becomes closer to the instantaneous rate. **The average rate will be equal to the instantaneous rate when the time interval approaches zero.** Thus the rate of reaction is defined as the instantaneous change in the concentration of a reactant or a product at a given moment of time.

$$\text{Rate of reaction} = \frac{dx}{dt}$$

Where “dx” is a very small change in the concentration of a product in a very small time interval “dt”.

The rate of a general reaction, $A \longrightarrow B$ can be expressed in terms of rate of disappearance of the reactant A or the rate of appearance of the product B. Mathematically,

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

Where d[A] and d[B] are the changes in the concentrations of A and B respectively. The negative sign in the term indicates a decrease in the concentration of the reactant. Since the concentration of product increase with time, the sign in the product should be positive.

SPECIFIC RATE CONSTANT

The relationship between the rate of a chemical reaction and the active masses (expressed as concentrations) of the reacting substances is summarized in the law of mass action. It states that the rate of reaction is proportional to the active mass of the reactant or the product of active masses if more than one reactants are in a chemical reaction (for dilute solutions, active mass is considered as equal to concentration). By applying the law of mass action to a general reaction.



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

This expression is called **rate equation**. The brackets [] represent the concentrations and the proportionality constant k is called **rate constant or velocity constant for the reactions**.

Let $[A] = 1 \text{ mole dm}^{-3}$ and $[B] = 1 \text{ mol dm}^{-3}$



$$\text{Rate of reaction} = k \times 1^a \times 1^b = k.$$

Hence the specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity. Under the given conditions, k remains constant but it changes with temperature. The unit of rate constant is “ $\text{mole dm}^{-3} \text{sec}^{-1}$ ”.

ORDER OF REACTION

“The sum of exponents of the concentrations of the reacting species in the observed rate law is called **order of reaction**.”

or “The number of reacting molecules whose concentrations alter as a result of chemical change.”

Order of a reaction cannot be predicted from a balance equation but must be determined from **rate law** which is obtained **experimentally**.



For a general reaction between A and B where ‘a’ moles of A and ‘b’ moles of B react to form ‘c’ moles of C and ‘d’ moles of D.

We can write the rate equations or rate law as:

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

The exponent ‘a’ or ‘b’ gives the order of reaction with respect to the individual reactant. Thus the reaction is of order ‘a’ with respect to A and order of b with respect to B. The overall order of reaction is (a + b).

The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation. The chemical reactions are classified as zero, first, second and third order reactions. The order of reactions provides valuable information about the mechanism of a reaction.

ZERO ORDER REACTIONS

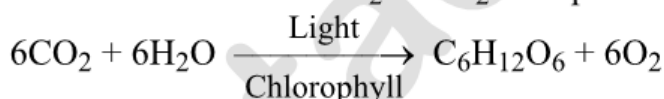
“The reactions in which rate of reaction does not depends upon the concentration of any reactant.”

A Product

$$\text{Rate} = k [A]^0$$

$$\text{Rate} = k$$

- (1) All photochemical reactions are of zero order. For example, rate does not depends upon the concentration of CO_2 or H_2O in photosynthesis.



- (2) Decomposition of NH_3 .



- (3) Decomposition of PH_3 .

- (4) Thermal decomposition of HI.



FIRST ORDER REACTION



“The reactions in which rate of reaction depends upon the concentration of only one substance are called **first order reaction**.”

For Examples:

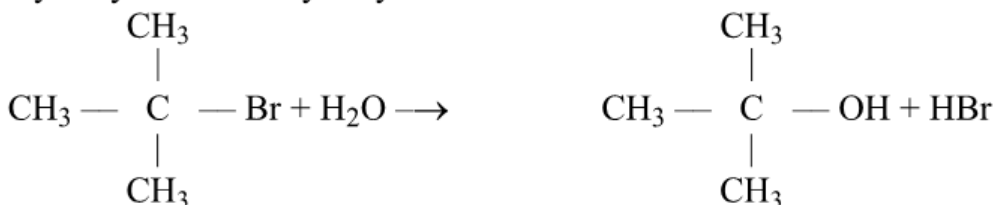
- (1) Decomposition of nitrogen pent-oxide involves the following equation.



The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

- (2) Hydrolysis of tertiary butyl bromide.

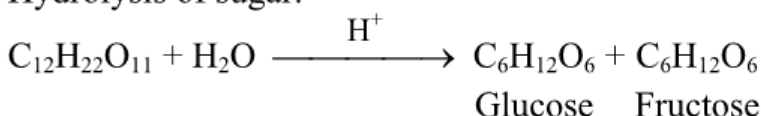


The rate equation determined experimentally for this reaction is

$$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such type of reactions have been named as **pseudo first order reactions**.

- (3) Hydrolysis of sugar.



- (4) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$

SECOND ORDER REACTIONS

For Example:

- (1) The rate equation for this reaction is which shows that it is second order reaction.



$$\text{Rate} = k [\text{NO}] [\text{O}_3]$$

- (2) Decomposition of HI in gas phase.



- (3) Decomposition of Acetaldehyde:



Third Order Reaction:

“The reactions in which rate of reaction depends upon the concentration of three molecules.”

For Example:

- (1) Consider the following reaction.

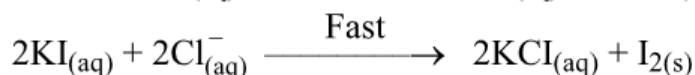
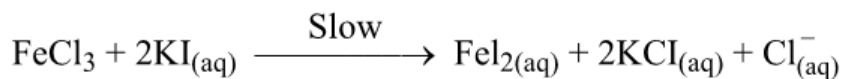


This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

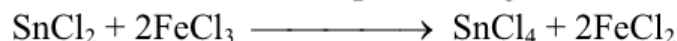
$$\text{Rate} = k [\text{FeCl}_3] [\text{KI}]^2$$

This rate equation suggests that the reaction is, in fact, taking place in more than one steps. The possible steps of the reaction are shown below.





(2) Reaction between SnCl_2 and FeCl_3 .



Fractional Orders:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Consider the formation of carbon tetrachloride from chloroform.



$$\text{Rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$$

The sum of exponents will be $1 + \frac{1}{2} = 1.5$, so the order of this reaction is 1.5.

HALF LIFE PERIOD

“Half life period of a reaction is the time required to convert 50% of the reactants into products.”

For example, the half life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

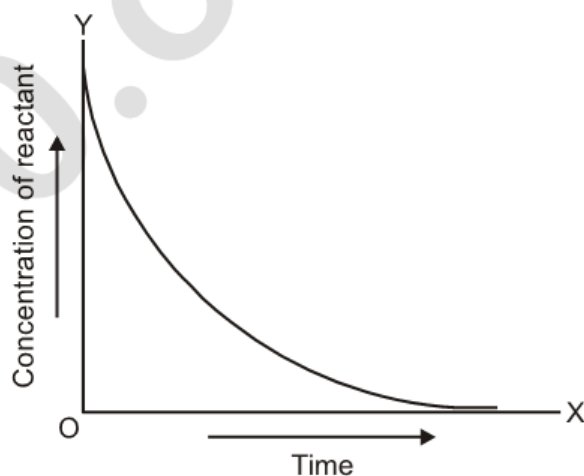
It means that if we decompose $0.10 \text{ mole dm}^{-3}$ of N_2O_5 at 45°C , then after 24 minutes $0.05 \text{ mole dm}^{-3}$ of N_2O_5 will be left behind. Similarly after 48 minutes $0.025 \text{ mole dm}^{-3}$ of N_2O_5 will remain un-reacted and after 72 minutes (3 half times) $0.0125 \text{ mole dm}^{-3}$ of N_2O_5 will remain un-reacted.

Decomposition of N_2O_5 is a first order reaction and the above experiment proves that the **half-life period of this reaction is independent of the initial concentration** of N_2O_5 . This is true for all first order reactions. The disintegration of radioactive ${}^{235}_{92}\text{U}$ has a half-life of 7.1×10^8 years or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of ${}^{235}_{92}\text{U}$ 0.25 kg disintegrates in the next 710 million year. So

the half-life period for the disintegration of radioactive substance is independent of the amount of that substance.

It is true for the half-life period of first order reactions. It is not true for the reactions having higher orders. In the case of 2nd order reaction, the half-life period is inversely proportional to the initial concentration of the reactant and for a 3rd order reaction, it is inversely proportional to the square of initial concentration of reactants.

Briefly we can say that;



First order reaction equation:

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

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

At half change:

$$x = 0.5a$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a-0.5a}$$



$$\begin{array}{l}
 [t_{1/2}] \propto \frac{1}{a^0}, \text{ Since } [t_{1/2}]_1 = \frac{0.693}{k} \\
 [t_{1/2}] \propto \frac{1}{a^1}, \text{ Since } [t_{1/2}]_2 = \frac{1}{ka} \\
 [t_{1/2}] \propto \frac{1}{a^2}, \text{ Since } [t_{1/2}]_3 = \frac{1.5}{ka^2}
 \end{array}
 \left|
 \begin{array}{l}
 t_{1/2} = \frac{2.303}{k} \log \frac{a}{0.5a} \\
 t_{1/2} = \frac{2.303}{k} \log 2 \\
 t_{1/2} = \frac{0.693}{k}
 \end{array}
 \right.$$

Where $[t_{1/2}]_1$, $[t_{1/2}]_2$ and $[t_{1/2}]_3$ are the half-life periods for 1st, and 2nd and 3rd order reactions respectively and 'a' is the initial concentration of reactants.

In general for the reaction of nth order:

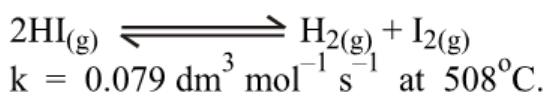
$$[t_{1/2}]_n \propto \frac{1}{a^{n-1}}$$

"The half-life period of any order reaction is, thus, inversely proportional to the initial concentration raised to the power one less than the order of that reaction."

So if one knows the initial concentration and half-life period of a reaction, then order of that reaction can be determined.

Example 1:

Calculate the half-life period of the following reaction when the initial concentrations is 0.05 M.



$$k = 0.079 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 508^\circ\text{C}.$$

$$\text{Rate} = k [\text{HI}]^2$$

$$\begin{aligned}
 \text{So } [t_{1/2}] &= \frac{1}{k \times a^{2-1}} \\
 &= \frac{1}{(0.079 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) (0.050 \text{ mol dm}^{-3})}
 \end{aligned}$$

$$[t_{1/2}] = 253 \text{ seconds.}$$

RATE DETERMINING STEP

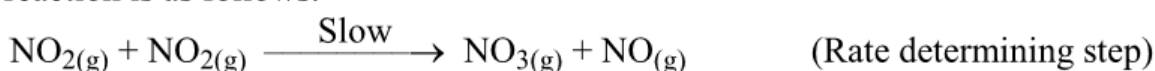
If a reaction occurs in several steps, one of the step is the **slowest**. The rate of this step determines to overall rate of reaction. This slowest step is called the **rate determining or rate limiting step**. The number of molecules (reacting species) taking part in the rate determining steps appear in the rate equation of the reaction. Let us consider the following reaction.

