CHEMISTRY

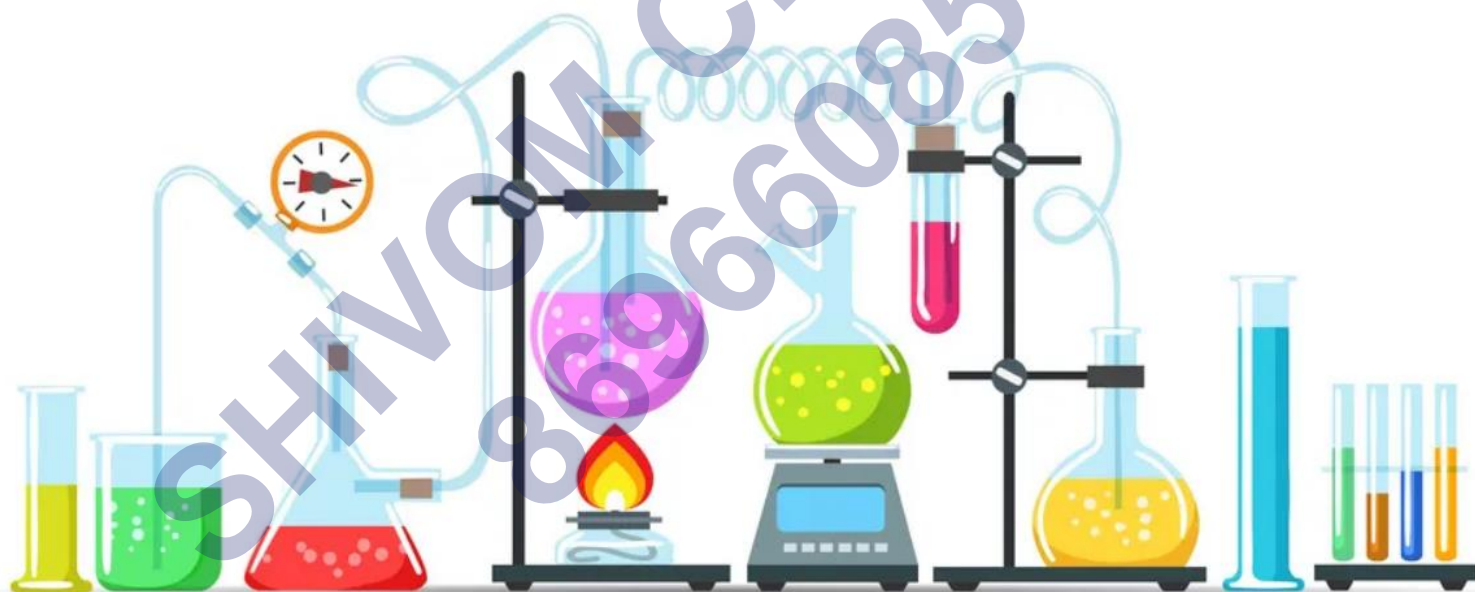## CHAPTER 4: CHEMICAL KINETICS

CHEMICAL KINETICS

Introduction

The stream of chemistry that governs the rate of reactions along with their mechanisms is termed as Chemical kinetics derived from a Greek word meaning chemical movement.

Combination of two or more reactants to produce a new product is called reaction.

Elementary Reaction: The reaction that occurs in a single step to give the product is called an elementary reactions.
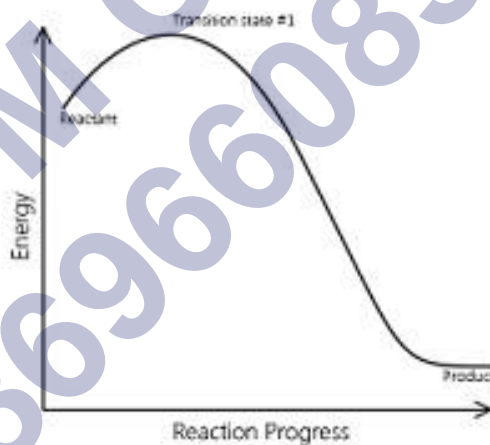
Complex reaction: The reactions that occur as a result of sequence of elementary reactions to give the product is called complex reactions.

Rate of reaction

The rate at which the concentration of reactant or product participating in a chemical reaction alters is called rate of reaction.

Rate of reaction = change in concentration/ time = (mol/litre)/time

Reactant (R) --> Product.

Rate [R]

Rate = k[R]

k = rate constant or velocity constant.

Let one mole of the reactant A produce one mole of the product B.

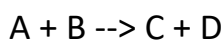Let at time t_1

[A]1 and [B]1 = Concentrations of A and B

Let at time t_2

[R]2 and [P]2 = Concentrations of A and B

Rate of disappearance of A = Decrease in concentration of R / Time taken = $-\Delta[A]/\Delta t$

Rate of appearance of B = Increase in concentration of P / Time taken = $+\Delta[B]/\Delta t$

When two or more reactants combine with each other the molecules of the respective reactants collide with each other to form the product. The collision between the molecules increases with the increase in concentration of the reactants and thereby increases the rate of reaction.
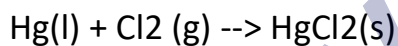
A + B --> C + D

Here molecules of reactant A and B collide to produce molecules of product C and D.
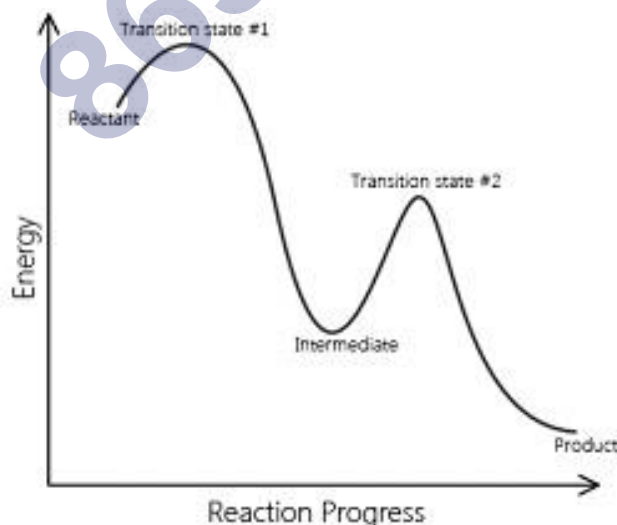
Therefore we can conclude that rate of reaction is directly proportional to the concentration of the participating reactants.
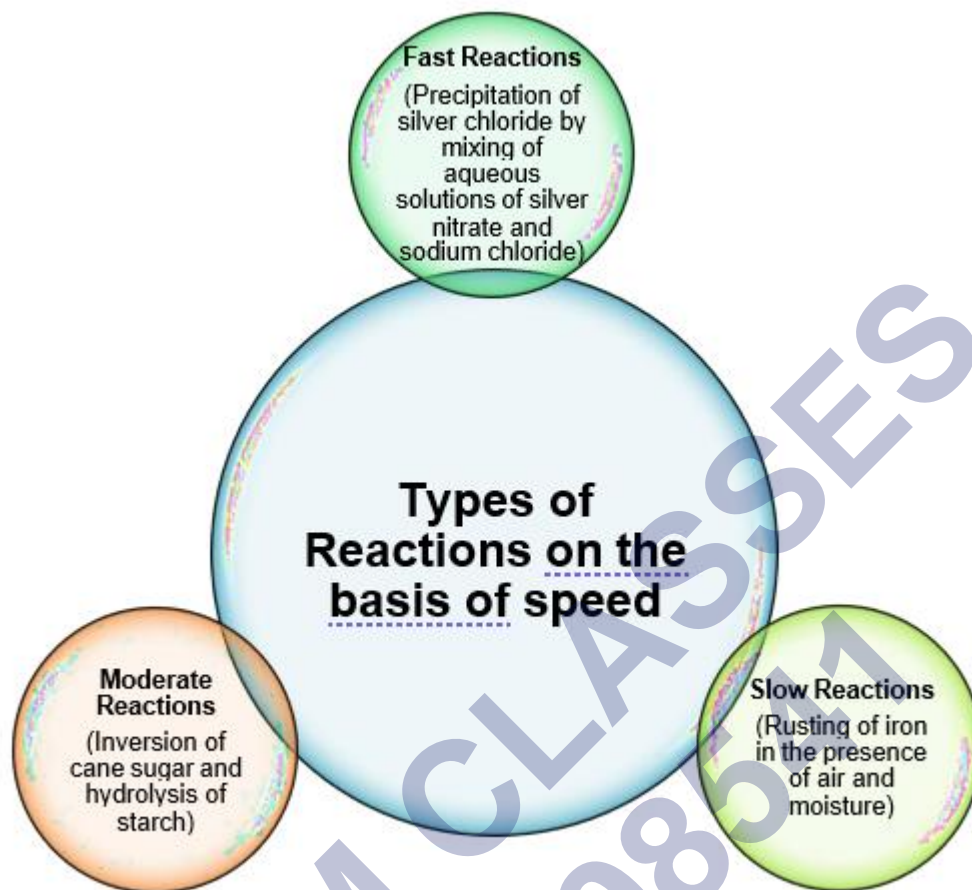
Rate $\propto$ [A]x [B]y

Or Rate = k[A]x [B]y

$Hg(l) + Cl_2 (g) \rightarrow HgCl_2(s)$

Rate of reaction= $-\Delta[Hg]/\Delta t = \Delta[Cl_2]/\Delta t = \Delta[Hg\ Cl_2]/\Delta t$

Rate of Chemical Reaction

Rate
of

Types of Reactions on the basis of speed

Fast Reactions (Precipitation of silver chloride by mixing of aqueous solutions of silver nitrate and sodium chloride)

Moderate Reactions (Inversion of cane sugar and hydrolysis of starch)

Slow Reactions (Rusting of iron in the presence of air and moisture)

Chemical Reaction

> The **rate of reaction** is the change in concentration of a reactant or productin unit time.
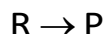
- Alternatively, the rate of reaction can also be expressed as

The rate of decrease in concentration of any one of the reactants.

