Chapter– 1  
Introduction

1.1 Precipitation Reactions:

In 1899 Nernst showed that the equilibrium between a solid ion and salt and its solutions in water was governed by the solubility product expression. The solubility of an ionic salt in pure water depends on the solubility product constant alone, provided that only cations and anions of salts are in solution.

For a Salt of the type MxNy

\[ MxNy \rightleftharpoons XM^{y+} + YN^{x-} \]

The solubility product expression can be given as

\[ K_{sp} = [M^{y+}]^x [N^{x-}]^y \]

Only a small fractions of all ionic salt that exist can be treated by this simple expression, because most salts yield a number of complex ions of solution in water, or are so soluble that the saturated solution is too concentrated to make reasonable activity coefficient corrections.

Consider an example where two solutions are mixed and a salt precipitates. Unless the two solutions are exactly in the stoichiometric ratio, the common ion effect will decrease the solubility of the salt and make the precipitation more complete.
One of the oldest methods of chemical separation is fractional precipitation. This involves the addition of a reagent which precipitates most of metal ion and leaves another mostly in solution. Many ions which form insoluble salts can be determined by titration, if a suitable method of estimating the equivalence point is available. The most convenient method is potentiometric, but chemical indicators are available for a number of cases. Plots of concentration of metal ion as a function of volume added resemble the titration curves calculated for acid base system.

K H Liesr\(^{(1)}\) have given the combined application of various methods of investigation (e.g. nephelometry, conductivity measurements, electron microscopy, isotope exchange, paper chromatography, co-precipitation etc) lead to refined insight into the course of precipitation reaction. The formation of a new solid phase within a solution. In the case of ionic crystals, be formally described as proceeding via a number of steps – nucleation, growth, ripening, and recrystallization – which overlap in time. The precipitation of hydroxides is a more complex process since additional chemical reactions (hydrolysis, condensation reaction) takes place within the newly formed solid phase.

Schneider and G. Inden\(^{(2)}\) have studied the Simulation of kinetics of precipitation reaction in ferric steel.
There are number of cases in which the solubility of an ionic salt can be calculated from its solubility product alone. A number of other factors also influence the solubility and must be taken into account. The solubility also depends on ionic strength of the solution. Addition of an inert electrolyte such as KNO$_3$ to a saturated solution of a slightly soluble salt such as AgIO$_3$ increases the solubility of that salt to a small extent. Even in dilute solutions however, other equilibrium, besides the solubility equilibrium occurs between ions in the solution.

Very common are the reactions of the cations or anions with water to produce hydroxide complexes or protonated anion species. Usually the hydrolysis of the anion is easily taken into account because the dissociations constant of most weak acids are known.  

Hydrolysis of the cation is more difficult, since transition metals forms rather complicated systems of hydroxide complexes and the equilibrium constant for their systems are often very approximate or completely unknown. Anion hydrolysis will be more extensive in acid solutions, and cation hydrolysis will be more extensive in basic solutions. Both will tend to remove the ion of the salt from solution and hence increase the value of solubility.

Another related phenomenon is the formation of complexes between the cation and anion of the salt. This is particularly
extensive in the silver and cuprous halide but ion-pairs formation occurs even in such salts as CaF$_2$ and CaSO$_4$. Again these reactions tend to increase the solubility over the value calculated from the solubility product alone.

There are several types of reactions in which concentration of the reactants and products affect the stability of various oxidation states. This can be understood through application of the Nernst equation.

**1.2 Kinetic Studies**: In physical chemistry, chemical kinetics or reaction kinetics is the study of reaction rates in a chemical reaction. Analyzing the influence of different reaction conditions on the reaction rate gives information about the reaction mechanism and the transition state of a chemical reaction. In 1864, Peter Waage pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

M.B. Bellakki$^{(3)}$ and others have given kinetic study of oxidative decarboxylation and de-amination of L-glutamine by di-periodato nickelate (IV) in aqueous alkaline medium.
Ashish Kumar Singh\(^{(4)}\) had studied kinetics of oxidation of crotonic acid by sodium N-chloro-p-toluene sulphonamide in the presence of Pd (II) and Os (VIII) as homogenous catalyst.