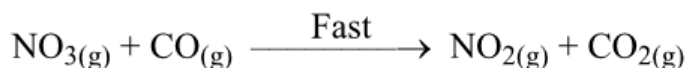


The rate equation of the reaction is found to be

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

This equation shows that the rate of reaction is independent of the concentration of carbon monoxide. In other words, the equation tells us that reaction involves more than one steps and two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.





The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the **reaction intermediate**. The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products. This is a species with normal bonds and may be stable enough to be isolated under special conditions. This reaction is a clear example of the fact that a balanced chemical equation may give any information about the way the reaction actually takes place.

DETERMINATION OF THE RATE OF A CHEMICAL REACTION

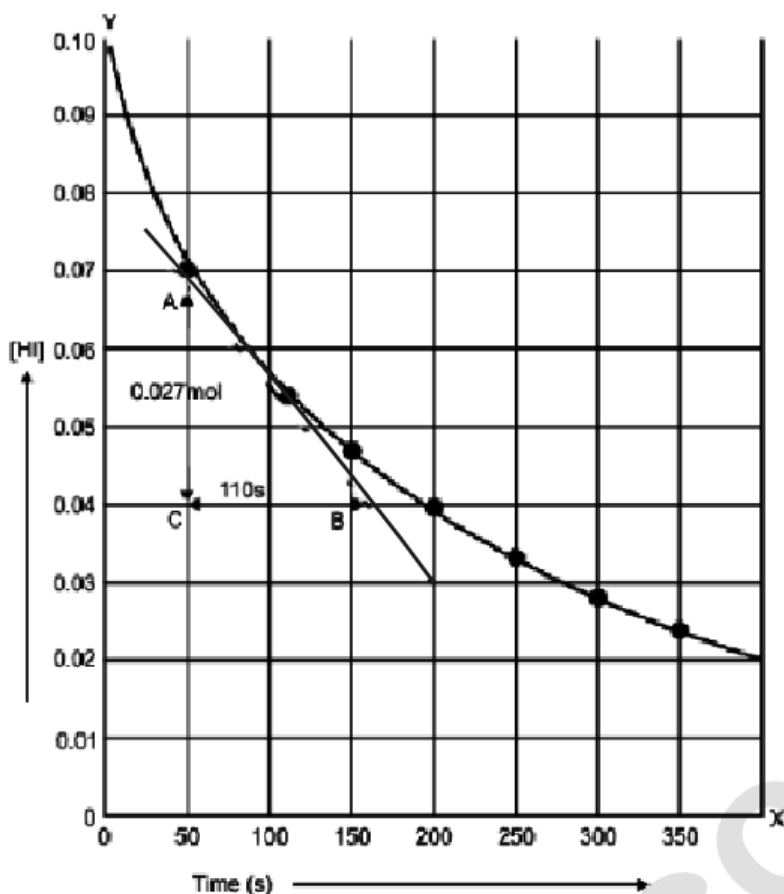
Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals as the reaction progresses. When the reaction goes on, the concentrations of reactants decrease and those of products increase the rate of a reaction, therefore, is expressed in terms of the rates at which the concentrations change.

$$\begin{aligned} \text{Rate of reaction} &= \frac{\Delta C}{\Delta t} = \frac{\text{moles dm}^{-3}}{\text{sec}} \\ &= \text{moles dm}^{-3} \text{ s}^{-1} \end{aligned}$$

Suppose the concentration of a reactant of any chemical reaction changes by $0.01 \text{ mole dm}^{-3}$ in one second, then rate of reaction is $0.01 \text{ mole dm}^{-3} \text{ s}^{-1}$.

Rate of a chemical reaction always decreases with the passage of time during the progress of reaction. To determine the rate of reaction for a given length of time, a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained.





The change in the HI concentration with time for the reaction $2\text{HI}_{(g)} \rightarrow \text{H}_{2(g)} + \text{I}_{2(g)}$ at 508°C .

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 508°C . Table tell us that the change in concentration of HI for first 50 seconds is $0.0284 \text{ mole dm}^{-3}$ but between 300 to 350 sec, the decrease is $0.0031 \text{ moles dm}^{-3}$. The steepness of the concentration time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Concentration of HI (mole dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.387	200
0.0336	250
0.0296	300
0.0265	450

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point



i.e. after 100 seconds. A right angle triangle ABC is completed with a tangent as hypotenuse. Figure shows that in 48 sec, the change in concentrations is $0.037 \text{ mole dm}^{-3}$, and hence the

$$\begin{aligned}\text{Slope or Rate} &= \frac{0.027 \text{ moles dm}^{-3}}{110 \text{ sec}} \\ &= 2.5 \times 10^{-4} \text{ moles dm}^{-3} \text{ s}^{-1}\end{aligned}$$

This value of rate means that in a period of one sec in dm^{-3} solution, the concentration of HI disappears by 2.5×10^{-4} moles, changing into the products.

The change in concentrations of reactants or products can be determined by both physical and chemical method depending upon the type of reactants or products involved.

(A) PHYSICAL METHODS

Some of the methods used for this purpose are the following:

1. Spectroscopy:

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiations. The rate of reaction can be measured by measuring the amount of radiations absorbed.

2. Electrical Conductivity Method:

The rate of reaction involving ions can be studied by electrical conductivity method. The **conductivity** of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of **change in the concentration** of the reacting ions or the ions formed.

3. Dilatometric Method:

This method is useful for those reactions, which involve small **volume changes** in solutions. The volume change is directly proportional to the extent of reactions.

4. Refractometric Method:

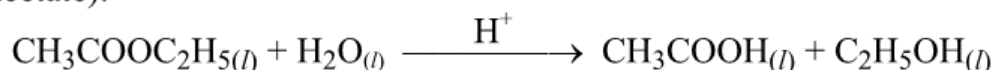
This method is applicable to reactions in solutions where there are changes in refractive indices of the substances taking part in the chemical reaction.

5. Optical Rotation Method:

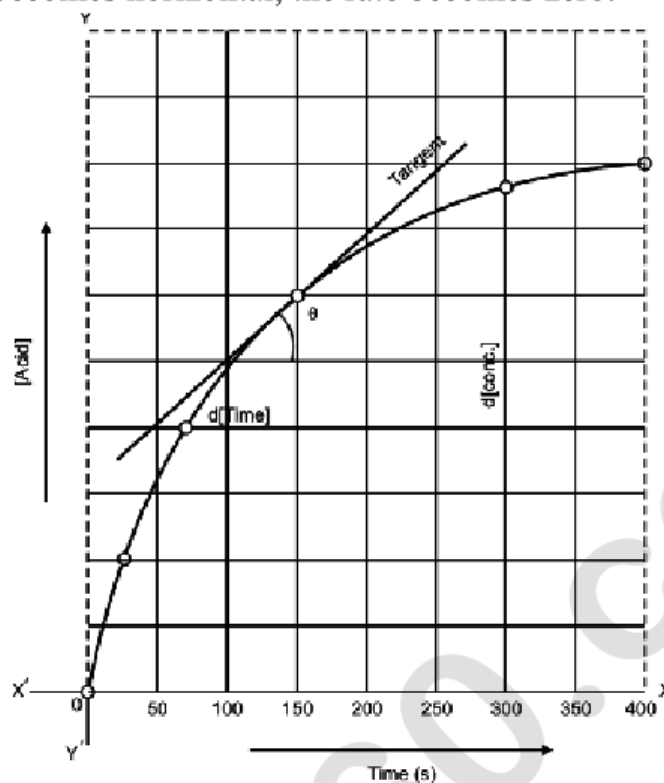
In this method, the angle through which **plane polarized light** is rotated by the reacting mixture is measured by a polarimeter. The extent of rotation determines the concentration of optically active substance. If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate reaction.

(B) CHEMICAL METHODS

This is particularly suitable for reaction in solution such as the acid hydrolysis an ester (ethyl acetate).



In case of **hydrolysis of an ester**, the solution of ester and the acid acting as a catalyst are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice cold water. The dilution and chilling stops the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator. The analysis is repeated at various time intervals. The different concentrations of acetic acid are plotted against the time whereby a curve is obtained. The slope of the curve at any point will give the rate of reaction. Initially the rate of reaction is high but it decreases with the passage of time. When the curve becomes horizontal, the rate becomes zero.



$$\tan \theta = \frac{d[\text{acid}]}{d[\text{time}]} = \frac{dx}{dt}$$

$$\frac{dx}{dt} = \text{Rate of reaction}$$

If we plot a graph for decreasing concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$, then falling curve is obtained.

This reaction is psuedo first order reaction because rate of reaction does not depend upon concentration of water. Actually water is in large excess as compared to ester and does not affect the rate.

COLLISION THEORY AND ENERGY OF ACTIVATION

For a chemical reaction to take place, the particles (atoms, ions or molecules) of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective they give rise to the products otherwise the colliding particles just bounce back. The **effective collisions** can take place only when the colliding particles will possess certain amount of energy and they approach each other with the **proper orientation**. The idea of proper



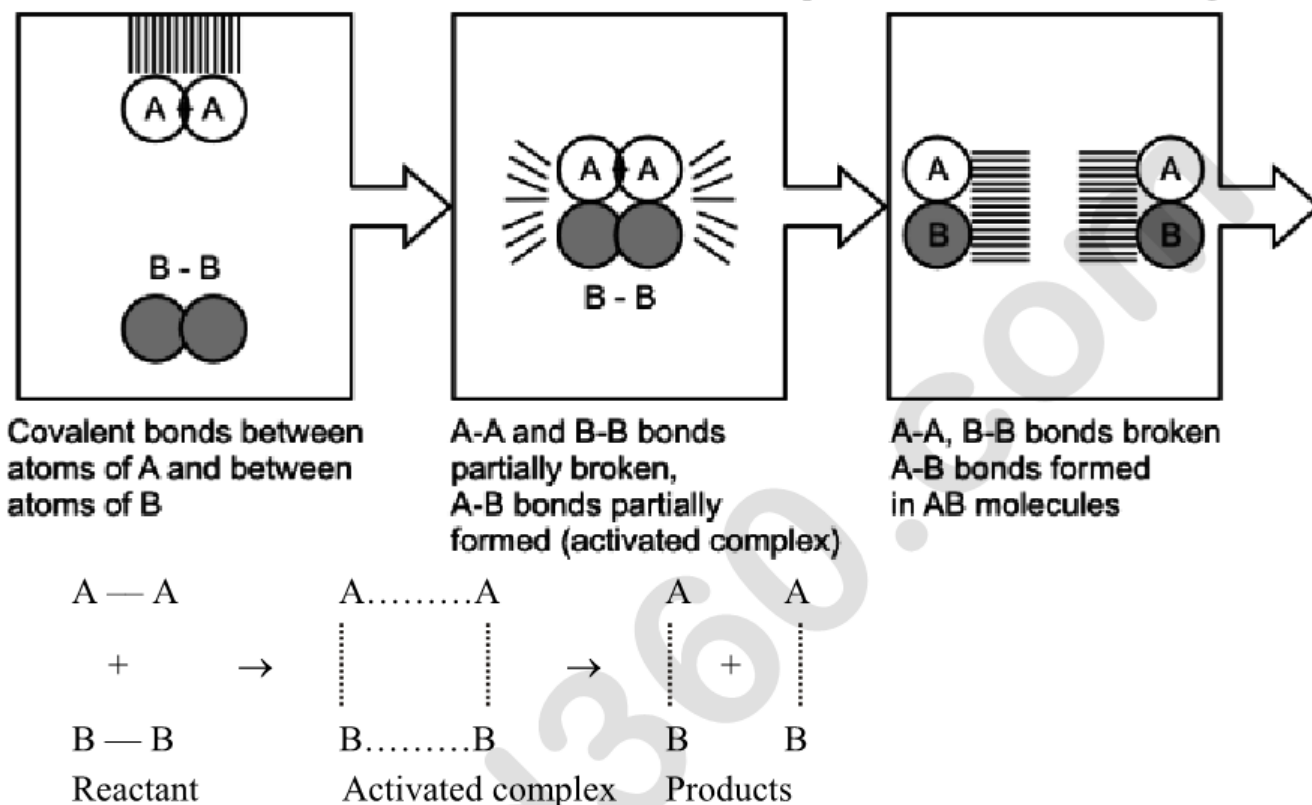
orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other.

