Chapter 11

Reaction Kinetics

Order of Reaction

Definition

The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised.

OR

The order of reaction may also be defined as the number of reacting molecules, whose concentrations alter as a result of the chemical change.

Importance

1. The order of reaction provides valuable information about the mechanism of a reaction.
2. The order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
3. The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.
4. The chemical reactions are classified as zero, first, second and third order reactions.

Explanation with Examples

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.

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

We can write the rate equation as:

$$R=k[A]^a[B]^b$$

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 of order b with respect to B.

The overall order of reaction is:

(a+b)

Decomposition of nitrogen pentoxide

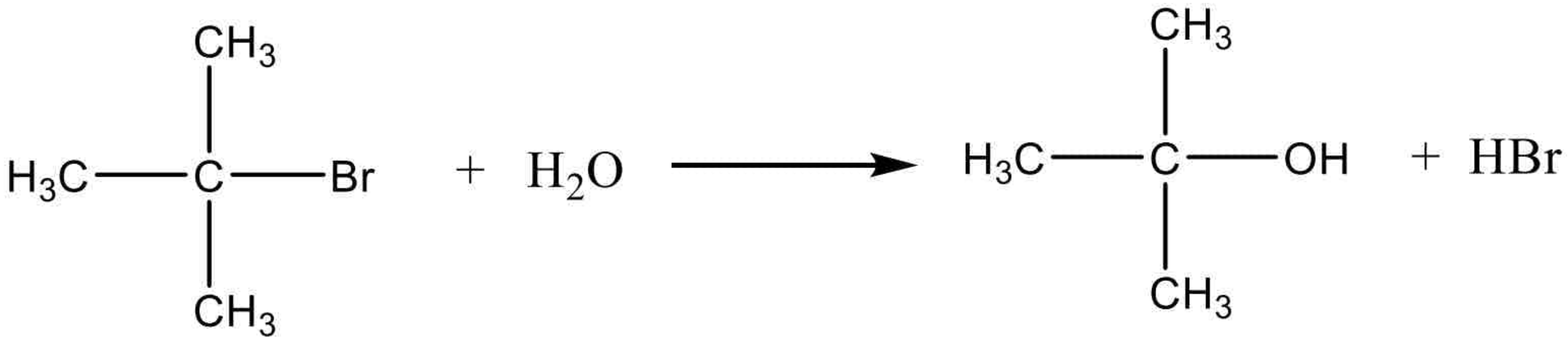
1. Decomposition of nitrogen pentoxide involves the following equation:

$$2N_2O_5\ (g) \longrightarrow 2N_2O_4\ (g) + O_2\ (g)$$

$$\text{Rate} = k\ [N_2O_5]$$

Order of reaction= one

Hydrolysis of tertiary butyl bromide



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

Order of reaction= pseudo first order reaction

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess.

Oxidation of nitric oxide

Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O_3.

$$NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$$

$$\text{Rate} = k\,[NO][O_3]$$

Order of reaction= two

Reaction of ferric chloride and potassium iodide

$$\text{Rate} = k[FeCl_3][KI]^2$$

Order of reaction= third

This rate equation suggests that the reaction is, in fact, taking place in more than one steps.

There are two possible steps of the reaction:

Slow step

$$FeCl_3\,(aq) + 2KI\,(aq) \xrightarrow{\text{slow}} FeI_2\,(aq) + 2KCl\,(aq) + Cl^-\,(aq)$$

Fast step

$$2KI\,(aq) + 2Cl^-\,(aq) \xrightarrow{\text{fast}} 2KCl\,(aq) + I_2\,(s)$$

Formation of carbon tetrachloride from chloroform

$$CHCl_3\,(l) + Cl_2\,(g) \longrightarrow CCl_4\,(l) + HCl\,(g)$$

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

Order of reaction= 1.5

Photochemical reactions

A reaction is said to be zero order if it is entirely independent of the concentration of reactant molecules. Photochemical reactions are usually zero order.

Half Life Period

Definition

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

Examples

First Order Reaction

1. Decomposition of N_2O_5 at 45°C takes 24 minutes.

After 24 minutes 0.10 mole dm^{-3} of N_2O_5 decomposes to 0.05 mol dm^{-3}.
After 48 minutes 0.025 (25%) mole dm^{-3} of N_2O_5 will remain unreacted.
After 72 minutes (3 half times) 0.0125 (12.5%) mole dm^{-3} of N_2O_5 will remain unreacted.

First order reaction.

2. The disintegration of radioactive ${}_{92}U^{235}$ has a half-life of 7.1×10^8 or 710 million years.

1 kg sample disintegrates to 0.5 kg in 710 million years.
0.5 kg disintegrates to 0.25kg in the next 710 million years.

First order reaction.
It is independent of the amount of that substance.

Second Order Reaction

The half-life period is inversely proportional to the initial concentration of the reactants.

Third Order Reaction

The half-life is inversely proportional to the square of the initial concentration of reactants.