Kabiruddin\(^{(5)}\) had studied role of manganese (III) micelles and inorganic salts on the kinetics of redox reaction of L-Sorbore and chromium (VI).

Kinetics deals with the experimental determination of reaction rates from which a rate law and reaction rate constant are derived. Essential rate laws exist for zero order reactions (for which reaction rates are independent of initial concentration), first order reactions, and second order reactions, and can be derived for others through calculus. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.
**Kinetics of zero order reaction:**

“A reaction is said to be of zero order, when its rate is independent of the concentration of the reactants. Alternatively, if the concentration of the reactants remains unaltered during the course of a reaction, it is said to be of zero order. As the velocity of a zero order reaction is constant, it can be written as

\[ \text{rate} = \text{constant} \]

or, in mathematical symbols,

\[ \frac{dx}{dt} = k_0 \]  \hspace{1cm} (1)

Where \( x \) is the concentration of product formed and \( k_0 \) is the rate constant for zero order reaction. On integrating above equation with respect to \( t \), we get

\[ \int dx = k_0 \int dt \]

or

\[ x = k_0 t + \text{constant} \]  \hspace{1cm} (2)

Since \( x = 0 \) when \( t = 0 \) (i.e. at the beginning of the reaction, no product has formed), the constant must be zero. Hence,

\[ 0 = k_0 \times 0 + \text{constant}, \]  \hspace{1cm} (3)

or

\[ \text{constant} = 0 \]

On substituting equation (3) in (2), we get

\[ x = k_0 t \]  \hspace{1cm} (4)
The dimensions of $k_0$ are concentration/time, \textit{i.e.}, mole/liter/time. In order to calculate the half-life of this reaction the condition that $t = t_{1/2}$

When $x = a/2$ (a being the initial concentration of the reactant) is substituted into eq. (4) to give

$$a/2 = k_0t_{1/2} \text{ or } t_{1/2} \propto a$$

Thus in a zero order reaction the half-life is proportional to the initial concentration of the reactant.

**Kinetics of First Order Reactions:**

The first order reaction is that in which the rate depends upon the concentration of a single reactant only. Consider a general first order reaction,

$$A \rightarrow \text{Products.} \quad (1)$$

Suppose ‘a’ is the initial concentration of the reacting substance $A$ in gm moles per liter. Let $x$ gm moles/liter of $A$ decompose in time $t$. The rate of the reaction at time $t$ is, according to the law of mass action, proportional to the concentration of $A$ at that instant, viz. $(a - x)$. This can be expressed mathematically as

$$\frac{dx}{dt} \propto (a - x) \text{ or } \frac{dx}{dt} = k_1 (a - x) \quad (2)$$

Where $dx/dt$ is called the reaction velocity and $k_1$ is usually referred to as the specific reaction rate or velocity coefficient. On rearranging Eq. (2), one gets the following equation:
\[
\frac{dx}{a-x} = k_1 \, dt
\]  

(3)

On integrating, we get

\[- \ln (a - x) = k_1 t + I_1 \]  

(4)

where \( I_1 \) is the constant of integration. When \( t = 0, x = 0 \); Eq. (4)
becomes as \(- \ln a = I_1 \). Substituting this in Eq. (4), we have

\[- \ln (a - x) = k_1 t - \ln a \text{ or } a - \ln (a-x) + k_1 t
\]
or

\[\ln \frac{a}{a-x} = k_1 t \quad (ln \frac{A}{B} = A - ln B) \]  

(5)

or

\[k_1 = \frac{1}{t} \ln \frac{a}{a-x} \]  

(6)

or

\[k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad [\text{ln} \, x = 2.303 \log_{10} x.] \]  

(7)

Equation (7) is known as kinetic equation for the first order reactions.