“The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collision is called **activation energy**.”

If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time.

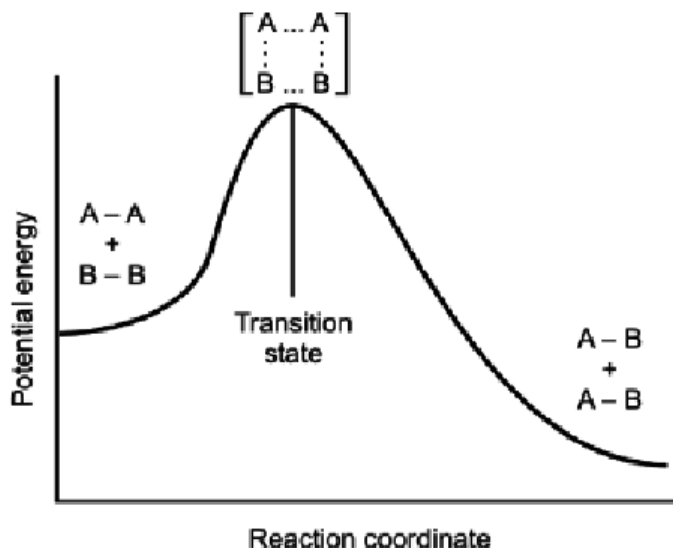
Most of the reactions, are however, slow showing that all the collisions are not equally effective.

Let us study a reaction between molecules A and B to form a new molecule AB. If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed. The phenomenon is shown in Figure.



Activated complex is an unstable combination of all the atoms involved in the reaction for products immediately. It has a transient existence, that is why it is also called a **transitions state**.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective then the molecules flying apart are chemically different otherwise the same molecules just bounce back. When the molecules slow down just before the collision, their kinetic energy decrease and this results in the corresponding increase in their potential energy. The process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules.



Transition state theory and the potential energy diagram for a reaction

The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a **potential energy hill** between reactants and the products. Only the colliding molecules with proper activation energy, will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a , they will be unable to reach the top of the hill and fall back chemically unchanged.

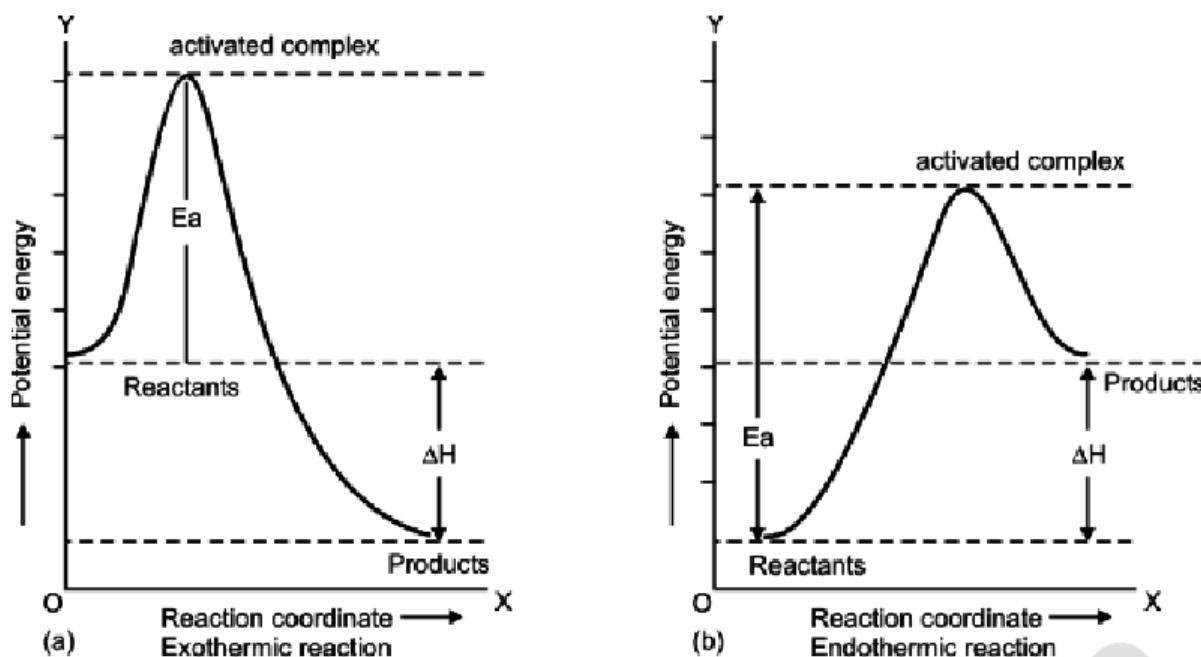
ACTIVATION ENERGY FOR EXOTHERMIC AND ENDOTHERMIC REACTIONS

The potential energy diagram can also be used to study the heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and the products. For **exothermic reactions**, the products are at a **lower energy level than the reactants** and the decrease in potential energy appears as increase in kinetic energy of the products.

For **endothermic reactions**, the products are at **higher energy level than the reactants** and for such reactions a continuous source of energy is needed to complete the reaction.

The energy of activation of forward and backward reactions are different for all the reactions. For exothermic reactions, the energy of activation of forward reaction is less than that of backward reaction, while reverse is true for endothermic reactions.





A graph between path of reaction and the potential energy of the reaction

Energy of activation of a reaction provided a valuable information about the way a reaction takes place and thus helps to understand the reaction.

FINDING THE ORDER OF REACTION

The order of a reaction is the sum of exponents of the concentration terms in the rate expression of that reaction. It can be determined by the following methods.

1. Method of hit and trial
2. Graphical method
3. Differential method
4. Half-life method
5. Method of large excess

1. Half – Life Method:

As mentioned earlier, half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

$$\text{Therefore, } (t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations 'a₁' and 'a₂' and their half-life periods are found to be t₁ and t₂ respectively.

$$(t_1)_n \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the two relations.

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

Taking log on both sides:

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

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



Rearranging

$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

So if we know the two initial concentrations and two half-life values we can calculate the order of reactions (n).

Example 2:

In the thermal decomposition of N_2O at $76^\circ C$ the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290 mm Hg and 212 seconds at the initial pressure of 360 mm Hg. Find the order of this reaction.

Solution:

$$a_1 = 290 \text{ mm Hg}$$

$$t_1 = 255 \text{ seconds}$$

$$a_2 = 360 \text{ mm Hg}$$

$$t_2 = 212 \text{ seconds}$$

$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

$$n = 1 + \frac{\log \left[\frac{255}{212} \right]}{\log \left[\frac{360}{290} \right]}$$

$$n = 1 + \frac{0.0802}{0.0940}$$

$$n = 1 + 0.85 = 1.85 = 2$$

Hence the reaction is of second order.

Method of Large Excess:

In this method, one of the reactants is taken in a small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance controls the rate, which is taken in small amount and the order is noted with respect to that.

In this way, the reaction is repeated by taking rest of the substances in small amount and overall order is calculated. The method will be further elaborated in factor of concentration.

FACTORS AFFECTING RATE OF REACTION

All the factors which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows.



1. Nature of Reactants:

The rate of reaction depends upon the nature of reacting substances and the chemical reactivity of the substances is controlled by the **electronic arrangements** in their outer most orbital. The elements of I – A group have one electron in their outermost s-orbital, and they react with water more swiftly than those of II – A group elements having two electrons in their outermost orbital. Similarly, the neutralization and double decomposition reactions are very fast as compared to those reactions in which bonds are rearranged. Oxidation – reduction reactions involve the transfer of electrons and are slower than ionic reactions.

2. Concentration of Reactants:

The frequency with which the molecules collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate while a decrease in the concentrations will have a reverse effect.

For Examples;

1. Combustion that occurs slowly in air (21% oxygen) will occur more rapidly in pure oxygen.
2. Similarly, lime stone reacts with different concentrations of hydrochloric acid at different rates.
3. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. therefore, a mixture of H_2 or Cl_2 is increased from 0.5 to 1.0 atmosphere in the presence of excess of the other component.

The effect of change in concentration on the rate of a chemical reaction can be understand from the following gaseous reactions.



In this reaction, four moles of the reactants form three moles of the products, so the pressure drop takes place during the progress of reaction. The rates of reaction between NO and H_2 at $800^\circ C$ are studied by noting the change in pressure. the following table has been obtained experimentally.

Experiment number	NO (mole dm^{-3})	H_2 (mole dm^{-3})	Initial rate atmosphere (min^{-1})
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.025
6	0.003	0.009	0.056



Table shows the results of six experiments. In the first three experiments the concentrations of H_2 is increased by keeping the concentration of NO constant by doubling the concentration of H_2 , the rate is doubled and by tripling the concentration of H_2 , the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2 .

$$\text{Rate} \propto [\text{H}_2]$$

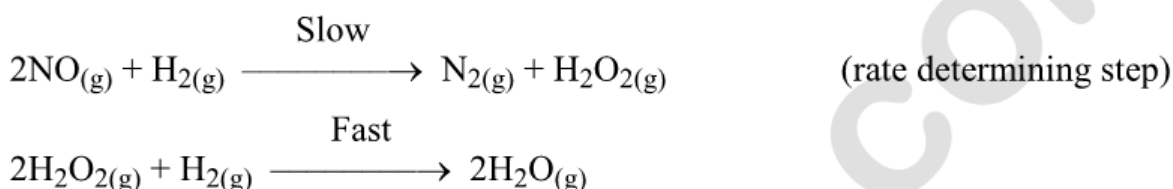
In the next three experiments, the concentration of H_2 is kept constant by doubling the concentration of NO , the rate is increases four times and by tripling the concentration of NO , the rate is increased nine times. So, the rate is proportional to square of concentration of NO .

