

UNIT 7

CHEMICAL KINETICS



Svante August Arrhenius
(1859 – 1927)

Svante August Arrhenius was a Swedish scientist. Arrhenius was one of the founders of the science of physical chemistry. He focused his attention on the conductivities of electrolytes. He proposed that crystalline salts dissociate into paired charged ions when dissolved in water, for which he received the Nobel Prize for Chemistry in 1903. He also proposed definitions for acids and bases. He formulated the concept of activation energy.



Learning Objectives

After studying this unit, the students will be able to

- * define the rate and order of a reaction,
- * derive the integrated rate equations for zero and first order reactions,
- * describe the half life period,
- * describe the collision theory,
- * discuss the temperature dependence of the rate of a reaction, and
- * explain various factors which affect the rate of a reaction.

INTRODUCTION

We have already learnt in XI standard that the feasibility of a chemical reaction under a given set of conditions can be predicted, using the principles of thermodynamics. However, thermodynamics does not provide an answer to a very important question of how fast a chemical reaction takes place. We know from our practical experience that all chemical reactions take some time for completion. Reaction speeds ranging from extremely fast (in femto seconds) to extremely slow (in years). For example, when the reactants BaCl_2 solution and dilute H_2SO_4 are just mixed, a white precipitate of BaSO_4 is immediately formed; on the other hand reactions such as rusting of Iron take many years to complete. The answers to the questions such as (i) how fast a chemical change can occur and (ii) What happens in a chemical reaction during the period between the initial stage and final stage are provided by the chemical kinetics. The word kinetics is derived from the Greek word “kinesis” meaning movement.

Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.

The study of chemical kinetics not only help us to determine the rate of a chemical reaction, but also useful in optimizing the process conditions of industrial manufacturing processes, organic and inorganic synthesis etc.

In this unit, we discuss the rate of a chemical reaction and the factors affecting it. We also discuss the theories of the reaction rate and temperature dependence of a chemical reaction.

7.1 Rate of a chemical reaction:

A rate is a change in a particular variable per unit time. You have already learnt in physics that change in the displacement of a particle per unit time gives its velocity. Similarly in a chemical reaction, the change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

Let us consider a simple general reaction



The concentration of the reactant ($[A]$) can be measured at different time intervals. Let the concentration of A at two different times t_1 and t_2 , ($t_2 > t_1$) be $[A_1]$ and $[A_2]$ respectively. The rate of the reaction can be expressed as

$$\text{Rate} = \frac{- [\text{Change in the concentration of the reactants}]}{(\text{Change in time})}$$

$$\text{i.e., Rate} = \frac{-([A_2] - [A_1])}{(t_2 - t_1)} = - \left(\frac{\Delta[A]}{\Delta t} \right) \dots (7.1)$$

During the reaction, the concentration of the reactant decreases i.e. $[A_2] < [A_1]$ and hence the change in concentration $[A_2] - [A_1]$ gives a negative value. By convention the reaction rate is a positive one and hence a negative sign is introduced in the rate expression (equation 7.1)

If the reaction is followed by measuring the product concentration, the rate is given by $\left(\frac{\Delta[B]}{\Delta t} \right)$ since $[B_2] > [B_1]$, no minus sign is required here.

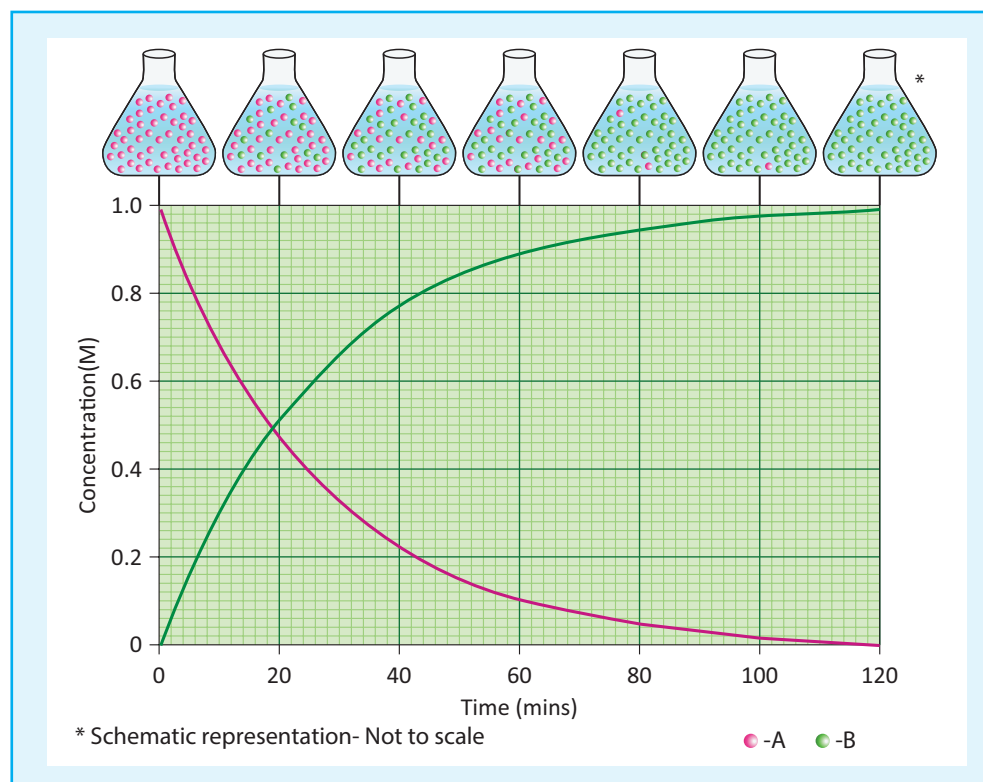


Fig 7.1 change in concentration of A and B for the reaction $A \longrightarrow B$

Unit of rate of a reaction:

$$\text{unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}}$$

Usually, concentration is expressed in number of moles per litre and time is expressed in seconds and therefore the unit of the rate of a reaction is $\text{mol L}^{-1}\text{s}^{-1}$. Depending upon the nature of the reaction, minute, hour, year etc can also be used.

For a gas phase reaction, the concentration of the gaseous species is usually expressed in terms of their partial pressures and in such cases the unit of reaction rate is atm s^{-1} .

7.1.1 Stoichiometry and rate of a reaction:

In a reaction $A \longrightarrow B$, the stoichiometry of both reactant and product are same, and hence the rate of disappearance of reactant (A) and the rate of appearance of product (B) are same.

Now, let us consider a different reaction



In this case, for every mole of A, that disappears two moles of B appear, i.e., the rate of formation of B is twice as fast as the rate of disappearance of A. therefore, the rate of the reaction can be expressed as below

$$\text{Rate} = \frac{+d[B]}{dt} = 2 \left(\frac{-d[A]}{dt} \right)$$

In other words,

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

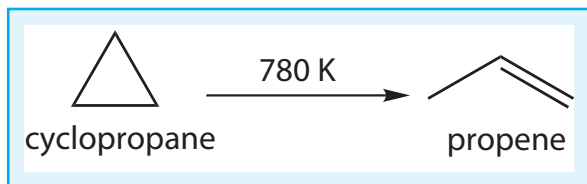
For a general reaction, the rate of the reaction is equal to the rate of consumption of a reactant (or formation of a product) divided by its coefficient in the balanced equation



$$\text{Rate} = \frac{-1}{x} \frac{d[A]}{dt} = \frac{-1}{y} \frac{d[B]}{dt} = \frac{1}{l} \frac{d[C]}{dt} = \frac{1}{m} \frac{d[D]}{dt}$$

7.1.2 Average and instantaneous rate:

Let us understand the average rate and instantaneous rate by considering the isomerisation of cyclopropane.



The kinetics of the above reaction is followed by measuring the concentration of cyclopropane at regular intervals and the observations are shown below. (Table 7.1)

Table 7.1 Concentration of cyclopropane at various times during its isomerisation at 780K

| Time (min) | [cyclopropane] (mol L ⁻¹) |
|--------------|---|
| 0 | 2.00 |
| 5 | 1.67 |
| 10 | 1.40 |
| 15 | 1.17 |
| 20 | 0.98 |
| 25 | 0.82 |
| 30 | 0.69 |

$$\text{Rate of the reaction} = \frac{-\Delta [\text{cyclopropane}]}{\Delta t}$$

$$\begin{aligned} \text{The rate over the entire 30 min} &= \frac{-(0.69-2) \text{ mol L}^{-1}}{(30-0) \text{ min}} \\ &= \frac{1.31}{30} = 4.36 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

It means that during the first 30 minutes of the reaction, the concentration of the reactant (cyclo propane) decreases as an average of $4.36 \times 10^{-2} \text{ mol L}^{-1}$ each minute.

Let us calculate the average rate for an initial and later stage over a short period.

$$\begin{aligned} (\text{Rate})_{\text{initial stage}} &= \frac{-(2.0-1.4)}{(10-0)} \\ &= \frac{0.6}{10} = 6 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} \\ (\text{Rate})_{\text{later stage}} &= \frac{-(0.69-0.98)}{(30-20)} \\ &= \frac{0.29}{10} = 2.9 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

From the above calculations, we come to know that the rate decreases with time as the reaction proceeds and the average rate cannot be used to predict the rate of the reaction at any instant. The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,

As $\Delta t \rightarrow 0$;

$$\frac{-\Delta [\text{cyclopropane}]}{\Delta t} = \frac{-d[\text{cyclopropane}]}{dt}$$

A plot of [cyclopropane] Vs (time) gives a curve as shown in the figure 7.2.

Instantaneous rate at a particular instant 't' $\frac{-d[\text{cyclopropane}]}{dt}$ is obtained by calculating the slope of a tangent drawn to the curve at that instant.

In general, the instantaneous reaction rate at a moment of mixing the reactants is calculated from the slope of the tangent drawn to the curve at mol L^{-1} , the rate calculated by this method is called initial rate of a reaction.

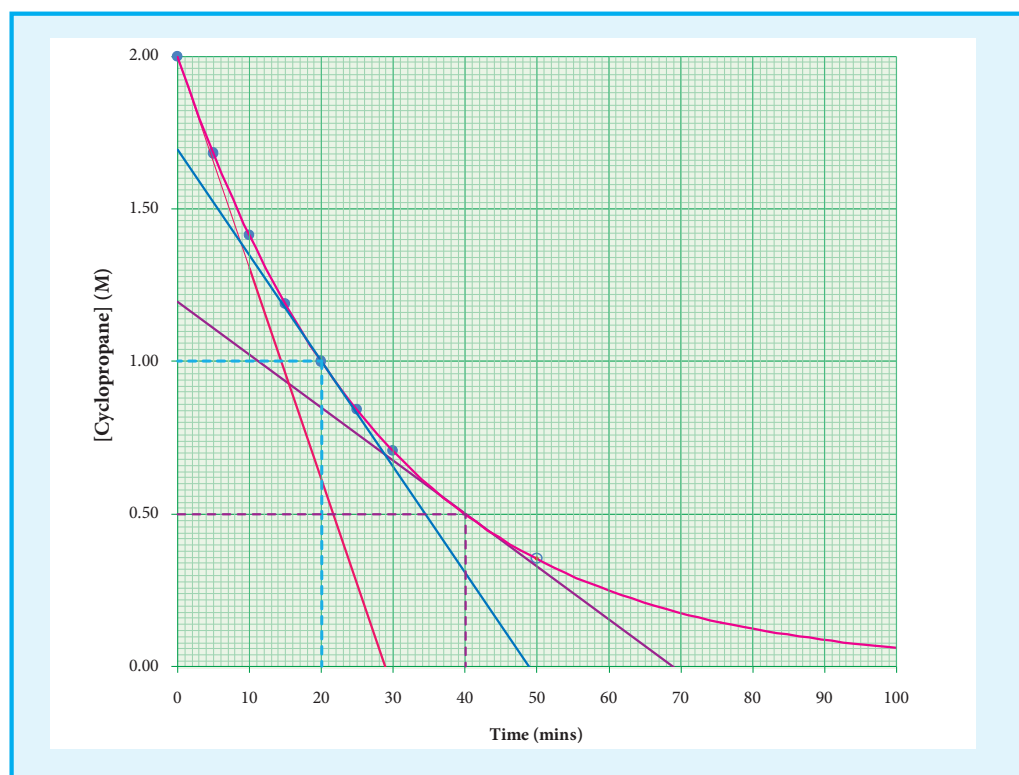


Fig 7.2 Concentration of cyclopropane vs time - graph

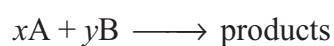
Let us calculate the instantaneous rate of isomerisation cyclopropane at different concentrations: 2 M, 1M and 0.5 M from the graph shown in fig 7.2, the results obtained are tabulated below.

| [cyclopropane] mol L ⁻¹ | Rate mol L ⁻¹ min ⁻¹ |
|---------------------------------------|--|
| 2 | 6.92×10^{-2} |
| 1 | 3.46×10^{-2} |
| 0.5 | 1.73×10^{-2} |

Table 7.2 Rate of isomerisation

7.3 Rate law and rate constant:

We have just learnt that, the rate of the reaction depends upon the concentration of the reactant. Now let us understand how the reaction rate is related to concentration by considering the following general reaction.



The rate law for the above reaction is generally expressed as

$$\text{Rate} = k [\text{A}]^m [\text{B}]^n$$

Where k is proportionality constant called the rate constant. The values of m and n represent the reaction order with respect to A and B respectively. The overall order of the reaction is given by $(m+n)$. The values of the exponents (m and n) in the rate law must be determined by experiment. They cannot be deduced from the Stoichiometry of the reaction. For example, consider the isomerisation of cyclopropane, that we discussed earlier.

The results shown in table 7.2 indicate that if the concentration of cyclopropane is reduced to half, the rate also reduced to half. It means that the rate depends upon [cyclopropane] raised to the first power

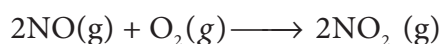
$$\text{i.e., Rate} = k[\text{cyclopropane}]^1$$

$$\Rightarrow \frac{\text{Rate}}{[\text{cyclopropane}]} = k$$

Table 7.3 Rate constant for isomerisation

| Rate mol L ⁻¹ min ⁻¹ | [cyclopropane] mol L ⁻¹ | $k = \frac{\text{Rate}}{[\text{cyclopropane}]}$ |
|---|---------------------------------------|---|
| 6.92×10^{-2} | 2 | 3.46×10^{-2} |
| 3.46×10^{-2} | 1 | 3.46×10^{-2} |
| 1.73×10^{-2} | 0.5 | 3.46×10^{-2} |

Let us consider an another example, the oxidation of nitric oxide (NO)



Series of experiments are conducted by keeping the concentration of one of the reactants constant and the changing the concentration of the others.

| Experiment | [NO] X 10 ⁻² (mol L ⁻¹) | [O ₂] X 10 ⁻² (mol L ⁻¹) | Initial rate x 10 ⁻² (mol L ⁻¹ min ⁻¹) |
|------------|---|--|---|
| 1 | 1.3 | 1.1 | 19.26 |
| 2 | 1.3 | 2.2 | 38.40 |
| 3 | 2.6 | 1.1 | 76.80 |

$$\text{Rate} = k [\text{NO}]^m [\text{O}_2]^n$$

For experiment 1, the rate law is

$$\begin{aligned} \text{Rate}_1 &= k [\text{NO}]^m [\text{O}_2]^n \\ 19.26 \times 10^{-2} &= k [1.3]^m [1.1]^n \quad \dots(1) \end{aligned}$$

Similarly for experiment 2

$$\text{Rate}_2 = k [\text{NO}]^m [\text{O}_2]^n$$

$$38.40 \times 10^{-2} = k [1.3]^m [2.2]^n \quad \dots(2)$$

For experiment 3

$$\text{Rate}_3 = k [\text{NO}]^m [\text{O}_2]^n$$

$$76.8 \times 10^{-2} = k [2.6]^m [1.1]^n \quad \dots(3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{38.40 \times 10^{-2}}{19.26 \times 10^{-2}} = \frac{k [1.3]^m [2.2]^n}{k [1.3]^m [1.1]^n}$$

$$2 = \left(\frac{2.2}{1.1} \right)^n$$

$$2 = 2^n \quad \text{i.e., } n=1$$

Therefore the reaction is first order with respect to O₂

$$\frac{(3)}{(1)} \Rightarrow \frac{76.8 \times 10^{-2}}{19.26 \times 10^{-2}} = \frac{k [2.6]^m [1.1]^n}{k [1.3]^m [1.1]^n}$$

$$4 = \left(\frac{2.6}{1.3} \right)^m$$

$$4 = 2^m \quad \text{i.e., } m=2$$

Therefore the reaction is second order with respect to NO

$$\text{The rate law is } \text{Rate}_1 = k [\text{NO}]^2 [\text{O}_2]^1$$

$$\text{The overall order of the reaction} = (2 + 1) = 3$$

Differences between rate and rate constant of a reaction:

| s.no | Rate of a reaction | Rate constant of a reaction |
|------|--|----------------------------------|
| 1 | It represents the speed at which the reactants are converted into products at any instant. | It is a proportionality constant |

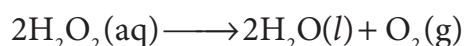
| s.no | Rate of a reaction | Rate constant of a reaction |
|------|--|---|
| 2 | It is measured as decrease in the concentration of the reactants or increase in the concentration of products. | It is equal to the rate of reaction, when the concentration of each of the reactants in unity |
| 3 | It depends on the initial concentration of reactants. | It does not depend on the initial concentration of reactants. |

7.4 Molecularity:

Kinetic studies involve not only measurement of a rate of reaction but also proposal of a reasonable reaction mechanism. Each and every single step in a reaction mechanism is called an elementary reaction.

An elementary step is characterized by its molecularity. The total number of reactant species that are involved in an elementary step is called molecularity of that particular step. Let us recall the hydrolysis of t-butyl bromide studied in XI standard. Since the rate determining elementary step involves only t-butyl bromide, the reaction is called a Unimolecular Nucleophilic substitution (S_N^1) reaction.

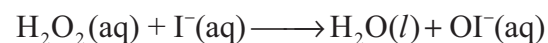
Let us understand the elementary reactions by considering another reaction, the decomposition of hydrogen peroxide catalysed by I^- .



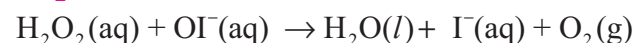
It is experimentally found that the reaction is first order with respect to both

H_2O_2 and I^- , which indicates that I^- is also involved in the reaction. The mechanism involves the following steps.

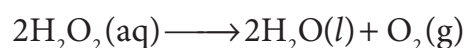
Step:1



Step : 2



Overall reaction is



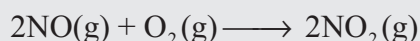
These two reactions are elementary reactions. Adding equ (1) and (2) gives the overall reaction. Step 1 is the rate determining step, since it involves both H_2O_2 and I^- , the overall reaction is bimolecular.

Differences between order and molecularity:

| s.no | Order of a reaction | Molecularity of a reaction |
|------|--|---|
| 1 | It is the sum of the powers of concentration terms involved in the experimentally determined rate law. | It is the total number of reactant species that are involved in an elementary step. |
| 2 | It can be zero (or) fractional (or) integer | It is always a whole number, cannot be zero or a fractional number. |
| 3 | It is assigned for a overall reaction. | It is assigned for each elementary step of mechanism. |

Example 1

Consider the oxidation of nitric oxide to form NO_2



(a). Express the rate of the reaction in terms of changes in the concentration of NO , O_2 and NO_2 .

(b). At a particular instant, when $[\text{O}_2]$ is decreasing at $0.2 \text{ mol L}^{-1}\text{s}^{-1}$ at what rate is $[\text{NO}_2]$ increasing at that instant?

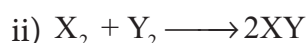
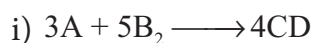
Solution:

$$\text{a) Rate} = \frac{-1}{2} \frac{d[\text{NO}]}{dt} = \frac{-d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

$$\begin{aligned} \text{b) } \frac{-d[\text{O}_2]}{dt} &= \frac{1}{2} \frac{d[\text{NO}_2]}{dt} \\ \frac{d[\text{NO}_2]}{dt} &= 2 \times \left(\frac{-d[\text{O}_2]}{dt} \right) = 2 \times 0.2 \text{ mol L}^{-1}\text{s}^{-1} \\ &= 0.4 \text{ mol L}^{-1}\text{s}^{-1} \end{aligned}$$

Evaluate yourself 1

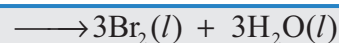
1). Write the rate expression for the following reactions, assuming them as elementary reactions.



2). Consider the decomposition of $\text{N}_2\text{O}_5(\text{g})$ to form $\text{NO}_2(\text{g})$ and $\text{O}_2(\text{g})$. At a particular instant N_2O_5 disappears at a rate of $2.5 \times 10^{-2} \text{ mol dm}^{-3}\text{s}^{-1}$. At what rates are NO_2 and O_2 formed? What is the rate of the reaction?

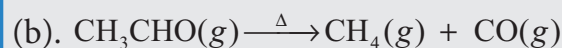
Example 2

1. What is the order with respect to each of the reactant and overall order of the following reactions?



The experimental rate law is

$$\text{Rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$$



the experimental rate law is

$$\text{Rate} = k [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$$

Solution:

a) First order with respect to Br^- , first order with respect to BrO_3^- and second order with respect to H^+ . Hence the overall order of the reaction is equal to $1 + 1 + 2 = 4$

b) Order of the reaction with respect to acetaldehyde is $\frac{3}{2}$ and overall order is also $\frac{3}{2}$

Example 3

2. The rate of the reaction $\text{x} + 2\text{y} \rightarrow \text{product}$ is $4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$, if $[\text{x}] = [\text{y}] = 0.2 \text{ M}$ and rate constant at 400K is $2 \times 10^{-2} \text{ s}^{-1}$, What is the overall order of the reaction.