The rate of increase in concentration of any one of the products.

- Consider a hypothetical reaction, assuming that the volume of the system remains

constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P.

- If $[R]_1$ and $[P]_1$ are the concentrations of R and P at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2, then

$$\Delta t = t_2 - t_1$$
$$\Delta[R] = [R]_2 - [R]_1$$
$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

$$\text{Rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad (1)$$

- $\Delta[R]$ is a negative quantity because the concentration of reactants is decreasing.

$$\text{Rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \qquad (2)$$

- Equations 1 and 2 represent the average rate of a reaction, r_{av}.

This average rate depends on the change in concentration of reactants or products and the timetaken for that change to occur.


Instantaneous and average rate of a reaction
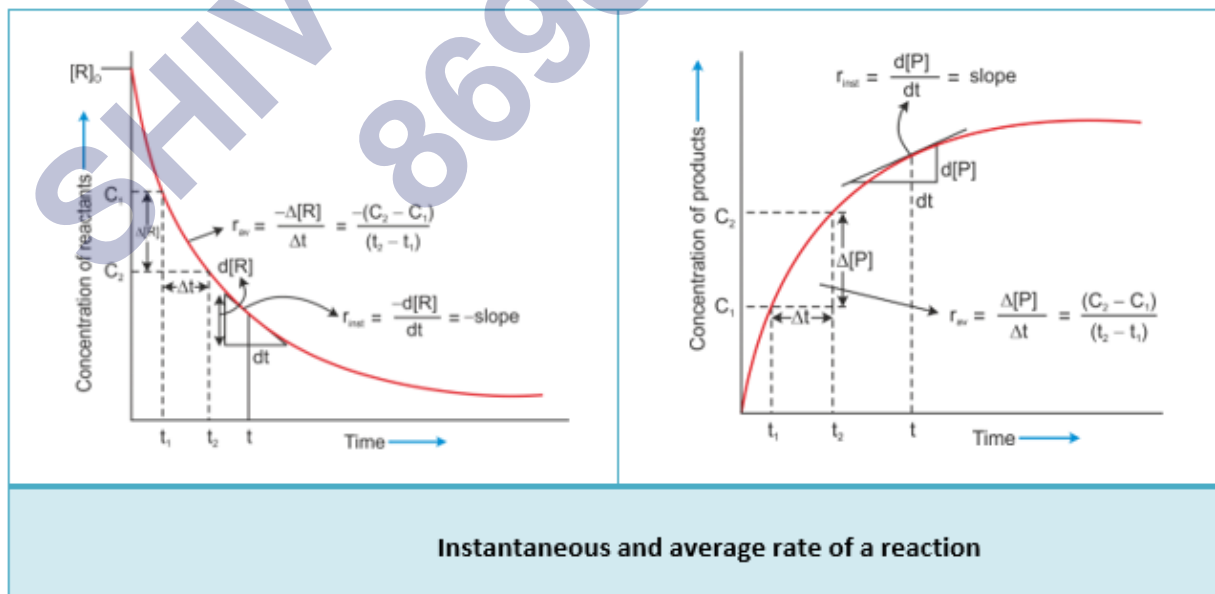
Units of Rate of a Reaction

- From Equations 1 and 2, it is clear that the units of rate are concentration time^{-1}.

- For example, if concentration is in mol L^{-1} and time is in seconds, then the units are mol $L^{-1}s^{-1}$.

- In gaseous reactions, the concentration of gases is expressed in terms of their partial pressures;hence, the units of the rate equation will be atm s^{-1}.

Instantaneous Rate of Reaction

- Consider the hydrolysis of butyl chloride (C_4H_9Cl).

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$
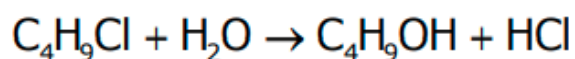
- We have provided the concentrations over different intervals of time below.

Time (s^{-1})	0	50	100	150	200	300	400	700	800
Concentration (mol L^{-1})	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

- We can determine the difference in concentration over different intervals of time, and thus, wedetermine the average rate by dividing Δ[R] by Δt.

- It can be seen from experimental data that the average rate falls from 1.90×10^{-4} mol $L^{-1}s^{-1}$ to 0.4×10^{-4} mol $L^{-1}s^{-1}$.

- However, the average rate cannot be used to predict the rate of reaction at a particular instant as itwould be constant for the time interval for which it is calculated.

- Hence, to express the rate at a particular moment of time, we determine the instantaneous rate.

- It is obtained when we consider the average rate at the smallest time interval, say dt, when Δt approaches zero.

  Therefore, for an infinitesimally small dt, the instantaneous rate is given by

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$
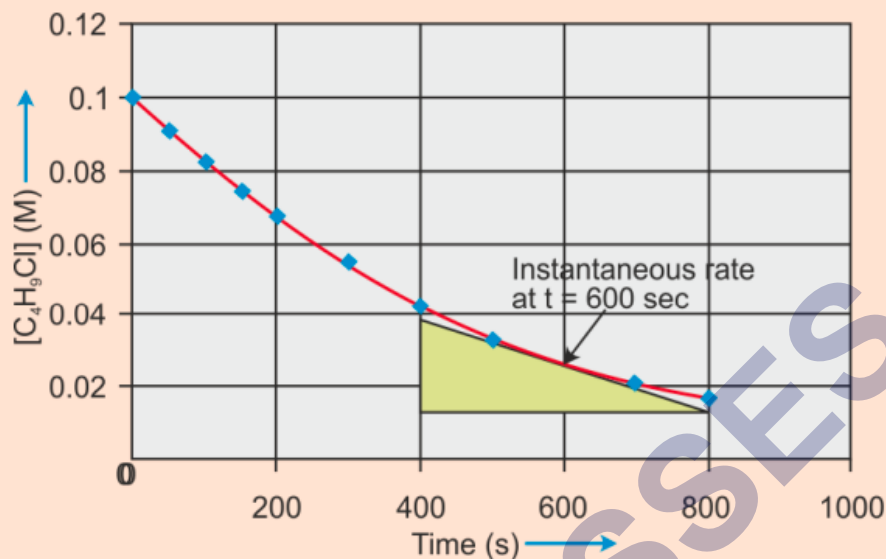
Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)

- By drawing the tangent at time t on either of the curves for the concentration of R versus time t orconcentration of P versus time t and calculating the slope of the curve, we can determine the instantaneous rate of reaction.

- Hence, in this example, r_{inst} at 600 s is calculated by plotting the graph of the concentration of butylchloride as against time t.
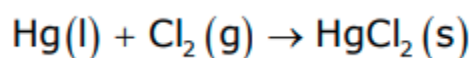
- A tangent is drawn on the curve at a point t = 600 s.

$$\therefore r_{inst} \text{ at } 600s = \left[\frac{0.0165-0.037}{(800-400)}\right] molL^{-1} = 5.12\times10^{-5}\, molL^{-1}s^{-1}$$

$$\text{At } t=250s \quad r_{inst} = 1.22\times10^{-4}\, molL^{-1}s^{-1}$$
$$t=350s \quad r_{inst} = 1.0\times10^{-4}\, molL^{-1}s^{-1}$$
$$t=450s \quad r_{inst} = 6.4\times10^{-5}\, molL^{-1}s^{-1}$$

- Now consider a reaction,

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Here, the stoichiometric coefficients of the reactants and products are the same; hence, the rate of reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

Therefore, we can say that from the above equation that the rate of disappearance of any of the reactants is the same as the rate of appearance of the products.

- Consider another reaction,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$
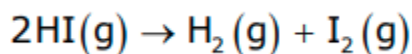
In this reaction, two moles of HI decompose to produce one mole each of H2 and I2, i.e. the stoichiometric coefficients of reactants or products are not equal to one; hence, we need to divide the rate of disappearance of any of the reactants or the rate of appearance of products by their respective stoichiometric coefficients.

Because the rate of consumption of HI is twice the rate of formation of H2 or I2, to make them equal, the term Δ[HI] is divided by 2.

The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species, and hence, the rate can be expressed as the rate of change in partial pressure of the reactant or the product.
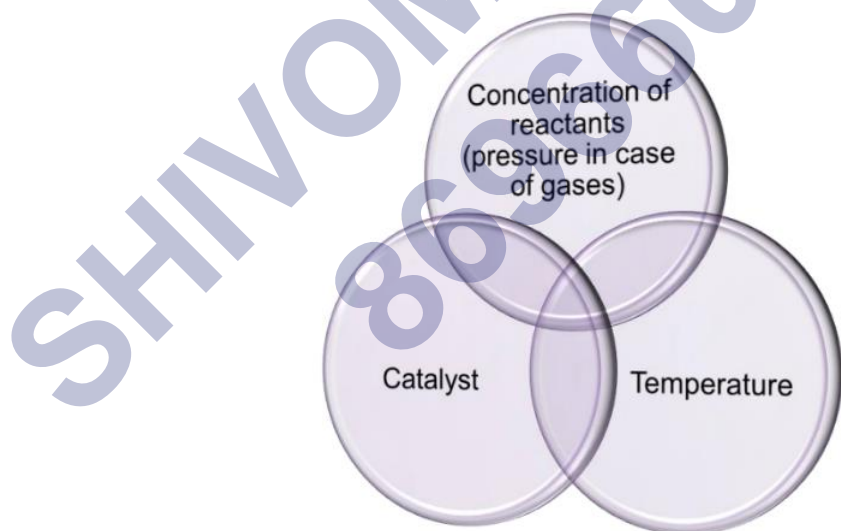

Instantaneous rate of reaction

The ratio of change in concentration in chemical reaction to the time period is termed as instantaneous rate of the reaction.

-d[R]/dt = change in chemical concentration over short period of time/ the short time elapsed = (mol/litre) / time

It can be calculated from the slope of the tangent on a concentration- time graph.