Mathematical expression

Determination of the Rate of a Chemical Reaction

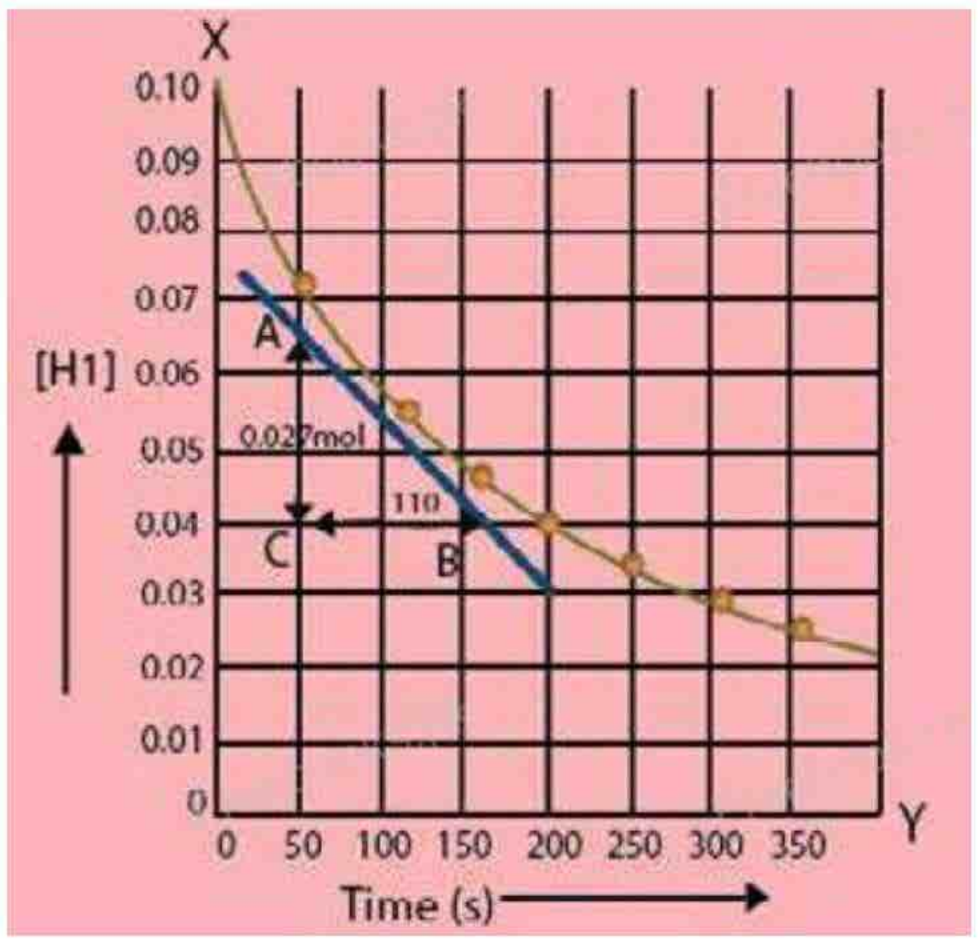
The rate of a reaction is expressed in terms of the rates at which the concentrations change.

When the reaction progresses the concentrations of reactants decrease and those of products increase and it is measured at regular time intervals.

Units

$$\text{Rate of reaction} = \frac{\triangle C}{\triangle t} = \frac{\underline{\text{mol}}\ \underline{\text{dm}}^{-3}}{\text{seconds}} = \text{mol dm}^{-3}\ \text{s}^{-1}$$

Graphical Explanation



Rate of a chemical reaction always decreases with the passage of time.

To determine the rate of reaction a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained.

$$2HI\,(g) \longrightarrow H_2\,(g) + I_2\,(g) \quad \text{at } 508\,^oC$$

The change in concentration of HI for first 50 seconds is 0.0284 mol dm^{-3}
Between 300 to 350 sec the decrease is 0.0031 mol dm^{-3}.

Since HI is a reactant, so it is a falling curve. The steepness of the curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Measurement of Rate of Reaction

In order to measure the rate of reaction, draw a tangent say, at 110 seconds, on the curve and measure the slope of that tangent. A right angled triangle ABC is completed with a tangent as hypotenuse.

$$\text{Slope or rate} = \frac{0.027 \text{ mol dm}^{-3}}{110 \text{ sec}}$$

$$= 2.5 \times 10^{-4} \text{ mol dm}^{-3}\ s^{-1}$$

In one sec in 1 dm^3 solution, the concentration of HI disappears by 2.5 x 10^{-4} moles, changing into the products. The right angled triangle ABC can be of any size, but the results for the rate of reaction will be the same.

Rising Curve

If we plot a graph between time on x-axis and concentration of any of the products then a rising curve is obtained. The value of the tangent will be the same.

Physical Methods

Following are the physical methods employed for determining the rate of reaction.

1. Spectrometry

If a reactant or a product absorbs ultraviolet, visible or infrared radiation then spectrometry is used. The rate of reaction can be measured by measuring the amount of radiation absorbed.

2. Electrical Conductivity Method

The rate of a 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.

Conductivity α rate of change in the concentration of such ions

3. Dilatometric Method

This method is useful for those reactions which involve small volume changes in solutions.