Solution :

$$\text{Rate} = k [\text{x}]^n [\text{y}]^m$$

$$4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1} = 2 \times 10^{-2} \text{ s}^{-1} (0.2 \text{ mol L}^{-1})^n (0.2 \text{ mol L}^{-1})^m$$

$$\frac{4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}}{2 \times 10^{-2} \text{ s}^{-1}} = (0.2)^{n+m} (\text{mol L}^{-1})^{n+m}$$

$$0.2 (\text{mol L}^{-1}) = (0.2)^{n+m} (\text{mol L}^{-1})^{n+m}$$

Comparing the powers on both sides

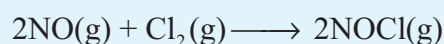
The overall order of the reaction $n + m = 1$

Evaluate yourself 2

1). For a reaction, $\text{X} + \text{Y} \longrightarrow \text{product}$; quadrupling $[\text{x}]$, increases the rate by a factor of 8. Quadrupling both $[\text{x}]$ and $[\text{y}]$,

increases the rate by a factor of 16. Find the order of the reaction with respect to x and y. what is the overall order of the reaction?

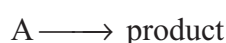
- 2). Find the individual and overall order of the following reaction using the given data.



| Experiment number | Initial concentration | | Initial rate |
|-------------------|-----------------------|-----|--|
| | NO | | NOCl mol L ⁻¹ s ⁻¹ |
| 1 | 0.1 | 0.1 | 7.8 x 10 ⁻⁵ |
| 2 | 0.2 | 0.1 | 3.12 x 10 ⁻⁴ |
| 3 | 0.2 | 0.3 | 9.36 x 10 ⁻⁴ |

7.5 The integrated rate equation:

We have just learnt that the rate of change of concentration of the reactant is directly proportional to that of concentration of the reactant. For a general reaction,



The rate law is

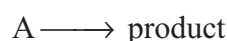
$$\text{Rate} = \frac{-d[\text{A}]}{dt} = k [\text{A}]^x$$

Where k is the rate constant, and x is the order of the reaction. The above equation is a differential equation, $\frac{-d[\text{A}]}{dt}$, so it gives the rate at any instant. However, using the above expression, we cannot answer questions such as how long will it take for a specific concentration of A to be used up in the reaction? What will be the concentration of

reactant after a time 't'? To answer such questions, we need the integrated form of the above rate law which contains time as a variable.

7.5.1 Integrated rate law for a first order reaction

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following Cl₂ first order reaction,



Rate law can be expressed as

$$\text{Rate} = k [\text{A}]^1$$

Where, k is the first order rate constant.

$$\frac{-d[\text{A}]}{dt} = k [\text{A}]^1$$

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

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration [A₀] to [A] at the later time.

$$\int_{[\text{A}_0]}^{[\text{A}]} \frac{-d[\text{A}]}{[\text{A}]} = k \int_0^t dt$$

$$(-\ln[\text{A}])_{[\text{A}_0]}^{[\text{A}]} = k(t)_0^t$$

$$-\ln[\text{A}] - (-\ln[\text{A}_0]) = k(t-0)$$

$$-\ln[\text{A}] + \ln[\text{A}_0] = kt$$

$$\ln\left(\frac{[\text{A}_0]}{[\text{A}]}\right) = kt \quad \dots(2)$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303 \log\left(\frac{[\text{A}_0]}{[\text{A}]}\right) = kt$$

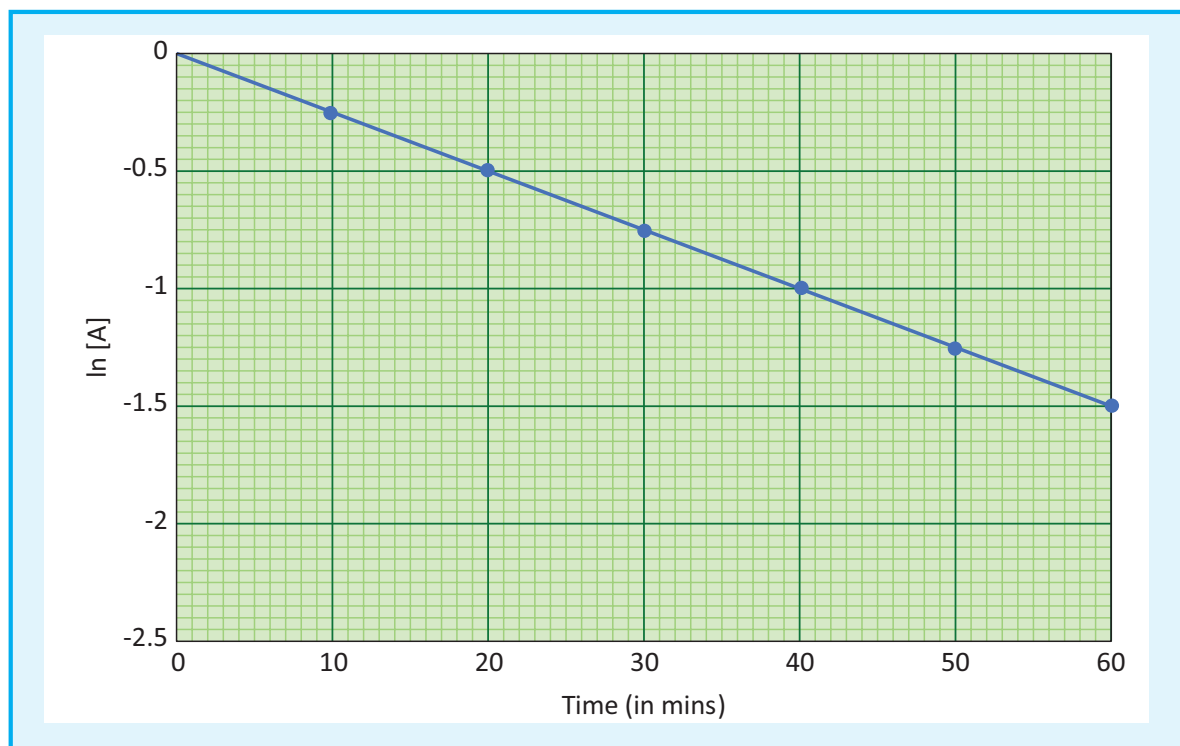


Fig: 7.3 A plot of $\ln[A]$ Vs t for a first order reaction, $A \longrightarrow \text{product}$ with initial concentration of $[A] = 1.00 \text{ M}$ and $k = 2.5 \times 10^{-2} \text{ min}^{-1}$.

$$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A]} \right) \text{ ----- (3)}$$

Equation (2) can be written in the form $y = mx + c$ as below

$$\ln[A_0] - \ln[A] = kt$$

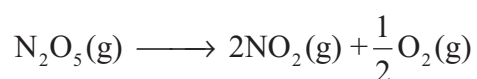
$$\ln[A] = \ln[A_0] - kt$$

$$\Rightarrow y = c + mx$$

If we follow the reaction by measuring the concentration of the reactants at regular time interval 't', a plot of $\ln[A]$ against 't' yields a straight line with a negative slope. From this, the rate constant is calculated.

Examples for the first order reaction

(i) Decomposition of dinitrogen pentoxide



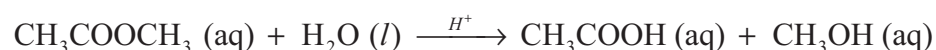
(ii) Decomposition of thionylchloride; $\text{SO}_2\text{Cl}_2(\text{l}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

(iii) Decomposition of the H_2O_2 in aqueous solution; $\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$

(iv) Isomerisation of cyclopropane to propene.

Pseudo first order reaction:

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, A second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction. Let us consider the acid hydrolysis of an ester,



$$\text{Rate} = k [\text{CH}_3\text{COOCH}_3] [\text{H}_2\text{O}]$$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e., concentration of water remains almost a constant.

Now, we can define $k [\text{H}_2\text{O}] = k'$; Therefore the above rate equation becomes

$$\text{Rate} = k' [\text{CH}_3\text{COOCH}_3]$$

Thus it follows first order kinetics.

7.5.2 Integrated rate law for a zero order reaction:

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

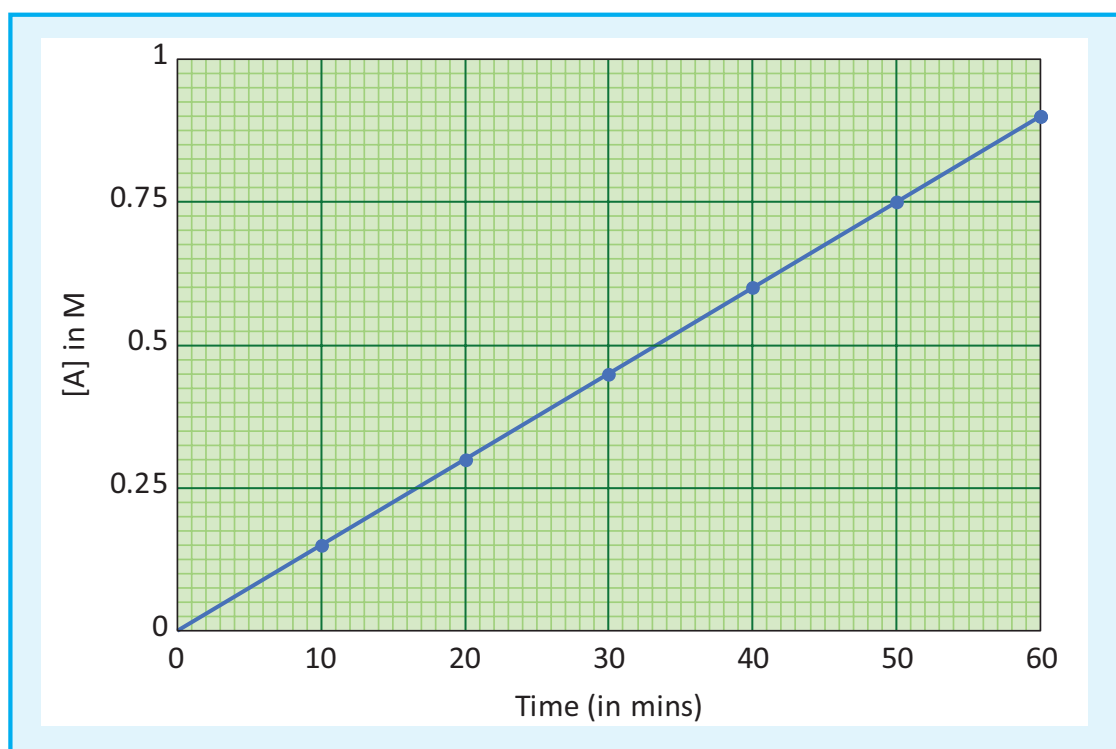
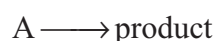


Fig 7.4 : A plot of $[A]$ Vs time for a zero order reaction $\text{A} \longrightarrow \text{product}$ with initial concentration of $[A] = 0.5\text{M}$ and $k = 1.5 \times 10^{-2} \text{mol}^{-1} \text{L}^{-1} \text{min}^{-1}$

The rate law can be written as,

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

$$\frac{-d[A]}{dt} = k (1) \quad (\because [A]^0 = 1)$$

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

Integrate the above equation between the limits of $[A_0]$ at zero time and $[A]$ at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k \int_0^t dt$$

$$-([A])_{[A_0]}^{[A]} = k(t)_0^t$$

$$[A_0] - [A] = kt$$

$$k = \frac{[A_0] - [A]}{t}$$

Equation (2) is in the form of a straight line $y = mx + c$

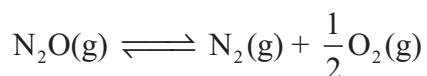
$$\text{I.e., } [A] = -kt + [A_0]$$

$$\Rightarrow y = c + mx$$

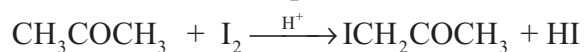
A plot of $[A]$ Vs time gives a straight line with a slope of $-k$ and y -intercept of $[A_0]$.

Examples for a zero order reaction:

1. Photochemical reaction between H_2 and I_2
 $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$
2. Decomposition of N_2O on hot platinum surface

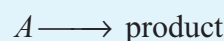


3. Iodination of acetone in acid medium is zero order with respect to iodine.



$$\text{Rate} = k [CH_3COCH_3] [H^+]$$

General rate equation for a n^{th} order reaction involving one reactant $[A]$.



$$\text{Rate law } \frac{-d[A]}{dt} = k[A]^n$$

Consider the case in which $n \neq 1$, integration of above equation between

$[A_0]$ and $[A]$ at time $t = 0$ and $t = t$ respectively gives $\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}} = (n-1)kt$

7.6 Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration.

The rate constant for a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$\text{at } t = t_{1/2}; [A] = \frac{[A_0]}{2}$$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A_0]}{[A_0]/2}$$

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

$$k = \frac{2.303 \times 0.3010}{t_{1/2}} = \frac{0.6932}{t_{1/2}}$$

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

Let us calculate the half life period for a zero order reaction.

$$\text{Rate constant, } k = \frac{[A_0] - [A]}{t}$$

$$\text{at } t = t_{1/2} ; [A] = \frac{[A_0]}{2}$$

$$k = \frac{[A_0] - \frac{[A_0]}{2}}{t_{1/2}}$$

$$k = \frac{[A_0]}{2t_{1/2}}$$

$$t_{1/2} = \frac{[A_0]}{2k}$$

Hence, in contrast to the half life of a first order reaction, the half life of a zero order reaction is directly proportional to the initial concentration of the reactant.

More to know

Half life for an n^{th} order reaction involving reactant A and $n \neq 1$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k [A_0]^{n-1}}$$

Example 4

- (i) A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. ($\log 5 = 0.6989$; $\log 10 = 1$)

Solution:

For a first order reaction,

$$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A]} \right) \quad \dots (1)$$

Let $[A_0] = 100M$

When

$t = t_{90\%}$; $[A] = 10M$ (given that $t_{90\%} = 8\text{hours}$)

$t = t_{80\%}$; $[A] = 20M$

$$k = \frac{2.303}{t_{80\%}} \log \left(\frac{100}{20} \right)$$

$$t_{80\%} = \frac{2.303}{k} \log (5) \quad \dots (2)$$

Find the value of k using the given data

$$k = \frac{2.303}{t_{90\%}} \log \left(\frac{100}{10} \right)$$

$$k = \frac{2.303}{8 \text{ hours}} \log 10$$

$$k = \frac{2.303}{8 \text{ hours}} (1)$$

Substitute the value of k in equation (2)

$$t_{80\%} = \frac{2.303}{\frac{2.303}{8 \text{ hours}}} \log (5)$$

$$t_{80\%} = 8\text{hours} \times 0.6989$$

$$t_{80\%} = 5.59\text{hours}$$

Example 5

- (ii) The half life of a first order reaction $x \longrightarrow \text{products}$ is $6.932 \times 10^4 \text{s}$ at 500K. What percentage of x would be decomposed on heating at 500K for 100 min. ($e^{0.06} = 1.06$)

Solution:

Given $t_{1/2} = 6.932 \times 10^4 \text{s}$

To solve : when $t = 100 \text{ min}$,

$$\frac{[A_0] - [A]}{[A_0]} \times 100 = ?$$

We know that

For a first order reaction, $t_{1/2} = \frac{0.6932}{k}$

$$k = \frac{0.6932}{6.932 \times 10^4}$$

$$k = 10^{-5} \text{s}^{-1}$$

$$k = \left(\frac{1}{t} \right) \ln \left(\frac{[A_0]}{[A]} \right)$$

$$10^{-5} \text{ s}^{-1} \times 100 \times 60 \text{ s} = \ln \left(\frac{[A_0]}{[A]} \right)$$

$$0.06 = \ln \left(\frac{[A_0]}{[A]} \right)$$

$$\frac{[A_0]}{[A]} = e^{0.06}$$

$$\frac{[A_0]}{[A]} = 1.06$$

$$\therefore \frac{[A_0] - [A]}{[A_0]} \times 100 \%$$

$$= \left(1 - \frac{[A]}{[A_0]} \right) \times 100 \%$$

$$= \left(1 - \frac{1}{1.06} \right) \times 100 \%$$

$$= 5.6 \%$$

Example 6

Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.

Let

$$[A_0] = 100;$$

$$\text{when } t = t_{99.9\%}; [A] = (100 - 99.9) = 0.1$$

$$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A]} \right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log \left(\frac{100}{0.1} \right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} \approx 10 \times \frac{0.69}{k}$$

$$t_{99.9\%} \approx 10 t_{1/2}$$

Evaluate yourself:

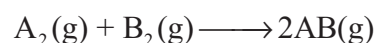
- (1) In a first order reaction $A \longrightarrow \text{products}$ 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?
- (2) The rate constant for a first order reaction is $2.3 \times 10^{-4} \text{ s}^{-1}$. If the initial concentration of the reactant is 0.01M. What concentration will remain after 1 hour?
- (3) Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.

| Time (min) | 0 | 30 | 60 | 90 |
|---|------|------|-------|------|
| Ester concentration mol L ⁻¹ | 0.85 | 0.80 | 0.754 | 0.71 |

Show that, the reaction follows first order kinetics.

7.7 Collision theory :

Collision Theory was proposed independently by Max Trautz in 1916 and William Lewis in 1918. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules. Let us understand this theory by considering the following reaction.



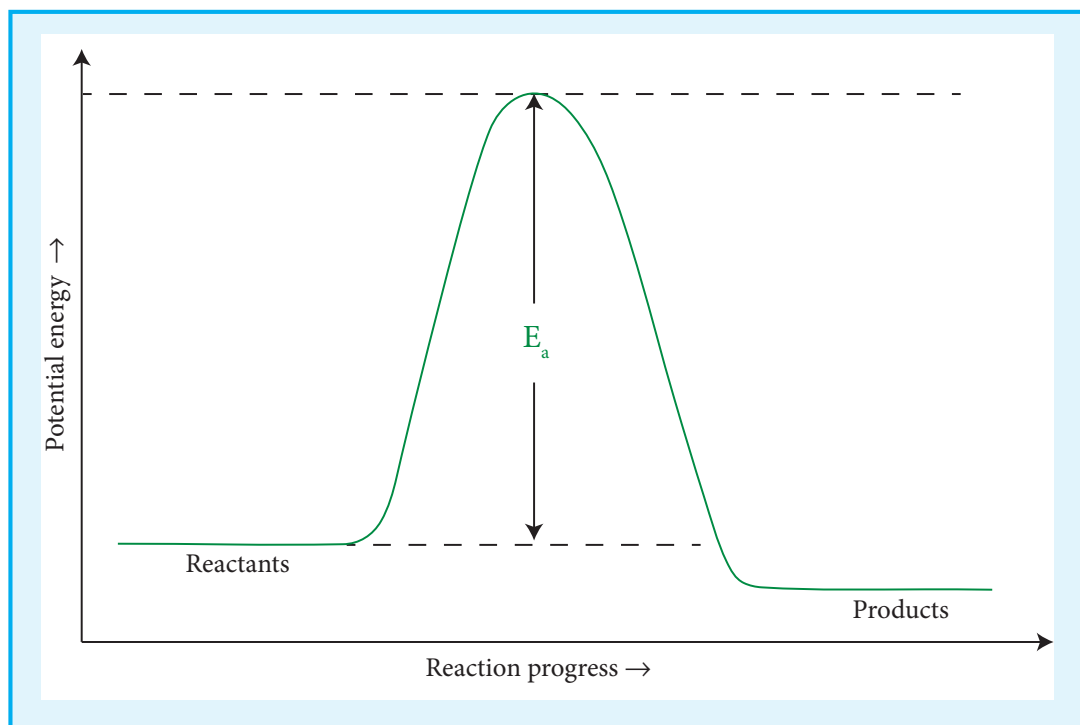


Fig 7.5 progress of the reaction

If we consider that, the reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate \propto number of molecules colliding per litre per second (collision rate)

The number of collisions is directly proportional to the concentration of both A_2 and B_2 .

$$\text{Collision rate} \propto [A_2][B_2]$$

$$\text{Collision rate} = Z [A_2][B_2]$$

Where, Z is a constant.

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., 1 collision in 10^{-9} second. Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second. In actual practice this does not happen. It implies that all collisions

are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions (f) is given by the following expression

$$f = e^{\frac{-E_a}{RT}}$$

To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of 100 kJ mol^{-1} at 300K.

$$f = e^{-\left(\frac{100 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}\right)}$$
$$f = e^{-40} \approx 4 \times 10^{-18}$$

Thus, out of 10^{18} collisions only four collisions are sufficiently energetic to convert reactants to products. This fraction of collisions is further reduced due to

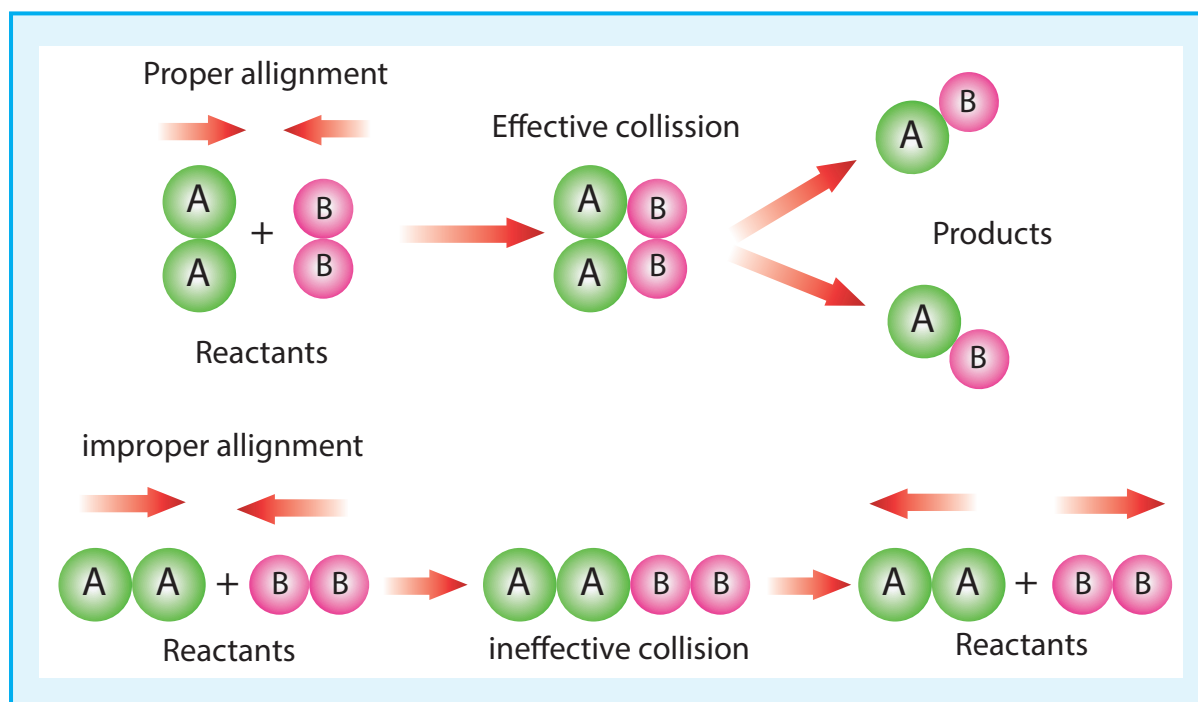


Fig 7.6 - Orientation of reactants - schematic representation

orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

The figure 7.6 illustrates the importance of proper alignment of molecules which leads to reaction.