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

So the overall equation of reaction.

$$\text{Rate} \propto [\text{H}_2]^1 [\text{NO}]^2$$

Hence the reaction is a **third order one**. This final equation is the rate law for this reaction. It should be kept in mind that rate law cannot be predicted from the balanced chemical equation. This set of experiments helps us to determine the order of reaction as well. The possible mechanism of the reaction is as follows.



3. Surface Area:

The increased surfaced area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance e.g. Al foil reacts with NaOH moderately when warmed but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.

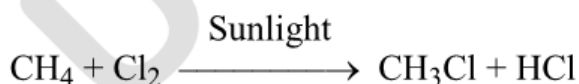


CaCO_3 in the powder form reacts with dilute HCl more efficiently than its big pieces.



4. Light:

Light consists of photons having definite amounts of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced. The reaction of CH_4 and Cl_2 required light.

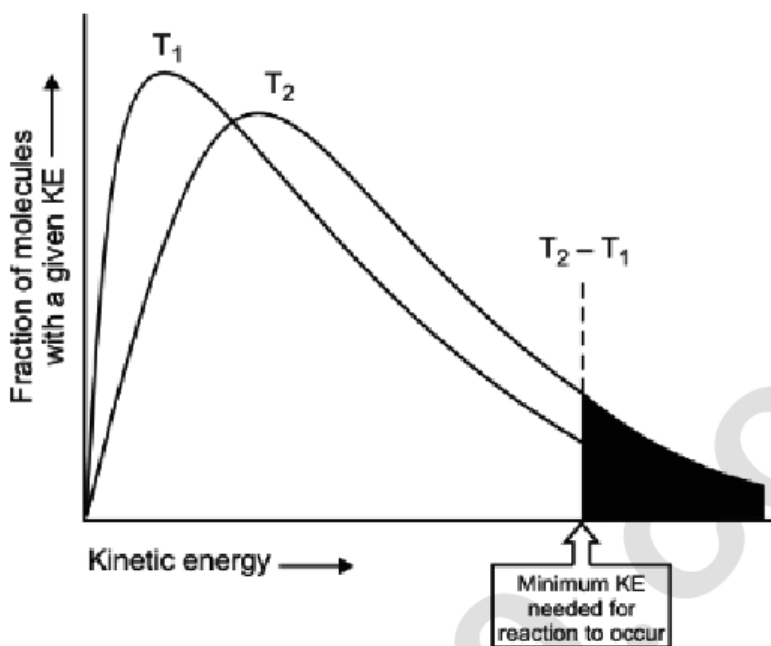


The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in day-light but explosive in sun-light. Similarly light is vital in photosynthesis. Photography is the commercial example in which reaction involving silver halides is influenced by light.



5. Effect of Temperature:

The collision theory of reaction rates convinces us that the rate of a reaction is proportional to the number of collisions among the reactant molecules. **Anything that can increase the frequency of collisions should increase the rate.** We also know that every collision does not lead to a reaction. For a collision to be effective the molecules must possess the activation energy and they must also be properly oriented. For nearly all chemical reactions, the activation energy is quite large and at ordinary temperature very few molecules are moving fast enough to have this minimum energy.



Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the **shaded areas** under the curves are proportional to the total fraction of the **molecules that possess the minimum activation energy**.

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded in Figure.

As the **temperature increases**, the number of molecules in this fraction also increases. So, the **number of effective collisions increases**, when the temperature of the reacting gases is raised by 10 K, the fraction of molecules with energy more than E_a , roughly doubles and so the reaction rate also doubles.

ARRHENIUS EQUATION AND EFFECT OF TEMPERATURE

Arrhenius equation explains the effect of temperature on the rate of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature. According to Arrhenius.

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



So 'k' is exponentially related to activation energy E_a and temperature. T.R is general gas constant and e is the base of logarithm. The equation shows that the **increase in temperature, increases the rate constant** and the reactions of high activation energy have low 'k' values. The factor 'A' is called **Arrhenius constant** and it depends upon the collision frequency of reacting substances. This equation helps us to determine the energy of activation of the reaction as well. For this purpose, we take natural log (ln) on Arrhenius equation.

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

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

Since $\ln e = 1$

Therefore,

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

$$\ln = 2.303 \log$$

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

Dividing the whole equation by 2.303.

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

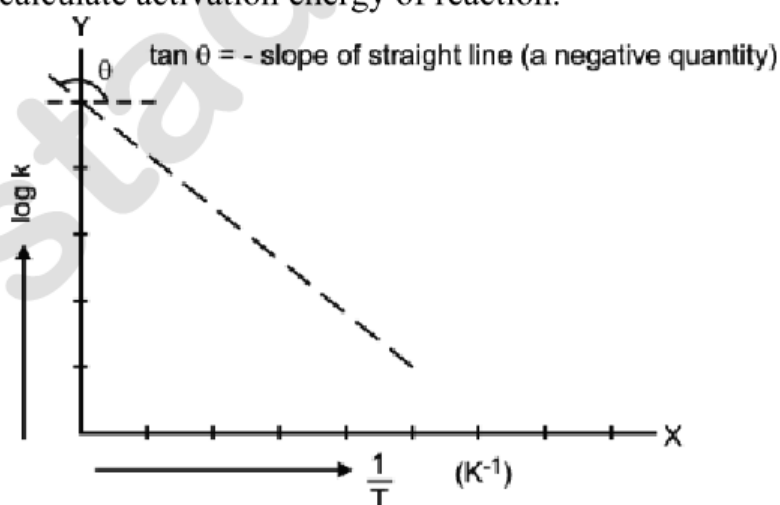
$$\log k = \frac{-E_a}{2.303 R} \cdot \frac{1}{T} + \log A$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad (y = mx + c \text{ is general equation of straight})$$

$$y = m \quad x \quad c$$

This is the equation of straight line. Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like E_a , R and A are constants for a given reactions.

When a graph is plotted between $\frac{1}{T}$ on x-axis and $\log k$ on y-axis, a straight line is obtained with a negative slope. The slope of the straight line is measured by taking tangent of that angle θ which this straight line makes with the x-axis. Thus the slope is equal to $\frac{-E_a}{2.303 R}$. This equation is helpful to calculate activation energy of reaction.



Arrhenius plot to calculate the energy of activation



$$\text{Slope} = \frac{-E_a}{2.303 R}$$

Therefore,

$$E_a = -\text{Slope} \times 2.303 R$$

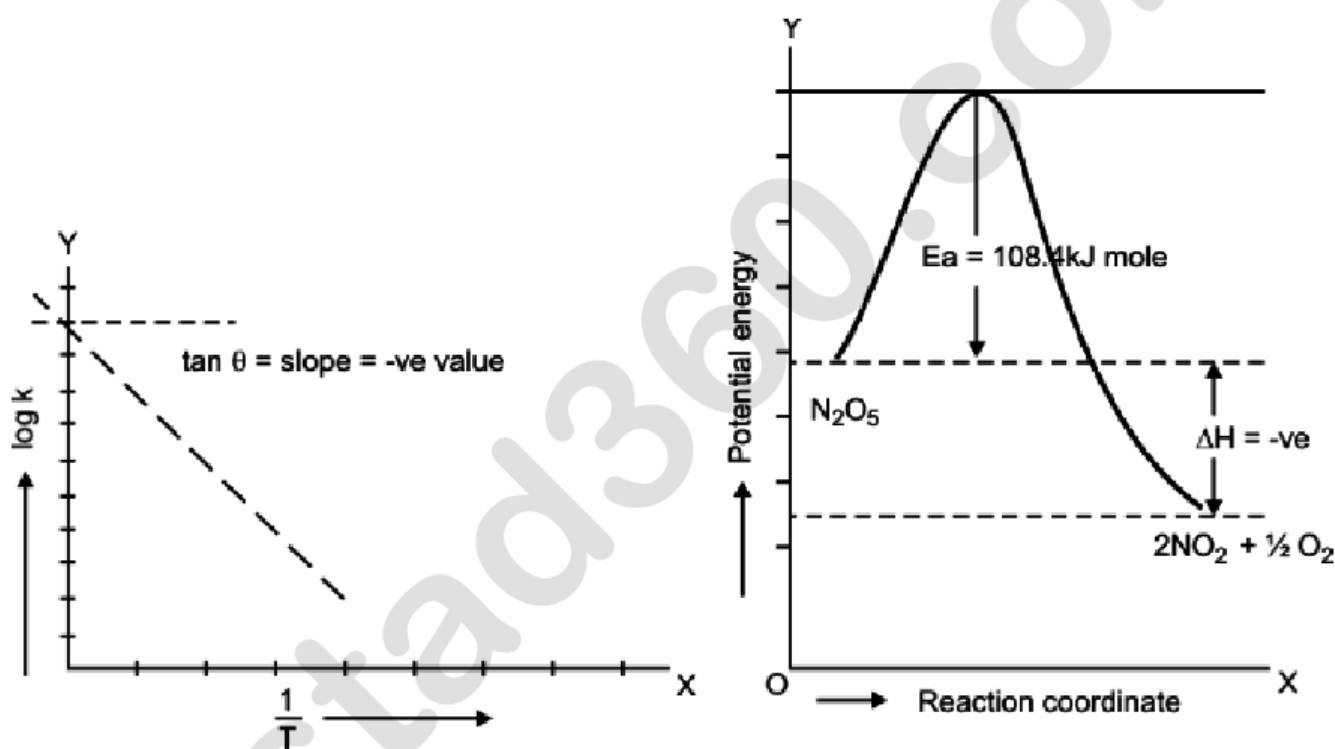
The straight lines of different reactions will have different slopes and different E_a values. The unit of slope of Kelvin (K).

$$\text{Slope} = \frac{-E_a}{2.303 R}$$

$$\text{Slope} = \frac{\text{J mol}^{-1}}{2.303 \text{ J K}^{-1} \text{ mol}^{-1}} = \text{K}$$

Example 3:

- (i) A plot of Arrhenius equation for the thermal decompositions of N_2O_5 is shown in the following Figure. The slope is found to be -5400 K . Calculate the energy of activation of this reaction.



Solution:

$$E_a = -\text{Slope} \times 2.303 R$$

$$= -(-5400 \text{ K}) \times 2.303 \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 103410 \text{ J mol}^{-1}$$

$$E_a = 103.410 \text{ kJ mol}^{-1}$$



- (ii) Hence the decomposition of N_2O_5 needs $103.4 \text{ kJ mol}^{-1}$ of the energy more than the average energy barrier.