Volume change α Extent of reaction

4. Refractrometric Method

This method is suitable for reactions in solutions, where change in refractive indices of the substances decides rate of reaction.

5. Optical Rotation Method

This method is applied to optically active species. The angle through which plane polarized light is rotated is measured by a polarimeter. The extent of rotation determines the concentration of optically active substance in the reaction mixture.

Chemical Method

This is particularly suitable for reactions in solution. Chemical analysis of a reactant or a product is done.

Example

The acid hydrolysis of ethyl acetate, an ester, in the presence of a small amount of an acid.

$$CH_3COOC_2H_5\,(l) + H_2O\,(l) \xrightleftharpoons{H^+\,(\text{catalyst})} CH_3COOH\,(l) + C_2H_5OH\,(l)$$

The solution of ester in water and the acid acting as a catalyst are allowed to react.

Determination of Rate of Reaction

1. 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.

2. The dilution and chilling stops the reaction.

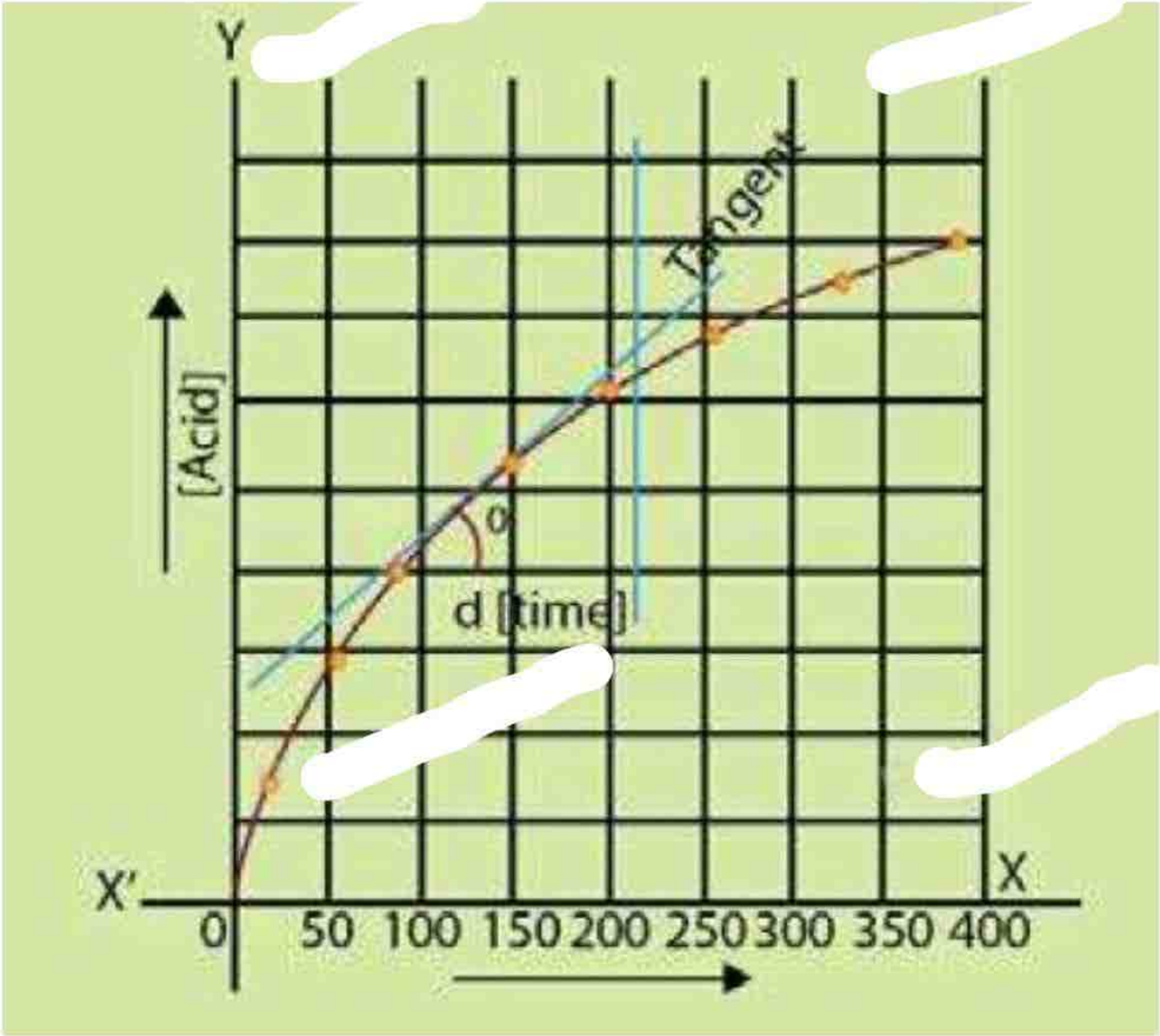
3. The acid formed is titrated against a standard alkali, say NaOH.

4. Phenolphthalein is used as an indicator.

5. The analysis is repeated at various time intervals after the start of reaction to get information about the change in concentration of acetic acid formed during the reaction at different time intervals.