The fraction of effective collisions (f) having proper orientation is given by the steric factor p .

$$\Rightarrow \text{Rate} = p \times f \times \text{collision rate}$$

$$\text{i.e., Rate} = p \times e^{\frac{-E_a}{RT}} \times Z [A_2][B_2] \dots (1)$$

As per the rate law,

$$\text{Rate} = k [A_2] [B_2] \dots (2)$$

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is ‘

$$k = p Z e^{\frac{-E_a}{RT}}$$

7.8 Arrhenius equation – The effect of temperature on reaction rate

Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10°C .

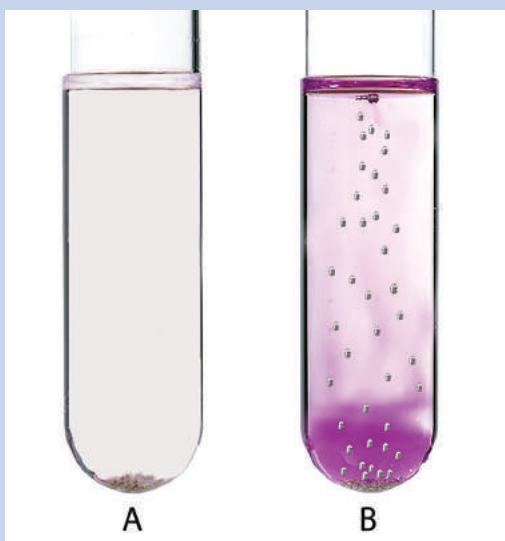
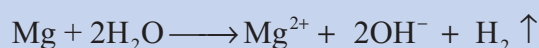
Activity

Let us understand the effect of temperature on reaction rate by doing this activity.

- Take two test tubes, label them as A and B
- Take 5 ml of cold water in A, add a drop of phenolphthalein indicator and then add Magnesium granules.
- Repeat the above with 5 ml of hot water in test tube B.

iv. Observe the two test tubes.

v. The observation shows that the solution in test tube B changes to pink colour and there is no such colour change in test tube A. That is, hot water reacts with magnesium according to the following reaction and there is no such reaction in cold water.



vi. The resultant solution is basic and it is indicated by phenolphthalein.

A large number of reactions are known which do not take place at room temperature but occur readily at higher temperatures. Example: Reaction between H_2 and O_2 to form H_2O takes place only when an electric spark is passed.

Arrhenius suggested that the rates of most reactions vary with temperature in such a way that the rate constant is directly proportional to $e^{-\left(\frac{E_a}{RT}\right)}$ and he proposed a relation between the rate constant and temperature.

$$k = Ae^{-\left(\frac{E_a}{RT}\right)} \quad \dots(1)$$

Where A the frequency factor,

R the gas constant,

E_a the activation energy of the reaction and,

T the absolute temperature (in K)

The frequency factor (A) is related to the frequency of collisions (number of collisions per second) between the reactant molecules. The factor A does not vary significantly with temperature and hence it may be taken as a constant.

E_a is the activation energy of the reaction, which Arrhenius considered as the minimum energy that a molecule must have to possess to react.

Taking logarithm on both side of the equation (1)

$$\ln k = \ln A + \ln e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \quad (\because \ln e = 1)$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right) \quad \dots(2)$$

$$y = c + m x$$

The above equation is of the form of a straight line $y = mx + c$.

A plot of $\ln k$ Vs $\frac{1}{T}$ gives a straight line with a negative slope $-\frac{E_a}{R}$. If the rate constant for a reaction at two different temperatures is known, we can calculate the activation energy as follows.

At temperature $T = T_1$; the rate constant $k = k_1$

$$\ln k_1 = \ln A - \left(\frac{E_a}{RT_1}\right) \quad \dots(3)$$

At temperature $T = T_2$; the rate constant $k = k_2$

$$\ln k_2 = \ln A - \left(\frac{E_a}{RT_2} \right) \quad \dots(4)$$

(4) - (3)

$$\ln k_2 - \ln k_1 = - \left(\frac{E_a}{RT_2} \right) + \left(\frac{E_a}{RT_1} \right)$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

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

$$\ln k_2 - \ln k_1 = - \left(\frac{E_a}{RT_2} \right) + \left(\frac{E_a}{RT_1} \right)$$

This equation can be used to calculate E_a from rate constants k_1 and k_2 at temperatures T_1 and T_2 .

Example 7

The rate constant of a reaction at 400 and 200K are 0.04 and 0.02 s^{-1} respectively. Calculate the value of activation energy.

Solution

According to Arrhenius equation

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

$$T_2 = 400K ; k_2 = 0.04 s^{-1}$$

$$T_1 = 200K ; k_1 = 0.02 s^{-1}$$

$$\log \left(\frac{0.04 s^{-1}}{0.02 s^{-1}} \right) = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{400K - 200K}{200K \times 400K} \right)$$

$$\log(2) = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{400K} \right)$$

$$E_a = \log(2) \times 2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 400K$$

$$E_a = 2305 \text{ J mol}^{-1}$$

Example 8

Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303R} \left(\frac{1}{T} \right)$$

Where E_a is the activation energy. When a graph is plotted for $\log k$ Vs $\frac{1}{T}$ a straight line with a slope of $-4000K$ is obtained. Calculate the activation energy

Solution

$$\log k = \log A - \frac{E_a}{2.303R} \left(\frac{1}{T} \right)$$

$$y = c + mx$$

$$m = - \frac{E_a}{2.303R}$$

$$E_a = -2.303 R m$$

$$E_a = -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (-4000K)$$

$$E_a = 76,589 \text{ J mol}^{-1}$$

$$E_a = 76.589 \text{ kJ mol}^{-1}$$

Evaluate yourself

For a first order reaction the rate constant at 500K is $8 \times 10^{-4} s^{-1}$. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol^{-1} .

7.9 Factors affecting the reaction rate:

The rate of a reaction is affected by the following factors.

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

7.9.1 Nature and state of the reactant:

We know that a chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product. The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

- 1). Redox reaction between ferrous ammonium sulphate (FAS) and KMnO_4
- 2). Redox reaction between oxalic acid and KMnO_4

The oxidation of oxalate ion by KMnO_4 is relatively slow compared to the reaction between KMnO_4 and Fe^{2+} . In fact heating is required for the reaction between KMnO_4 and Oxalate ion and is carried out at around 60°C .

The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster

than the reaction between solid sodium and solid iodine.

Let us consider another example that you carried out in inorganic qualitative analysis of lead salts. If you mix the aqueous solution of colorless potassium iodide with the colorless solution of lead nitrate, precipitation of yellow lead iodide take place instantaneously, whereas if you mix the solid lead nitrate with solid potassium iodide, yellow coloration will appear slowly.



7.9.2 Concentration of the reactants:

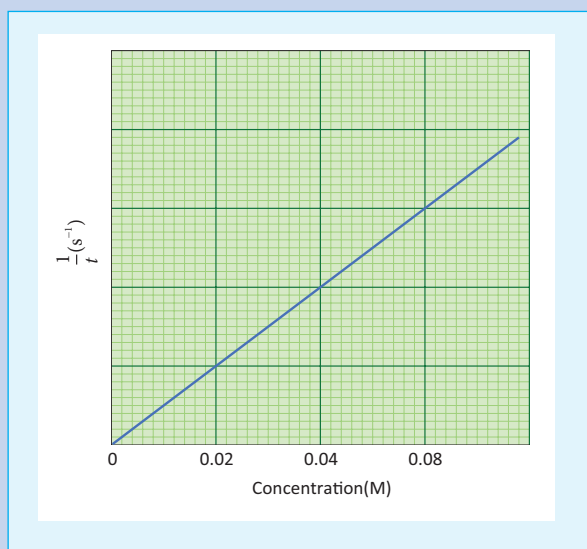
The rate of a reaction increases with the increase in the concentration of the reactants. The effect of concentration is explained on the basis of collision theory of reaction rates. According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules. Higher the concentration, greater is the possibility for collision and hence the rate.

Activity

1. Take three conical flasks and label them as A, B, and C.
2. using a burette, add 10, 20 and 40 ml of 0.1M sodium thiosulphate solution to the flask A, B and C respectively. And then add 40, 30 and 10 ml of distilled water to the respective flasks so that the volume of solution in each flask is 50ml.
3. Add 10 ml of 1M HCl to the conical flask A. Start the stop watch when half of the HCl has been added. Shake the contents carefully and place it on the tile with a cross mark as shown in the figure. Observe the conical flask from top and stop the stops watch when the cross mark just becomes invisible. Note the time.
4. Repeat the experiment with the contents on B and C. Record the observation.

| Flask | Volume of $\text{Na}_2\text{S}_2\text{O}_3$ | Volume of water | Strength of $\text{Na}_2\text{S}_2\text{O}_3$ | Time taken (t) |
|-------|---|-----------------|---|------------------|
| A | 10 | 40 | 0.02 | |
| B | 20 | 30 | 0.04 | |
| C | 40 | 10 | 0.08 | |

Draw a graph between $\frac{1}{t}$ Vs concentration of sodium thiosulphate. A graph like the following one is obtained.



$\frac{1}{t}$ is a direct measure of rate of reaction and therefore, the increase in the concentration of reactants i.e $\text{Na}_2\text{S}_2\text{O}_3$, increases the rate.



7.9.3 Effect of surface area of the reactant:

In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased. For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of CaCO_3 as marble

Activity

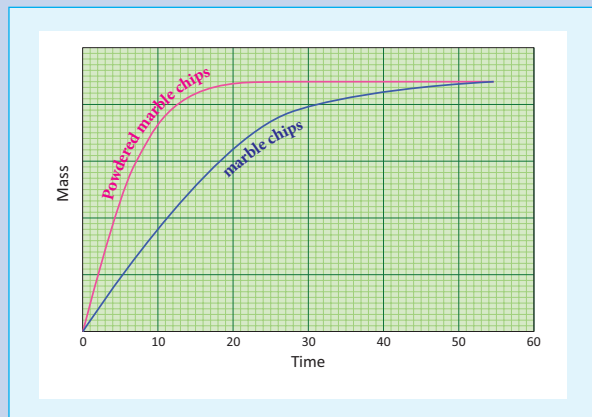
A Known mass of marble chips are taken in a flask and a known volume of dilute HCl is added to the content, a stop clock is started when half the volume of HCl is added. The mass is noted at regular intervals until the reaction is complete. Same experiment is repeated with the same mass of powdered marble chips and the observations are recorded.

Reaction



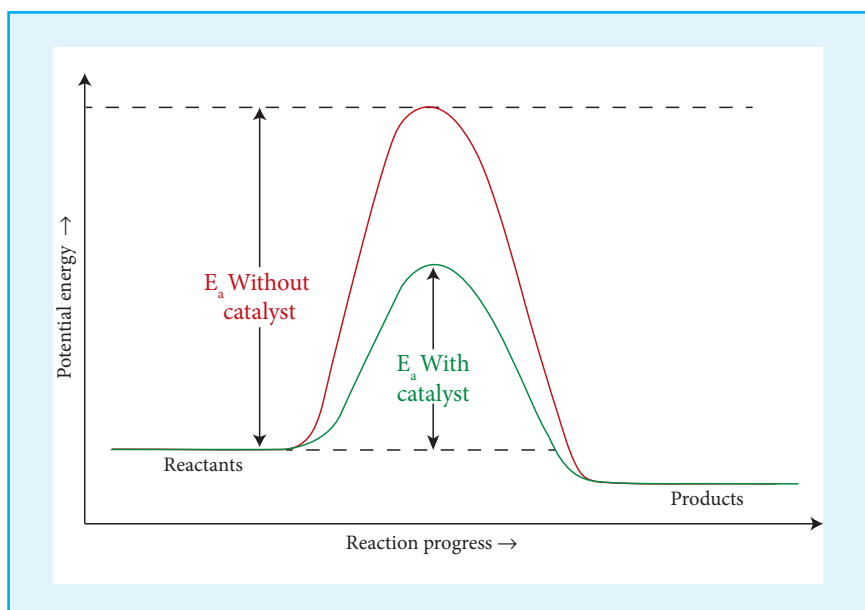
Since, carbon dioxide escapes during reaction, the mass of the flask gets lighter as the reaction proceeds. So, by measuring the flask, we can follow the rate of the reaction. A plot of loss in mass Vs time is drawn and it looks like the one as shown below.

For the powdered marble chips, the reaction is completed in less time. i.e., rate of a reaction increases when the surface area of a solid reactant is increased.



7.9.4 Effect of presence of catalyst:

So far we have learnt, that rate of reaction can be increased to certain extent by increasing the concentration, temperature and surface area of the reactant. However significant changes in the reaction can be brought out by the addition of a substance called catalyst. A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change. They may participate in the reaction, but again regenerated and the end of the reaction. In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.



Activity

Take two test tubes and label them as A and B. Add 7 ml of 0.1N oxalic acid solution, 5 ml of 0.1N KMnO_4 solution and 5 ml of 2N dilute H_2SO_4 in both the test tubes. The colour of the solution is pink in both the test tubes.

Now add few crystals of manganese sulphate to the content in test tube A. the pink colour fades up and disappears. In this case, MnSO_4 acts as a catalyst and increases the rate of oxidation of $\text{C}_2\text{O}_4^{2-}$ by MnO_4^- .



Chemical kinetics in pharmaceuticals

Chemical kinetics has many applications in the field of pharmaceuticals. It is used to study the lifetimes and bioavailability of drugs within the body and this branch of study is called **pharmacokinetics**. Doctors usually prescribe drugs to be taken at different times of the day. i.e. some drugs are to be taken twice a day, while others are taken three times a day, or just once a day. Pharmacokinetic studies are used to determine the prescription (dosage and frequency). For example, Paracetamol is a well known anti-pyretic and analgesic that is prescribed in cases of fever and body pain. Pharmacokinetic studies showed that Paracetamol has a half-life of 2.5 hours within the body i.e. the plasma concentration of a drug is halved after 2.5 hrs. After 10 hours (4 half-lives) only 6.25 % of drug remains. Based on such studies the dosage and frequency will be decided. In case of paracetamol, it is usually prescribed to take once in 6 hours depending upon the conditions.

Summary

- Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.
- The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.
- The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,
- The rate represents the speed at which the reactants are converted into products at any instant.
- The rate constant is a proportionality constant and It is equal to the rate of reaction, when the concentration of each of the reactants is unity
- Molecularity of a reaction is the total number of reactant species that are involved in an elementary step.
- The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant

i.e., it does not depend on the initial concentration.

- According to collision theory, chemical reactions occur as a result of collisions between the reacting molecules.
- Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10°C .
- According to Arrhenius, activation energy of the reaction is the minimum energy that a molecule must have to posses to react.
- The rate of a reaction is affected by the following factors.
 1. Nature and state of the reactant
 2. Concentration of the reactant
 3. Surface area of the reactant
 4. Temperature of the reaction
 5. Presence of a catalyst



EVALUATION



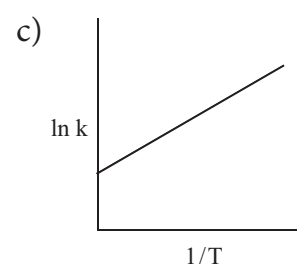
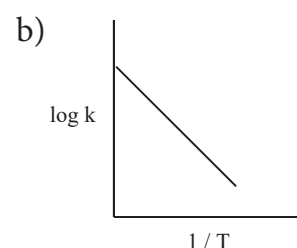
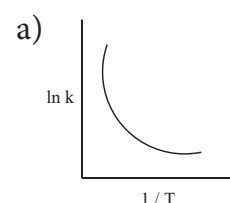
1. For a first order reaction $A \longrightarrow B$ the rate constant is $x \text{ min}^{-1}$. If the initial concentration of A is 0.01M , the concentration of A after one hour is given by the expression.

- a) $0.01 e^{-x}$
- b) $1 \times 10^{-2} (1 - e^{-60x})$
- c) $(1 \times 10^{-2}) e^{-60x}$
- d) none of these

2. A zero order reaction $X \longrightarrow \text{Product}$, with an initial concentration 0.02M has a half life of 10 min. if one starts with concentration 0.04M , then the half life is

- a) 10 s
- b) 5 min
- c) 20 min
- d) cannot be predicted using the given information

3. Among the following graphs showing variation of rate constant with temperature (T) for a reaction, the one that exhibits Arrhenius behavior over the entire temperature range is



- d) both (b) and (c)

4. For a first order reaction $A \longrightarrow \text{product}$ with initial concentration $x \text{ mol L}^{-1}$, has a half life period of 2.5 hours. For the same reaction with initial concentration $\left(\frac{x}{2}\right) \text{ mol L}^{-1}$ the half life is




- a) (2.5×2) hours
b) $\left(\frac{2.5}{2}\right)$ hours
c) 2.5 hours
d) Without knowing the rate constant, $t_{1/2}$ cannot be determined from the given data
5. For the reaction, $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$
, if $\frac{-d[\text{NH}_3]}{dt} = k_1 [\text{NH}_3]$,
 $\frac{d[\text{N}_2]}{dt} = k_2 [\text{NH}_3]$, $\frac{d[\text{H}_2]}{dt} = k_3 [\text{NH}_3]$
then the relation between k_1, k_2 and k_3 is
a) $k_1 = k_2 = k_3$
b) $k_1 = 3 k_2 = 2 k_3$
c) $1.5 k_1 = 3 k_2 = k_3$
d) $2k_1 = k_2 = 3 k_3$
6. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the (NEET)
a) rate is proportional to the surface coverage
b) rate is inversely proportional to the surface coverage
c) rate is independent of the surface coverage
d) rate of decomposition is slow
7. For a reaction $\text{Rate} = k[\text{acetone}]^{3/2}$ then unit of rate constant and rate of reaction respectively is
a) $(\text{mol L}^{-1} \text{s}^{-1}), (\text{mol}^{1/2} \text{L}^{1/2} \text{s}^{-1})$
b) $(\text{mol}^{1/2} \text{L}^{1/2} \text{s}^{-1}), (\text{mol L}^{-1} \text{s}^{-1})$
c) $(\text{mol}^{1/2} \text{L}^{1/2} \text{s}^{-1}), (\text{mol L}^{-1} \text{s}^{-1})$
d) $(\text{mol}^{1/2} \text{L}^{1/2} \text{s}^{-1}), (\text{mol L}^{-1} \text{s}^{-1})$
8. The addition of a catalyst during a chemical reaction alters which of the following quantities? (NEET)
a) Enthalpy b) Activation energy
c) Entropy d) Internal energy
9. Consider the following statements :
(i) increase in concentration of the reactant increases the rate of a zero order reaction.
(ii) rate constant k is equal to collision frequency A if $E_a = 0$
(iii) rate constant k is equal to collision frequency A if $E_a = 0$
(iv) a plot of $\ln(k)$ vs T is a straight line.
(v) a plot of $\ln(k)$ vs $\left(\frac{1}{T}\right)$ is a straight line with a positive slope.
Correct statements are
a) (ii) only b) (ii) and (iv)
c) (ii) and (v) d) (i), (ii) and (v)
10. In a reversible reaction, the enthalpy change and the activation energy in the forward direction are respectively $-x \text{ kJ mol}^{-1}$ and $y \text{ kJ mol}^{-1}$. Therefore, the energy of activation in the backward direction is
a) $(y-x) \text{ kJ mol}^{-1}$
b) $(x+y) \text{ J mol}^{-1}$
c) $(x-y) \text{ kJ mol}^{-1}$
d) $(x+y) \times 10^3 \text{ J mol}^{-1}$



11. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 200K to 400K? ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

- a) $234.65 \text{ kJ mol}^{-1} \text{ K}^{-1}$
- b) $434.65 \text{ kJ mol}^{-1} \text{ K}^{-1}$
- c) $434.65 \text{ J mol}^{-1} \text{ K}^{-1}$
- d) $334.65 \text{ J mol}^{-1} \text{ K}^{-1}$

12. ; This reaction follows first order kinetics. The rate constant at particular temperature is $2.303 \times 10^{-2} \text{ hour}^{-1}$. The initial concentration of cyclopropane is 0.25 M. What will be the concentration of cyclopropane after 1806 minutes? ($\log 2 = 0.3010$)

- a) 0.125M b) 0.215M
- c) $0.25 \times 2.303 \text{ M}$ d) 0.05M

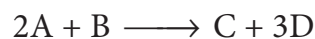
13. For a first order reaction, the rate constant is 6.909 min^{-1} . The time taken for 75% conversion in minutes is

- a) $\left(\frac{3}{2}\right) \log 2$ b) $\left(\frac{2}{3}\right) \log 2$
- c) $\left(\frac{3}{2}\right) \log\left(\frac{3}{4}\right)$ d) $\left(\frac{2}{3}\right) \log\left(\frac{4}{3}\right)$

14. In a first order reaction $x \longrightarrow y$; if k is the rate constant and the initial concentration of the reactant x is 0.1M, then, the half life is

- a) $\left(\frac{\log 2}{k}\right)$ b) $\left(\frac{0.693}{(0.1) k}\right)$
- c) $\left(\frac{\ln 2}{k}\right)$ d) none of these

15. Predict the rate law of the following reaction based on the data given below



| Reaction number | [A] (min) | [B] (min) | Initial rate (M s^{-1}) |
|-----------------|-----------|-----------|------------------------------------|
| 1 | 0.1 | 0.1 | x |
| 2 | 0.2 | 0.1 | $2x$ |
| 3 | 0.1 | 0.2 | $4x$ |
| 4 | 0.2 | 0.2 | $8x$ |

- a) $\text{rate} = k[A]^2[B]$ b) $\text{rate} = k[A][B]^2$
- c) $\text{rate} = k[A][B]$
- d) $\text{rate} = k[A]^{1/2}[B]^{3/2}$

16. Assertion: rate of reaction doubles when the concentration of the reactant is doubles if it is a first order reaction.