For example, consider the following graph.
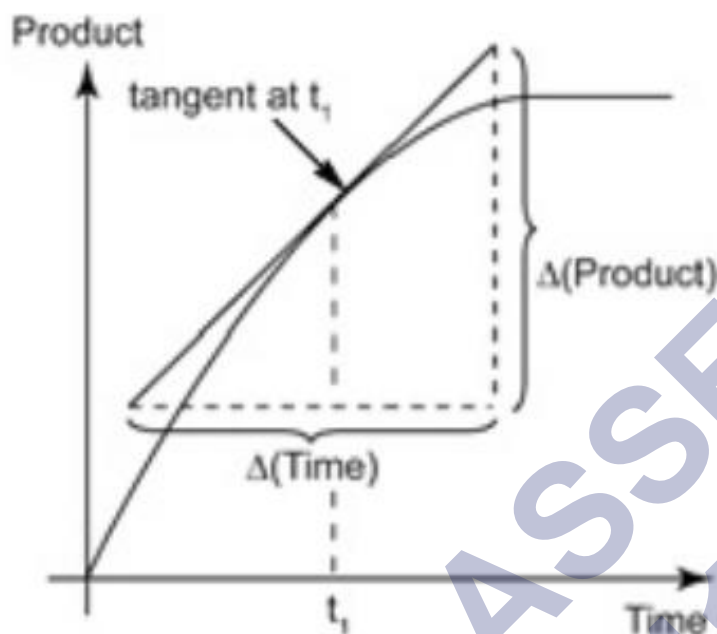
The rate of reaction at t = 40s in the above graph can be calculated by following method:

Rate of reaction = gradient of the tangent at 40s = (120-70)/(65-5) = 50/60= 0.83 cm3s^{-1}

Rate of reaction

The rate at which the concentration of reactant or product participating in a chemical reaction alters is called rate of reaction.

Rate of reaction = change in concentration/ time = (mol/litre)/time

Reactant (R) --> Product.

Rate [R]

Rate = k[R]

k = rate constant or velocity constant.

Let one mole of the reactant A produce one mole of the product B.

Let at time t1

[A]1 and [B]1 = Concentrations of A and B
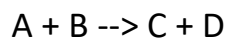
Let at time t2

[R]2 and [P]2 = Concentrations of A and B

Rate of disappearance of A = Decrease in concentration of R / Time taken = $-\Delta[A]/\Delta t$

Rate of appearance of B = Increase in concentration of P / Time taken = $+\Delta[B]/\Delta t$

When two or more reactants combine with each other the molecules of the respective reactants collide with each other to form the product. The collision between the molecules increases with the increase in concentration of the reactants and thereby increases the rate of reaction.
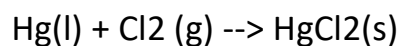
A + B --> C + D

Here molecules of reactant A and B collide to produce molecules of product C and D.

Therefore we can conclude that rate of reaction is directly proportional to the concentration of the participating reactants.

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

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

$Hg(l) + Cl2 (g) \rightarrow HgCl2(s)$

Rate of reaction= $-\Delta[Hg]/\Delta t = \Delta[Cl2]/\Delta t = \Delta[Hg Cl2]/\Delta t$

Average rate of reaction

The average rate of the reaction is the ratio of change in concentration of reactants to the change in time. It is determined by the change in concentration of reactants or products and the time taken for the change as well. As the reaction precedes forward the collisions between the molecules of the participating reactants reduces thereby decreasing the average rate of the reaction.

Mathematically, Average rate of reaction = Change in concentration / Time = (mol/litre)/time

Problem 1. For the reaction R $\rightarrow$ P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Solution: R2= 0.02 M

R1= 0.03M

t2 - t1= 25 minutes

$\Delta[R]/\Delta t = \Delta[R2-R1]/ t2- t1 = - (0.02-0.03)/25 = 6.67 \times 10^{-6} Ms^{-1}$

= $0.005 ML^{-1} min^{-1}$

Problem 2. In a reaction, 2A $\rightarrow$ Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

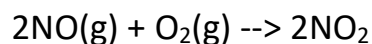**Solution:** $-1/2 (\Delta[A]/\Delta t) = -1/2(\Delta[A2-A1]/\Delta t) = -1/2 (0.4-0.5/10)$

= $0.005 ML^{-1} min^{-1}$

= $5 \times 10^{-3} M min^{-1}$

Rate expression

The representation of rate of reaction in terms of concentration of the reactants is called rate equation or rate expression.
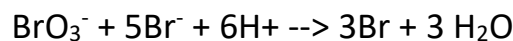
For example, in the reaction

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

The rate expression is given as

Rate $= k[NO]2[O2]$

Let us consider another reaction

$BrO_3^- + 5Br^- + 6H+ \longrightarrow 3Br + 3 H_2O$

Rate expression for this reaction is given as

$k[BrO_3^-][Br^-][H+]^2$

Order of a Reaction

The order of a reaction is defined as:

the sum of the powers to which the concentration terms are raised in the rate law equation to express the observed rate of the reaction.

The power of the concentration of a particular reactant in the rate law is called the order of the reaction with respect to that reactant.

If the rate of a reaction,

$aA + bB + cC \longrightarrow$ Products
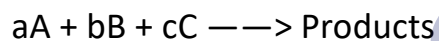
is given by the rate law as:

$k[A]p [B]q [C]r$

Rate $= -dx /dt = k[A]p [B]q [C]r$

then, the order of the reaction, n, is $n = p+q+r$

where p, q and r are the orders with respect to individual reactants and overall order of the reaction is sum of these exponents, i.e., p + q +r.

When n =1, the reaction is said to be first order reaction, if n = 2, the reaction is said to be second order reaction and so on.

Some Examples of Reactions of Different Orders

(a) Reactions of first order

(1) Decomposition of nitrogen pentoxide (N2O5)

$2N_2O_5 (g) \longrightarrow 2 NO_2 (g) + ½ O_2 (g)$
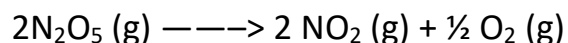
Rate $= k [N_2O_5]$

(2) Decomposition of ammonium nitrite in aqueous solution

$NH_4NO_2 ———> N_2 + 2H_2O$
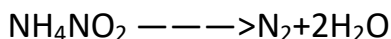
Rate = $k[NH_4NO_2]$

(3) Decomposition of H_2O_2 in the presence of I^- ions

$H_2O_2 ———-> H_2O + \frac{1}{2} O_2$
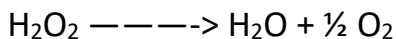
Rate = $k[H_2O_2]$

(b) Reactions of second order

(1) Decomposition of nitrogen peroxide

$2NO_2 ——-> 2NO + O_2$
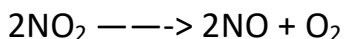
Rate = $k[NO_2]2$

(2) Reaction between H_2 and I_2 to give HI

$H_2 + I_2 ——-> 2HI$
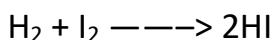
Rate = $k[H_2][I_2]$

(c) Reactions of third order

(1) Reaction between nitric oxide and oxygen

$2NO + O_2 ——-> 2NO_2$
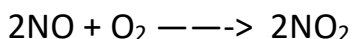
Rate = $k[NO]_2[O_2]$

(2) Reaction between nitric oxide and Cl_2

$2NO + Cl_2 ——> 2NOCl$
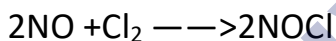
Rate = $k[NO]_2[Cl2]$

(d) Reactions of fractional order

(1) Decomposition of acetaldehyde is a fractional order reaction

$CH3CHO ——-> CH4 + CO$

Rate = $k[CH3CHO]3/2$

Order = 3/2 or 1.5

(2) The reaction between hydrogen and bromine to form hydrogen bromide is a fractional order reaction.

$H2(g) + Br2(g) ——> 2HBr$
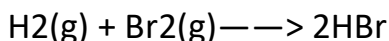
Rate = $k[H2][Br2]\frac{1}{2}$

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

(e) Zero order reaction

A number of zero order reactions are known in which the rate of the reaction is independent of the concentration of the reactants.

For example: the decomposition of ammonia at the surface of metals like gold, platinum etc., is a zero order reaction.

$2NH_3 \longrightarrow N_2 + 3H_2$
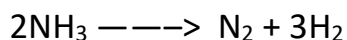
The rate of the reaction is independent of the concentration of ammonia, i.e.,

Rate = -dx/dt = $k[NH_3]^0$

Rate = k

order = 0

Molecularity of a Reaction

For a chemical reaction to occur, the reacting molecules must collide with each other. The number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction is called molecularity of a reaction.

If a reaction involves the decomposition of only a single species, the molecularity is one or it is called unimolecular reaction.

For example:

1) The decomposition of hydrogen peroxide involves single species which undergoes the change to form the products. Hence, it is a unimolecular reaction.

$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$

2) Decomposition of ammonium nitrite

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$
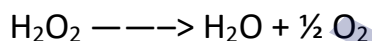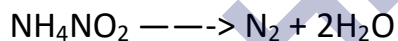
If the reaction involves the collision of two species, it is bimolecular and if three species take part in a collision leading to the formation of the products it is called trimolecular and so on.

The examples of bimolecular reactions are given below:

1) Dissociation of hydrogen iodide is a bimolecular reaction because two molecules collide to bring about the reaction.

$2HI (g) \longrightarrow H_2 (g) + I_2 (g)$
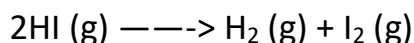
2) Combination of NO and O3 is a bimolecular reaction

$NO(g) + O_3 (g) \longrightarrow NO_2 (g) + O_2 (g)$
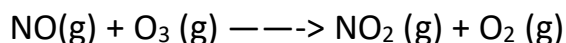
The examples of trimolecular reactions are

The reaction of nitric oxide and oxygen is a trimolecular reaction because it involves collision

of three reacting molecules.

$2NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$
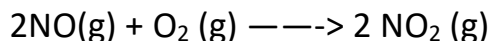
Reactions involving three or more molecules are uncommon because such reactions requires the simultaneous collision of three or more than three molecules.

Simultaneous collision of three molecules means that the third molecule must collide the other two molecules at the same time when they are in the process of collision. The chances of the occurrence of such collisions are very small.

Some reactions involving more than three molecules are quite fast.