6. The different concentrations of acetic acid are plotted against the time.

7. A rising 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.

Falling Curves

1. If we plot the graph for decreasing concentrations of $CH_3COOC_2H_5$, then falling curves are obtained.
2. If we have any laboratory technique to record the changing concentration of ester or alcohol, we can measure the rate of the reaction.
3. This is a pseudo first order reaction as water is in large excess.

Finding the Order of Reaction

Following methods are used to determine the order of reaction.

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

Half Life Method

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.

Mathematical Expression

$$(t_{1/2})_n \quad a \quad 1/a^{n-1}$$

Two different initial concentrations ‘a_1’ and ‘a_2’ are taken in a reaction and their half-life periods are found to be t_1 and t_2, respectively.

Dividing the two relations

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

Taking log on both sides

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

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

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

If we know the two initial concentrations and two half life values we can calculate the order of reaction (n).

Method of Large Excess

One of the reactants is taken in a very small amount.
The active masses of the substances in large excess remain constant throughout.
That substance taken in small amount controls the rate and the order is noted with respect to that.

Reason

A small change in concentration of a substance taken in very small amount affects the value of rate more appreciably.

Example

The hydrolysis of ethyl acetate shows that water being in large excess does not determine the order.

Overall Order Calculation

The reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated.

Factors Affecting Rates of Reactions

Some of the important factors affecting rates of reactions are given below:

1. Nature of Reactants

The rate of reaction depends upon the nature of reacting substances.

Electronic configuration

The chemical reactivity of the substances is controlled by their electronic configuration.

Example

The elements of I-A group have one electron in their outermost s-orbital. They react with water more swiftly than those of II-A group elements having two electrons in their outermost s-orbital.

Type of reactions

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

An increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate due to more collisions, while a decrease in the concentrations will have a reverse effect.

Example

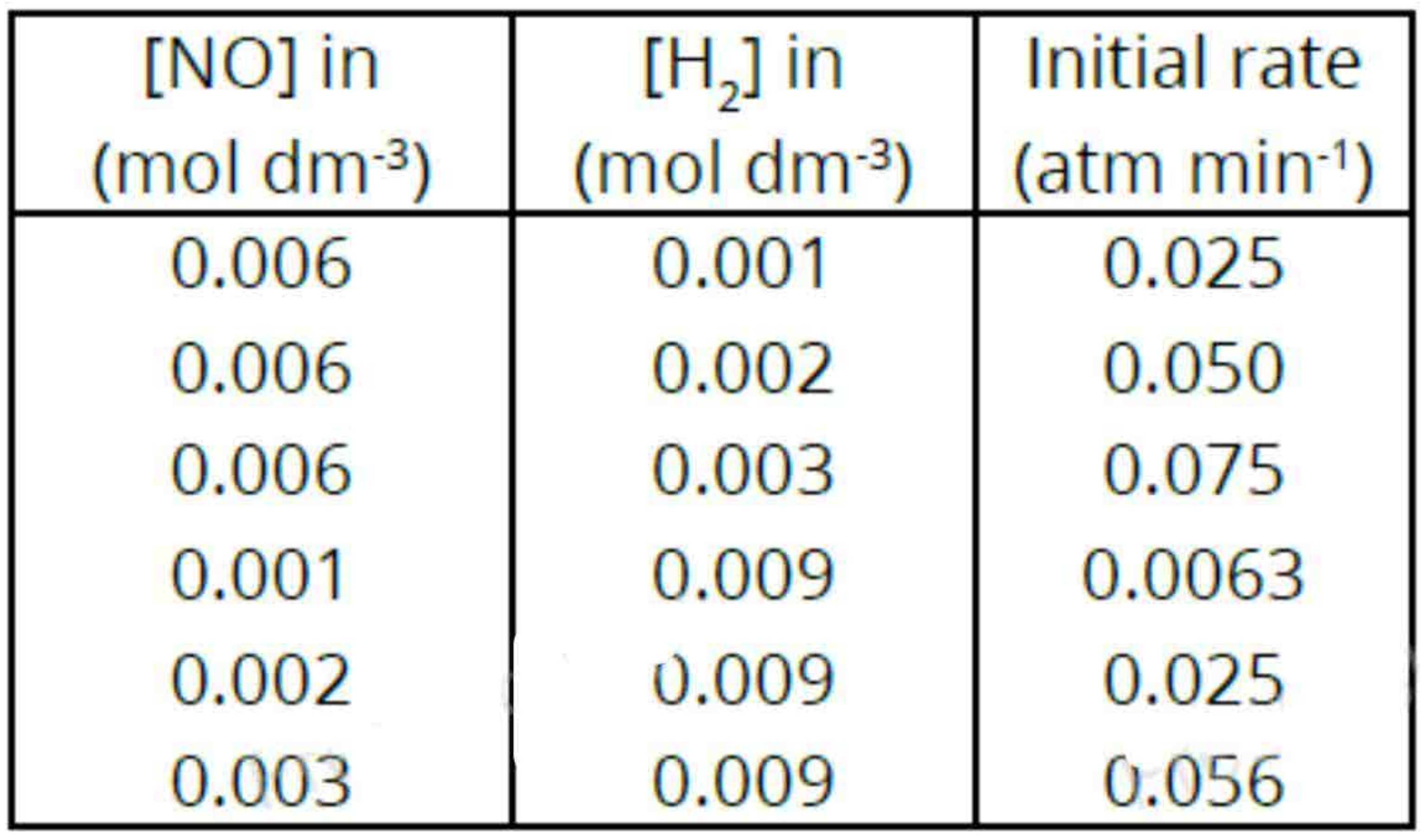
1. Combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen. 2. Limestone reacts with different concentrations of hydrochloric acid at different rates. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. Increasing the partial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