Reason: rate constant also doubles

- a) Both assertion and reason are true and reason is the correct explanation of assertion.
- b) Both assertion and reason are true but reason is not the correct explanation of assertion.
- c) Assertion is true but reason is false.
- d) Both assertion and reason are false.

17. The rate constant of a reaction is $5.8 \times 10^{-2} \text{ s}^{-1}$. The order of the reaction is

- a) First order b) zero order
- c) Second order d) Third order

18. For the reaction $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, the value of rate of disappearance of N_2O_5 is given as $6.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of formation of NO_2 and O_2 is given



respectively as

- a) $(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1})$ and $(1.3 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1})$
- b) $(1.3 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1})$ and $(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1})$
- c) $(1.3 \times 10^{-1} \text{ mol L}^{-1}\text{s}^{-1})$ and $(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1})$
- d) None of these
19. During the decomposition of H_2O_2 to give dioxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is
- a) $0.75 \text{ mol min}^{-1}$
- b) 1.5 mol min^{-1}
- c) $2.25 \text{ mol min}^{-1}$
- d) 3.0 mol min^{-1}
20. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is
- a) Zero b) one
- c) Fraction d) none
21. In a homogeneous reaction $\text{A} \longrightarrow \text{B} + \text{C} + \text{D}$, the initial pressure was P_0 and after time t it was P . expression for rate constant in terms of P_0 , P and t will be

- a) $k = \left(\frac{2.303}{t} \right) \log \left(\frac{2P_0}{3P_0 - P} \right)$
- b) $k = \left(\frac{2.303}{t} \right) \log \left(\frac{2P_0}{P_0 - P} \right)$
- c) $k = \left(\frac{2.303}{t} \right) \log \left(\frac{3P_0 - P}{2P_0} \right)$

d) $k = \left(\frac{2.303}{t} \right) \log \left(\frac{2P_0}{3P_0 - 2P} \right)$

22. If 75% of a first order reaction was completed in 60 minutes, 50% of the same reaction under the same conditions would be completed in
- a) 20 minutes b) 30 minutes
- c) 35 minutes d) 75 minutes
23. The half life period of a radioactive element is 140 days. After 560 days, 1 g of element will be reduced to
- a) $\left(\frac{1}{2} \right) \text{ g}$ b) $\left(\frac{1}{4} \right) \text{ g}$
- c) $\left(\frac{1}{8} \right) \text{ g}$ d) $\left(\frac{1}{16} \right) \text{ g}$
24. The correct difference between first and second order reactions is that (NEET)
- a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.
- b) The half life of a first order reaction does not depend on $[A_0]$; the half life of a second order reaction does depend on $[A_0]$.
- c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.
- d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.
25. After 2 hours, a radioactive substance becomes $\left(\frac{1}{16} \right)^{\text{th}}$ of original amount.



Then the half life (in min) is

- a) 60 minutes b) 120 minutes
c) 30 minutes d) 15 minutes

Answer the following questions:

1. Define average rate and instantaneous rate.
2. Define rate law and rate constant.
3. Derive integrated rate law for a zero order reaction $A \longrightarrow \text{product}$.
4. Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.
5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.
6. Explain the rate determining step with an example.
7. Describe the graphical representation of first order reaction.
8. Write the rate law for the following reactions.
 - (a) A reaction that is $3/2$ order in x and zero order in y.
 - (b) A reaction that is second order in NO and first order in Br_2 .
9. Explain the effect of catalyst on reaction rate with an example.
10. The rate law for a reaction of A, B and C has been found to be $\text{rate} = k[A]^2[B][L]^{3/2}$. How would the rate of reaction change when
 - (i) Concentration of [L] is quadrupled
 - (ii) Concentration of both [A] and [B] are doubled
 - (iii) Concentration of [A] is halved
 - (iv) Concentration of [A] is reduced to $\left(\frac{1}{3}\right)$ and concentration of [L] is quadrupled.
11. The rate of formation of a dimer in a second order reaction is $7.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant.
12. For a reaction $x + y + z \longrightarrow \text{products}$ the rate law is given by $\text{rate} = k[x]^{3/2}[y]^{1/2}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.
13. Explain briefly the collision theory of bimolecular reactions.
14. Write Arrhenius equation and explain the terms involved.
15. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s^{-1} .
16. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of an ester at different temperatures is given below.
17. Explain pseudo first order reaction with an example.
18. Identify the order for the following reactions
 - (i) Rusting of Iron
 - (ii) Radioactive disintegration of ${}_{92}\text{U}^{238}$
 - (iii) $2\text{A} + 3\text{B} \longrightarrow \text{products}$; $\text{rate} = k[\text{A}]^{1/2}[\text{B}]^2$
19. A gas phase reaction has energy of activation 200 kJ mol^{-1} . If the frequency factor of the reaction is $1.6 \times 10^{13} \text{ s}^{-1}$



. Calculate the rate constant at 600 K.
($e^{-40.09} = 3.8 \times 10^{-18}$)

20. For the reaction $2x + y \longrightarrow L$ find the rate law from the following data.

| [x] (min) | [y] (min) | rate (M s ⁻¹) |
|--------------|--------------|------------------------------|
| 0.2 | 0.02 | 0.15 |
| 0.4 | 0.02 | 0.30 |
| 0.4 | 0.08 | 1.20 |

21. How do concentrations of the reactant influence the rate of reaction?
22. How do nature of the reactant influence rate of reaction.
23. The rate constant for a first order reaction is $1.54 \times 10^{-3} \text{ s}^{-1}$. Calculate its half life time.
24. The half life of the homogeneous gaseous reaction $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?
25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?
26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?
27. The activation energy of a reaction is 225 k Cal mol⁻¹ and the value of rate constant at 40°C is $1.8 \times 10^{-5} \text{ s}^{-1}$. Calculate the frequency factor, A.
28. Benzene diazonium chloride in aqueous solution decomposes according to the equation $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$. Starting with an initial concentration of

10 g L⁻¹, the volume of N₂ gas obtained at 50 °C at different intervals of time was found to be as under:

| | | | | | | |
|---------------------------------|------|------|------|------|------|------|
| t (min): | 6 | 12 | 18 | 24 | 30 | ∞ |
| Vol. of N ₂ (ml): | 19.3 | 32.6 | 41.3 | 46.5 | 50.4 | 58.3 |

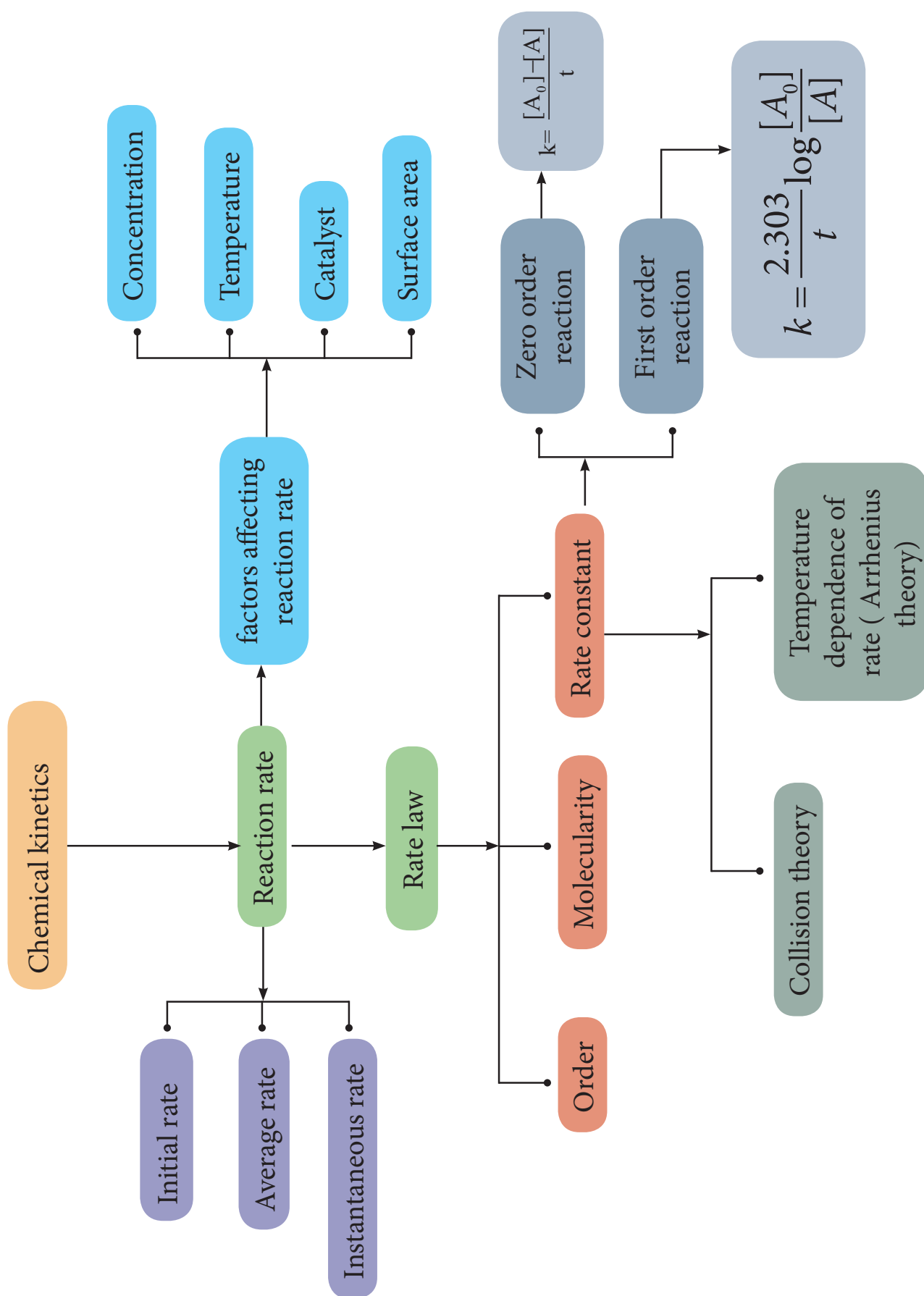
Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:

| | | | |
|---------|------|------|------|
| t (min) | 0 | 10 | 20 |
| V (ml) | 46.1 | 29.8 | 19.3 |

Where t is the time in minutes and V is the volume of standard KMnO_4 solution required for titrating the same volume of the reaction mixture.

30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?





CHEMICAL KINETICS

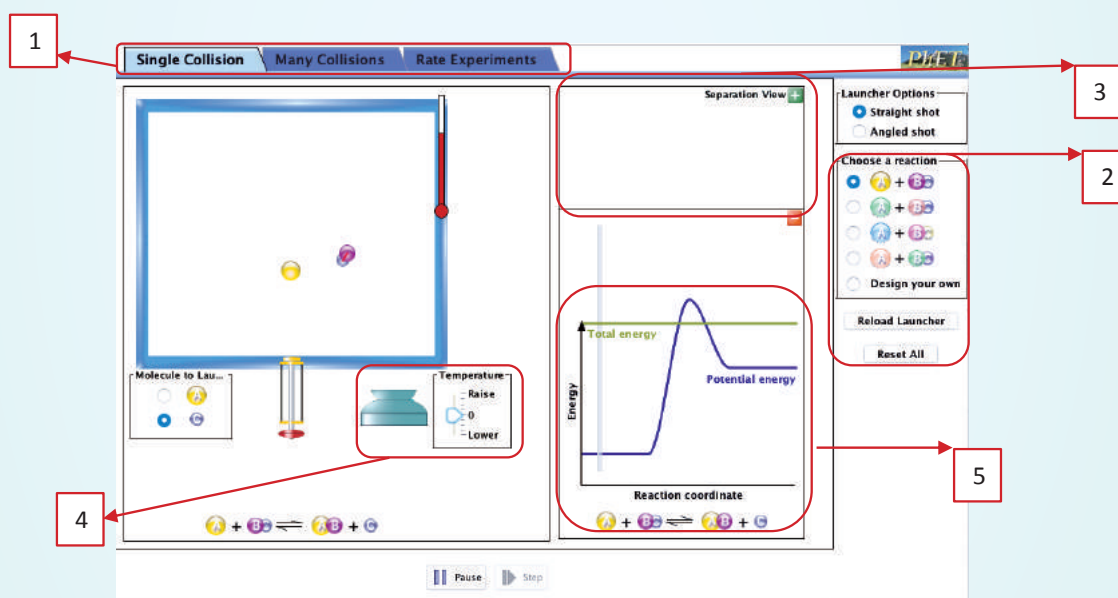
By using this tool you can understand collision and the activation energy. You can also perform virtual kinetic experiment to understand the effect of temperature on reaction rate.

Please go to the URL
<https://phet.colorado.edu/en/simulation/legacy/reactions-and-rates>
(or) Scan the QR code on the right side



Steps

- Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage which displays the java applet called reactions and rates. You can click it and you will get a window as shown in the figure. This applet contains three modules which can be selected by clicking the appropriate tab (box 1).
- Select single collision tab (tab 1) to visualise collision between two molecules. You can visualise the progress of the reaction (box 5) by varying the temperature using the slider (box 2). You can visualise that the raise in temperature, will raise the energy of the system and allows the reactants to cross the energy barrier to form products. You can repeat this simulation with more molecules in the many collisions tab (box 1).
- You can also perform virtual kinetic experiment, using rate experiments mode. Choose the types reacting molecules and their stoichiometry using the options provided (box 2). The number of reactant and product molecules at a given time will be displayed in panel (box-3). You can see the effect of temperature on reaction rate by varying the temperature (box 4).





UNIT-I

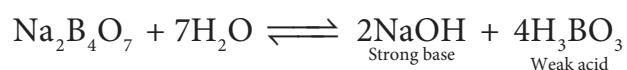
Choose the correct answer

1. b) $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ 2. c) SO_2 3. c) $\text{MgCO}_3 \longrightarrow \text{MgO} + \text{CO}_2$
4. b) Al_2O_3 5. a) Al
6. d) Carbon and hydrogen are suitable reducing agents for metal sulphides.
7. c) A-iv , B-ii , C-iii , D-i
8. d) Electromagnetic separation
9. b) $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \longrightarrow \text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$
10. c) sodium 11. b) Infusible impurities to soluble impurities
12. c) Galena 13. a) Lower the melting point of alumina
14. a) Carbon reduction 15. a) Silver
16. c) Displacement with zinc 17. c) Mg
18. b) van Arkel process 19. d) Both (a) and (c)
20. d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution
21. b) Impure copper 22. b) ΔG^0 Vs T
23. c) $\left(\frac{\Delta G^0}{\Delta T} \right)$ is negative 24. b) $\text{Al}_2\text{O}_3 + 2\text{Cr} \longrightarrow \text{Cr}_2\text{O}_3 + 2\text{Al}$
25. b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

UNIT-2

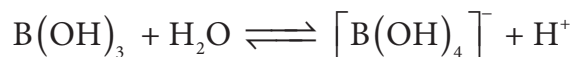
Choose the correct answer:

1. c) basic





2. d) accepts OH^- from water, releasing proton.



3. b) B_3H_6

nido borane : B_nH_{4+n}

aracno borane : B_nH_{6+n}

B_3H_6 is not a borane

4. a) Aluminium

5. c) four

There are two $3\text{c} - 2\text{e}^-$ bonds i.e., the bonding in the bridges account for 4 electrons.

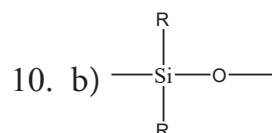
6. c) Lead

7. c) sp^2 hybridised

8. a) +4

Example : CH_{4+} in which the oxidation state of carbon is +4

9. d) $(\text{SiO}_4)^{4-}$



11. a) Me_3SiCl

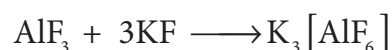
12. d) dry ice

dry ice – solid CO_2 in which carbon is in sp hybridized state

13. a) Tetrahedral

14. d) Feldspar is a three dimensional silicate

15. b) $\text{K}_3[\text{AlF}_6]$



16. a) A-b, B-1, C-4, D-3

17. d) Al, Cu, Mn, Mg

Al-95%, Cu-4%, Mn-0.5%, Mn-0.5%

18. b) graphite

19. a) Metal borides

20. a) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$

stability of +1 oxidation state decreases down the group due to inert pair effect

UNIT-3

Choose the correct answer:

1. a) Nessler's reagent

2. d) ability to form $p\pi - p\pi$ bonds with itself

3. d) $1s^2 2s^2 2p^6 3s^2 3p^3$

4. b) P_4 (white) and PH_3

5. b) Nitroso ferrous sulphate

6. a) H_3PO_3

7. a) H_3PO_3

8. b) 2

9. a) 6N

10. d) Both assertion and reason are wrong.
The converse is true.

11. b) F_2

12. b) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

13. d) NeF_2

14. c) He

15. c) XeO_3

16. c) SO_4^{2-}

17. a) HI

18. d) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

19. d) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

20. c) $\text{Cu}(\text{NO}_3)_2$ and NO_2

UNIT-4

Choose the correct answer:

1. b) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled
2. a) Cr

$$\text{Cr} \Rightarrow [\text{Ar}]3d^5 4s^1$$
3. a) Ti
4. c) Ni^{2+}
5. a) 5.92BM

$$\text{Mn}^{2+} \Rightarrow 3d^5 \text{ contains 5 unpaired electrons}$$

$$n=5 ; \therefore \sqrt{n(n+2)} \text{ BM}$$

$$\therefore \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$
6. b) Ti^{4+}
 Ti^{4+} contains no unpaired electrons in d orbital, hence no d-d transition.
7. c) their ability to adopt variable oxidation states
8. a) $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$

$$\overset{+5}{\text{V}}\text{O}_2^+ < \overset{+6}{\text{Cr}_2}\text{O}_7^{2-} < \overset{+7}{\text{Mn}}\text{O}_4^-$$
 greater the oxidation state, higher is the oxidising power
9. d) brass
 Brass contains 70% Cu + 30% Zn
10. b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

$$2\text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow 2\text{K}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \left(\frac{3}{2}\right)\text{O}_2$$

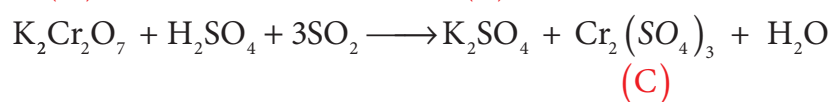
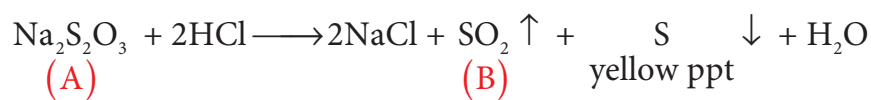
$$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} + \text{N}_2$$

$$\text{KClO}_3 \longrightarrow \text{KCl} + \left(\frac{3}{2}\right)\text{O}_2$$

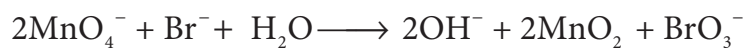
$$\text{Zn}(\text{ClO}_3)_2 \longrightarrow \text{ZnCl}_2 + 3\text{O}_2$$
11. b) Carbon dioxide

$$5(\text{COO})_2^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 \uparrow + 8\text{H}_2\text{O}$$
12. b) $\text{Na}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{K}_2\text{Cr}_2\text{O}_7$ in volumetric analysis
13. b) Mn^{2+}

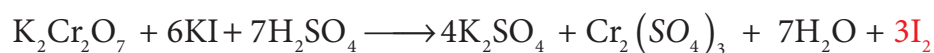
$$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
14. a) Na_2SO_3 , SO_2 , $\text{Cr}_2(\text{SO}_4)_3$



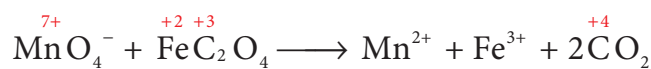
15. a) BrO_3^- , MnO_2



16. c) 3



17. c) 0.6



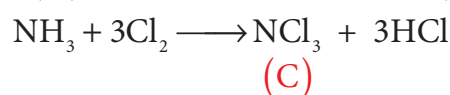
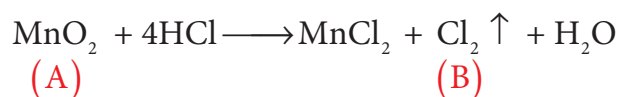
$5e^-$ acception $3e^-$ release

5 moles of $\text{FeC}_2\text{O}_4 \equiv$ 3 moles of KMnO_4

1 mole of $\text{FeC}_2\text{O}_4 \equiv \left(\frac{3}{5}\right)$ moles of KMnO_4

1 mole of $\text{FeC}_2\text{O}_4 \equiv$ 0.6 moles of KMnO_4

18. a) MnO_2 , Cl_2 , NCl_3



19. c) All the lanthanons are much more reactive than aluminium.