For example:

a) The reaction of bromide ions with bromate ions in the presence of an acid:

$5Br^-(aq) + BrO_3^-(aq) + 6H+(aq) \longrightarrow 3\,Br_2(aq) + 3H_2O(l)$
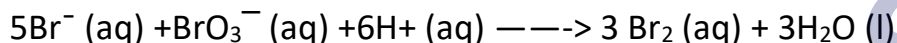
The experimentally measured rate law for this reaction is given as:

Rate = $k[Br^-][BrO_3^-][H+]2$

This rate is first order with respect to Br^- and BrO_3^- ion and second order with respect to H+ ions and the overall order of the reaction is 1+1+2=4.

b) The reaction of potassium chlorate with ferrous sulphate in the presence of sulphuric acid involves ten species.

$KClO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow KCl + 3Fe_2(SO_4)3 + 3H_2O$
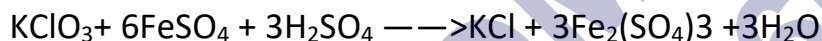
The above reaction appears to be of tenth order but actually it is a second order reaction. If this reaction were to take place in a single step, the 10 particles (1 $KClO_3$, 6 $FeSO_4$, and 3 H_2SO_4) would have to collide simultaneously.

But chances of such events are extremely small, so much so that a reaction which takes place by such collision will not occur at all.

Type of reactions which take place through a sequence of two or more consecutive steps are called complex reactions.

The detailed description of various steps by which reactants change into the products is called mechanism of the reaction.

The steps which contribute to the overall reaction are called elementary processes.

Integrated Rate Expression

The concentration dependence of rate is called differential rate equation. Integrated rate equation gives a relation between directly measured experimental quantities i.e. concentrations at different times. The integrated rate equations are different for reactions of different orders.

The instantaneous rate of a reaction is given by differential rate law equations.

For example: For a general reaction

aA +bB ——–> Products
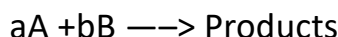
the differential rate law equation is :

dx/dt = k[A]a [B]b

The differential form of rate law is transformed to integrated form of rate law by simple mathematics (calculus).

Zero Order Reaction

A reaction is said to be of zero order, if its rate is independent of the concentration of the reactants. Consider the general zero order reaction:

R ——–> Product
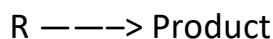
Let [R] be the concentration of the reactant R and k0 is the rate constant for the zero order reaction. For the zero order reaction, the rate of the reaction is independent of the concentration of R. Thus,

$$\text{Rate} = -\frac{d[R]}{dt} = k_0 \, [R]^\circ = k_0$$

This form of rate law is known as differential rate equation, Rearranging the above equation,

-d [R] =k0 dt

Integrating the above equation

-∫ d[R] = k0 ∫ dt

-[R]= k0t + I

where I is the constant of integration. The value of I can be calculated from the initial concentration.

For example: the initial concentration of R be [R]0, at t=0

-[R]0 = k0 × 0 + I

I = – [R]0

– [R] = K0t – [R]0

K0t = [R]0 – [R]

[R] = -K0t + [R]0

If we plot a graph between [R] against t, we get a straight line with slope as -k0 and intercept equal to [R]0.
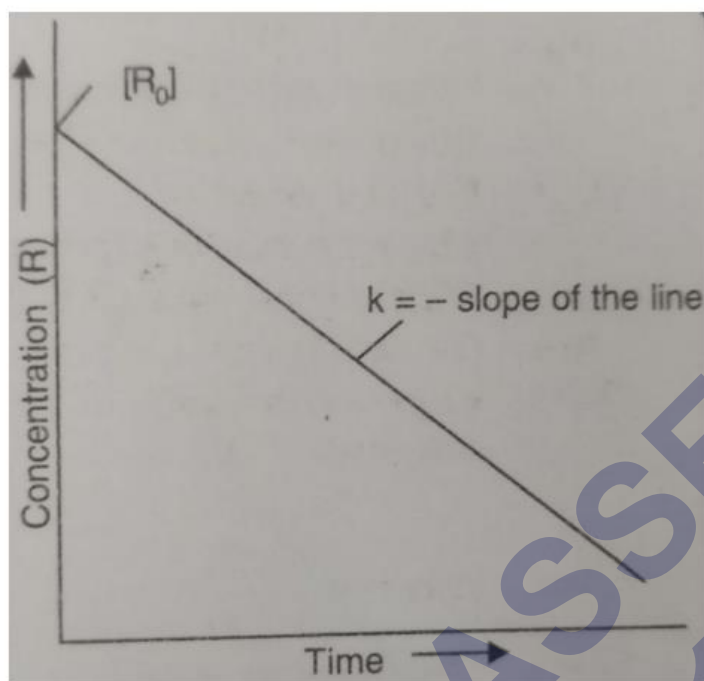
Alternatively, rate constant, k0 can be calculated if we know the concentration of R at any time t and [R]0. Thus,

$k0 = \{ [R]0 - [R] \} / t$

where [R]0, is the initial concentration of R, [R] is the concentration at time t.

Alternatively, if the initial concentration of R is 'a' moles per litre and let x moles of reactants get changed to products in time t. Then, concentration of R left after time t be (a – x)

R ——-> Products
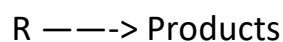
[R]0 =a

[R] = a – x so that

[R]0 -[R] = a- (a-x) = x

k0 = x/t

x=k0 t

The amount of the substance reacted is proportional to the time.

Zero order reactions generally take place in heterogeneous systems. In such systems the reactant is adsorbed on the surface of a solid catalyst, where it is converted into product. The fraction of the surface of the catalyst covered by the reactant is proportional to the concentration of the reactants at low values.

After certain concentration limit of the reactant, the surface of the catalyst becomes fully covered. On further increasing the concentration of the reactant, the reaction rate does not change. The rate becomes independent of the concentration and, therefore, becomes zero

order reaction.

Collision Theory

Pseudo Chemical Reactions

Some reactions are first order each with respect to two different reactants i.e.,

A+B——-> Products
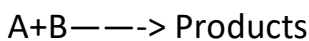
Rate = k[A] [B]

If one of the reactants is present in high concentration (solvent) then there is very little change in its concentration. The concentration of that reactant remains practically constant during the reaction.

For example, if [A] = 0.01 M and that of solvent water [B] = 55.5 M, the concentration of B changes only from 55.50 to 55.49 M even after the completion of the reaction.

The reaction, therefore, behaves as a first order reaction in A. Such reactions are called pseudo first order reactions.

Consider the hydrolysis of ethyl acetate:

$CH_3COOC_2H_5 + H_2O \Leftrightarrow CH_3COOH + C_2H_5OH$

The molecularity of the reaction is two because it involves two reacting species, namely ethyl acetate and water. However, the concentration of ethyl acetate changes during the reaction while water is present in such a large excess that its concentration remains practically unchanged. Therefore, the rate of the reaction depends only the order of the reaction is one.

Rate = k' $[CH_3COOC_2H_5]$ $[H_2O]$

on the concentration of ethyl acetate and hence

$[H_2O]$ can be takes as constant so that

Rate = k $[CH_3COOC_2H_5]$

k= k' $[H_2O]$

Thus, the reaction appears to be second order but follows the first order kinetics. Such reactions which appear to be of higher order but actually follow lower order kinetics are called pseudo chemical reactions.

For example: The hydrolysis of cane sugar or inversion of cane sugar to give glucose

and fructose:

$C_12H_{22}O_{11} + H_2O ——> C_6H_{12}O_6 + C_6H_{12}O_6$
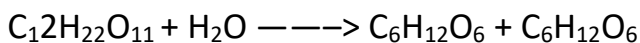
Molecularity is two while order is one.

Collision Theory

Collision theory was put forward by Max Trautz and William Lewis in 1916-18. It is based on kinetic theory of gases.

According to this theory,

1) the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

2) The number of collisions that takes place per second per unit volume of the reaction mixture is known as collision frequency Z. The value of collision frequency is normally very high.

3) For instance, under ordinary conditions of temperature and pressure, in a gaseous system, the collision frequency of binary collisions is of the order of 1025 to 1028.

4) If all the collisions are effective in forming the products, the reactions must be completed in a very short time.

5) All the collisions among the reacting species at a temperature are not effective in bringing about the chemical reaction.

The collisions which actually produce the products and therefore, result in the chemical reactions are called effective collisions.

There are two important barriers to a reaction namely

(i) energy barrier (ii) orientation barrier

(i) Energy barrier: For the reacting species to make effective collisions, they should have sufficient energy to break the chemical bonds in the reacting molecules. The minimum amount of energy which the colliding molecules must possess is known as threshold energy. This means that only those collisions of reactants will give products which possess energies greater than threshold energy.

(ii) Orientation barrier: The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed.

Consider the reaction

NO_2 (g) + NO_2 (g) ——> N_2O_4 (g)
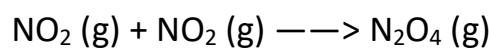
During this reaction, the products molecules are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.

When the molecules do not have proper orientation at the time of collision, they result in ineffective collisions and do not form the products.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$
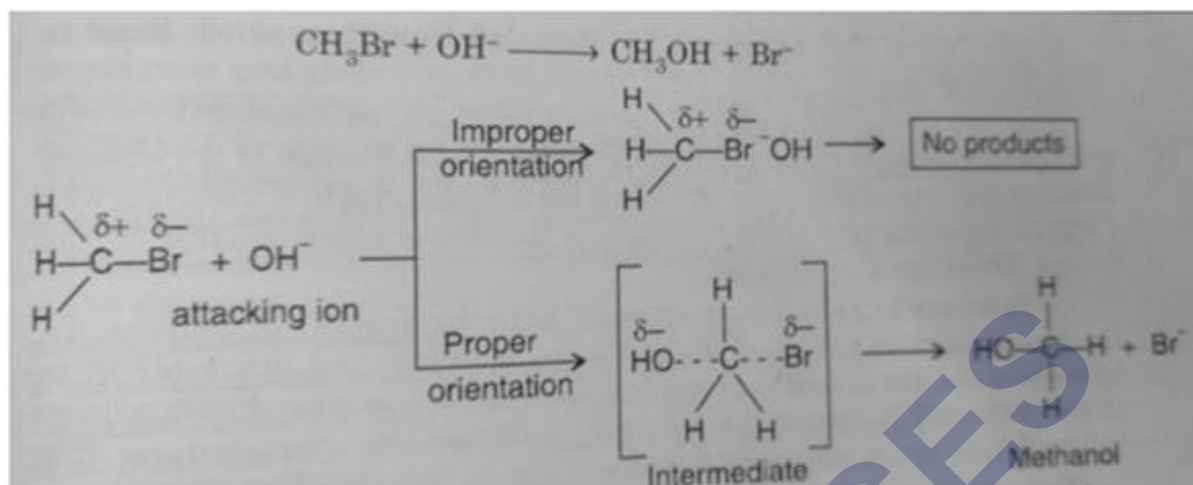
Effect of Catalyst on Reaction Rate

The rate of a reaction can be increased by raising the temperature. However, temperature can be raised within certain limits because in certain cases, the reactants become unstable at higher temperatures and decompose.