Example for explanation

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

$$2NO\,(g) + 2H_2\,(g) \longrightarrow 2H_2O\,(g) + N_2\,(g)$$

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°C are studied by noting the change in pressure.



[NO] in (mol dm^{-3})	[H$_2$] in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

First three experiments

The concentration 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.

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

Next three experiments

The concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. The rate is proportional to the square of concentration of NO.

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

Rate Equation

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

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

Order of reaction: 3rd order reaction

Possible Mechanism

The mechanism has two steps:

1. $2NO(g) + H_2(g) \xrightarrow{\text{slow}} N_2(g) + H_2O_2(g)$ (rate determining)

2. $$H_2O_2(g) + H_2(g) \xrightarrow{fast} 2H_2O(g)$$

3. Surface Area

The increased surface area of reactants increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance.

Examples

1. Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2$$

2. $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces.

4. Light

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced.

Examples

1. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight.
2. Light is vital in photosynthesis and the rate is influenced by light.

5. Temperature

Collision theory

The rate of a reaction is proportional to the number of collisions among the reactant molecules.

Effective collisions

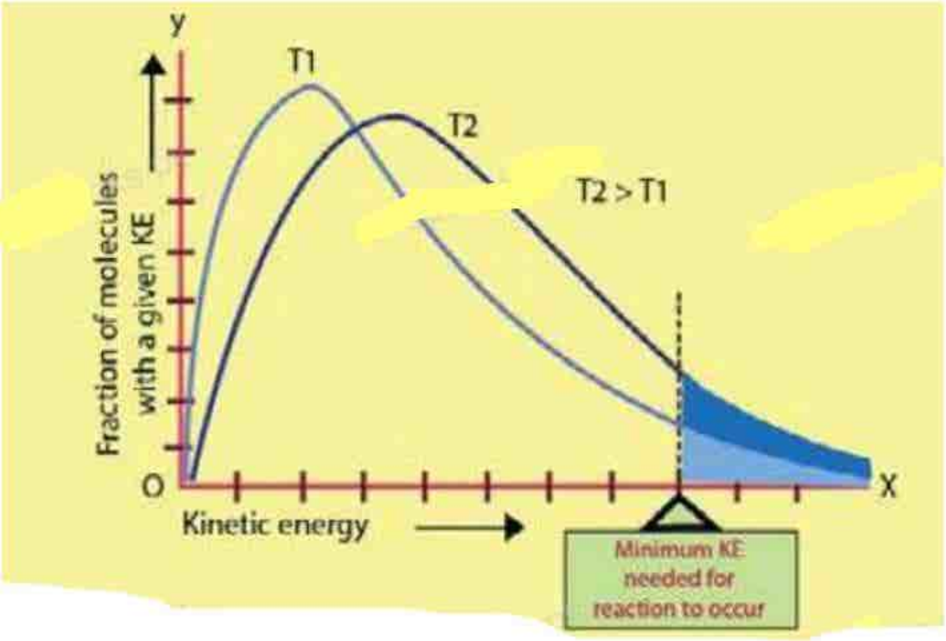
The effective collisions are the ones which lead to the formation of product.

Condition for effective collision

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.

Temperature and 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 area. As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution of velocities. The curve at higher temperature T2 has flattened. It shows that molecules having higher energies have increased and those with less energies have deceased. So, the number of effective collisions increases and hence the rate increases. When the temperature of the reacting gases is raised by 10K, the fraction of molecule with energy more than Ea roughly doubles and so the reaction rate also doubles.



6. Arrhenius Equation

Arrheinus studied the quantitative relationship between temperature, energy of activation and rate constant of a reaction.

Main idea

The rate constant ‘k’ for many simple reactions is found to vary with temperature.

Arrhenius Equation

$$k=Ae^{-Ea/RT} \text{..... (1)}$$

Ea =activation energy
T =temperature
R =general gas constant
e =base of natural logarithm.

Explanation of equation

The equation shows that the increase in temperature increases the rate constant and the reactions of high activation energy have low ’k’ values.

A =Arrhenius constant and it depends upon the collision frequency of the reacting substances.