As we move from La to Lu, their metallic behaviour becomes almost similar to that of aluminium.

20. b) Yb^{2+}

$\text{Yb}^{2+} - 4f^{14}$ - no unpaired electrons - diamagnetic

21. d) 3

22. a) Both assertion and reason are true and reason is the correct explanation of assertion.

23. c) +4

24. a) Np, Pu, Am

25. a) $\text{La}(\text{OH})_3$ is less basic than $\text{Lu}(\text{OH})_3$

UNIT-5

Choose the correct answer:

1. In the complex $[M(en)_2(Ox)]Cl$ For the central metal ion M^{3+}

The primary valance is $= +3$

The secondary valance $= 6$

sum of primary valance and secondary valance $= 3+6 = 9$

Answer : option (d)

2. The complex is $[M(H_2O)_5Cl]Cl_2$

1000 ml of 1M solution of the complex gives 2 moles of Cl^- ions

1000 ml of 0.01M solution of the complex will give

$$\frac{100 \text{ ml} \times 0.01M \times 2Cl^-}{1000 \text{ ml} \times 1M} = 0.002 \text{ moles of } Cl^- \text{ ions}$$

Answer : option (b)

3. Molecular formula: $MSO_4Cl \cdot 6H_2O$.

Formation of white precipitate with Barium chloride indicates that SO_4^{2-} ions are outside the coordination sphere, and no precipitate with $AgNO_3$ solution indicates that the Cl^- ions are inside the coordination sphere. Since the coordination number of M is 6, Cl^- and 5 H_2O are ligands, remaining 1 H_2O molecular and SO_4^{2-} are in the outer coordination sphere.

Answer : option (c)

4. $[Fe(H_2O)_5NO]^{2+} SO_4^{2-}$

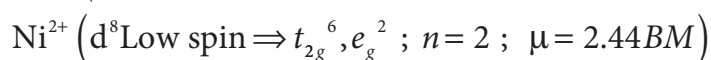
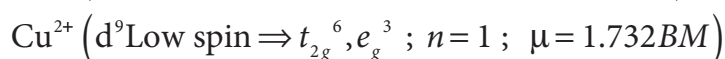
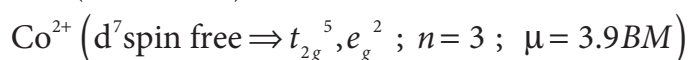
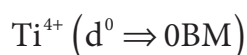
+1 and +1 respectively

Answer : option(d)

5. Answer : option(d)

6. Answer : option(d)

7. Answer : option(c)



8. Answer : option(b)

The electronic configuration t_{2g}^3, e_g^2

$$[3 \times (-0.4) + 2(0.6)]\Delta_0$$

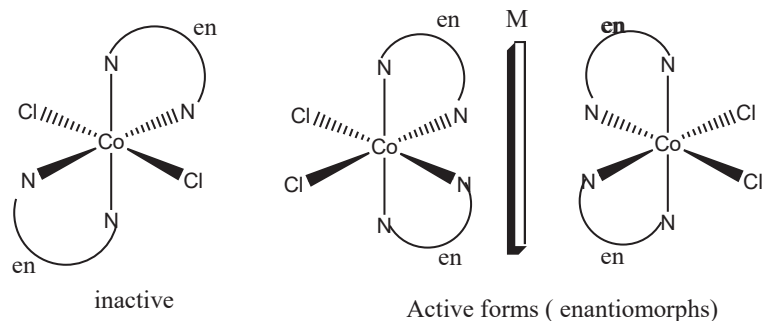


$$[-1.2 + 1.2]\Delta_0 = 0$$

9. Answer : option(a)

In all the complexes, the central metal ion is Co^{3+} , among the given ligands CN^- is the strongest ligand, which causes large crystal field splitting i.e maximum Δ_0

10. Answer : option(b)



Complexes given in other options (a), (c) and (d) have symmetry elements and hence they are optically inactive.

11. Answer : option(d)



12. Three isomers. If we consider any one of the ligands as reference (say Py), the arrangement of other three ligands (NH_3 , Br $^-$ and Cl $^-$) with respect to (Py) gives three geometrical isomers.

13. Answer : option(c)

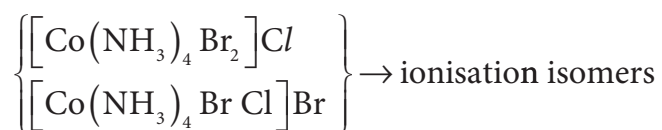
(a) coordination isomers

(b) no isomerism (different molecular formula)

(c) $\leftarrow \text{NCS}$, $\leftarrow \text{SCN}$ coordinating atom differs : linkage isomers

14. Answer : option(a)

For $[\text{MA}_4\text{B}_2]^{n+}$ complexes-geometrical isomerism is possible



15. Answer : option(d)

Option (a) and (b) – geometrical isomerism is possible

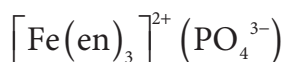
Option (c) – ionization isomerism is possible

Option (d) – no possibility to show either constitutional isomerism or stereo isomerism

16. Answer : option(c)

(a) Fe^{2+} (b) Fe^{3+} (c) Fe^0

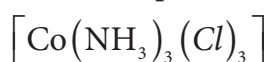
17. Answer : option(d)



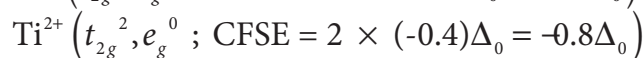
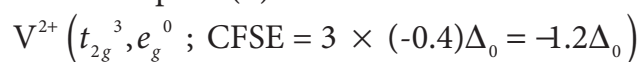
18. Answer : option(c)

- (a) $\text{Zn}^{2+} (\text{d}^{10} \Rightarrow \text{diamagnetic})$
 (b) $\text{Co}^{3+} (\text{d}^6 \text{ Low spin} \Rightarrow t_{2g}^6, e_g^0 ; \text{diamagnetic})$
 (c) $\text{Ni}^{2+} (\text{d}^8 \text{ Low spin} \Rightarrow t_{2g}^6, e_g^2 ; \text{paramagnetic})$
 (d) $[\text{Ni}(\text{CN})_4]^{2-} (\text{dsp}^2 ; \text{square planar, diamagnetic})$

19. Answer : option(c)



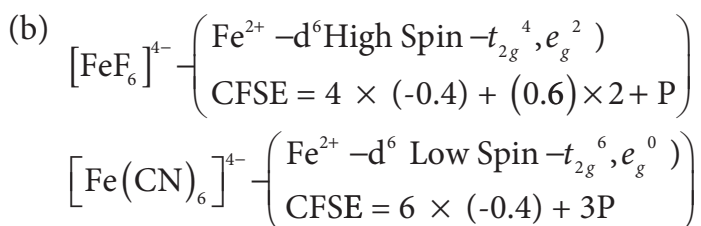
20. Answer : option(d)



Statements given in option (a), (b), and (c) are wrong.

The current statements are

(a) since, the crystal field stabilization is more in octahedral field, octahedral complexes are more stable than square planar complexes.



UNIT-6

Choose the correct answer:

1. c) both covalent crystals

2. b) AB_3

$$\text{number of A ions} = \left(\frac{N_c}{N_f} \right) = \left(\frac{8}{8} \right) = 1$$

$$\text{number of B ions} = \left(\frac{N_c}{2} \right) = \left(\frac{6}{2} \right) = 3$$

simplest formula AB_3

3. b) 1:2

if number of close packed atoms = N; then,

The number of Tetrahedral holes formed = 2N

number of Octahedral holes formed = N

therefore $\text{N}:2\text{N} = 1:2$

4. c) molecular solid

lattice points are occupied by CO_2 molecules

5. a) Both assertion and reason are true and reason is the correct explanation of assertion.

6. c) 8 and 4

CaF_2 has cubical close packed arrangement

Ca^{2+} ions are in face centered cubic

arrangement, each Ca^{2+} ions is surrounded by 8 F^- ions and each F^- ion is surrounded by 4 Ca^{2+} ions.

Therefore coordination number of Ca^{2+} is 8 and of F^- is 4

7. b) 6.023×10^{22}

in bcc unit cell,

2 atoms \equiv 1 unit cell

Number of atoms in 8g of element is ,

Number of moles = $\frac{8\text{g}}{40\text{ g mol}^{-1}} = 0.2\text{ mol}$

1 mole contains 6.023×10^{23} atoms

0.2 mole contains $0.2 \times 6.023 \times 10^{23}$ atoms

$\left(\frac{1\text{ unit cell}}{2\text{ atoms}}\right) \times 0.2 \times 6.023 \times 10^{23}$

6.023×10^{22} unit cells

8. a) 8

in diamond carbon forming fcc. Carbon occupies corners and face centres and also occupying half of the tetrahedral voids.

$\left(\frac{N_c}{8}\right) + \left(\frac{N_f}{2}\right) + 4\text{ C atoms in Td voids}$

$\left(\frac{8}{8}\right) + \left(\frac{6}{2}\right) + 4 = 8$

9. d) M_3N_2

if the total number of M atoms is n, then the number of tetrahedral voids

$= 2n$

given that $\left(\frac{1}{3}\right)^{\text{rd}}$ of tetrahedral voids are occupied i.e., $\left(\frac{1}{3}\right) \times 2n$ are occupied by N atoms

$\therefore \text{M:N} \Rightarrow n : \left(\frac{2}{3}\right)n$

$1 : \left(\frac{2}{3}\right)$

$3 : 2 \Rightarrow \text{M}_3\text{N}_2$

10. b) 15.05%

let

the number of Fe^{2+} ions in the crystal be x

the number of Fe^{3+} ions in the crystal be y

total number of Fe^{2+} and Fe^{3+} ions is

$x + y$

given that $x + y = 0.93$

the total charge = 0

$x(2+) + (0.93 - x)(+3) - 2 = 0$

$2x + 2.97 - 3x - 2 = 0$

$x = 0.79$

Percentage of Fe^{3+}

$= \left(\frac{(0.93 - 0.79)}{(0.93)}\right) 100 = 15.05\%$

11. c) 6

$\frac{r_{\text{C}^+}}{r_{\text{A}^-}} = \frac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.54$

it is in the range of 0.414 - 0.732,

hence the coordination number of each ion is 6

12. d) $\left(\frac{\sqrt{3}}{2}\right) \times 400\text{pm}$



$$\sqrt{3} a = r_{Cs^+} + 2r_{Cl^-} + r_{Cs^+}$$

$$\left(\frac{\sqrt{3}}{2}\right) a = (r_{Cs^+} + r_{Cl^-})$$

$$\left(\frac{\sqrt{3}}{2}\right) 400 = \text{inter ionic distance}$$

13. a) $\left(\frac{100}{0.414}\right)$
 for an fcc structure $\frac{r_{x^+}}{r_{y^-}} = 0.414$
 given that $r_{x^+} = 100 \text{ pm}$
 $r_{y^-} = \frac{100 \text{ pm}}{0.414}$

14. c) 32%
 packing efficiency = 68%
 therefore empty space percentage =
 $(100 - 68) = 32\%$

15. b) 848.5 pm
 let edge length = a
 $\sqrt{2}a = 4r$
 $a = \frac{4 \times 300}{\sqrt{2}}$
 $a = 600 \times 1.414$
 $a = 848.4 \text{ pm}$

16. b) $\left(\frac{\pi}{6}\right)$
 $\left(\frac{\frac{4}{3}\pi r^3}{a^3}\right) = \left(\frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3}\right) = \left(\frac{\pi}{6}\right)$

17. a) excitation of electrons in F centers

18. c) $\left(\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a\right)$

$$sc \Rightarrow 2r = a \Rightarrow r = \frac{a}{2}$$

$$bcc \Rightarrow 4r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}a}{4}$$

$$fcc \Rightarrow 4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$

$$\left(\frac{a}{2}\right) : \left(\frac{\sqrt{3}a}{4}\right) : \left(\frac{a}{2\sqrt{2}}\right)$$

19. d) $\left(\frac{\sqrt{3}}{2}\right)a$

if a is the length of the side, then the length of the leading diagonal passing through the body centered atom is $\sqrt{3}a$

$$\text{Required distance} = \left(\frac{\sqrt{3}}{2}\right)a$$

20. a) 915 kg m⁻³

$$\rho = \frac{n \times M}{a^3 N_A}$$

for bcc

$$n = 2$$

$$M = 39$$

$$\text{nearest distance } 2r = 4.52$$

$$a = \frac{4r}{\sqrt{3}} = \frac{2 \times 4.52 \times 10^{-10}}{\sqrt{3}} = 5.21 \times 10^{-10}$$

$$\rho = \frac{2 \times 39}{(5.21 \times 10^{-10})^3 \times (6.023 \times 10^{23})}$$

$$\rho = 915 \text{ Kg m}^{-3}$$

$$N_A$$

21. b) equal number of anions and anions are missing from the lattice

22. c) Frenkel defect

23. d) Both assertion and reason are false

24. b) FeO

25. a) XY₈

UNIT-7

Choose the correct answer:

1. option (c)

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{[A_0]}{[A]} \right)$$

$$k = \left(\frac{1}{t} \right) \ln \left(\frac{[A_0]}{[A]} \right)$$

$$e^{kt} = \left(\frac{[A_0]}{[A]} \right)$$

$$[A] = [A_0] e^{-kt}$$

In this case

$$k = x \text{ min}^{-1} \text{ and } [A_0] = 0.01\text{M} = 1 \times 10^{-2}\text{M}$$

$$t = 1 \text{ hour} = 60 \text{ min}$$

$$[A] = 1 \times 10^{-2} (e^{-60x})$$

2. option (c)

$$\text{for } n \neq 1 \quad t_{1/2} = \frac{2^{n-1} - 1}{(n-1) k [A_0]^{n-1}}$$

$$\text{for } n = 0 \quad t_{1/2} = \frac{1}{2 k [A_0]^{-1}}$$

$$t_{1/2} = \frac{[A_0]}{2 k}$$

$$t_{1/2} \propto [A_0] \text{ ————— (1)}$$

given

$$[A_0] = 0.02\text{M} ; t_{1/2} = 10 \text{ min}$$

$$[A_0] = 0.04\text{M} ; t_{1/2} = ?$$

substitute in (1)

$$10 \text{ min} \propto 0.02\text{M} \text{ ————— (2)}$$

$$t_{1/2} \propto 0.04\text{M} \text{ ————— (3)}$$

$$\frac{(3)}{(2)}$$

$$\Rightarrow \frac{t_{1/2}}{10 \text{ min}} = \frac{0.04 \text{ M}}{0.02 \text{ M}}$$

$$t_{1/2} = 2 \times 10 \text{ min} = 20 \text{ min}$$

3. option (b)

$$k = A e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

this equation is in the form of a straight line equation

$$y = c + m x$$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

4. option(d)

For a first order reaction

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

$t_{1/2}$ does not depend on the initial concentration and it remains constant (whatever may be the initial concentration)

$$t_{1/2} = 2.5 \text{ hrs}$$

5. option(c)

$$\text{Rate} = \left(\frac{-1}{2}\right) \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \left(\frac{1}{3}\right) \frac{d[\text{H}_2]}{dt}$$

$$\left(\frac{1}{2}\right) k_1 [\text{NH}_3] = k_2 [\text{NH}_3] = \left(\frac{1}{3}\right) k_3 [\text{NH}_3]$$

$$\left(\frac{3}{2}\right) k_1 = 3k_2 = k_3$$

$$1.5 k_1 = 3k_2 = k_3$$

6. option(c)

Given :

At low pressure the reaction follows first order, therefore

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

$$\text{Rate} \propto (\text{surface area})$$

At high pressure due to the complete coverage of surface area, the reaction follows zero order.

$$\text{Rate} \propto [\text{reactant}]^0$$

Therefore the rate is independent of surface area.

7. option(b)

$$\text{rate} = k[A]^n$$

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

$$\text{unit of rate} = \frac{\text{mol L}^{-1}}{s} = \text{mol L}^{-1} s^{-1}$$

$$\text{unit of rate constant} = \frac{(\text{mol L}^{-1} s^{-1})}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n} \text{L}^{n-1} s^{-1}$$

in this case

$$\text{rate} = k[\text{Acetone}]^{3/2}$$

$$n = \frac{3}{2}$$

$$\text{mol}^{1-(3/2)} \text{L}^{(3/2)-1} s^{-1}$$

$$\text{mol}^{-(1/2)} \text{L}^{(1/2)} s^{-1}$$

8. option(b)

A catalyst provides a new path to the reaction with low activation energy. i.e., it lowers the activation energy.

9. option(a)

In zero order reactions, increase in the concentration of reactant does not alter the rate. So statement (i) is wrong.

$$k = A e^{-\left(\frac{E_a}{RT}\right)}$$

if $E_a = 0$ so, statement (ii) is correct, and statement (iii) is wrong

$$k = A e^0$$

$$k = A$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right)$$

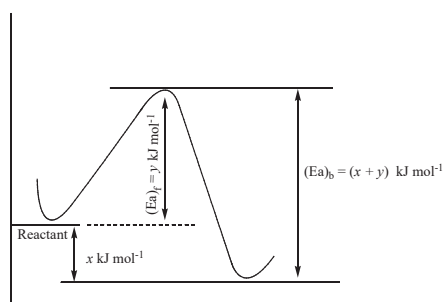
this equation is in the form of a straight line equation

$$y = c + m x$$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

so statements (iv) and (v) are wrong.

10. option(d)



$$(x + y) \text{ kJ mol}^{-1}$$

$$(x + y) \times 10^3 \text{ J mol}^{-1}$$

11. option(c)

$$T_1 = 200\text{K} ; k = k_1$$

$$T_2 = 400\text{K} ; k = k_2 = 2k_1$$

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

$$\log\left(\frac{2 k_1}{k_1}\right) = \frac{2.303 E_a}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{400 \text{ K} - 200 \text{ K}}{200 \text{ K} \times 400 \text{ K}}\right)$$

$$E_a = \frac{0.3010 \times 8.314 \text{ J mol}^{-1} \times 200 \times 400}{2.303 \times 200}$$

$$E_a = 434.65 \text{ J mol}^{-1}$$

12. option(b)

$$k = \left(\frac{2.303}{t}\right) \log\left(\frac{[A_0]}{[A]}\right)$$

$$2.303 \times 10^{-2} \text{ hour}^{-1} = \left(\frac{2.303}{1806 \text{ min}}\right) \log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{2.303 \times 10^{-2} \text{ hour}^{-1} \times 1806 \text{ min}}{2.303}\right) = \log\left(\frac{0.25}{[A]}\right)$$



$$\left(\frac{1806 \times 10^{-2}}{60} \right) = \log \left(\frac{0.25}{[A]} \right)$$

$$0.301 = \log \left(\frac{0.25}{[A]} \right)$$

$$\log 2 = \log \left(\frac{0.25}{[A]} \right)$$

$$2 = \left(\frac{0.25}{[A]} \right)$$

$$[A] = \left(\frac{0.25}{2} \right) = 0.125M$$

13. option(b)

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{[A_0]}{[A]} \right)$$

$$[A_0] = 100 ; [A] = 25$$

$$6.909 = \left(\frac{2.303}{t} \right) \log \left(\frac{100}{25} \right)$$

$$t = \left(\frac{2.303}{6.909} \right) \log(4)$$

$$t = \left(\frac{1}{3} \right) \log 2^2$$

$$t = \left(\frac{2}{3} \right) \log 2$$

14. option(c)

$$k = \left(\frac{1}{t} \right) \ln \left(\frac{[A_0]}{[A]} \right)$$

$$[A_0] = 0.1 ; [A] = 0.05$$

$$k = \left(\frac{1}{t_{1/2}} \right) \ln \left(\frac{0.1}{0.05} \right)$$

$$k = \left(\frac{1}{t_{1/2}} \right) \ln(2)$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

15. option(b)

$$\text{rate}_1 = k[0.1]^n [0.1]^m \text{ —————(1)}$$

$$\text{rate}_2 = k[0.2]^n [0.1]^m \text{ —————(2)}$$

$$\frac{(2)}{(1)}$$

$$\frac{2x}{x} = \frac{k[0.2]^n [0.1]^m}{k[0.1]^n [0.1]^m}$$

$$\frac{2x}{x} = 2^n \quad \therefore n = 1$$

$$\text{rate}_3 = k[0.1]^n [0.2]^m \text{ —————(3)}$$

$$\text{rate}_4 = k[0.2]^n [0.2]^m \text{ —————(4)}$$

$$\frac{(4)}{(2)}$$

$$\frac{8x}{2x} = \frac{k[0.2]^n [0.2]^m}{k[0.2]^n [0.1]^m}$$

$$\frac{8}{2} = 2^m \quad \therefore m = 2$$

$$\therefore \text{rate} = k[A]^1 [B]^2$$

16. option(c)

For a first reaction, If the concentration of reactant is doubled, then the rate of reaction also doubled.

Rate constant is independent of concentration and is a constant at a constant temperature,

17. option(a)

The unit of rate constant is s^{-1} and it indicates that the reaction is first order.