The intercept of the straight line is $\log A$ and by taking the anti-log of intercept the value of Arrhenius constant A can be determined. Value of A is 4.3×10^{13} for thermal decomposition of N_2O_5 . Its units are the same as of k , so the Arrhenius rate equation for N_2O_5 is

$$K = 4.3 \times 10^{13} e^{\frac{-E_a}{2.303 RT}}$$

- (iii) With the help of this equation, it is possible to predict the rate of decomposition of N_2O_5 at any temperature.

CATALYST

“The substance which alters the rate of a chemical reaction is called **catalyst**.”

A catalyst is often present in very small amount.

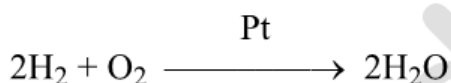
There are two types of catalyst.

- (i) Positive catalyst (ii) Negative catalyst

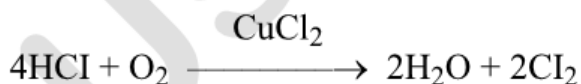
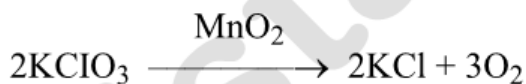
(i) POSITIVE CATALYST

“The substance which increases the rate of reaction is called **positive catalyst**.”

For example, the reaction between H_2 and O_2 is very slow at ordinary conditions of temperature but proceeds more rapidly in the presence of platinum catalyst.

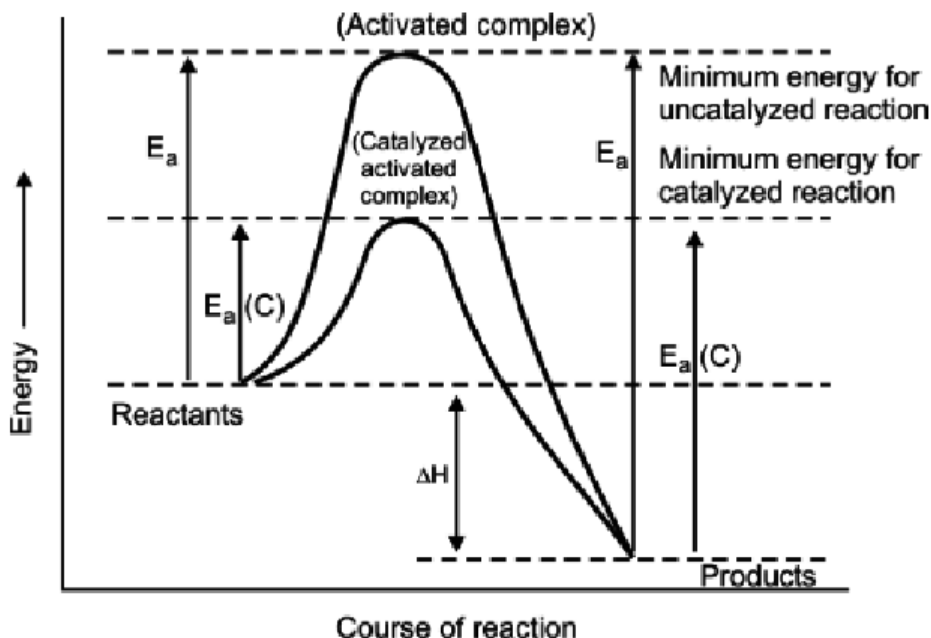


Similarly, KClO_3 decomposes much more rapidly in the presence of a small amount of MnO_2 . HCl is oxidized to Cl_2 in the presence of CuCl_2 .



By using a catalyst, the number of effective collisions increases and the rate of reaction increases. A catalyst changes the reaction mechanism, by providing a different, low energy mechanism for the formation of product. ΔH or enthalpy change will remain the same for each path. A path of catalyzed and uncatalyzed reaction is shown in the Figure.





Catalyzed and uncatalyzed reactions.

(ii) NEGATIVE CATALYST

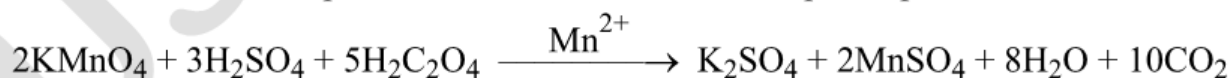
When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

AUTO CATALYSIS

“In some reactions, a product formed act as catalyst and this phenomena is called **auto catalysis**.”

For Examples;

- (i) In hydrolysis of ethyl acetate, acetic acid acts as catalyst for further reaction,
- (ii) When copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally becomes very fast. This is due to the **formation of nitrous acid** (HNO_2) during the reaction, which accelerates the process.
- (iii) The reaction of oxalic acid and acidified KMnO_4 is slow at the beginning, but after sometime Mn^{2+} are produced in the reaction, which speed up the reaction.



PROMOTER OR ACTIVATOR

“Such a substance which promotes the activity of a catalyst is called a **promoter or an activator**. It is also called “**catalyst for a catalyst**”.



For Examples:

- (a) Hydrogenation of vegetable oils is accelerated by nickel. The catalytic activity of nickel can be increased by using copper and tellurium.
- (b) In Haber's process for the manufacture of ammonia, iron is used as a catalyst. If small amounts of some higher melting oxides like aluminum oxide, chromium oxide or rare earth oxides are added, they increase the efficiency of iron.

Catalysis:

"The reactions which take place in the presence of catalyst are called **catalysis**."

There are two types of catalysis.

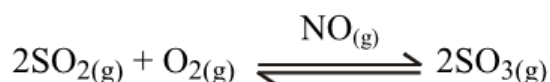
- (i) Homogeneous catalyst (ii) Heterogeneous catalyst

(i) Homogeneous Catalyst:

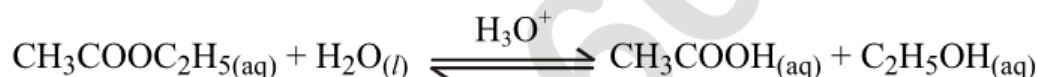
"In the process, the catalysts and reactants have same phase and the reacting system is homogeneous throughout."

For Examples:

- (i) The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphur acid, needs NO as a catalyst. Both the reactants and the catalyst are gases.



- (ii) Esters are hydrolyzed in the presence of H_2SO_4 . Both the reactants and the catalyst are in the solution state.

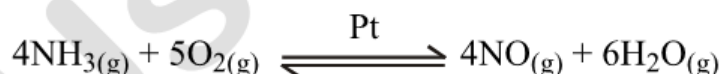
**(ii) Heterogeneous Catalysis:**

"If the catalyst and reactants have different phases, it is called **heterogeneous catalysis**."

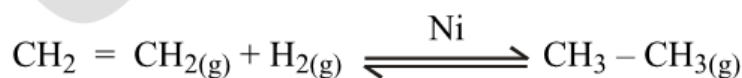
Mostly the catalyst is in the solid phase, while reactants are in the gaseous or liquid phase.

For Examples:

- (i) Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3 .



- (ii) Hydrogenation of unsaturated organic compounds are catalyzed by finely divided Ni .



- (iii) $\text{CO}_{(g)} + 2\text{H}_{2(g)} \xrightarrow{\text{ZnO} - \text{Cr}_2\text{O}_{3(s)}} \text{CH}_3\text{OH}_{(l)}$



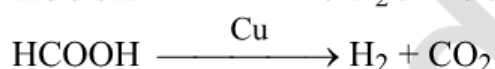
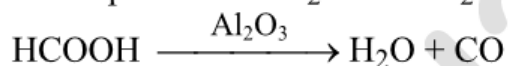
CHARACTERISTIC OF CATALYST

There are many types of catalyst with varying chemical compositions, but the following features are common to most of them.

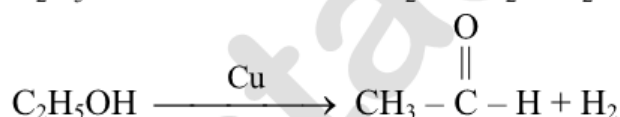
1. A catalyst **remains unchanged** in mass and chemical compositions at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition of KClO_3 in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.
2. Sometimes we need a **traces amount** of a metal catalyst to affect very large amount of reactants. For example, 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water. Dry HCl and NH_3 do not combine but in the presence of trace of moisture, they give dense white fumes of NH_4Cl . Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.
3. A catalyst is **more effective** when it is present in a **finely divided** form. For example, a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used. Fine catalyst has greater surface area.
4. A catalyst **cannot affect the equilibrium constant** of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
5. A catalyst cannot start a reaction, which is **not thermodynamically** feasible. The mechanism of a catalyzed reaction is different from that of an un-catalyzed reactions.
6. A catalyst is **specific in its action**. When a particular catalyst works for one reaction it may not necessarily work for any other reaction. If different catalysts are used for the same reactant than the products may change.

For Examples;

- (i) Formic acid is decomposed by Al_2O_3 to water and CO while Cu causes its decomposition to H_2 and CO_2 .



- (ii) $\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Al}_2\text{O}_3} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$



7. **Temperature affects the role of catalyst.** Some catalysts are physically altered by a change in temperature and hence their catalytic power will be decreased. For example, colloidal catalysts like platinum may be coagulated with rise in temperature.
8. **“Deactivation of catalyst by small amount of impurities is called poisoning of a catalyst.”** Catalytic poisoning happens due to presence of trace amounts of foreign substances which render them ineffective. Such substances are called **poisons**. The poisoning of a catalyst may be temporary or permanent. In permanent poisoning, the poison reacts chemically with the catalyst. The compounds of sulphur and arsenic behave as poisons to many metallic catalysts.



For Examples:

- (a) The presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst in the Haber's process for the manufacture of NH_3 .
- (b) The manufacture of H_2SO_4 in the contact process needs platinum as a catalyst. The traces of arsenic present as impurities in the reacting gases makes platinum ineffective. That's why arsenic purifier is employed in the contact process.

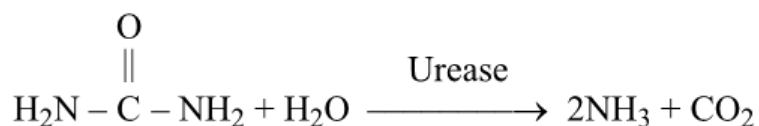
ENZYME CATALYSIS

Enzyme are complex proteins which catalyzed the chemical reactions in living systems. They are often called **biological catalysts or biocatalysts**. The reaction in which enzymes are used as catalyst are called **enzyme catalysis**.

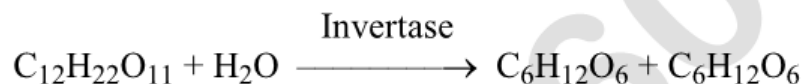
Many enzymes have been identified and obtained in the pure crystalline state. However, first enzyme was prepared in the laboratory in 1969.

For Examples:

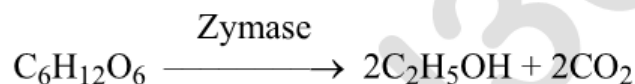
- (a) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soybean.