Determination of energy of activation

We take natural log of Arrhenius equation, which is expressed as n. The base of natural log is e and its value is 2.718281.

$$\ell nk = \ell n(Ae^{-Ea/RT})$$

$$\ell nk = \ell nA + \ell ne^{-Ea/RT}$$

$$\ell nk = \ell nA + \frac{-E}{RT}\ell ne$$

$l$ne=1 (log of a quantity with same base is unity)

$$lnk = -Ea/RT + lnA \text{..... (2)}$$

Calculation of slope

Equation (1) is a straight line equation and from the slope of straight line E_a can be calculated. In order to convert this natural log into common log of base 10, we multiply the ln term with 2.303.

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

(The base of common log is 10)

Divide the whole equation by 2.303

$$\log k = \frac{-E_a}{2.303RT} + \log A \quad \text{....(3)}$$

The eq (3) is a straight line equation like $y= - mx + c$

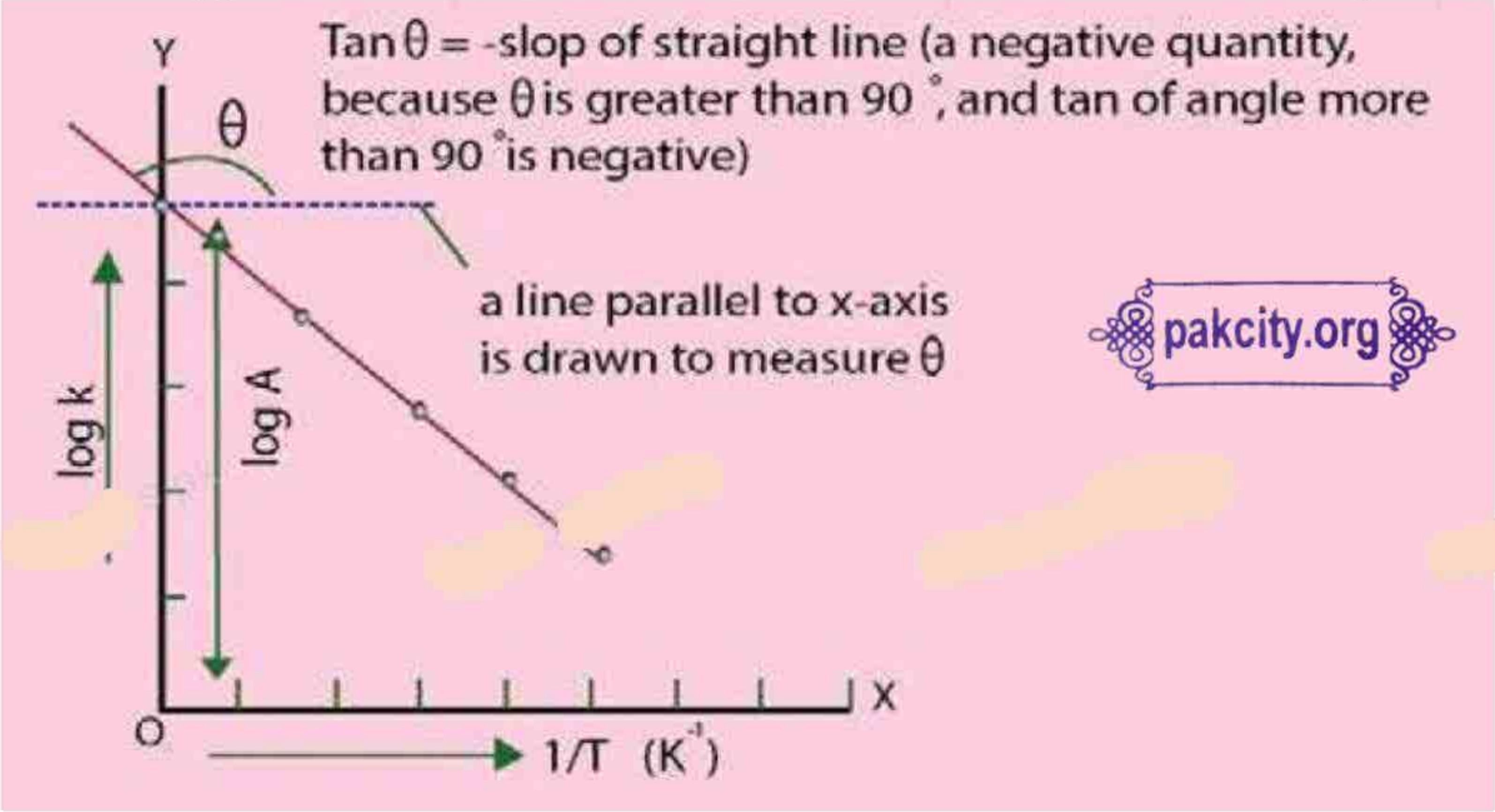
m= slope of straight line

c= intercept of straight line

Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like Ea, R and A are constants for a given reaction.

Plotting graph

A graph is plotted between 1/T on x-axis and log k on y-axis. A straight line is obtained with a negative slope. Ea/RT has negative sign so the straight line has two ends in second and fourth quadrants.