18. option(c)

$$\text{Rate} = \frac{d[N_2O_5]}{dt} = \left(\frac{1}{2}\right) \frac{d[NO_2]}{dt} = \frac{2}{dt} \frac{d[O_2]}{dt}$$

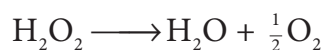
Given that

$$\frac{d[N_2O_5]}{dt} = 6.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[NO_2]}{dt} = 2 \times 6.5 \times 10^{-2} = 1.3 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[O_2]}{dt} = \frac{6.5 \times 10^{-2}}{2} = 3.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

19. option(d)



$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt}$$

$$\text{no of moles of oxygen} = \left(\frac{48}{32}\right) = 1.5 \text{ mol}$$

$$\therefore \text{rate of formation of oxygen} = 2 \times 1.5 = 3 \text{ mol min}^{-1}$$

20. option(a)

For a first order reaction $t_{1/2}$ is independent of initial concentration i.e., $\therefore n \neq 1$; for such cases

$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}} \text{ ————— (1)}$$

$$\text{If } [A_0] = 2[A_0]; \text{ then } t_{1/2} = 2t_{1/2}$$

$$2t_{1/2} \propto \frac{1}{[2A_0]^{n-1}} \text{ ————— (2)}$$

$$\frac{(2)}{(1)} \Rightarrow$$

$$2 = \frac{1}{[2A_0]^{n-1}} \times \frac{[A_0]^{n-1}}{1}$$

$$2 = \frac{[A_0]^{n-1}}{[2A_0]^{n-1}}$$

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

$$2 = (2^{-1})^{n-1}$$

$$2^1 = (2^{-n+1})$$

$$n = 0$$

21. Answer : option(a)

| | A | → | B | C | D |
|-----------------------|-------|------------|---|---|---|
| Initial | a | | 0 | 0 | 0 |
| Reacted at time t | x | | x | x | x |
| After time t | (a-x) | | x | x | x |
| Total number of moles | | = (a + 2x) | | | |

$$a \propto P_0$$

$$(a + 2x) \propto P$$

$$\frac{a}{(a + 2x)} = \frac{P_0}{P}$$

$$x = \frac{(P - P_0)a}{2P_0}$$

$$(a - x) = a - \left(\frac{(P - P_0)a}{2P_0}\right)$$

$$(a - x) = a \left\{ \frac{3P_0 - P}{2P_0} \right\}$$

$$k = \left(\frac{2.303}{t}\right) \log \frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t}\right) \log \left(\frac{a}{a - x}\right)$$

$$k = \left(\frac{2.303}{t}\right) \log \left(\frac{a}{a \left\{ \frac{3P_0 - P}{2P_0} \right\}} \right)$$

$$k = \left(\frac{2.303}{t}\right) \log \left(\frac{2P_0}{3P_0 - P} \right)$$



22. Answer : option(d)

$$t_{75\%} = 2t_{50\%}$$

$$t_{50\%} = \left(\frac{t_{75\%}}{2} \right) = \left(\frac{60}{2} \right) = 30 \text{ min}$$

23. Answer : option(d)

in 140 days \Rightarrow initial concentration reduced to $\left(\frac{1}{2} \right) g$

in 280 days \Rightarrow initial concentration reduced to $\left(\frac{1}{4} \right) g$

in 420 days \Rightarrow initial concentration reduced to $\left(\frac{1}{8} \right) g$

in 560 days \Rightarrow initial concentration reduced to $\left(\frac{1}{16} \right) g$

24. Answer : option(b)

For a first order reaction

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

For a second order reaction

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1) k [A_0]^{n-1}}$$

$$n = 2$$

$$t_{1/2} = \frac{2^{2-1} - 1}{(2-1) k [A_0]^{2-1}}$$

$$t_{1/2} = \frac{1}{k [A_0]}$$

25. Answer : option(c)

$$1 \xrightarrow{t_{1/2}} \left(\frac{1}{2} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{4} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{8} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{16} \right)$$

$$\therefore 4 t_{1/2} = 2 \text{ hours}$$

$$t_{1/2} = 30 \text{ min}$$

Answer the following:

10 solution

$$\text{Rate} = k[A]^2[B][L]^{\frac{3}{2}} \text{ -----(1)}$$

(i) when $[L] = [4L]$

$$\text{Rate} = k[A]^2[B][4L]^{\frac{3}{2}}$$

$$\text{Rate} = 8 \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(2)}$$

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) when $[A] = [2A]$ and $[B] = [2B]$

$$\text{Rate} = k[2A]^2[2B][L]^{\frac{3}{2}}$$

$$\text{Rate} = 8 \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(3)}$$

Comparing (1) and (3) ; rate is increased by 8 times.

(iii) when $[A] = \left[\frac{A}{2} \right]$

$$\text{Rate} = k \left[\frac{A}{2} \right]^2 [B][L]^{\frac{3}{2}}$$

$$\text{Rate} = \left(\frac{1}{4} \right) \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(4)}$$

Comparing (1) and (4) ; rate is reduced to $\frac{1}{4}$ times.

(iv) when $[A] = \left[\frac{A}{3} \right]$ and $[L] = [4L]$

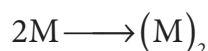
$$\text{Rate} = k \left[\frac{A}{3} \right]^2 [B][4L]^{\frac{3}{2}}$$

$$\text{Rate} = \left(\frac{8}{9} \right) \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(5)}$$

Comparing (1) and (5) ; rate is reduced to $\frac{8}{9}$ times.

11. solution

Let us consider the dimerisation of a monomer M



$$\text{Rate} = k[M]^n$$

Given that $n=2$ and $[M] = 0.05 \text{ mol L}^{-1}$

$$\text{Rate} = 7.5 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$$

$$k = \frac{\text{Rate}}{[M]^n}$$

$$k = \frac{7.5 \times 10^{-3}}{(0.05)^2} = 3 \text{ mol}^{-1}\text{Ls}^{-1}$$

12. Solution

$$\text{rate} = k[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$$

$$\text{overall order} = \left(\frac{3}{2} + \frac{1}{2}\right) = 2$$

i.e., second order reaction.

Since the rate expression does not contain the concentration of z, the reaction is zero order with respect to z.

15. Solution:

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{1 \text{ min}} \log \frac{[0.08]}{[0.04]}$$

$$k = 2.303 \log 2$$

$$k = 2.303 \times 0.3010$$

$$k = 0.6932 \text{ min}^{-1}$$

$$k = \left(\frac{0.6932}{60}\right) \text{ s}^{-1}$$

$$k = 1.153 \times 10^{-2} \text{ s}^{-1}$$

19. Solution

$$k = A e^{\left(\frac{E_a}{RT}\right)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} e^{\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 600 \text{ K}}\right)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} e^{-(40.1)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} \times 3.8 \times 10^{-18}$$

$$k = 6.21 \times 10^{-5} \text{ s}^{-1}$$

20. Solution

$$\text{rate} = k[x]^n [y]^m$$

$$0.15 = k[0.2]^n [0.02]^m \text{ ———(1)}$$

$$0.30 = k[0.4]^n [0.02]^m \text{ ———(2)}$$

$$1.20 = k[0.4]^n [0.08]^m \text{ ———(3)}$$

$$\frac{(3)}{(2)}$$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n [0.08]^m}{k[0.4]^n [0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]} \right)^m$$

$$4 = (4)^m$$

$$\therefore m = 1$$

$$\frac{(2)}{(1)}$$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n [0.02]^m}{k[0.2]^n [0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]} \right)^n$$

$$2 = (2)^n$$

$$\therefore n = 1$$

$$\text{Rate} = k[x]^1 [y]^1$$

$$0.15 = k[0.2]^1 [0.02]^1$$

$$\frac{0.15}{[0.2]^1 [0.02]^1} = k$$

$$k = 37.5 \text{ mol}^{-1} \text{L s}^{-1}$$

23 Solution:

We know that, $t_{1/2} = 0.693/k$

$$t_{1/2} = 0.693/1.54 \times 10^{-3} \text{ s}^{-1} = 450 \text{ s}$$

24. Solution:

We know that, $k = 0.693/t_{1/2}$

$$k = 0.693/8.0 \text{ minutes} = 0.087 \text{ minutes}^{-1}$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.087 \text{ min}^{-1}} \log \left(\frac{100}{1} \right)$$

$$t = 52.93 \text{ min}$$

25 Solution:

i) Order of a reaction = 1; $t_{1/2} = 60$; seconds, $k = ?$

We know that, $k = \frac{2.303}{t_{1/2}}$

$$k = \frac{2.303}{60} = 0.01155 \text{ s}^{-1}$$

ii) $[A_0] = 100\%$ $t = 180 \text{ s}$, $k = 0.01155 \text{ seconds}^{-1}$, $[A] = ?$

For the first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$0.01155 = \frac{2.303}{180} \log \left(\frac{100}{[A]} \right)$$

$$\frac{0.01155 \times 180}{2.303} = \log \left(\frac{100}{[A]} \right)$$

$$0.9207 = \log 100 - \log [A]$$

$$\log [A] = \log 100 - 0.9207$$

$$\log [A] = 2 - 0.9207$$

$$\log [A] = 1.0973$$

$$[A] = \text{antilog of } (1.0973)$$

$$[A] = 12.5\%$$

26 Solution:

i) Let $A = 100\text{M}$, $[A_0] - [A] = 20\text{M}$,

For the zero order reaction

$$k = \left(\frac{[A_0] - [A]}{t} \right)$$

$$k = \left(\frac{20M}{20\text{min}} \right) = 1 \text{ Mmin}^{-1}$$

Rate constant for a reaction = 1 Mmin^{-1}

ii) To calculate the time for 80% of completion

$$k = 1 \text{ Mmin}^{-1}, [A_0] = 100M, [A_0] - [A] = 80M, t = ?$$

Therefore,

$$t = \left(\frac{[A_0] - [A]}{k} \right) = \left(\frac{80M}{1 \text{ Mmin}^{-1}} \right) = 80 \text{ min}$$

27 Solution:

Here, we are given that

$$E_a = 22.5 \text{ kcal mol}^{-1} = 22500 \text{ cal mol}^{-1}$$

$$T = 40^\circ\text{C} = 40 + 273 = 313 \text{ K}$$

$$k = 1.8 \times 10^{-5} \text{ sec}^{-1}$$

Substituting the values in the equation

$$\log A = \log k + \left(\frac{E_a}{2.303RT} \right)$$

$$\log A = \log(1.8 \times 10^{-5}) + \left(\frac{22500}{2.303 \times 1.987 \times 313} \right)$$

$$\log A = \log(1.8) - 5 + (15.7089)$$

$$\log A = 10.9642$$

$$A = \text{antilog}(10.9642)$$

$$A = 9.208 \times 10^{10} \text{ collisions s}^{-1}$$

28.Solution:

For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

In the present case, $V_\infty = 58.3 \text{ ml}$.

The value of k at different time can be calculated as follows:

| $t \text{ (min)}$ | V_t | $V_\infty - V_t$ | $\frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$ |
|-------------------|-------|----------------------|--|
| 6 | 19.3 | $58.3 - 19.3 = 39.0$ | $k = \frac{2.303}{6} \log \left(\frac{58.3}{39} \right) = 0.0670 \text{ min}^{-1}$ |
| 12 | 32.6 | $58.3 - 32.6 = 25.7$ | $k = \frac{2.303}{12} \log \left(\frac{58.3}{25.7} \right) = 0.0683 \text{ min}^{-1}$ |
| 18 | 41.3 | $58.3 - 41.3 = 17.0$ | $k = \frac{2.303}{18} \log \left(\frac{58.3}{17} \right) = 0.0685 \text{ min}^{-1}$ |
| 24 | 46.5 | $58.3 - 46.5 = 11.8$ | $k = \frac{2.303}{24} \log \left(\frac{58.3}{11.8} \right) = 0.0666 \text{ min}^{-1}$ |

Since the value of k comes out to be nearly constant, the given reaction is of the first order. The mean value of $k = 0.0676 \text{ min}^{-1}$

29. Solution:

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{V_0}{V_t} \right)$$

In the present case, $V_0 = 46.1 \text{ ml}$.

The value of k at each instant can be calculated as follows:

| $t \text{ (min)}$ | V_t | $k = \left(\frac{2.303}{t} \right) \log \left(\frac{V_0}{V_t} \right)$ |
|-------------------|-------|--|
| 10 | 29.8 | $k = \frac{2.303}{10} \log \left(\frac{46.1}{29.8} \right) = 0.0436 \text{ min}^{-1}$ |
| 20 | 19.3 | $k = \frac{2.303}{20} \log \left(\frac{46.1}{19.3} \right) = 0.0435 \text{ min}^{-1}$ |

Thus, the value of k comes out to be nearly constant. Hence it is a reaction of the first order.

30. Solution:

i) For the first order reaction $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

Assume, $[A_0] = 100 \%$, $t = 50 \text{ minutes}$

Therefore, $[A] = 100 - 40 = 60$

$$k = (2.303 / 50) \log (100 / 60)$$

$$k = 0.010216 \text{ min}^{-1}$$

Hence the value of the rate constant is $0.010216 \text{ min}^{-1}$

ii) $t = ?$, when the reaction is 80% completed,

$$[A] = 100 - 80 = 20 \%$$

From above, $k = 0.010216 \text{ min}^{-1}$

$$t = (2.303 / 0.010216) \log (100 / 20)$$

$$t = 157.58 \text{ min}$$

The time at which the reaction will be 80% complete is 157.58 min.



+2

PRACTICALS

I-ORGANIC QUALITATIVE ANALYSIS

| S.no | Experiment | Observation | Inference |
|--------------------------|--|--|--|
| Preliminary tests | | | |
| 1 | Odour: Note the Odour of the organic compound. | (i) Fish odour (ii) Bitter almond odour (iii) Phenolic odour (iv) Pleasant fruity odour | (i) May be an amine (ii) May be benzaldehyde (iii) May be phenol (iv) May be an ester |
| 2 | Test with litmus paper: Touch the Moist litmus paper with an organic compound. | (i) Blue litmus turns red (ii) Red litmus turns blue (iii) No colour change is noted | (i) May be a carboxylic acid or phenol (ii) May be an amine (iii) Absence of carboxylic acid, phenol and amine |
| 3 | Action with sodium bicarbonate: Take 2 ml of saturated sodium bi carbonate solution in a test tube. Add 2 or 3 drops (or a pinch of solid) of an organic compound to it. | (i) Brisk effervescence (ii) No brisk effervescence | (i) Presence of a carboxylic acid. (ii) Absence of a carboxylic acid. |
| 4 | Action with Borsche's reagent: Take a small amount of an organic compound in a test tube. Add 3 ml of Borsche's reagent, 1 ml of Conc HCl to it, then warm the mixture gently and cool it. | yellow or orange or red precipitate | Presence of an aldehyde or ketone |

| | | | |
|--|--|--|---|
| 5 | Charring test: Take a small amount of an organic compound in a dry test tube. Add 2 ml of conc H_2SO_4 to it, and heat the mixture. | Charring takes place with smell of burnt sugar | Presence of carbohydrate |
| Tests for Aliphatic or Aromatic nature: | | | |
| 6 | Ignition test: Take small amount of the organic compound in a Nickel spatula and burn it in Bunsen flame. | (i) Burn with sooty flame (ii) Burns with non sooty flame | (i) Presence of an aromatic compound (ii) Presence of an aliphatic compound |
| Tests for an unsaturation: | | | |
| 7 | Test with bromine water: Take small amount of the organic compound in a test tube add 2 ml of distilled water to dissolve it. To this solution add few drops of bromine water and shake it well. | (i) Orange - yellow colour of bromine water is decolourised (ii) No Decolourisation takes place (iii) Decolourisation with formation of white precipitate. | (i) Substance is unsaturated. (ii) Substance is saturated. (iii) Presence of an aromatic amine or phenol. |
| 8 | Test with KMnO_4 solution: Take small amount of the organic compound in a test tube add 2 ml of distilled water to dissolve it. To this solution add few drops of very dilute alkaline KMnO_4 solution and shake it well. | (i) Pink colour of KMnO_4 solution is decolourised (ii) No Decolourisation takes place | (i) Substance is unsaturated. (ii) Substance is unsaturated. |
| TEST FOR SELECTED ORGANIC FUNCTIONAL GROUPS | | | |
| Test For Phenol | | | |
| 9 | Neutral FeCl_3 test: Take 1 ml of neutral ferric chloride solution is taken in a dry clean test tube. Add 2 or 3 drops (or a pinch of solid) of organic compound to it. If no colouration occurs add 3 or 4 drops of alcohol. | (i) Violet colouration is seen (ii) violet – blue colouration is seen (iii) green colouration is seen | (i) Presence of phenol. (ii) Presence of α -naphthol (iii) Presence of β -naphthol |



| TEST FOR CARBOXYLIC ACIDS | | | |
|---------------------------|---|-----------------------------------|-------------------------------|
| 10 | Esterification reaction: Take 1 ml (or a pinch of solid) of an organic compound in a clean test tube. Add 1 ml of ethyl alcohol and 4 to 5 drops of conc. sulphuric acid to it. Heat the reaction mixture strongly for about 5 minutes. Then pour the mixture into a beaker containing dil. Sodium carbonate solution and note the smell. | A Pleasant fruity odour is noted. | Presence of carboxylic group. |
| Test for aldehydes. | | | |
| 11 | Tollen's reagent test: Take 2 ml of Tollen's reagent in a clean dry test tube. Add 3-4 drops of an organic compound (or 0.2 g of solid) to it, and warm the mixture on a water bath for about 5 minutes. | Shining silver mirror is formed. | Presence of an aldehyde |
| 12 | Fehling's test: Take 1 ml each of Fehling's solution A and B are taken in a test tube. Add 4-5 drops of an organic compound (or 0.2g of solid) to it, and warm the mixture on a water bath for about 5 minutes. | Red precipitate is formed. | Presence of an aldehyde |
| Test for ketones | | | |
| 13 | Legal's test: A small amount of the substance is taken in a test tube. 1 ml sodium nitro prusside solution is added. Then sodium hydroxide solution is added dropwise. | Red colouration. | Presence of a ketone. |
| Test for an amine. | | | |



| | | | |
|-------------------------------|--|---|---------------------------------------|
| 14 | Dye test: Take A small amount of an organic substance in a clean test tube, add 2 ml of HCl to dissolve it. Add few crystals of NaNO_2 , and cool the mixture in ice bath. Then add 2 ml of ice cold solution of β -naphtholin NaOH. | Scarlet red dye is obtained. | Presence of an aromatic primary amine |
| Test for diamide | | | |
| 15 | Biuret test: Take A small amount of an organic compound in a test tube. Heat strongly and then allow to cool. Dissolve the residue with 2 ml of water. To this solution Add 1 ml of dilute copper sulphate solution and few drops of 10% NaOH solution drop by drop. | Violet colour is appeared. | presence of a diamide |
| Test for carbohydrates | | | |
| 16 | Molisch's test: Take A small amount of an organic compound in a test tube. It is dissolved in 2 ml of water. Add 3-4 drops of alpha naphthol to it. Then add conc H_2SO_4 through the sides of test tube carefully. | Violet or purple ring is formed at the junction of the two liquids. | Presence of carbohydrate |
| 17 | Osazone test: Take A small amount of an organic compound in a test tube. Add 1 ml of phenyl hydrazine solution and heat the mixture for about 5 minutes on a boiling water bath. | Yellow crystals are obtained | Presence of carbohydrate |

Report:

The given organic compound contains /is

- (i) Aromatic / aliphatic
- (ii) Saturated / unsaturated
- (iii) _____ functional group

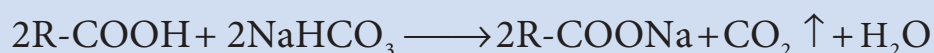
List of organic compounds for analysis:

- | | | |
|-------------------|------------------|--------------------|
| 1. Benzaldehyde | 5. Benzoic acid | 9. Aniline |
| 2. Cinnamaldehyde | 6. Cinnamic acid | 10. Salicylic acid |
| 3. Acetophenone | 7. Urea | |
| 4. Benzophenone | 8. Glucose | |

REASONING

3. Action with sodium bicarbonate:

Carboxylic acids react with sodium bi carbonate and liberate CO_2 . Evolution of carbon dioxide gives brisk effervescence.



4. Action with Borsches reagent:

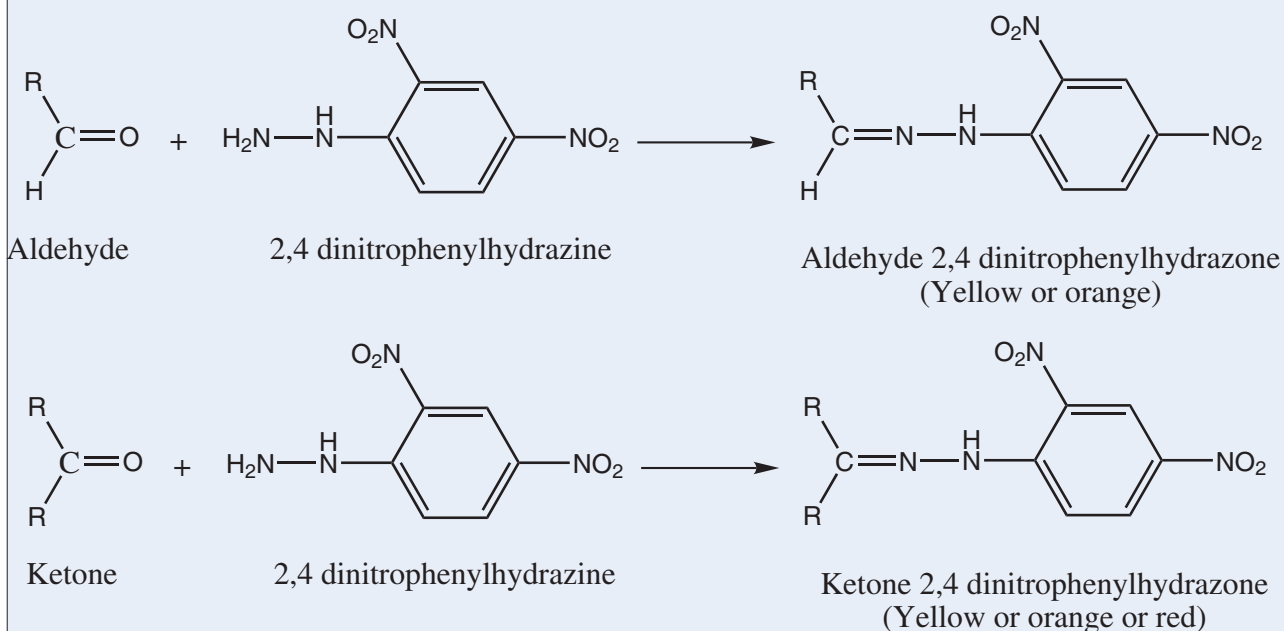
Borsches reagent is prepared by dissolving 2,4-dinitrophenylhydrazine in a solution containing methanol and little of conc sulphuric acid.