Many reactions are made to proceed at an increased rate by the presence of some other substance.

For example: a mixture of H_2 and O_2 does not react at room temperature. However, in the presence of finely divided platinum, the reaction becomes quite vigorous.

Manganese dioxide, a black powder speeds up the thermal decomposition of potassium chlorate.

$$2 \text{ KClO3 (s)} \longrightarrow 2KCl \text{ (s)} + 3 O_2$$
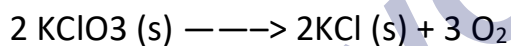
Catalysts

The substances which accelerate the rate of reactions without itself undergoing permanent change are called catalysts.

The substances which increase the rate of a reaction and can be recovered chemically unchanged in mass and composition after the reaction are called catalysts.

The phenomenon of increasing the rate of a reaction by the use of catalyst is called catalysis. A catalyst is not consumed in the reaction.
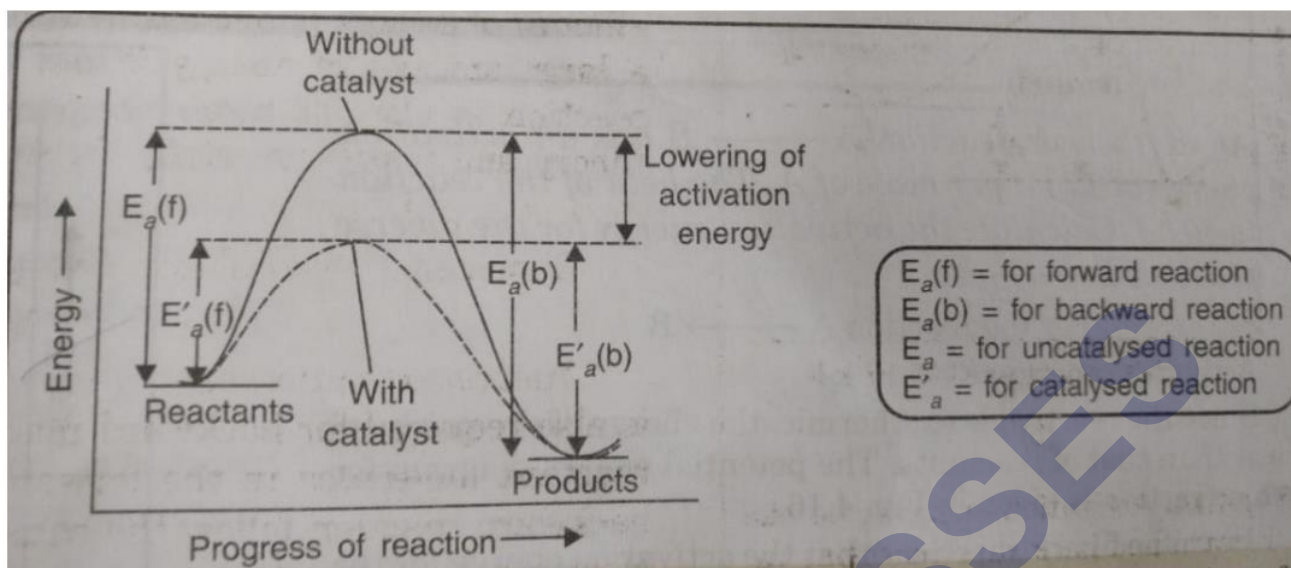
In a catalysed reaction the catalyst is used in one step and is regenerated in subsequent step and thus, it is used up again and again without undergoing any permanent change.

Catalyst provides an entirely new path for the reaction in which the reactants are converted to products quickly. The catalyst forms a new activated complex of lower potential energy. This means that the activation energy becomes lower for the catalysed reaction than that for uncatalysed reaction. The fraction of the total number of collisions possessing lower activation energy increased and hence, the rate of reaction also increase.

The solid line shows the path for uncatalysed reaction and dotted line shows the path adopted by catalysed reaction. Consider a hypothetical reaction

A + B ——–> AB
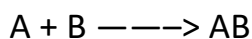
The reaction proceeds through the formation of activated complex

A+B ——> [A...B] ——> AB

Addition of a catalyst C result into the formation of new activated complex of lower activation energy.
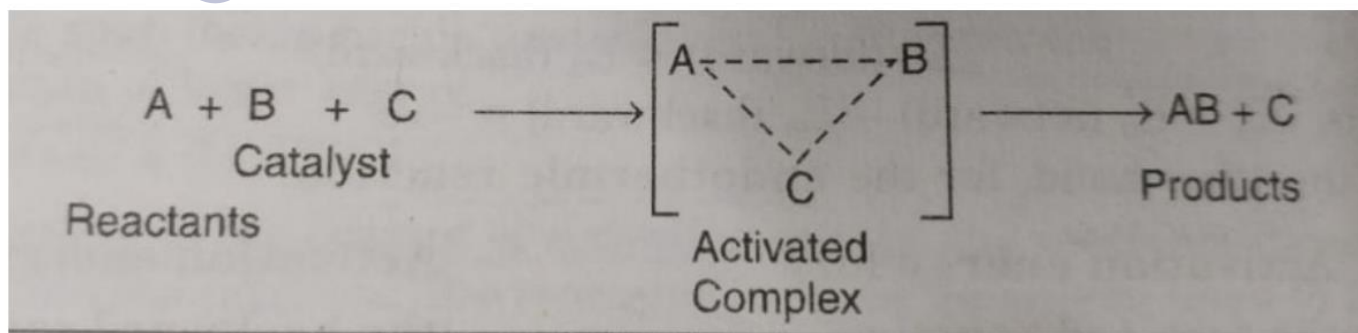
The Function of Catalyst

(1) A catalyst may undergo intermediate physical changes and it may even form temporary

chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction.

(2) A catalyst speeds up the reaction but it does not shift the position of equilibrium. The presence of a catalyst reduces the height of barrier by providing an alternative path for the reaction and lowers the activation energy. The lowering in activation energy is to the same extent for the forward as well as for the backward reaction.

(3) Catalysts are highly specific in nature. A catalyst which can catalyse one reaction may have no effect on another reaction even, if that reaction is very similar.

(4) The catalyst does not change ΔE (or ΔH) of the reaction.

Half Life Period of a Reaction

Half life period of a reaction is defined as the time during which the concentration of a reactant is reduced to half of its initial concentration.

or

The time in which half of a reaction is completed. It is generally denoted as t½

The half life period of a first order reaction may be calculated as given below:

The first order rate equation for the reaction

A → Products

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

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

Half life period of a reaction

Now, half life period corresponds to time during which the initial concentration, [A]0 is reduced to half i.e.

[A] = [A]0 /2   at t= t½

Then half life period, t½ becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k}$$

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

Half life period of a reaction

Thus, half life period of a first order reaction is independent of the initial concentration of the reactant. Half life period for the first order reaction is inversely proportional to the rate constant.

For example,

(i) time required to complete 1/3 of the reaction will be given as:

$[A]_o = a$, $[A] = a - a/3 = 2/3a$

$$t_{1/3} = \frac{2.303}{k} \log \frac{a}{1/3a} = \frac{2.303}{k} \log \frac{3}{2}$$

time required to complete 1/3 of the reaction

(ii) time required to complete 3/4 of the reaction will be

$[A]_o = a$, $[A] = a - 3/4\, a = 1/4\, a$

time required to complete 3/4 of the reaction

$$t_{3/4} = \frac{2.303}{k} \log \frac{a}{1/4a} = \frac{2.303}{k} \log 4$$

Half Life period of zero order and second order reactions

The integrated rate equation is ,

$kt = [A]_o - [A]$

For half life period, t½ , $[A] = [A]_0/2$

$t½ = [A]_0\, /2k$

Similarly for second order reaction,

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

For half life period, $t_{1/2} = [A] = [A]_0/2$

$$\therefore \quad kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

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

Type of reaction	Rate equation	$t_{1/2}$
Zero order	Rate $= k[A]^0$	$\dfrac{[A]_0}{2k}$
First order	Rate $= k[A]$	$\dfrac{0.693}{k}$
Second order	Rate $= k[A]^2$	$\dfrac{1}{k[A]_0}$

Class : 12th Chemistry
Chapter-4 : Chemical Kinetics (Part_1)

E_a and proper orientation of the molecules determine the criteria for an effective collision.