- (b) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called **invertase**, present in the yeast.



- (c) Glucose is converted into ethanol by the enzyme zymase present in the yeast.

**MODE OF ENZYME ACTION**

Enzymes have active centres on their surfaces. The molecules of a substrate fit into their cavities just as a key fits into a lock. The substrate molecule enters the cavities, form complex, reacts and the product get out of the cavity immediately.

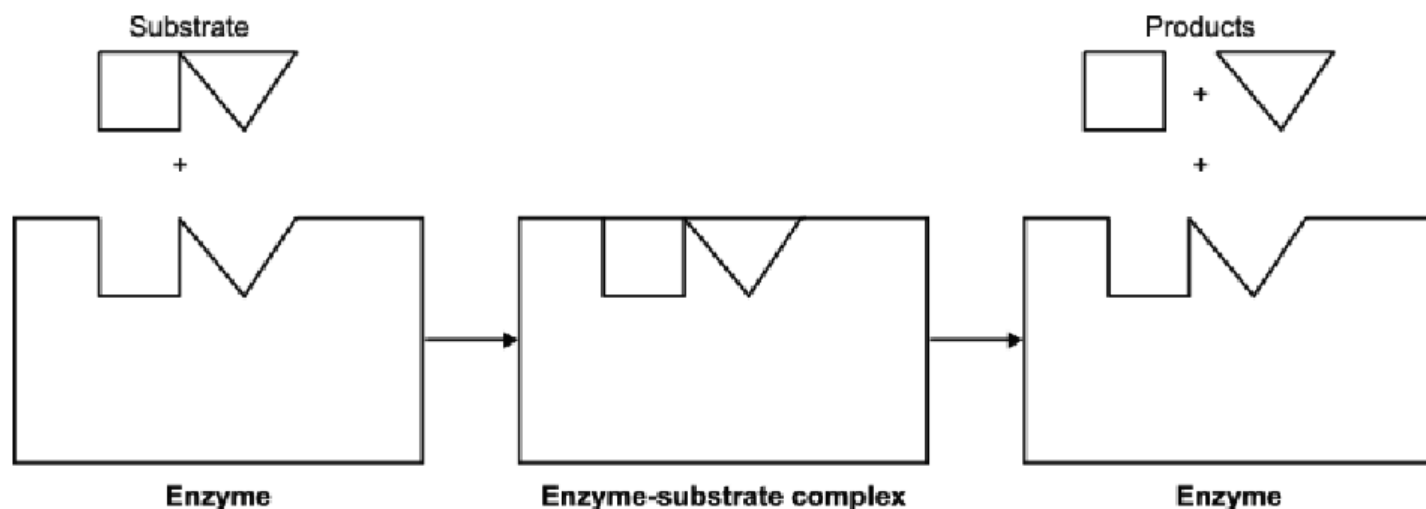
In 1913, Lenore Michaels and his student M.L. Manton, studied the mechanism of enzyme catalysis.



Where E = Enzyme, S = Substrate

ES = Activated complex (Reactant)

P = Product



CHARACTERISTICS OF ENZYMES CATALYSIS

The role of enzymes as catalysts is like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity.

For Examples:

- Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.
- Enzyme catalysis is highly specific, for example, urea's catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.
- Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- The pH of the medium also control the rates of the enzyme catalyzed reactions and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.
- The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.

Co-enzyme:

"A substance needed by enzyme in order to function is called **co-enzyme**."



EXERCISE

Q.1 Multiple choice questions:

- (i) In zero order reaction, the rate is independent of:
- (a) temperature of reaction (b) concentration of reactants
- (c) concentration of products (d) none of these
- (ii) If the rate equation of a reaction $2A + B \rightarrow \text{products}$ is, $\text{rate} = k[A]^2[B]$, and A is present in large excess, then order of reaction is:
- (a) 1 (b) 2
- (c) 3 (d) none of these
- (iii) The rate of reaction:
- (a) increases as the reaction proceeds
- (b) decreases as the reaction proceeds
- (c) remains the same as the reaction proceeds
- (d) may decrease or increase as the reaction proceeds
- (iv) With increase of 10°C temperature the rate of reaction doubles. This increase in rate of reaction is due to:
- (a) decrease in activation energy of reaction.
- (b) decrease in the number of collisions between reactant molecules.
- (c) increase in activation energy of reactants.
- (d) increase in number of effective collisions.
- (v) The unit of the rate constant is the same as that of the rate of reaction in:
- (a) first order reaction (b) second order reaction
- (c) zero order reaction (d) third order reaction



ANSWERS

Answers	Reasons
(i) (b)	The reaction whose rate is independent of concentration of reactants is said to have zero order.
(ii) (a)	The substance which is taken in large excess and does not affect the rate of reaction and the order with respect to that reactant is zero. The order with respect to "A" is zero and that with respect to "B" is one. Hence overall order is also one.
(iii) (b)	As the reaction proceeds, concentration of reactants decreases and rate of reaction also decreases.
(iv) (d)	The rate of reaction depends upon no of effective collisions between reactant molecules. For every 10°C rise of temperature no of effective collisions are almost doubled and so the rate of reaction.
(v) (c)	For zero order reaction, rate of reaction is independent of concentration of reactants.
	Hence, $\text{Rate} = K[\text{Reactants}]^0$ $= K \times 1$ $\text{Rate} = K$
	For zero order reaction, units of rate and rate constant of reaction are same.

Q.2 Fill in the blanks:

- (i) The rate of an endothermic reaction _____ with the increase in temperature.
- (ii) All radioactive disintegration nuclear reactions are of _____ order.
- (iii) For a fast reaction the rate constant is relatively _____ and half-life is _____.
- (iv) The second order reaction becomes _____ if one of the reactants is in large excess.
- (v) Arrhenius equation can be used to find out _____ of a reaction.

ANSWERS

Answers	Explanation
(i) Increases	In endothermic reactions, heat is absorbed during the reaction. Hence rise of temperature will increase the rate of reaction.
(ii) First order	
(iii) Greater, short	
(iv) First order	
(v) Activation energy	



Q.3 Indicate true or false as the case may be:

- (i) The half-life of a first order reaction increases with temperature.
- (ii) The reactions having zero activation energies are instantaneous.
- (iii) A catalyst makes a reaction more exothermic.
- (iv) There is difference between rate law and the law of mass action.
- (v) The order of reaction is strictly determined by the stoichiometry of the balanced equation.

ANSWERS

Answers	Correct Statement
(i) False	The half-life of a first order reaction decreases with temperature.
(ii) True	Activation energy is the energy barrier between reactants and products. If its value is zero, then reactants can instantly be converted into products.
(iii) False	A catalyst makes the reaction faster.
(iv) True	
(v) False	The order of reaction is not strictly determined by the stoichiometry of balance equation.

Q.4 What is chemical kinetics? How do you compare chemical kinetics with chemical equilibrium and thermodynamics?

Ans. **Chemical Kinetics:** The study of rates of chemical reactions and factors affecting the rate is called as “chemical kinetics”.

Difference between chemical kinetics and chemical equilibrium:

Chemical Kinetics	Chemical Equilibrium
(i) The study of rates and mechanism of reaction is called chemical kinetics.	(i) A state of reversible reaction at which forward and backward rates become equal is called chemical equilibrium.
(ii) Rate study is possible for both reversible and irreversible reactions.	(ii) Chemical equilibrium is the characteristics of reversible reactions only.
(iii) It is related to rate of reactions and factors affecting it.	(iii) It is related to state of equilibrium and factors affecting it.

Q.5 The rate of a chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with a negative sign. Explain it with reference to the following hypothetical reaction.

Ans. The rate of reaction can be written with respect to reactants or products concentration. The rate of reaction with respect to concentration of reactants is written with negative sign because concentration of reactants decrease with the passage of time.

$$\text{Rate} = \frac{-d[A]}{dt} \quad \text{or} \quad \frac{-d[B]}{dt}$$



The rate of reaction with respect to concentration of products is written with positive sign because concentration of products increases as the time passes.

$$\text{Rate} = \frac{+d[C]}{dt} \quad \text{or} \quad \frac{+d[D]}{dt}$$

Q.6 What are instantaneous and average rates? Is it true that the instantaneous rate of a reaction at the beginning of the reaction is greater than average rate and becomes far less than the average rate near the completion of reaction?

Ans. The rate measured at any moment of reaction during the progress is called instantaneous rate, whereas rate of reaction between two time intervals is called average rate.

Instantaneous rate is very fast at the start. It slows down with decreasing concentration of reactants and very slow at the end, but average rate has an intermediate value (neither very slow nor very fast) because it is obtained by dividing the whole change in concentration with time.

It clearly shows that instantaneous rate is faster than average rate at start but slower than average rate at the end.

Q.7 Differentiate between:

- (i) Rate and rate constant of a reaction.
- (ii) Homogeneous and heterogeneous catalyses.
- (iii) Fast step and the rate determining step.
- (iv) Enthalpy change of reaction and energy of activation of reaction.

Ans.

(i)

Rate of Reaction	Rate Constant of Reaction
(i) It is the change in concentration of reactant or product per unit time. $\text{Rate} = \frac{dx}{dt}$	(i) It is the proportionality constant and is the ratio of rate and concentration of reactants $K = \frac{\text{Rate}}{[A]^a [B]^b}$
(ii) Its units are $\text{moles} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$.	(ii) Its units are variable depending upon order of reaction.
(iii) It is a variable parameter.	(iii) It is always constant under given conditions.



(ii)

Homogeneous Catalysis	Heterogeneous Catalysis
(i) A catalysed reaction in which catalyst and reaction mixture are in same phase is called homogeneous catalysis.	(i) A catalysed reaction in which catalyst and reaction mixture are in different phases is called heterogeneous catalysis.
(ii) Example: $2\text{SO}_{2(g)} + \text{O}_{2(g)} \xrightleftharpoons{\text{NO}_{(g)}} 2\text{SO}_{3(g)}$	(ii) Example: $\text{CH}_2 = \text{CH}_{2(g)} + \text{H}_{2(g)} \xrightarrow{\text{Ni}_{(s)}} \text{CH}_3 - \text{CH}_{3(g)}$
(iii) In this case, catalyst is distributed uniformly throughout the system.	(iii) In this case, catalyst is not uniformly distributed throughout the system.

(iii)

Fast Step	Rate Determining Step
(i) A step in a multi-step reaction that has high speed and does not affect the overall rate of reaction is called fast step.	(i) A step in a multi-step reaction that is the slowest one and controls the overall rate of reaction is called rate determining step.
(ii) The reactants in fast step are not involved in rate equation.	(ii) Reactants in rate determining step are involved in rate equation.
(iii) Example: $\text{NO}_2 + \text{NO}_2 \xrightarrow{\text{Slow}} \text{NO}_3 + \text{NO}$ $\text{NO}_3 + \text{CO} \xrightarrow{\text{Fast}} \text{NO}_2 + \text{CO}_2$ Second step is fast step.	(iii) Example: $\text{NO}_2 + \text{NO}_2 \xrightarrow{\text{Slow (RDS)}} \text{NO}_3 + \text{NO}$ $\text{NO}_3 + \text{CO} \xrightarrow{\text{Fast}} \text{NO}_2 + \text{CO}_2$ First slow step is rate determining step.