Aldehydes and ketones react with borsches reagent to form yellow, orange or red precipitate (dinitro phenylhydrazone)

Aliphatic carbonyl compounds give deep yellow precipitate.

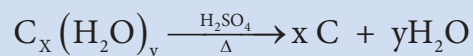
Aromatic carbonyl compounds give red precipitate.

2,4-dinitrophenyl hydrazine can be used to qualitatively detect the carbonyl group of an aldehyde or ketone. A positive result is indicated by the formation of an yellow or orange-red precipitate of 2,4-dinitrophenyl hydrazone.



5. Charring test:

When carbohydrates are treated with concentrated sulphuric acid, dehydration of carbohydrates results in charring.

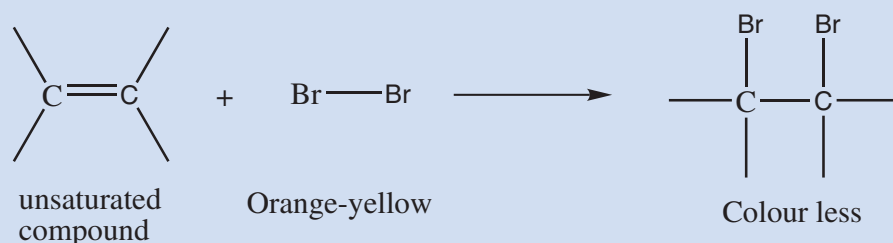


6. Ignition test

Aromatic compounds burn with a strong sooty yellow flame because of the high carbon-hydrogen ratio. Aliphatic compounds burn with non-sooty flame.

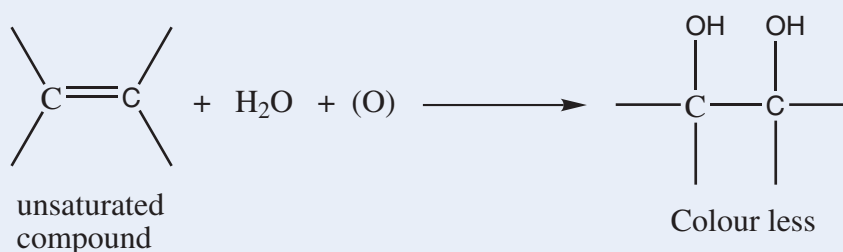
7. Test with bromine water:

In this test, the orange-red colour of bromine solution disappears when it is added to an unsaturated organic compound.



8. Test with $KMnO_4$ (Baeyer's Test)

In this test, pink colour of $KMnO_4$ disappears, when alkaline $KMnO_4$ is added to an unsaturated hydrocarbon. The disappearance of pink colour may take place with or without the formation of brown precipitate of MnO_2 .



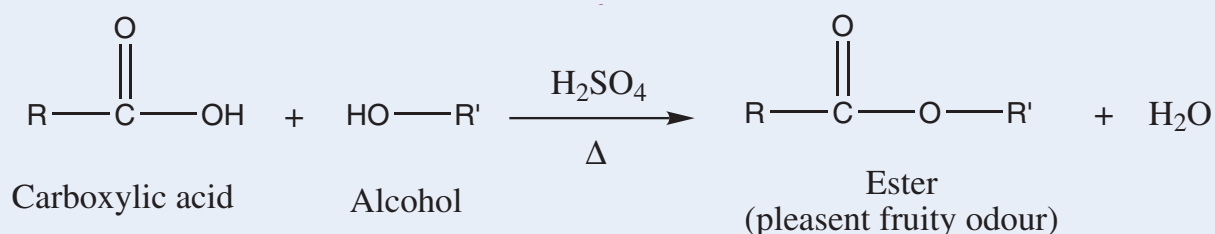
9. Neutral $FeCl_3$ test:

Phenol reacts with ferric ions to form violet coloured complex.

Aqueous solution Naphthols do not give any characteristic colour with neutral ferric chloride. But alcoholic solution of α and β naphthols give blue-violet and green colouration respectively due to the formation of binaphthols.

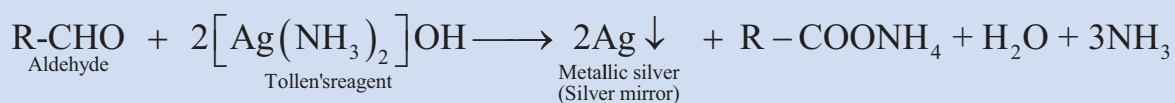
10. Esterification test:

Alcohols react with carboxylic acids to form fruity smelling compounds called esters. This esterification is catalysed by an acid such as concentrated sulphuric acid.



11. Tollen's reagent test:

Aldehydes react with Tollen's reagent to form elemental silver, accumulated onto the inner surface of the test tube. Thus silver mirror is produced on the inner walls of the test tube.



Tollen's reagent preparation:

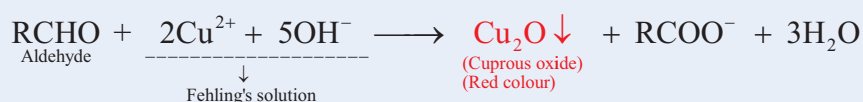
Tollen's reagent is ammoniacal silver nitrate. It is prepared as follows. About 1 g of silver nitrate crystals are dissolved in distilled water in a clean dry test tube. To this aqueous solution of silver nitrate, add 2 ml of dilute NaOH solution to it. A brown precipitate of silver oxide is formed. This precipitate is dissolved by adding dilute ammonia solution drop wise.

12. Fehling's Test

Fehling's solution A is an aqueous solution of copper sulphate.

Fehling's solution B is a clear solution of sodium potassium tartrate (Rochelle salt) and strong alkali (NaOH).

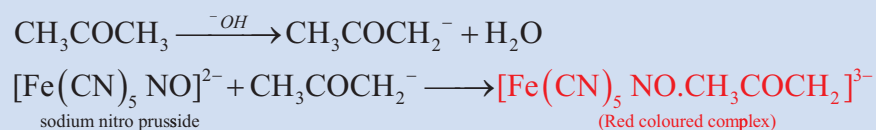
The Fehling's solution is obtained by mixing equal volumes of both Fehling's solution A and Fehling's solution B that has a deep blue colour. In Fehling's solution, copper (II) ions form a complex with tartrate ions in alkali. Aldehydes reduces the Cu(II) ions in the Fehling's solution to red precipitate of cuprous oxide(copper (I) oxide).



Note: Benzaldehyde may not give this test as the reaction is very slow.

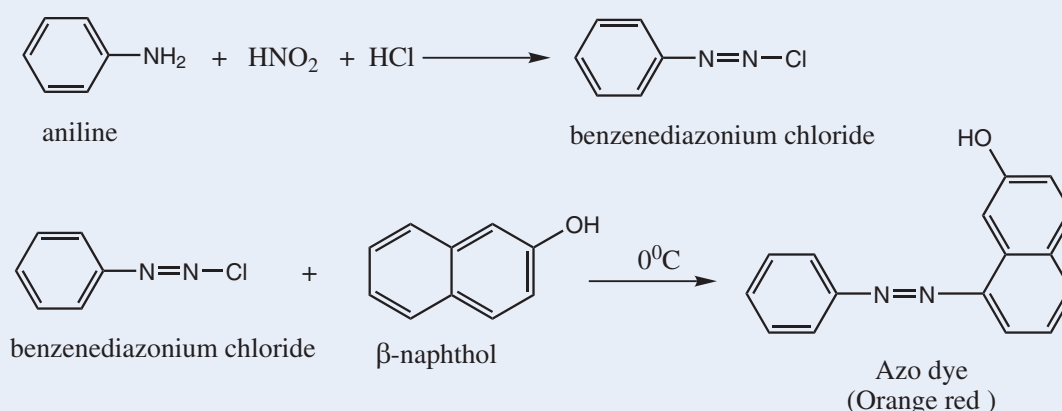
13. Sodium nitroprusside Test

The anion of the ketone formed by a alkali reacts with nitroprusside ion to form a red coloured complex. this test is not given by aldehydes.



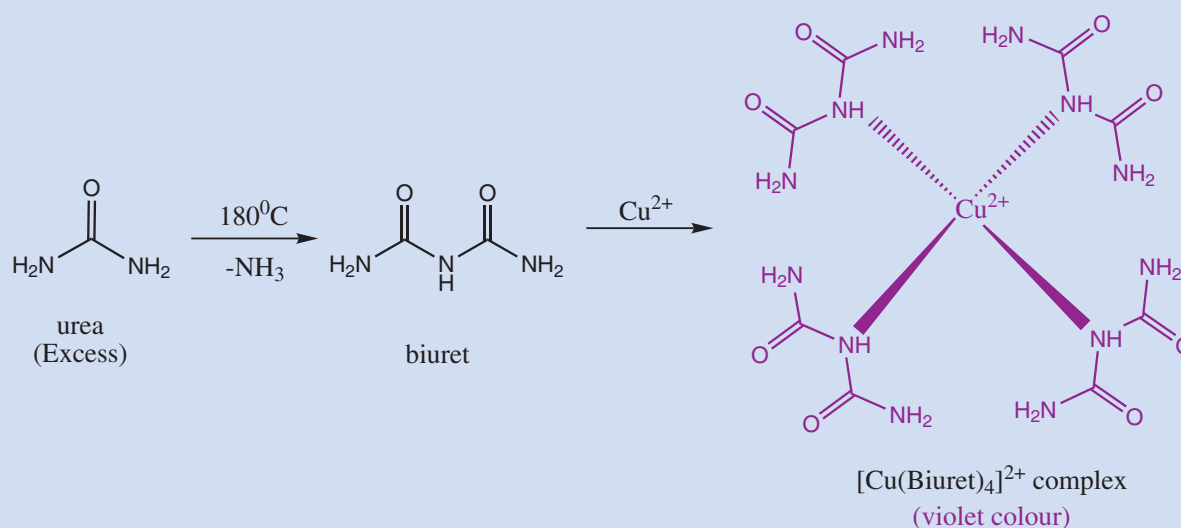
14. Azo-Dye Test

This test is given by aromatic primary amines. Aromatic primary amines react with nitrous acid to form diazonium salts. These diazonium salts undergo coupling reaction with β -naphthol to form orange coloured azo dye.



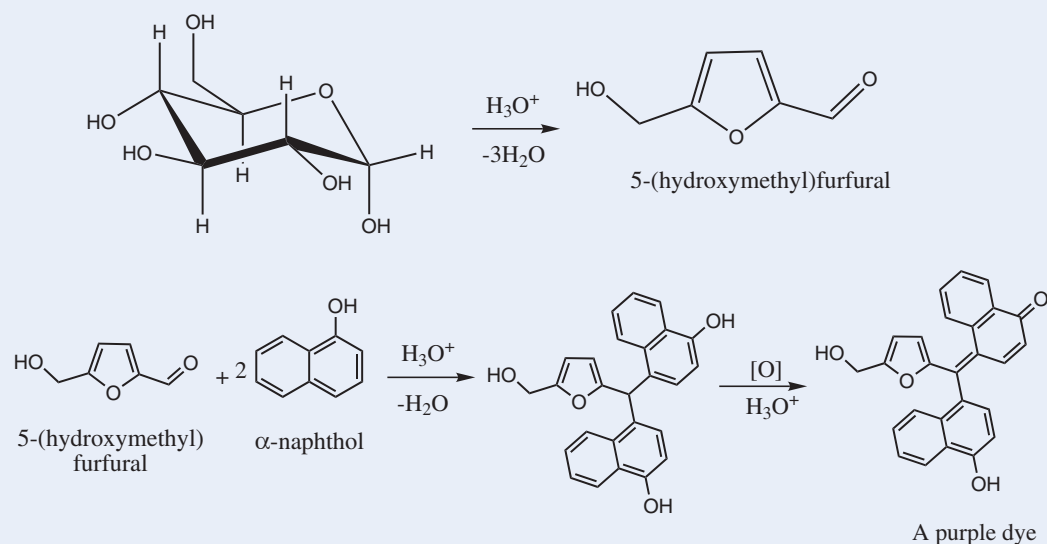
15. Biuret test

On strong heating Diamide (like urea) form biuret, which forms a copper complex with Cu^{2+} ions from copper sulphate solution. This copper –biuret complex is deep violet coloured.



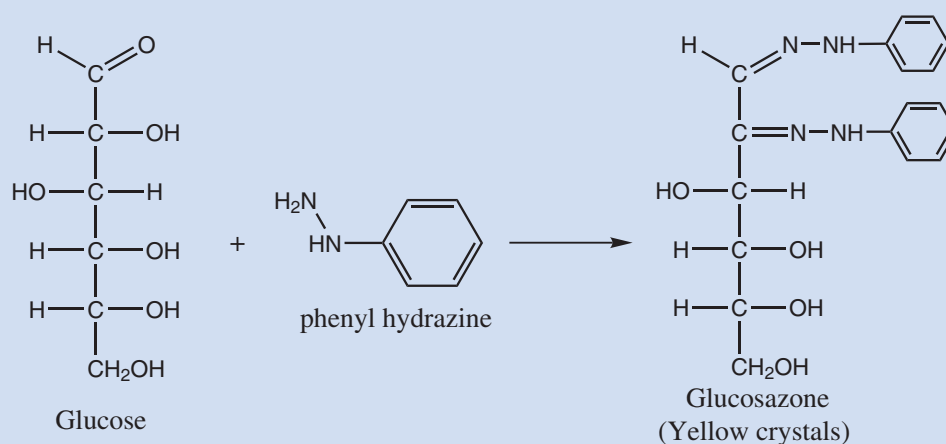
16. Molisch's test:

Disaccharides, and polysaccharides are hydrolysed to Monosaccharides by strong mineral acids. Pentoses are then dehydrated to furfural, while hexoses are dehydrated to 5-hydroxymethylfurfural. These aldehydes formed will condense with two molecules of α -Naphthol to form a purple-coloured product, as shown below.



17. Osazone test:

Phenyl hydrazine in acetic acid, when boiled with reducing sugars forms Osazone. The first two carbon atoms are involved in this reaction. The sugars that differ in their configuration on these carbon atoms give the same type of Osazone. Thus glucose, fructose and mannose give the same needle type yellow crystals.



II-VOLUMETRIC ANALYSIS

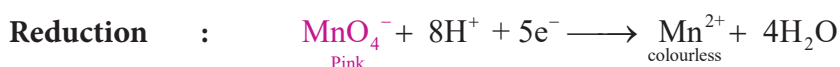
1. Estimation of Ferrous Sulphate (Fe^{2+})

Aim :

To estimate the amount of ferrous sulphate dissolved in 750 ml of the given unknown solution volumetrically. For this you are given with a standard solution of ferrous ammonium sulphate (FAS) of normality 0.1102 N and potassium permanganate solution as link solution.

Principle:

During these titrations, Fe^{2+} ions (from ferrous salts) are oxidised to MnO_4^- ions and MnO_4^- ion (from Mn^{2+}) is reduced to Mn^{2+} ion.



| S.no | Content | Titration-I | Titration-II |
|------|--|---|---|
| 1 | Burette solution | KMnO_4 | KMnO_4 |
| 2 | Pipette solution | 20 ml of standard FAS | 20 ml of unknown FeSO_4 |
| 3 | Acid to be added | 20ml of 2N H_2SO_4 (approx) | 20ml of 2N H_2SO_4 (approx) |
| 4 | Temperature | Lab temperature | Lab temperature |
| 5 | Indicator | Self-indicator (KMnO_4) | Self-indicator (KMnO_4) |
| 6 | End point | Appearance of permanent pale pink colour | Appearance of permanent pale pink colour |
| 7 | Equivalent weight of $\text{FeSO}_4 = 278$ | | |

Procedure :

Titration-I

(Link KMnO_4) Vs (Standard FAS)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same KMnO_4 solution up to the zero mark. Exactly 20 ml of standard FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted, and the same procedure is repeated to get concordant values.

Titration –I

(Link KMnO_4) Vs (Standard FAS)

| S.no | Volume of standard FAS (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|-----------------------------|------------------|------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of KMnO_4 (link) solution (V_1) = -----ml

Normality KMnO_4 (link) solution (N_1) =-----N

Volume of standard FAS solution (V_2) = 20 ml

Normality of standard FAS solution (N_2) = 0.1102 N

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of KMnO_4 (link) solution (N_1) = _____ X _____ N

Titration-II

(Unknown FeSO_4) Vs (Link KMnO_4)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same KMnO_4 solution up to the zero mark. Exactly 20 ml of unknown FeSO_4 solution is pipetted out into the clean, washed conical flask. To this FeSO_4 solution approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link FeSO_4) Vs (Unknown FeSO_4 solution)

| s.no | Volume of Unknown FeSO_4 (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|--|------------------|------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of Unknown FeSO_4 solution $V_1 = 20 \text{ ml}$

Normality of Unknown FeSO_4 solution $N_1 = ? \text{ N}$

Volume of KMnO_4 (link) solution $V_2 = \text{ml}$

Normality KMnO_4 (link) solution $N_2 = X \text{ N}$

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

$$N_1 = \frac{Y}{\quad} \text{ N}$$

The normality of unknown FeSO_4 solution = $\frac{Y}{\quad} \text{ N}$

Weight calculation:

The amount of FeSO_4 dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of FeSO_4 dissolved in 750 ml of the solution = $\frac{\text{Normality} \times \text{equivalent weight} \times 750}{1000}$

$$N_1 = \frac{Y \times 278 \times 3}{4}$$

$$= \quad \text{ g}$$

Report :

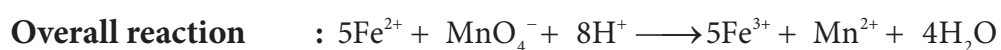
The amount of FeSO_4 dissolved in 750 ml of the solution = $\quad \text{ g}$

2. Estimation of Ferrous Ammonium Sulphate (FAS)

Aim :

To estimate the amount of ferrous ammonium sulphate (FAS) dissolved in 1500 ml of the given unknown solution volumetrically. For this you are given with a standard solution of ferrous sulphate (FeSO_4) of normality 0.1024 N and potassium permanganate solution as link solution.

Principle:



Short procedure:

| s.no | Content | Titration-I | Titration-II |
|------|--------------------------------|---|---|
| 1 | Burette solution | KMnO_4 | KMnO_4 |
| 2 | Pipette solution | 20 ml of standard FeSO_4 | 20 ml of unknown FAS |
| 3 | Acid to be added | 20ml of 2N H_2SO_4 (approx) | 20ml of 2N H_2SO_4 (approx) |
| 4 | Temperature | Lab temperature | Lab temperature |
| 5 | Indicator | Self-indicator (KMnO_4) | Self-indicator (KMnO_4) |
| 6 | End point | Appearance of permanent pale pink colour | Appearance of permanent pale pink colour |
| 7 | Equivalent weight of FAS = 392 | | |

Procedure :

Titration-I

(Link KMnO_4) Vs (Standard FeSO_4)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same FeSO_4 solution up to the zero mark. Exactly 20 ml of standard FeSO_4 solution is pipetted out into the clean, washed conical flask. To this solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading are noted, the same procedure is repeated to get concordant values.

Titration –I

(Link KMnO_4) Vs (Standard FeSO_4)

| s.no | Volume of standard FeSO_4 (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|---|------------------|------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

| | | | |
|--|-------|---|----------|
| Volume of KMnO_4 (link) solution | V_1 | = | ml |
| Normality KMnO_4 (link) solution | N_1 | = | ?N |
| Volume of standard FeSO_4 solution | V_2 | = | 20 ml |
| Normality of standard FeSO_4 solution | N_2 | = | 0.1024 N |

According to normality equation:

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of KMnO_4 (link) solution (N_1) = _____ X _____ N

Titration–II

(Unknown FAS) Vs (Link KMnO_4)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same KMnO_4 solution up to the zero mark. Exactly 20 ml of unknown FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link KMnO_4) Vs (Unknown FAS)

| s.no | Volume of Unknown FAS (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|----------------------------|------------------|------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of Unknown FAS solution $V_1 = 20\text{ml}$

Normality of Unknown FAS solution $N_1 = ? \text{ N}$

Volume of KMnO_4 (link) solution $V_2 = \text{ml}$

Normality KMnO_4 (link) solution $N_2 = \text{N}$

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

$$N_1 = \frac{Y}{\text{ml}} \text{ N}$$

The normality of unknown FAS solution = $\frac{Y}{\text{ml}} \text{ N}$

Weight calculation:

The amount of FAS dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of FAS dissolved in 1500 ml of the solution = $\frac{\text{Normality} \times \text{equivalent weight} \times 1500}{1000}$

$$= \frac{Y \times 392 \times 1500}{1000}$$

$$= \text{g}$$

Report :

The amount of FAS dissolved in 1500 ml of the solution = g

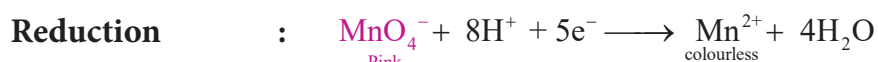
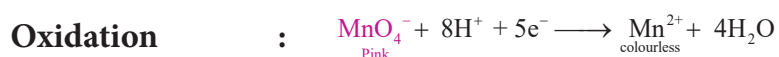
3. Estimation of oxalic acid

Aim :

To estimate the amount of oxalic acid dissolved in 500 ml of the given solution volumetrically. For this you are given with a standard solution of ferrous ammonium sulphate (FAS) of normality 0.1 N and potassium permanganate solution as link solution.

Principle:

During these titrations, oxalic acid is oxidized to CO_2 and MnO_4^- ions (from KMnO_4) is reduced to Mn^{2+} ion.