Taking slope

The slope of the straight line is measured by taking the tangent of that angle θ which this straight line makes with the x-axis. To measure the slope, draw a line parallel to x-axis and measure angle θ. Take tan θ which is slope. This slope is equal to

$$-\frac{Ea}{2.303\ R}$$

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

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

Units of slope

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

$$= K$$

Catalysis

Definition of catalysis

The process which takes place in the presence of a catalyst is called catalysis.

Definition of catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small proportion.

Importance

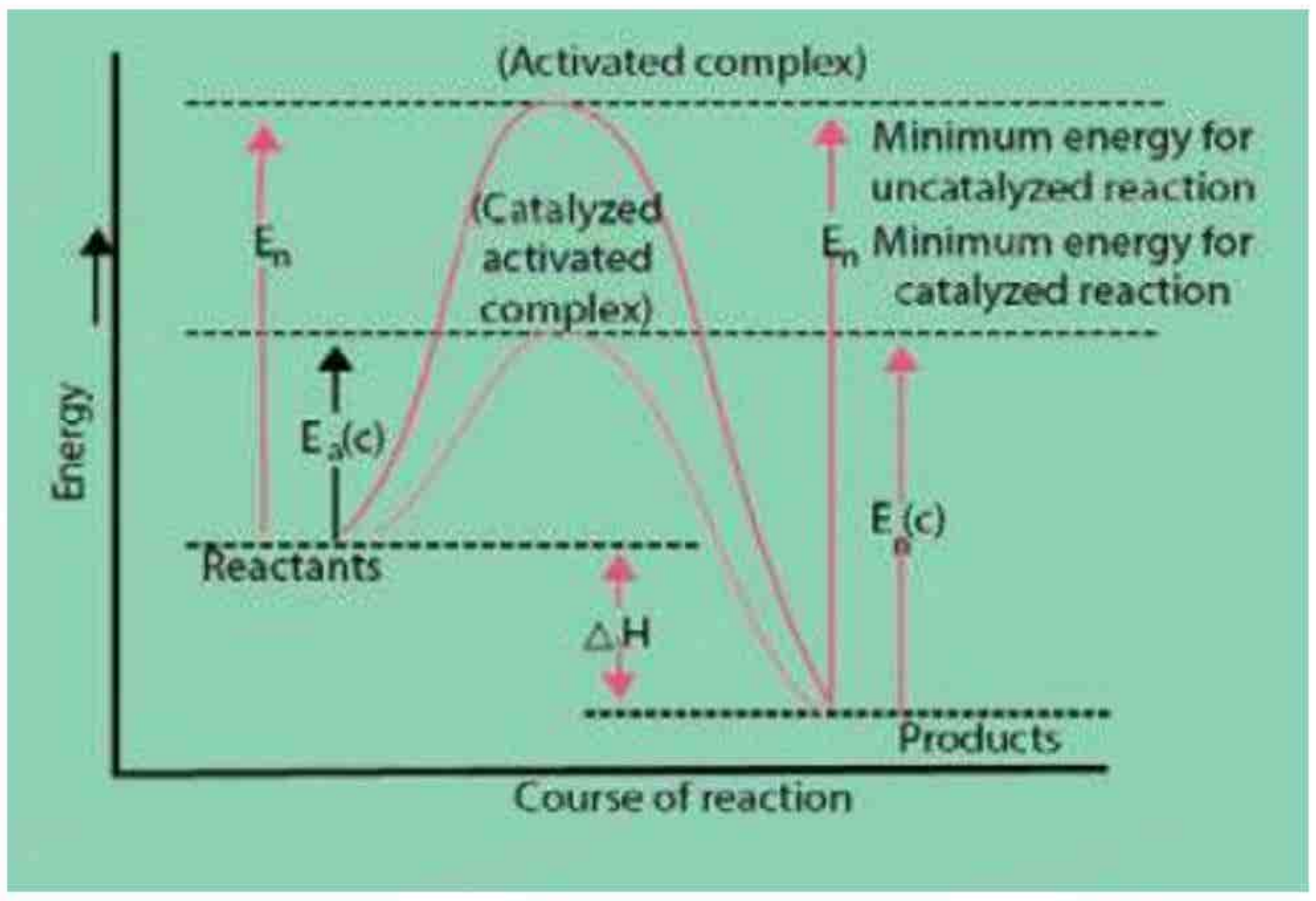
A catalyst provides a new reaction path with a low activation energy barrier. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

Examples

1. The reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst.

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

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$



Types of Catalysis

Following are the two types of catalysis:
1. Homogeneous catalysis
2. Heterogeneous catalysis

1. Homogeneous Catalysis

The catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system.

Examples

1. The formation of SO_3 (g) from SO_2 (g) and O_2 (g) in the lead chamber process for the manufacture of sulphuric acid needs NO (g) as a catalyst.

$$2SO_2 (g) + O_2 (g) \xrightarrow{NO (g)} 2SO_3 (g)$$

2. Esters are hydrolyzed in the presence of H_2SO_4.

$$CH_3COOC_2H_5 (aq) + H_2O (l) \xrightarrow{H_3O^+/H_2SO_4} CH_3COOH (aq) + C_2H_5OH (aq)$$

2. Heterogeneous Catalysis

The catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase.