(iv)

Enthalpy Change of Reaction	Energy of Activation of Reaction
(i) Heat change accompanied by chemical reaction is called enthalpy change.	(i) The minimum amount of energy in addition to average K.E, sufficient to convert reactants into products is called activation energy.
(ii) It is denoted by ΔH .	(ii) It is denoted by E_a .
(iii) It is the difference of enthalpies of reactants and products.	(iii) It is the energy barrier between reactants and products.
(iv) It may be negative or positive.	(iv) It is always positive.



Q.8 Justify the following statements:

- (i) Rate of chemical reaction is an ever changing parameter under the given conditions.
- (ii) The reaction rate decreases every moment but rate constant 'k' of the reaction is a constant quantity, under the given conditions.
- (iii) 50% of a hypothetical first order reaction completes in one hour. The remaining 50% needs more than one hour to complete.
- (iv) The radioactive decay is always a first order reaction.
- (v) The unit of rate constant of a second order reaction is $\text{dm}^3 \text{mol}^{-1} \cdot \text{s}^{-1}$, but the unit of rate of reaction is $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$.
- (vi) The sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction.
- (vii) The order of a reaction is obtained from the rate expression of a reaction and the rate expression is obtained from the experiment.

Ans.

- (i) The rate of a reaction is directly proportional to concentration of reactants. As the concentration of reactants is maximum at start, the rate is fast. As the time passes, the concentration of reactants decreases and rate of reaction also slows down.

During the progress of reaction, the rate of reaction slows down every moment with the decreasing concentration of reactants. Hence, it is ever changing parameter.

- (ii) The rate of reaction decreases every moment with decreasing concentration of reactants. For understanding of rate constant, consider the following hypothetical reaction.



$$\text{Rate} = K [\text{A}] [\text{B}]$$

or
$$K = \frac{\text{Rate}}{[\text{A}] [\text{B}]}$$

From above equation, it is clear that rate constant "K" is the ratio of rate of reaction and concentration of reactants. As the concentration of reactants decreases, rate of reaction also decreases but the ratio remains constant.

Hence, rate constant "K" always a constant quantity.

- (iii) 50% of hypothetical reaction is completed in one hour and 50% left behind.

From this 50% reaction, 25% will be completed in one hour and 25% will be left behind. Among this 12.5% will need one more hour to be completed.

37.5% of remaining 50% reaction took 2 hours and 12.5% will still left behind. Hence this remaining 50% requires more than one hour to complete.

$$(100\% \xrightarrow{1 \text{ hour}} 50\% \xrightarrow{1 \text{ hour}} 25\% \xrightarrow{1 \text{ hour}} 12.5\% \dots)$$



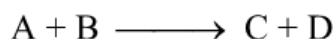
- (iv) During radioactive decay, nuclei of only one type are broken up and no other specie is involved. The rate of this decay depends upon concentration of nuclei of only one type. Hence, it follows first order kinetics.

- (v) Equation for rate of reaction is:

$$\begin{aligned}\text{Rate} &= \frac{DC}{Dt} = \frac{\text{Change in conc.}}{\text{Change in time}} \\ &= \frac{\text{moles.dm}^{-3}}{\text{s}^{-1}}\end{aligned}$$

$$\text{Rate} = \text{moles.dm}^{-3}.\text{s}^{-1}$$

Second order reaction:



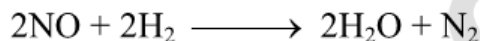
$$\text{Rate} = K [A] [B]$$

$$\begin{aligned}K &= \frac{\text{Rate}}{[A] [B]} \\ &= \frac{\text{moles.dm}^{-3}.\text{s}^{-1}}{\text{moles.dm}^{-3} \times \text{moles.dm}^{-3}}\end{aligned}$$

$$K = \text{dm}^3.\text{mol}^{-1}.\text{s}^{-1}$$

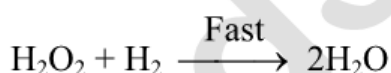
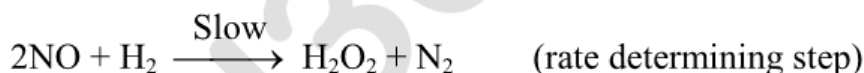
- (vi) For many reactions, the order is not equal to the sum of co-efficient of balanced because reaction proceeds in more than one steps and order and rate expression is derived from slowest step (rate determining step).

Consider the reaction:



The sum of coefficients is four and order is three. This order is experimentally determined from mechanism of reaction.

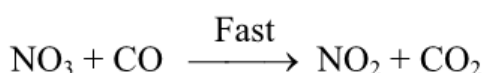
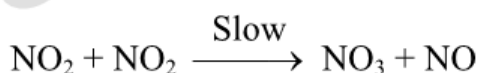
Mechanism:



$$\text{Rate} = K [\text{H}_2]^1 [\text{NO}]^2$$

- (vii) Many reactions that consists of more than one steps. There is always one step which is slowest one and controls the overall rate and order of reaction. This slow step is called rate determining step and is experimentally determined. And rate expression is written on the basis of this step.

Experimentally determined mechanism of reaction is:



and rate expression is:

$$\text{Rate} = K [\text{NO}_2]^2$$



Q.9 Explain that half-life method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.

Ans. Descriptive question consult text book for details.

Q.10 A curve is obtained when a graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points give us the instantaneous rates of reaction. Explain with suitable examples.

Ans. Descriptive question consult text book for details.

Q.11 The rate determining step of a reaction is found out from the mechanism of that reaction. Explain with few examples.

Ans. Detailed question for answer see text book.

Q.12 Discuss the factors which influence the rates of chemical reactions.

Ans. Descriptive question see text book.

Q.13 Explain the following facts about the reaction.



- (i) The changing concentrations of reactants, change the rates of this reaction.
- (ii) Individual orders with respect to NO and H₂ can be measured.
- (iii) The overall order can be evaluated by keeping the concentration of one of the substances constant.

Ans.

- (i) The effect of changing concentration or rates of this reaction can be studied from following experimental data.

	[NO]	[H ₂]	Rates
1.	0.006	0.001	0.025
2.	0.006	0.002	0.050
3.	0.006	0.003	0.075
4.	0.001	0.009	0.0063
5.	0.002	0.009	0.025
6.	0.003	0.009	0.056

The data shows that rate of reaction is changed when concentration of one reactant is changed by keeping the other's constant.

- (ii) Above data shows that when rate is studied by changing the concentration of H₂ and by keeping the concentration of NO constant. It comes out to be that rate of reaction is directly proportional to the concentration of H₂.

$$\text{Rate} = K [\text{H}_2]^1$$

And individual order with respect to hydrogen is one.

Similarly, rate of reaction is directly proportional to the square of concentration of NO. It is clear from data, when concentration of NO is increased to two times, rate increases four times.

$$\text{Rate} = K [\text{NO}_2]^2$$

And individual order with respect to NO is 2 and reaction is of 2nd order.



- (iii) When concentration of NO is kept constant, the rate of reaction comes out to be directly proportional to concentration of H_2 and order is 1.

$$\text{Rate} = K [H_2]^1$$

When concentration of H_2 is kept constant, the rate of reaction comes out to be directly proportional to square of concentration of NO and order is 2.

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

Hence, overall rate expression is:

$$\text{Rate} = K [H_2]^1 [NO]^2$$

So, overall order is 3 and reaction is of third order.

- Q.14** The collision frequency and the orientation of molecules are necessary conditions for determining the proper rate of reaction. Justify the statement.

Ans. Descriptive question consult text book.

- Q.15** How does Arrhenius equation help us to calculate the energy of activation of reaction?

Ans. Detailed question see text book for answer.

- Q.16** Define the following terms and give examples:

- | | |
|--------------------------------|------------------------------|
| (i) Homogeneous catalysis | (ii) Heterogeneous catalysis |
| (iii) Activation of a catalyst | (iv) Auto-catalysis |
| (v) Catalytic poisoning | (vi) Enzyme catalysis |

Ans. For definitions consult text book.

- Q.17** Briefly describe the following with examples:

- Change of physical state of a catalyst at the end of reaction.
- A very small amount of a catalyst may prove sufficient to carry out a reaction.
- A finely divided catalyst may prove more effective.
- Equilibrium constant of a reversible reaction is not changed in the presence of a catalyst.
- A catalyst is specific in its action.

Ans.

- (i) A catalyst remains chemically unchanged but changes physically at the end of reaction.

Example:

- Granular catalyst (MnO_2) for the decomposition of $KClO_3$ is converted into powder form.
- Shining surface of Pt is made dull, when it is used as catalyst for hydrogenation of vegetable oil.



- (ii) Since, catalyst itself is not used up, it can catalyse a reaction between large amount of reactants.

Example:

- (i) 1 g of Pt can catalyse a reaction between 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to form water.
 - (ii) Thousands of dm^3 of H_2O_2 can decompose in the presence of 1 g of colloidal platinum.
- (iii) When catalyst is finely divided, it has greater surface area and is more effective.

Example:

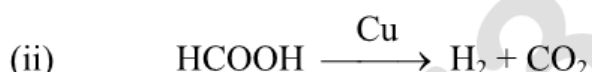
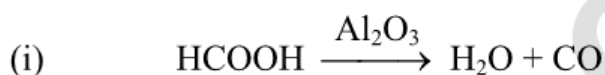
- (i) Colloidal platinum has far more catalytic activity than lump of Pt.
 - (ii) For hydrogenation of vegetable oils, finely divided Nickel is used.
- (iv) When catalyst is added at the equilibrium position of a reversible reaction, it equally speed up the rate of forward and backward reaction. Hence, equilibrium is not disturbed and equilibrium constant remains constant.

Example:



- (v) When a particular catalyst works for one reaction, it may not necessarily work for any other reaction. If different catalysts are used for same reactants then the product may change.

Example:



Q.18 What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis.

Ans. Detailed question consult text book.

Q.19 In the reaction of NO and H_2 , it was observed that equimolecular mixture of gases at 340.5 mm of Hg, was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction.

Ans. Initial pressure of NO and H_2 are the initial concentrations of reactants and denoted by “a” and “a₂”. The half life period are t₁ and t₂.

$$a_1 = 340.5 \text{ mm Hg}$$

$$\text{Half-life period } t_1 = 102 \text{ seconds}$$

$$a_2 = 288 \text{ mm Hg}$$



Half-life period $t_2 = 140$ seconds

$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

Putting the values:

$$n = 1 + \frac{\log \left[\frac{102}{140} \right]}{\log \left[\frac{288}{340.5} \right]}$$

$$n = 1 + \frac{\log (0.728)}{\log (0.845)}$$

$$n = 1 + \frac{-0.1378}{-0.0731}$$

$$n = 1 + 1.88 = 2.88$$

The value of n is very close to three, so, the reaction is third order.