Since one mole oxalic acid releases 2 moles of electrons, the equivalent weight of oxalic acid = $\frac{106}{2} = 63$ (oxalic acid is dihydrated)

Short procedure:

| s.no | Content | Titration-I | Titration-II |
|------|---------------------------------------|---|---|
| 1 | Burette solution | KMnO_4 | KMnO_4 |
| 2 | Pipette solution | 20 ml of standard FAS | 20 ml of unknown oxalic acid |
| 3 | Acid to be added | 20ml of 2N H_2SO_4 (approx) | 20ml of 2N H_2SO_4 (approx) |
| 4 | Temperature | Lab temperature | 60 – 70 °C |
| 5 | Indicator | Self-indicator (KMnO_4) | Self-indicator (KMnO_4) |
| 6 | End point | Appearance of permanent pale pink colour | Appearance of permanent pale pink colour |
| 7 | Equivalent weight of oxalic acid = 63 | | |

Procedure :

Titration-I

(Link KMnO_4) Vs (Standard FAS)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same KMnO_4 solution up to the zero mark. Exactly 20 ml of standard FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(Link KMnO_4) Vs (Standard FAS solution)

| s.no | Volume of standard FAS (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|-----------------------------|------------------|------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

| | | | |
|---|-------|---|-------|
| Volume of KMnO_4 (link) solution | V_1 | = | ml |
| Normality KMnO_4 (link) solution | N_1 | = | ? N |
| Volume of standard FAS solution | V_2 | = | 20 ml |
| Normality of standard FAS solution | N_2 | = | 0.1 N |

According to normality equation:

$$V_1 \times N_1 = V_2 \times N_2$$

$$N_1 = \frac{V_2 \times N_2}{V_1} =$$

Normality KMnO_4 (link) solution $N_1 =$ _____ N

Titration–II

(Unknown oxalic acid) Vs (Link KMnO_4)

Burette is washed with water, rinsed with KMnO_4 solution and filled with same KMnO_4 solution up to the zero mark. Exactly 20 ml of unknown oxalic acid solution is pipetted out into the clean, washed conical flask. To this oxalic acid solution approximately 20ml of 2N sulphuric acid is added. This mixture is heated to 60 – 70°C using Bunsen burner and that hot solution is titrated against KMnO_4 Link solution from the burette. KMnO_4 is added drop wise till the appearance of permanent pale pink colour. Burette reading are noted, the same procedure is repeated to get concordant values.

Titration –II

(Link KMnO_4) Vs (Unknown oxalic acid)

| s.no | Volume of Unknown oxalic acid (ml) | Burette readings | | Concordant value (Volume of KMnO_4) (ml) |
|------|------------------------------------|------------------|---------------|--|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of Unknown oxalic acid solution $V_1 = 20 \text{ ml}$

Normality of Unknown oxalic acid solution $N_1 = ? \text{ N}$

Volume of KMnO_4 (link) solution $V_2 = \text{ml}$

Normality KMnO_4 (link) solution $N_2 = \text{N}$

According to normality equation:

$$V_1 \times N_1 = V_2 \times N_2$$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of Unknown oxalic acid solution $N_1 = \frac{Y}{\quad} \text{ N}$

Weight calculation:

The amount of oxalic acid dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of oxalic acid dissolved in 500 ml of the solution = $\frac{Y \times 63 \times 500}{1000}$

$$= \frac{Y \times 63 \times 500}{1000}$$

$$= \text{g}$$

Report :

The amount of oxalic acid dissolved in 500 ml of given the solution = g

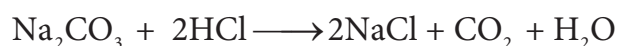
4. Estimation of sodium hydroxide

Aim :

To estimate the amount of sodium hydroxide dissolved in 250 ml of the given unknown solution volumetrically. For this you are given with a standard solution of sodium carbonate solution of normality 0.0948 N and hydrochloric acid solution as link solution.

Principle:

Neutralization of Sodium carbonate by HCl is given below. To indicate the end point, methyl orange is used as an indicator.



Neutralization of Sodium hydroxide by HCl is given below. To indicate the end point, phenolphthalein is used as an indicator.



Short procedure:

| s.no | Content | Titration-I | Titration-II |
|------|--------------------------------|---|--------------------------------|
| 1 | Burette solution | HCl (link solution) | HCl (link solution) |
| 2 | Pipette solution | 20 ml of standard Na_2CO_3 solution | 20 ml of unknown NaOH solution |
| 4 | Temperature | Lab temperature | Lab temperature |
| 5 | Indicator | Methyl orange | Phenolphthalein |
| 6 | End point | Colour change from straw yellow to pale pink | Disappearance of pink colour |
| 7 | Equivalent weight of NaOH = 40 | | |

Procedure :

Titration-I

(Link HCl)Vs (standard Na_2CO_3)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of standard Na_2CO_3 solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of methyl orange indicator is added and titrated against HCl link solution from the burette. HCl is added drop wise till the colour change from straw yellow to pale pink. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(Link HCl) Vs (standard Na_2CO_3)

| s.no | Volume of standard Na_2CO_3 (ml) | Burette readings | | Concordant value (Volume of HCl) (ml) |
|------|--|------------------|------------|---------------------------------------|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of HCl (link) solution $V_1 =$ ml

Normality HCl (link) solution $N_1 = ?$ N

Volume of standard Na_2CO_3 solution $V_2 =$ 20 ml

Normality of standard Na_2CO_3 solution $N_2 =$ 0.0948 N

According to normality equation:

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of HCl (link) solution (N_1) = _____ X _____ N

Titration–II

(Unknown NaOH) Vs (Link HCl)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of unknown NaOH solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against HCl link solution from the burette. HCl is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link HCl)Vs (Unknown NaOH solution)

| s.n | Volume of Unknown NaOH (ml) | Burette readings | | Concordant value (Volume of HCl) (ml) |
|-----|-----------------------------|------------------|------------|---------------------------------------|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of Unknown NaOH solution $V_1 = 20 \text{ ml}$

Normality of Unknown NaOH solution $N_1 = ? \text{ N}$

Volume of HCl (link) solution $V_2 = \text{ml}$

Normality HCl (link) solution $N_2 = \text{N}$

According to normality equation:

$$V_1 \times N_1 = V_2 \times N_2$$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of Unknown HCl solution $N_1 = \underline{\hspace{2cm} Y \hspace{2cm}} \text{ N}$

Weight calculation:

The amount of NaOH dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of NaOH dissolved in 250 ml of the solution = $\frac{\text{Normality} \times \text{equivalent weight} \times 250}{1000}$

$$= \frac{Y \times 40 \times 250}{1000}$$

$$= \frac{\text{ } \times 40 \times 250}{1000} \text{ g}$$

Report :

The amount of NaOH dissolved in 750 ml of the solution = $\text{ } \text{ g}$

5. Estimation of oxalic acid

Aim :

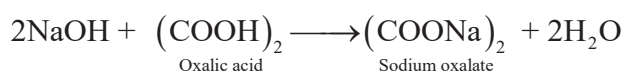
To estimate the amount of oxalic acid dissolved in 1250 ml of the given unknown solution volumetrically. For this you are given with a standard solution of HCl solution of normality 0.1010 N and sodium hydroxide solution as link solution.

Principle:

Neutralization of Sodium hydroxide by HCl is given below. To indicate the end point, phenolphthalein is used as an indicator.



Neutralization of Sodium hydroxide by oxalic acid is given below. To indicate the end point, phenolphthalein is used as an indicator.



Short procedure:

| s.no | Content | Titration-I | Titration-II |
|------|---------------------------------------|------------------------------|---------------------------------|
| 1 | Burette solution | HCl (standard solution) | Oxalic acid (unknown solution) |
| 2 | Pipette solution | 20 ml of NaOH link solution | 20 ml of NaOH link solution |
| 4 | Temperature | Lab temperature | Lab temperature |
| 5 | Indicator | Phenolphthalein | Phenolphthalein |
| 6 | End point | Disappearance of pink colour | Disappearance of pink colour |
| 7 | Equivalent weight of oxalic acid = 63 | | |

Procedure :

Titration-I

(standard HCl)Vs (link NaOH)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of NaOH is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against HCl solution from the burette. HCl is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(standard HCl) Vs (link NaOH)

| s.no | Volume of NaOH(ml) | Burette readings | | Concordant value (Volume of std HCl) (ml) |
|------|--------------------|------------------|---------------|---|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

Volume of NaOH(link) solution $V_1 = 20 \text{ ml}$

Normality NaOH(link) solution $N_1 = ? \text{ N}$

Volume of standard HCl solution $V_2 = \text{ml}$

Normality of standard HCl solution $N_2 = 0.1010 \text{ N}$

According to normality equation:

$$V_1 \times N_1 = V_2 \times N_2$$

$$N_1 = \frac{\times 0.1010}{20} =$$

Normality NaOH (link) solution $N_1 = \text{X} \text{ N}$

Titration–II

(Unknown oxalic acid) Vs (Link NaOH)

Burette is washed with water, rinsed with oxalic acid solution and filled with same oxalic acid solution up to the zero mark. Exactly 20 ml of NaOH solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against oxalic acid solution from the burette. oxalic acid is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link NaOH)Vs (Unknown oxalic acid solution)

| s.no | Volume of NaOH link (ml) | Burette readings | | Concordant value (Volume of oxalic acid) (ml) |
|------|--------------------------|------------------|---------------|---|
| | | Initial (ml) | Final (ml) | |
| 1 | 20 | | | |
| 2 | 20 | | | |
| 3 | 20 | | | |

Calculation :

| | | | |
|---|-------|---|-------|
| Volume of Unknown oxalic acid solution | V_1 | = | ml |
| Normality of Unknown oxalic acid solution | N_1 | = | ? N |
| Volume of NaOH solution | V_2 | = | 20 ml |
| Normality NaOH solution | N_2 | = | N |

According to normality equation:

$$V_1 \times N_1 = V_2 \times N_2$$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of Unknown oxalic acid solution $N_1 = \frac{Y}{\quad} N$

Weight calculation:

The amount of oxalic acid dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

$$\text{The amount of oxalic acid dissolved in 1250 ml of the solution} = \frac{\text{Normality} \times \text{equivalent weight} \times 1250}{1000}$$

$$= \frac{Y \times 63 \times 1250}{1000}$$

$$= \frac{Y \times 63 \times 1250}{1000}$$

$$= \frac{Y \times 63 \times 1250}{1000}$$

$$= \frac{Y \times 63 \times 1250}{1000} \text{ g}$$

Report :

The amount of oxalic acid dissolved in 1250 ml of the solution = g

Glossary - கலைச்சொற்கள்

| | |
|-------------------------------|-----------------------------|
| Acidic oxide | அமிலஆக்சைடு |
| Activated complex | கிளர்வுற்ற அணைவு |
| Activation energy | கிளர்வுறு ஆற்றல் |
| Ambidentate ligand | இருமுனைஈனி |
| Amorphous solid | படிகவடிவமற்றதிண்மம் |
| Amphoteric oxide | ஈரியல்புத்தன்மைகொண்டஆக்சைடு |
| Anionic complex | எதிரயனிஅணைவு |
| Anisotropy | திசையொப்புபண்புஅற்றவை |
| Antiferromagnetic | எதிர்பெற்றோகாந்ததன்மை |
| Basic oxide | காரஆக்சைடு |
| Blast furnace | ஊதுஉலை |
| Bleaching | வெளுப்பான் |
| BM | போர்மேக்னடான் |
| Body centered cubic unit cell | பொருள்மையகனசதுரஅலகுக்குடு |
| Brass | பித்தளை |
| Bronze | வெண்கலம் |
| Brown ring test | பழுப்புவளையசோதனை |
| Cast iron | வார்ப்பிரும்பு |
| Catalysts | வினைவேகமாற்றி |
| Cationic complex | நேரயனிஅணைவு |
| Central metal ion | மையஉலோகஅயனி |
| CFT | படிகபுலக்கொள்கை |
| Chalcogens | சால்கோஜன்கள்(தாதீனிகள்) |
| Chelating ligand | கொடுக்கிணைப்புஈனி |
| Chemiluminescence | வேதி ஒளிர்தல் |
| Chile saltpeter | சிலிவெடியுப்பு |
| Chromatography | வண்ணப்பிரிகைமுறை |
| Close packed arrangement | நெருங்கிபொதிந்தகட்டமைப்பு |
| Coinage metals | நாணயஉலோகங்கள் |
| Collision theory | மோதல் கொள்கை |
| Column chromatography | குழாய்வண்ணப்பிரிகைமுறை |
| Completely filled | முழுவதுமாகநிரம்பிய |
| Concentration of the ore | தாதுக்களை செறிவுட்டல் |



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| Conductivity | கடத்துத்திறன் |
| Coordination compounds | அணைவுச்சேர்மங்கள் |
| Coordination isomerism | அணைவுமாற்றியம் |
| Coordination number | அணைவுஎண் |
| Coordination sphere | அணைவுக்கோளம் |
| Crystal defect | படிகக்குறைபாடு |
| Crystal field splitting | படிகபுலப்பிரிப்பு |
| Crystalline solid | படிகவடிவமுடையதிண்மம் |
| Cupellation | புடமிடுதல் |
| Decay | சிதைவு |
| Degenerate orbitals | சமஆற்றல்கொண்டஆர்பிட்டால்கள் |
| Deliquescent | நீர்உறிஞ்சிநீர்மமாதல் |
| Density | அடர்த்தி |
| Dibasic acid | இருகாரத்துவஅமிலம் |
| Diffraction | விளிம்புவளைவுவிளைவு |
| Double salts | இரட்டைஉப்புகள் |
| Ductility | கம்பியாகஇழுபடும்தன்மை |
| Earth's crust | புவிமேலடுக்கு |
| Edge | விளிம்பு |
| Electro metallurgy | மின்வேதிஉலோகவியல் |
| Electrolytic refining | மின்னாந்தூய்மையாக்கல் |
| Electroplating | மின்முலாம்பூசுதல் |
| Enameling | கனிமபூச்சிடுதல் |
| Excited state | கிளர்வுநிலை |
| Extraction | பிரித்தெடுத்தல் |
| Extrinsic semiconductor | புற மாசுக்குறைக்கடத்தி (புறமார்ந்த குறைகடத்தி) |
| Face | முகப்பு |
| Face cantered cubic unit cell | முகப்புமையகனசதுரஅலகுக்கூடு |
| Facial isomer | முகப்பு மாற்றியம் |
| Ferromagnetic | பெர்ரோகாந்ததன்மை |
| Flash photolysis | துடிப்பு ஒளிப்பகுப்பாய்வு |
| Flints | தீக்கல் |
| Fluorescence | ஒளிர்தல் |
| Fluorescing surface | ஒளிரும்பரப்புகள் |



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| Froth floatation | நுரைமிதப்புமுறை |
| Galvanizing | துத்தநாகமுலாம்பூசுதல் |
| Gangue | கனிமக்கழிவு |
| Garlic | உள்ளிப்பூண்டு |
| Geometrical isomerism | வடிவமாற்றியம் |
| Gravity separation | புவியர்ப்புபிரித்தெடுத்தல் |
| Half filled | பாதிநிரம்பிய |
| Halogens | ஹேலஜன்கள் (உப்பீனிகள்) |
| Hardness of water | நீரின் கடினத்தன்மை |
| Heteroleptic complex | பல்லினாணி அணைவு |
| High spin complex | நிறைசுழற்சி அணைவு |
| Hole | துளை |
| Homoleptic complex | ஒரினாணி அணைவு |
| Hybrid orbitals | இனக்கலப்பு ஆர்பிட்டால்கள் |
| Hydration energy | நீரேற்ற ஆற்றல் |
| Hydro metallurgy | நீர்ம உலோகவியல் |
| Hygroscopic | நீர் உறிஞ்சி இறுத்திவைத்தல் |
| Incompressibility | அமுக்க இயலாத்தன்மை |
| Indian saltpeter | இந்திய வெடியுப்பு |
| Inert gases | மந்தவாயுக்கள் |
| Inert pair effect | மந்த இணைவிளைவு |
| Inner d orbital complex | உள் d ஆர்பிட்டால் அணைவு |
| Inner transition metals | உள் இடைநிலைத்தனிமங்கள் |
| Instantaneous rate of reaction | வினைவேகம் |
| Interfacial angle | முகப்பிடைக்கோணம் |
| Interstitial defect | இடைச்செறுகல்படிகுறைபாடு |
| Interstitial void | இடைவெளிவெற்றிடம் |
| Intrinsic semiconductor | இயல்குறைக்கடத்தி (உள்ளார்ந்த குறைகடத்தி) |
| Ionisation enthalpy | அயனியாக்களன்தால்பி |
| Ionisation isomerism | அயனியாதல்மாற்றியம் |
| Isotropy | திசையொப்பு பண்பு உடையவை |
| Kinetic stability | வேகவியல் நிலைப்புத் தன்மை |
| Lanthanide contraction | லாந்தனைடு குறுக்கம் |
| Lattice plane | அணிக்கோவைத்தளம் |



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| Leaching | வேதிக்கழுவதல்முறை |
| LFT | ஈனியுலக்கொள்கை |
| Ligands | ஈனிகள் |
| Linkage isomerism | இணைதல்மாற்றியம் |
| Low spin complex | குறைசுழற்சிஅணைவு |
| Luminescence | ஒளிர்தல் |
| Magnetic resonance imaging | காந்தஒத்ததிர்வுபடமாக்கி |
| Magnetic separation | காந்தப்பிரிப்பு |
| Malleability | தகடாகநெகிழும் தன்மை |
| Meridional isomer | நெடுவரை மாற்றியம் |
| Metal deficiency defect | குறை உலோக அயனிக்குறைபாடு |
| Metal excess defect | அதி உலோக அயனிக்குறைபாடு |
| Metallic lustre | உலோகப் பளபுத்தன்மை |
| Metalloids | உலோகபோலிகள் |
| Metallurgy | உலோகவியல் |
| Minerals | கனிமங்கள் |
| Molecularity | வினைமூலக்கூறு எண் |
| Molten state | உருகியநிலை |
| Monobasic acid | ஒருகாரத்துவஅமிலம் |
| MOT | மூலக்கூறு ஆர்பிட்டால்கொள்கை |
| Mustard | கடுகு |
| Negative catalyst | வினை தளர்த்தி (எதிர்வினைவேக மாற்றி) |
| Nitrogenous fertilizers | நைட்ரஜன் உரங்கள் |
| Octahedral | எண்முகி |
| Opaque | ஒளிபுகா |
| Optical isomerism | ஒளியியல்மாற்றியம் |
| Orbital angular momentum | ஆர்பிட்டால்கோண உந்தம் |
| Order of the reaction | வினைவகை |
| Ores | தாதுக்கள் |
| Outer d orbital complex | வெளி d ஆர்பிட்டால் அணைவு |
| Oxidation number | ஆக்ஸிஜனேற்ற எண் |
| Oxoanion | ஆக்சோ எதிரயனி |
| Oxocations | ஆக்சோ நேரயனி |
| Packing fraction | பொதிவுபின்னம் |
| Phosphorescence | நின்றொளிர்தல் |



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| Photo sensitizer | ஒளிவேதிவினைத் தூண்டி |
| Photochemical reaction | ஒளி வேதி வினை |
| Pickling of steel | எஃகுவேதித்தூய்மையாக்கல் |
| Pig iron | கசடுஇரும்பு |
| Planar | ஒருதளவடிவம் |
| Positive catalyst | வினையூக்கி (நேர்வினைவேக மாற்றி) |
| Preservative | பதப்படுத்தி |
| Primary valency | முதன்மைஇணைதிறன் |
| Pulverization | மீநுண்துகளாக்குதல் |
| Pyro metallurgy | வெப்பவேதிஉலோகவியல் |
| Quantum efficiency | ஒளிவேதி வினைத்திறன் |
| Radioactive | கதிரியக்கம் |
| Rate constant | வினைவேக மாறிலி |
| Refrigerant | குளிரூட்டி |
| Rigid | கட்டிறுக்கம் |
| Roasting | வறுத்தல் |
| Rocket fuels | ராக்கெட்எரிபொருள் |
| Seaweeds | கடற்பாசி |
| Secondary valency | இரண்டாம்நிலைஇணைதிறன் |
| Self-reduction | சுயஒடுக்கம் |
| Simple cubic unit cell | எளியகனசதுரஅலகுக்கூடு |
| Slag | கசடு |
| Smelting | உருக்கிபிரித்தல் |
| Solvate isomerism | கரைப்பானேற்றமாற்றியம் |
| Spectrochemical series | வேதிநிறமலைதொடர் |
| Square planar | சதுரதளம் |
| Stability constant | நிலைப்புத்தன்மைமாறிலி |
| Stabilizers | நிலைநிறுத்திகள் |
| Strong field ligands | நிறைபுலஈனி |
| Structural isomerism | அமைப்புமாற்றியம் |
| Successive reaction | அடுத்தடுத்து நிகழும் வினைகள் |
| Super conducting magnets | அதிமின்கடத்துகாந்தங்கள் |
| Superconductivity | அதிமின்கடத்துத்திறன் |
| Symmetry | சமச்சீர்த்தன்மை |
| Synergic effect | ஒருங்கிணைந்த விளைவு |



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| Tetrahedral | நான்முகி |
| Thermal decomposition | வெப்பச்சிதைவு |
| Thermodynamic stability | வெப்பஇயக்கவியல்நிலைப்புத்தன்மை |
| Transition metals | இடைநிலைத்தனிமங்கள் |
| Transition state | பரிமாற்ற நிலை |
| Tribasic acid | மூக்காரத்துவஅமிலம் |
| Trigonal bipyramidal | முக்கோணஇருபிரமிடு |
| Trigonal pyramid | முக்கோணபிரமிடு |
| Unit cell | அலகுக்கூடு |
| Unpaired electrons | இணைசேராளக்ட்ரான்கள் |
| Unpleasant | நறுமனமற்ற |
| Vapour phase refining | வாயுநிலைதூய்மையாக்கல் |
| VBT | இணைதிறன்பிணைப்புகொள்கை |
| Void | வெற்றிடம் |
| Weak field ligand | குறைபுலாணி |
| Wool | கம்பளி |
| Wrought iron | தேனிரும்பு |
| Zone refining | கரைதிறவேறுபாட்டுபிரித்தெடுத்தல் |

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