$\text{Rate} = PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor
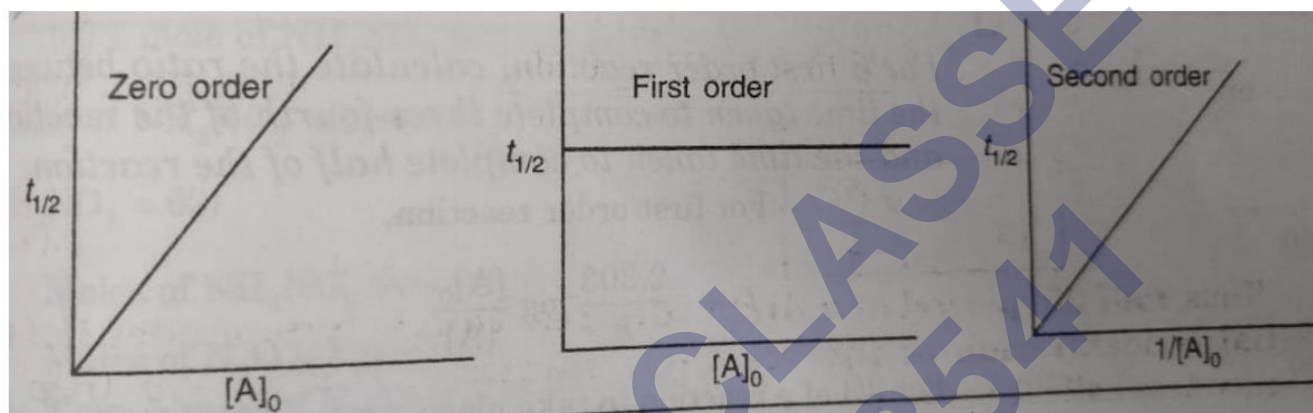
Pseudo First Order Reaction
•Are not truly of first order but under certain conditions behave as first order reaction
•Acid hydrolysis of ethyl acetate
•Inversion of sugar

Collision Frequency
Number of collisions per unit volume of reaction mixture
$\text{Rate} = PZ_{AB}e^{-Ea/RT}$

Molecularity of a Reaction
Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Effective Collision
Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

Collision Theory: Rate of Reaction depends on the collision frequency and effective collisions

Chemical Kinetics

Half-life of a Reaction
Time in which the concentration of a reactant is reduced to one half of its initial concentration
1st Order
$t_{1/2} = \dfrac{0.693}{K}$
0 Order
$t_{1/2} = \dfrac{[R]_0}{2K}$

Order of a Reaction
Sum of powers of concentration of the reactants in the rate law.

Integrated Rate Equation
Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol L^{-1}s^{-1}
1	$kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	s^{-1}

Arrhenius Equation
$K = Ae^{-Ea/RT}$
$\log k = \log A - \dfrac{E_a}{2.303RT}$
$\log = \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303RT}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

Activation Energy: E_a
Energy required to form an intermediate called activated complex (c)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

Class : 12th Chemistry
Chapter-4 : Chemical Kinetics (Part_2)

Rate of disappearance of R
$= \dfrac{\text{Decease in concentration of R}}{\text{Time taken}} = \dfrac{-\triangle[R]}{\triangle t}$

Rate of appearance of P
$= \dfrac{\text{Increase in concentration of P}}{\text{Time taken}} = \dfrac{+\triangle[P]}{\triangle t}$

$R \rightarrow P$

Average Rate
Appearance of products or disappearance of reactants over a long time interval.
$$r_{av} = \frac{d[P]}{dt} = \text{slope}$$
$$r_{av} = \frac{-d[R]}{dt} = -\text{slope}$$

Instantaneous Rate
Rate of change in concentration of reactant/product at a particular time
$$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$

Chemical Kinetics

Rate of Chemical Reaction
Change in concentration of reactants or products in unit time;
Unit : $\text{mol L}^{-1}\text{s}^{-1}$ or atm s^{-1}

Rate Law
Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. aA + bB - cC + dD
$$\text{Rate} = K[A]^{X}[B]^{y} = \frac{d[R]}{dt}$$

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity

Order	Unit
0	$\text{molL}^{-1}\text{s}^{-1}$
1	s^{-1}
2	$\text{mol}^{-1}\text{Ls}^{-1}$

Factor Influencing
Concentration: Higher the concentration of reactants, faster is the rate of reaction.
Temperature: Increases with increase in temperature. becomes almost double with 10°C rise.
Presence of Catalyst: Increases with a catalyst.
Surface Area: Greater is the surface area, faster is the rate of reaction.
Activation Energy: Lower the activation energy, faster is the reaction.

Important Questions

Multiple Choice questions-

Question 1.A first order reaction has a half life period of 34.65 seconds. Its rate constant is

(a) 2×10^{-2} s^{-1}

(b) 4×10^{-4} s^{-1}

(c) 20 s^{-1}

(d) 2×10^{-4} s^{-1}

Question 2.If a graph is plotted between In k and 1/T for the first order reaction, the slope of the straight line so obtained is given by

(a) $-\dfrac{E_a}{R}$

(b) $\dfrac{E_a}{2.303R}$

(c) $\dfrac{2.303}{E_a.R}$

(d) $\dfrac{E_a}{2.303}$

Question 3.The unit of rate constant for a zero order reaction is

(a) mol L^{-1}s^{-1}

(b) s^{-1}

(c) L mol^{-1}s^{-1}

(d) L2mol^{-2}s^{-1}

Question 4.A catalyst increases the speed of a chemical reaction by

(a) increasing activation energy

(b) decreasing activation energy

(c) increasing reactant energy

(d) decreasing threshold energy

Question 5.The units of the rate constant for the second order reaction are:

(a) mol^{-1} litre s^{-1}

(b) mol $litre^{-2}$ s^{-1}

(c) s^{-1}

(d) mol $litre^{-1}$ s^{-1}

Question 6.The value of k for a reaction is 2.96×10^{-30} s^{-1}. What is the order of the reaction?

(a) Zero

(b) 3

(c) 2

(d) 1

Question 7.A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will

(a) triple

(b) increase by a factor of 4

(c) double

(d) remain unchanged

Question 8. If the concentrations are expressed in mol litre-1 and time in s, then the units of rate constant for the first-order reactions are

(a) mol $litre^{-1}$ s^{-1}

(b) mol^{-1} litre s^{-1}

(c) s^{-1}

(d) mol^2 $litre^{-2}$ s^{-1}

Question 9.The half life of a first order reaction having rate constant 200 s^{-1} is

(a) 3.465×10^{-2} s

(b) 3.465×10^{-3} s

(c) 1.150×10^{-2} S

(d) 1.150×10^{-3} S

Question 10. The rate of a reaction is $1.209 \times 10^{-4} L^2 \, mol^{-2} s^{-1}$. The order of the reaction is:

(a) zero

(b) first

(c) second

(d) third

Very Short Question:

Question 1. Is rate of reaction always constant?

Question 2. Can order of reaction be zero? Give example.

Question 3. What do you understand by rate law expression?

Question 4. Is it possible to determine or predict the rate law theoretically by merely looking at the equation?

Question 5. Define the term chemical kinetics?

Question 6. Define – Rate of reaction and the factors affecting the rate of reaction.

Question 7. What is average rate of a reaction? How is it determined?

Question 8. What are the units of rate of a reaction?

Question 9. Identify the reaction order for from each of the following rate constant –

(a) $k = 2.3 \times 10^{-5} L \, mol -1 s^{-1}$

(b) $k = 3.1 \times 10^{-4} s^{-1}$

Question 10. Consider the equation $2NO(q) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

The rate law for this equation is first order with respect to H_2 and second order with respect to NO. write the rate law for this reaction.

Short Questions:

Question 1 For the reaction A+B $\rightarrow$ C+D, the rate of reaction doubles when the concentration of A doubles, provided the concentration of B is constant. To what order does A enter into the rate expression?

Question 2. . A chemical reaction 2A $\Leftrightarrow$ 4B+C in gas phase occurs in a closed vessel. The concentration of B is found to be increased by $5\times10^{-3} mole\ L^{-1}$ in 10 second. Calculate (i) the rate of appearance of B (ii) the rate of disappearance of A?

Question 3. For the following reactions, write the rate of reaction expression in terms of reactants and products?

$4NH_3(g)+5O_2(g)4\rightarrow NO(g)+6H_2O(g)$

ii) $2N_2O_5\ 2NO_2+O_2$
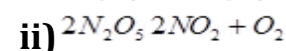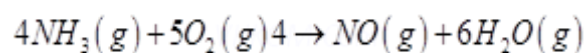
Question 4. **.** The reaction $2N_2O_5(g)\rightarrow 2NO_2(g)+O_2(g)$ was studied and the following data were collected:

S.no (mol/L/min)	$[N_2O_5]$ $mol\ L^{-1}$	Rate of disappearance of $[N_2O_5]$ (mol/L/min
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine

i) **The order**
ii) **The rate law.**
iii) **Rate constant for the reaction.**

Question 5. The following experimental data was collected for the reaction:

$Cl_2(g)+2NO(g)\rightarrow 2NOCl(g)$
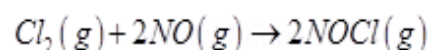
Trial	Intial conc. Of $Cl_2(mol/L)$	NO mol/L	Initial Rate,(mol/L/s)
1	0.10	0.010	1.2×10^{-4}
2	0.10	0.030	10.8×10^{-4}

3	0.20	0.030	21.6×10^{-4}

Construct the rate equation for the reaction.

Question 6. Draw a graph for

a)   Concentration   of   reactant   against   time   for   a   zero   order   reaction.
b) Log Ro/ R against time for a first order reaction.

Question 7. In general it is observed that the rate of a chemical reaction doubles with every 10^0 rise in temperature. If this generalization holds for a reaction in the temperature range 295K to 305K, what would be the activation energy for this reaction? $\left(R = 8.314 Jk^{-1}mol^{-1}\right)$

Question 8. The rate constant for a reaction is $1.5\times10^7 s^{-1}$ at $50^0 C$ and $4.5\times10^7 s^{-1}$ at $100^0 C$. Calculate the value of activation energy for the reaction $R = 8.314\ JK^{-1}mol^{-1}$?