Q.20 A study of chemical kinetics of a reaction



gave the following data at 25°C . Calculate the rate law.

[A]	[B]	Rate
1.00	0.15	4.2×10^{-6}
2.00	0.15	8.4×10^{-6}
1.00	0.2	5.6×10^{-6}

Ans.

The rate of this chemical reaction is directly proportional to A and B concentrations with certain exponents. We have to determine those exponents.

In first two experiments it is clear that when the concentration of A is doubled, the rate is doubled. Hence, rate of reaction with respect to A is with exponent as unity.

$$\text{So, Rate} \propto [A]^1$$

Reaction is first order with respect to A.

Compare experiment 1 and 3. When the concentration of B is increased from 0.15 to 0.2, the rate increases for 4.2×10^{-6} to 5.6×10^{-6} . The increase is proportional to the first power of B;

$$\text{Rate} \propto [B]^1$$

In order words, the reaction is first order with respect to B.

The overall rate law is:

$$\text{Rate} \propto [A][B]$$

$$\text{Rate} = K[A][B]$$

So, the reaction is of second order.



Q.21 Some reactions taking place around room temperature have activation energies around 50 KJ mol^{-1} :

- (i) What is the value of the factor $e^{-\frac{E_a}{RT}}$ at 25°C ?
- (ii) Calculate this factor at 35°C and 45°C and note the increase in this factor for every 10°C rise in temperature.
- (iii) Prove that for every 10°C rise in of temperature, the factor doubles and so rate constant also doubles.

Ans.

- (i) To calculate the exponential factor at 25°C , we put E_a and T in Arrhenius factor.

$$\begin{aligned}
 E_a &= 50 \text{ KJ mol}^{-1} = 50000 \text{ J mol}^{-1} \\
 T &= 25^\circ\text{C} = 298 \text{ K} \\
 R &= 8.3143 \text{ JK}^{-1} \text{ mol}^{-1} \\
 e^{-\frac{E_a}{RT}} &= ?
 \end{aligned}$$

Putting the values:

$$\begin{aligned}
 &= e^{-\frac{50000}{8.3143 \times 298}} \\
 &= e^{-\frac{50000}{2477.6}} \\
 &= e^{-20.188} = 1.72 \times 10^{-9}
 \end{aligned}$$

- (ii) Exponential factor at 35°C :

$$\begin{aligned}
 E_a &= 50000 \text{ J mol}^{-1} \\
 R &= 8.3143 \text{ K}^{-1} \text{ J mol}^{-1}
 \end{aligned}$$

Putting values:

$$\begin{aligned}
 e^{-\frac{E_a}{RT}} &= e^{-\frac{50000 \text{ J mol}^{-1}}{8.3143 \times 308}} \\
 &= e^{-19.52} = 3.31 \times 10^{-9}
 \end{aligned}$$

- (iii) Exponential factor at 45°C :

$$\begin{aligned}
 E_a &= 50000 \text{ J mol}^{-1} \\
 R &= 8.3143 \text{ K}^{-1} \text{ mol}^{-1} \\
 T &= 45^\circ\text{C} = 318 \text{ K} \\
 &= e^{-\frac{50000}{8.314 \times 318}} \\
 &= e^{-18.91} = 6.12 \times 10^{-9}
 \end{aligned}$$

The results indicate that:

$$\text{Exponential factor at } 25^\circ\text{C} = 1.72 \times 10^{-9}$$

$$\text{Exponential factor at } 35^\circ\text{C} = 3.31 \times 10^{-9}$$

$$\text{Exponential factor at } 45^\circ\text{C} = 6.12 \times 10^{-9}$$



(iii) $\text{Rate} = A e^{-\frac{E_a}{RT}}$

Since the factor A is almost constant for a particular reaction, hence, when the exponential factor doubles, then rate is doubled. For every 10°C increase of temperature, the rate has almost doubled.

Q.22 H_2 and I_2 react to produce HI . Following data for rate constant at various temperatures (K) have been collected:

Temp. (K)	Rate constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) (k)
500	6.814×10^{-1}
550	2.64×10^{-2}
600	0.56×10^0
650	7.31×10^0
700	66.67×10^0

- (i) Plot a graph between $\frac{1}{T}$ on x-axis and $\log k$ on the y-axis.
- (ii) Measure the slope of this straight line and calculate the energy for activation of this reaction.

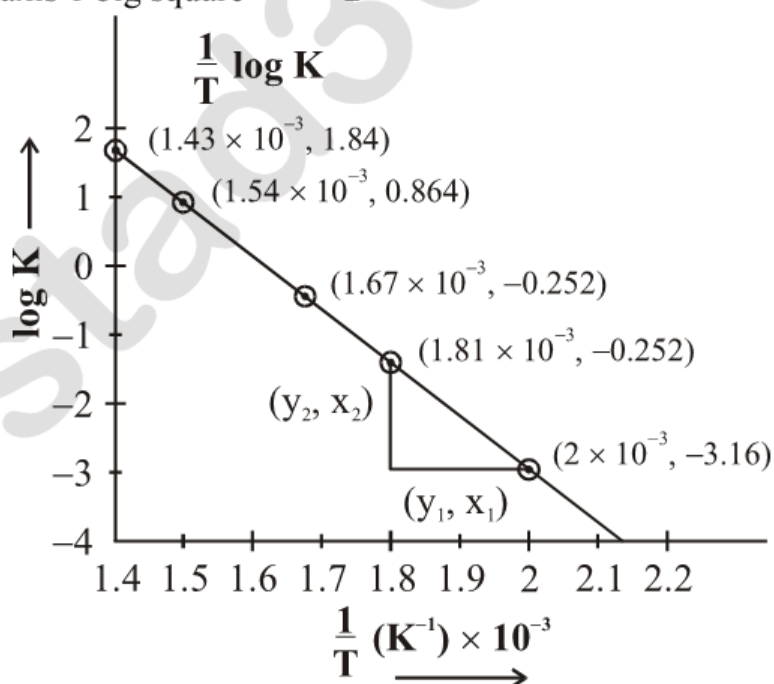
Ans.

(i)

$\frac{1}{T} (\text{K}^{-1})$ units	$\log K$
1. 2×10^{-3}	-3.16
2. 1.8×10^{-3}	-1.578
3. 1.67×10^{-3}	-0.252
4. 1.54×10^{-3}	0.864
5. 1.43×10^{-3}	1.824

GRAPH:

Scale: On x-axis 1 big square = 0.2×10^{-3}
On y-axis 1 big square = 2



(ii) Slope:

$$\begin{aligned}
 m &= \frac{y_2 - y_1}{x_2 - x_1} \\
 &= \frac{-1.578 - (-3.16)}{1.81 \times 10^{-3} - 2 \times 10^{-3}} \\
 &= \frac{1.582}{-0.19 \times 10^{-3}}
 \end{aligned}$$

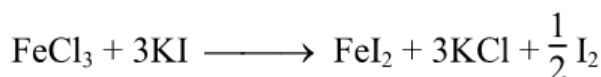
$$\text{Slope} = -8326.32$$

$$\begin{aligned}
 E_a &= -\text{Slope} \times 2.303 R \\
 &= -(-8326.32) \times 2.303 \times 8.314 \\
 &= 159425.15 \text{ J/mol} \\
 &= 159.42515 \text{ kJ/mol} \\
 &\sim 160 \text{ kJ/mol}
 \end{aligned}$$

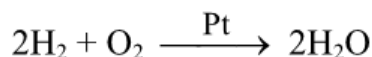
DO YOU KNOW?

- Units of rate of reaction = moles $\text{dm}^{-3} \text{ sec}^{-1}$.
- The rate of reaction between two specific times is called average rate.
- The rate of any one instant in a specific interval of time is called instantaneous rate.
- The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction.
- Total number of molecules taking part in a chemical reaction is called molecularity.
- The sum of exponents of the concentrations of the reacting species in the observed rate law is called order of a reaction.
- The reaction in which rate of reaction does not depend upon the concentration of any reactant is called zero order reaction.
- All photochemical reactions are of the zero order.
- The reaction in which rate of reaction depends upon the concentration of only one substance is called first order reaction. For example: decomposition of N_2O_5 .
- The reaction in which rate of reaction depends upon the concentration of two molecules of the reacting substances is called second order reaction. For example:

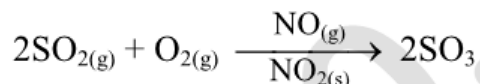
$$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$$
- The reaction in which rate of reaction depends upon the concentration of three molecules of the reacting substances is called third order reaction. For example:



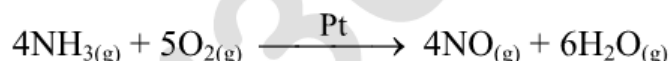
12. The time required to convert 50% of the reactants into the products is called “half-life period”.
13. In the first order reaction, half-life period of the reaction is independent of the initial concentration.
14. The minimum amount of energy in addition to average kinetic energy which the molecules must possess for effective collision is called activation energy.
15. The increased surface area increases the rate of reaction.
16. Increase in temperature also increase the rate of reaction.
17. The substance which alters the rate of chemical reaction is called catalyst.
18. The catalyst which increases the rate of chemical reaction is called positive catalyst. For example:



19. The substance which decreases the rate of chemical reaction is called negative catalyst. For example: Tetra ethyl lead is negative catalyst in the combustion of petrol.
20. In some reaction, one of the products formed acts as a catalyst. It is called auto-catalysis. For example: In the hydrolysis of ethyl acetate, acetic acid produced acts as catalyst.
21. The substance which promotes the activity of a catalyst is called promoter or activator. It is also called “catalyst for a catalyst”. For example: In the hydrogenation of vegetable oils, Ni is used as catalyst. The catalytic activity of Ni, is increased by adding copper or tellurium.
22. The process in which the catalyst and reactants have same phase is called homogeneous catalysis. For example: In the lead chamber process for the manufacture of H_2SO_4 .



23. The process in which catalyst and the reactants have different phases is called heterogeneous catalysis. For example: In the oxidation of NH_3 to form NO in the Ostwald's process Pt is used as catalyst.



24. Units of rate of reaction = $\text{mol dm}^{-3} \text{sec}^{-1}$

$$\left[\begin{array}{l} \text{Units of K for zero-order reaction and} \\ \text{Units of K and reaction of reaction are same} \end{array} \right] \longrightarrow \text{mol dm}^{-3} \text{sec}^{-1}$$

$$\text{Units of K for the first order reaction} = \text{s}^{-1}$$

$$\text{Units of K for the second order reaction} = \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$$

$$\text{Units of K for the third order reaction} = \text{dm}^6 \text{mol}^{-2} \text{sec}^{-1}$$