Examples

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

$$4NH_3 (g) + 5O_2 \xrightarrow{Pt (s)} 4NO (g) + 6H_2O (g)$$

(ii) Hydrogenation of unsaturated organic compounds is catalyzed by finely divided Ni, Pd or Pt.

$$CH_2{=}CH_2 (g) + H_2 (g) \xrightarrow{Ni (s)} CH_3{-}CH_3 (g)$$

Characteristics of a Catalyst

Following are the characteristics of a catalyst:

1. Catalyst remains unchanged

A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.

Example

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. Needed in small amounts

We need a trace of a metal catalyst to affect very large amount of reactants.

Example

1. 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.
2. Dry HCl and NH_3 don't combine, but in the presence of trace of moisture they give dense white fumes of NH_4Cl.
3. Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

3. Effectiveness of catalyst

A catalyst is more affective, when it is present in a finely divided form.

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.

4. Establishment of equilibrium

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. Initiation of reaction

A catalyst cannot start a reaction, which is not thermodynamically feasible. It is now considered that a catalyst can initiate a reaction but the mechanism of it is different.

Enzyme Catalysis

Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells. Many enzymes have been identified and obtained in the pure crystalline state. The first enzyme was prepared in the laboratory in 1969.

Examples

1. Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.

$$NH_2\text{-}CO\text{-}NH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

2. Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

3. Glucose is converted into ethanol by the enzyme zymase present in the yeast.

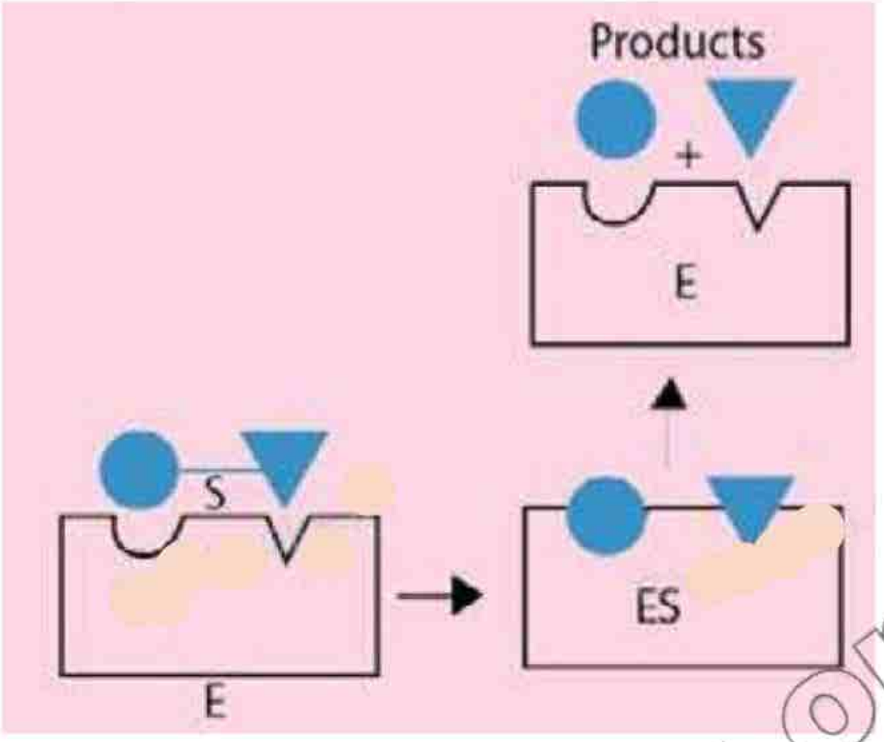
$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Lock and Key Model

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 molecules enter the cavities, form the complex and reactants and the products get out of the cavity immediately. Michaulis and Menter(1913) proposed the following mechanism for enzyme catalysis.

$$E + S \longrightarrow ES \longrightarrow P + E$$

E = enzyme, S = substrate (reactant)
ES = activated complex, P = product



Characteristics of Enzyme Catalysis

Following are the characteristics of enzyme catalysis:

1. Efficiency

Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.

2. Specificity

Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.

3. Optimum temperature

Enzyme catalytic reactions have the maximum rates at an optimum temperature.

4. Optimum pH

The pH of the system also controls the rates of the enzyme catalyzed reaction 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.

5. Co-enzyme or activator

The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.

Important long questions from past papers

1. How does Arrhenius equation help us to calculate the energy of activation of a reaction?
2. How rate of reaction depends on the following factors?
    a. Nature of reactants
    b. Surface area
3. Explain effect of temperature on rate of reaction.
4. What is order of reaction? Describe two methods (half life method and large excess method) for finding the order of reaction.
5. Define half life period. Describe half life method for the determination of order of reaction**.**
6. Define Order of reaction. Describe it with three examples.
7. Write a brief note on the following:

    a. Homogeneous catalysis
    b. Heterogeneous catalysis
8. What are enzymes? Write any four characteristics of enzyme catalysis.
9. Explain any four characteristics of catalysts**.**