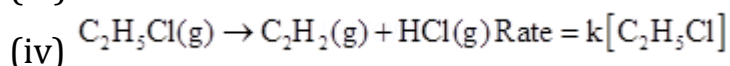Question 9. Plot a graph showing variation of potential energy with reaction. coordinate?
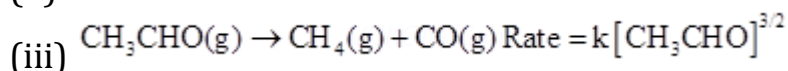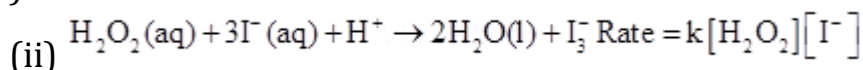
Question 10. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Long Questions:

Question 1. .The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a

Question 2. The activation energy for the reaction $2HI_{(g)} \rightarrow H_2 + I_{2(g)}$ is $209.5\,kJ\,mol^{-1}$ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Question 3. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

) $3NO(g) \rightarrow N_2O(g)\ Rate = k[NO]^2$

(ii) $H_2O_2(aq) + 3I^-(aq) + H^+ \rightarrow 2H_2O(l) + I_3^-\ Rate = k[H_2O_2][I^-]$

(iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)\ Rate = k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)\ Rate = k[C_2H_5Cl]$
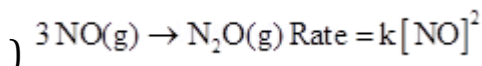
Question 4. The decomposition of NH_3 on platinum surface is zero order reaction. What are

the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \, mol^{-1} L \, s^{-1}$?

Question 5. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by Rate = $k[CH_3OCH_3]^{3/2}$. The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the

partial pressure of dimethyl ether, i.e., $Rate = k\left(P_{CH_3OCH_3}\right)^{3/2}$ If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: The rate ofreaction is always negative.

Reason: Minus sign used in expressing the rate shows that concentration of product is decreasing.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertionss.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Kinetics explains the reaction mechanism.

Reason: Kinetics explains the formation of products.

Case Study Questions:

1. In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction'. Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.
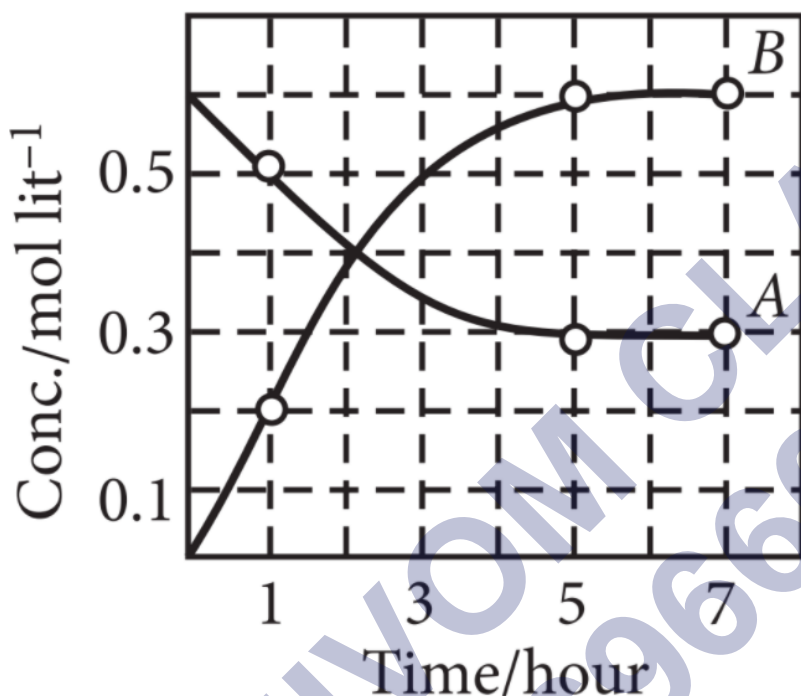
The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The rate constant of a reaction is found to be 3×10^{-3} mol^{-2} L^2 sec^{-1}. The order of the reaction is:

    a) 0.5
    b) 2
    c) 3
    d) 1

(ii) In the reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is:

    a) The same as rate of consumption of A.
    b) The same as the rate of consumption of B.
    c) Twice the rate of consumption of A.
    d) 3232 times the rate of consumption of B.

(iii) Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2 [B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

    a) 9 times
    b) 27 times
    c) 18 times
    d) 8 times

(iv) The rate of a certain reaction is given by, rate = $k[H^+]^n$. The rate increases 100 times when the pH changes from 3 to 1. The order (n) of the reaction is:

    a) 2
    b) 0
    c) 1
    d) 1.5

(v) In a chemical reaction A + 2B → products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. The order of the reaction is:

    a) 1
    b) 2
    c) 3
    d) 4

2. The progress of the reaction, A ⇌ nB with time is represented in the following figure:

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) What is the value of n?

    a) 1
    b) 2
    c) 3
    d) 4

(ii) Find the value of the equilibrium constant.

    a) 0.6M
    b) 1.2M
    c) 0.3M
    d) 2.4M

(iii) The initial rate of conversion of A will be:

    a) 0.1 mol $L^{-1}hr^{-1}$
    b) 0.2 mol $L^{-1}hr^{-1}$
    c) 0.4 mol $L^{-1}hr^{-1}$
    d) 0.8 mol $L^{-1}hr^{-1}$

(iv) For the reaction, if $\dfrac{d[B]}{dt} = 2 \times 10^{-4}$, value of $\dfrac{d[A]}{dt}$ will be:

    a) 2×10^{-4}
    b) 10^{-4}
    c) 4×10^{-4}
    d) 0.5×10^{-4}

(v) Which factor has no effect on rate of reaction?

    a) Temperature.
    b) Nature of reactant.
    c) Concentration of reactant.
    d) Molecularity.

Answers key

MCQ Answer:

1.   Answer: (a) $2 \times 10^{-2}\ s^{-1}$

2.   Answer: (a) $-\dfrac{E_a}{R}$

3.   Answer: (a) mol $L^{-1}s^{-1}$

4.   Answer: (b) decreasing activation energy

5.   Answer: (a) mol^{-1} litre s^{-1}

6.   Answer: (d) 1

7.   Answer: (b) increase by a factor of 4

8.   Answer: (c) s^{-1}

9.   Answer: (b) 3.465×10^{-3} s

10. Answer: (d) third

Very Short Answers:

1. No. rate of a reaction is not always constant. It depends on many factors such as concentration, temperature etc.

2. Yes, decomposition of ammonia on a hot platinum surface is a zero order of reaction at high pressure

3. Answer: The rate law is the expression in which rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

4. Answer: No, the rate law cannot be predicted by merely looking at the balanced chemical equation but must be determined experimentally.

5. Answer: The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical Kinetics.

6. Answer: Rate of reaction can be defined as the change in concentration of a reactant or product per unit time. Factors affecting the rate of reaction are temperature, concentration of reactants and catalyst.

7. Answer: Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration of reactant or product by the time interval
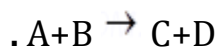
   For the reaction: $A \rightarrow B$ R_{av}

   $$= \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

8. The units of rate of a reaction are Mol $L^{-1}S^{-1}$ In gaseous reaction the unit of rate of reaction is atom .

9. a) Since the units of rate constant are $Lmol^{-1}s^{-1}$ The reactions is of second order.
   b) Since the units of rate constant are s^{-1}, The reaction is of first order

10. The rate law will be $R = K[NO]^2[H_2]$

Short Answers:

1. Answer

. A+B $\rightarrow$ C+D

$Rate[A]^x$

Rate = 1 when A = 1 ———- 1)
Rate = 2 when A = 2————-2)
Dividing equation 2) by 1)

$\frac{2}{1} \alpha \frac{(2)^x}{1^x}$

$2^1 \alpha (2)^x$

$\therefore x = 1$

The reaction is first order reaction.

2. Answer:

2A $\rightarrow$ 4B
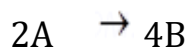
$-\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt} = \frac{d[C]}{dt}$

i)   Rate of disappearance of B

$= \frac{\frac{5 \times 10^{-3}}{10\ 5} mol\ /L^{-1}}{} = 5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

$\frac{-d[A]}{dt} = \frac{2}{4} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$

ii) $= \frac{1}{2} \times 5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$ $= 2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

3. Answer:

In terms of reactant	In terms of products
i) $R_1 = \frac{-1}{4} \frac{\Delta[NH_3]}{\Delta t}$	$R_3 = \frac{1}{4} \frac{\Delta[NO]}{\Delta t}$
$R_2 = \frac{-1}{5} \frac{\Delta[O_2]}{\Delta t}$	$R_4 = \frac{1}{6} \frac{\Delta[H_2O]}{\Delta t}$

$\frac{1}{4} R_1 = \frac{1}{5} R_2 = \frac{1}{4} R_3 = \frac{1}{6} R_4$

$-\frac{1}{4} \frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[O_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO]}{\Delta t} = \frac{1}{6} \frac{\Delta[H_2O]}{\Delta t}$

II) In terms of reactant	In terms of product
$R1 = -\dfrac{\Delta[N_2O_5]}{\Delta t}$	$R_2 = \dfrac{\Delta[NO_2]}{\Delta t}$
	$R_3 = \dfrac{\Delta[O_2]}{\Delta t}$

$$\frac{1}{2}R_1 = \frac{1}{2}R_2 = R_3 \quad -\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

4. Answer:

Let the order of reaction be x

$Rate = K[N_2O_5]^x$

i) From the data –

$34 \times 10^{-5} = (1.13 \times 10^{-2})^x$ ————-1)

$25 \times 10^{-5} = (0.84 \times 10^{-2})^x$ ————-2)

$18 \times 10^{-5} = (0.62 \times 10^{-2})^x$ ————-3)

Dividing 1) by 2)

$$\frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \left(\frac{1.13 \times 10^{-2}}{0.84 \times 10^{-2}}\right)^x$$

$(1.36) = (1.35)^x$

X=1

The order of reaction with respect with respect to N_2O_5 is 1
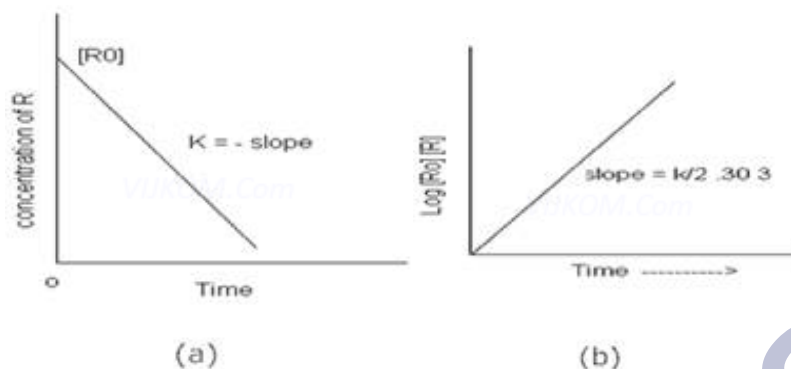
ii) Rate law $R = K[N_2O_5]$

iii) Rate constant , K = $\dfrac{Rate}{[N_2O_5]}$ = $\dfrac{18 \times 10^{-5} \text{ mol/L/min}}{0.62 \times 10^{-2} \text{ mol/L}}$ = $0.29 \ min^{-1}$

5. Answer :

Order of NO is 2

Rate law = $K[Cl_2][NO]^2$

6. Answer

(a)   (b)

7. Answer:

$$T_1 = 295K \quad T_2 = 305K$$

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

$$K_2 = 2k_1$$

$$E_a = 2.303 \times 8.314 \times \left[\frac{305 \times 295}{305 - 295} \right] \log \frac{2k_1}{k_1}$$

$$= 2.303 \times 8.314 \times 8997.5 K \log 2$$
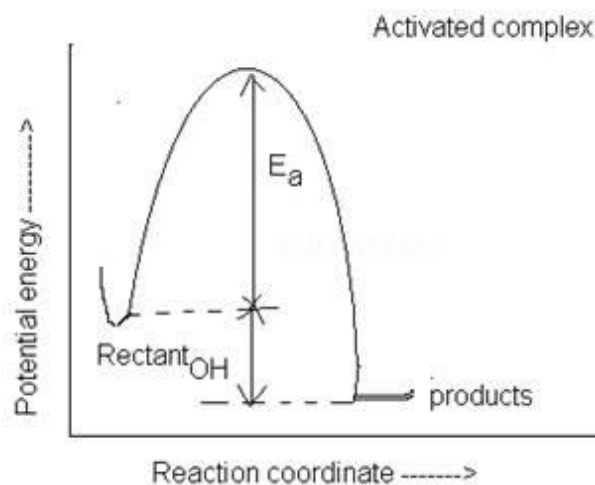
= 51855.2 J/mol   (log2 = 0.3010)

8. Answer:

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{Ea}{2.303 \times 3.314} \left(\frac{373 - 323}{373 \times 323} \right)$$

$$\log 1.5 = \frac{Ea}{2.303 \times 3.314} \left(\frac{50}{373 \times 323} \right)$$

$$Ea = \left(\frac{2.303 \times 3.314 \times 373 \times 323}{50} \right) \times \log 1.5$$

$$= 22 \, KJ \, / \, mol$$

9. Answer :

10. Answer :

The reaction $X \rightarrow Y$ follows second order kinetics.
Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)

Let X = a mol^{-1}, then equation (1) can be written as:

$Rate_1 = k.(a)_2$

$= ka_2$

If the concentration of X is increased to three times, then X = $3 \, a \, mol \, L^{-1}$
Now, the rate equation will be:

Rate = $k(3a)_2$

$= 9(ka^2)$

Hence, the rate of formation will increase by 9 times.

Long Answers:

1. **Answer:**

It is given that $T1 = 298$ K
Therefore, $T_2 = (298+10)K$
= 308 K
We also know that the rate of the reaction doubles when temperature is increased by $10°$.

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$
Also, $R = 8.314 \, JK^{-1} mol^{-1}$
Now, substituting these values in the equation:

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

We get:

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

$$= 52897.78 \, J \, mol^{-1}$$

$$= 52.9 \, kJ \, mol^{-1}$$

2. Answer:

In the given case:

$$E_a = 209.5 \, kJ \, mol^{-1} = 209500 \, J \, mol^{-1}$$

$T = 581$ K

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

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

$$x = e^{-E_a/RT}$$

In $x = -E_a / RT$

$$\log x = -\frac{E_a}{2.303 \, RT}$$

$$\log x = \frac{209500 \, J \, mol^{-1}}{2.303 \times 8.314 \, J \, K^{-1} \, mol^{-1} \times 581} = 18.8323$$

Now, x = Anti log (18.8323)

= Anti log $\overline{19.1677}$

1.471×10^{-19}

3. Answer:

(i) Given rate = $k[NO]^2$

Therefore, order of the reaction = 2

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

Dimension of

$$= \frac{mol \, L^{-1} s^{-1}}{(mol \, L^{-1})^2}$$

$$= \frac{mol \, L^{-1} s^{-1}}{mol^2 L^{-2}}$$

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

(ii) Given rate = $k[H_2O_2][I^-]$

Therefore, order of the reaction = 2

Dimension of $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]}$

$= \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})}$

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

(iii) Given rate = $k[CH_3CHO]^{3/2}$

Therefore, order of reaction = $\dfrac{3}{2}$

Dimension of $k = \dfrac{\text{Rate}}{[CH_3CHO]^{\frac{3}{2}}}$

$= \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{\frac{3}{2}}}$

$= \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol}^{\frac{3}{2}}\text{L}^{-\frac{3}{2}}}$

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

(iv) Given rate = $k[C_2H_5Cl]$

Therefore, order of the reaction = 1
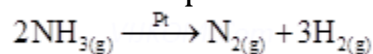
Dimension of $k = \dfrac{\text{Rate}}{[C_2H_5Cl]}$

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

$= \text{s}^{-1}$

4. Answer:

The decomposition of NH_3 on platinum surface is represented by the following equation.

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

Therefore, $\text{Rate} = -\dfrac{1}{2}\dfrac{d[NH_3]}{dt} = \dfrac{d[N_2]}{dt} = \dfrac{1}{3}\dfrac{d[H_2]}{dt}$

However, it is given that the reaction is of zero order.

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$

Therefore, $= 2.5 \times 10^{-4} \, mol \, L^{-1} s^{-1}$

Therefore, the rate of production of N_2 is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \, mol \, L^{-1} s^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \, mol \, L^{-1} s^{-1}$$
$$= 7.5 \times 10^{-4} \, mol \, L^{-1} s^{-1}$$

5. **Answer:**

   If pressure is measured in bar and time in minutes, then

   Unit of rate = $bar \, min^{-1}$

   $$Rate = k \left(P_{CH_3OCH_3} \right)^{3/2}$$

   $$k = \frac{Rate}{\left(P_{CH_3OCH_3} \right)^{3/2}}$$

   Therefore, unit of rate constants $(k) = \dfrac{bar \, min^{-1}}{bar^{3/2}}$

   $= bar^{-1/2} \, min^{-1}$

Assertion and Reason Answers:

1. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

Kinetics deals with the reaction mechanism i.e., how the atoms rearrange themselves in the reactant molecules in a single step or a number of steps, finally leading to the product molecules.

Case Study Answers:

1. Answer :

i. (c) 3

Explanation:

Unit of k for n^{th} order = $(mot \ L^{-1})^{1-n} \ sec^{-1}$

Here, k = $3 \times 10^{-3} \ mol^{-2} \ L^2 \ sec^{-1}$

Unit of k = $mol^{-2} \ L^2 \ sec^{-1} \Rightarrow (mol \ L^{-1})^{-2} \ sec^{-1}$

Comparing (i) and (ii) we get, 1 - n = -2 $\Rightarrow$ n = 3

ii. (c) twice the rate of consumption of A.

Explanation:

$$Rate = \frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

iii. (c) 18 times

Explanation:

Given, $R_1 = k[A]^2 [B]$

According to question, $R_2 = k[3A]^2 [2B]$

$= k \times 9 [A]^2 \times 2[B] = 18 \times k[A]^2 [B] = 18 R_1$

iv. (c) 1

Explanation:

Rate (r) = $k[H^+]^n$

When pH = 3 ; $[H^+] = 10^{-3}$

and when pH = 1 ; $[H^+] = 10^{-1}$

$$\therefore \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \Rightarrow \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n (\because r_2 = 100r_1)$$

$$\Rightarrow (10^{-2})^1 = (10^{-2})^n \Rightarrow n = 1$$

V. (b) 2

Explanation:

Let the order of reaction w.r.t. A is x and w.r.t. B is y.

$$r_1 = k[A]^x[B]^y$$

$$r_2 = k[2A]^x[B]^y$$

$$r_3 = k[A]^x[2B]^y$$

$$\frac{r_1}{r_2} = \frac{k[A]^x[B]^y}{k[2A]^x[B]^y}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly, $\dfrac{r_1}{r_3} = \dfrac{k[A]^x[B]^y}{k[A]^x[2B]^y}$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Hence the rate law equation is

Rate = $k[A]^2[B]^0 \Rightarrow$ Order of reaction = 2

2. Answer :

i. (b) 2

Explanation:

According to the figure,

in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3M,

while in the same time concentration of B increases from 0.2 to 0.6 M.

Decrease in concentration of A in 4 hours

= 0.5 - 0.3 = 0.2M

Increase in concentration of B in 4 hours

= 0.6 - 0.2 = 0.4M

Thus, increase in concentration of B in a given time is

twice the decrease in concentration of A. Thus, n = 2.

ii. (b) 1.2M

Explanation:
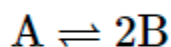
$$K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2M$$

iii. (a) 0.1 mol $L^{-1}hr^{-1}$

Explanation:

From t = 0 to t = 1hr,

For A, dx = 0.6 - 0.5 = 0.1 mol L^{-1}

$\therefore$ Initial rate of conversion of $A = \frac{dx}{dt}$

$$= \frac{0.1 \text{ mol } L^{-1}}{1hr} = 0.1 \text{ mol } L^{-1}hr^{-1}$$

iv. (b) 10^{-4}

Explanation:

$$A \rightleftharpoons 2B$$

$$-\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$$

$$= \frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$$

v. (d) Molecularity.

Explanation:

The number of reacting species (atoms, ions or molecules)

taking part in an elementary reaction is called molecularity

and it has no influence on the rate of reaction.