Second form: In certain reactions the initial concentration is not
known definitely because the time when the reaction starts in
uncertain. The value of \( a \) is eliminated by integrating Eq. (3) within
limits as:

\[\int_{x_1}^{x_2} \frac{dx}{a-x} = \int_{t_1}^{t_2} k_1 \, dt \]  

(8)

Where \( x_1 \) and \( x_2 \) represent gram moles of A which have
decomposed in time \( t_1 \) and \( t_2 \) respectively. Eq. (8) is simplified as
Kinetics of Second order Reactions:

If the rate of a reaction is determined by the change in concentration of the two reactants or the square of the concentration of a single reactant, it is said to be of the second order. Such a reaction can be represented in the general way as

(I) \[ A + B \rightarrow \text{Products} \]

(II) \[ 2A \rightarrow \text{Products} \]

Equation of second order reactions: There two cases:

Case I:
Let us consider the case I, \( A + B \rightarrow \text{Products} \).

Suppose \( a \) and \( b \) are the initial concentrations is gm moles/litre of A and B respectively. Let \( x \) gm. moles/litre of A and B decompose in time \( t \). Then the concentrations of A and B will be \( (a - x) \) and \( (b - x) \) gm. moles/litre respectively. According to the law of mass action, the rate of such a second order reaction is represented as

\[
\frac{dx}{dt} = k_2 (a - x)(b - x) \quad (1)
\]

Where \( k_2 \) is the rate constant for the second order reaction.
On separating the variables, equation (1) may be put as
\[ \frac{dx}{(a - x)(b - x)} = k_2 \, dt \]  \hspace{1cm} (2)

By using partial fractions, equation (2) may be written as
\[ \frac{1}{(1 - x)} \left[ \frac{1}{(b - x)} - \frac{1}{(a - x)} \right] \, dx = k_2 \, dt \]

Or
\[ \frac{1}{(a-b)} \left[ \frac{dx}{(b - x)} - \frac{dx}{(a - x)} \right] = k_2 \, dt \]

On integrating it, we obtain
\[ \frac{1}{(a-b)} \left[ - \ln (b - x) + \ln (a - x) \right] = k_2 t + I_2 \]  \hspace{1cm} (3)

where \( I_2 \) is known as constant of integration. When \( t = 0, \ x = 0 \), equation (3) takes the form
\[ \frac{1}{(a-b)} \left[ - \ln b + \ln a \right] = I_2 \quad \text{or} \quad \frac{1}{(a-b)} \ln \frac{a}{b} = I_2 \]  \hspace{1cm} (4)

Substituting the value of \( I_2 \) in equation (3), we obtain
\[ \frac{1}{(a-b)} \left[ - \ln (b - x) + \ln (a - x) \right] = k_2 t + \frac{1}{(a-b)} \ln \frac{a}{b} \]

or
\[ \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = k_2 t + \frac{1}{(a-b)} \ln \frac{a}{b} \]

or
\[ k_2 \ t = \frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln \frac{a}{b} = \frac{1}{(a-b)} \left[ \ln \frac{(a-x)}{(b-x)} \ln \frac{a}{b} \right] \]
or \[ k_2 = \frac{1}{(a-b)t} \ln \left[ \frac{\ln (a-x)}{\ln b} \right] \]

Equation (5) is known as the kinetic equation for the second order reaction.

### 1.3 Induced Reactions:

There are several reactions, which can be carried out simultaneously. Some of them are spontaneous and other is non-spontaneous. When the systems of two reactions proceeding in one phase in which one depends on the other i.e. a spontaneous reaction causes or accelerates a non-spontaneous process, this is called as Chemical induction. A few examples can be given to elucidate this.

1. Oxygen readily oxidizes Sodium sulphite Na$_2$SO$_3$; it does not oxidize Na$_3$AsO$_3$, when these substances are taken separately. If their mixture is taken together, however, they both are easily oxidized by oxygen. Thus the oxidation of Na$_2$SO$_3$, proceeding in a system causes the oxidation of Na$_3$AsO$_3$.

2. H$_2$O$_2$ oxidises Ferrous salt, but does not oxidise HI in aqueous solution, If HI is added to the mixture of FeSO$_4$ & H$_2$O$_2$, it also gets oxidized simultaneously along with ferrous sulphate.
3. Indigo will not react with oxygen, but if benzaldehyde is added to indigo, benzaldehyde will get oxidized to benzoic acid and simultaneously indigo oxidizes to give Isatin and solution will decolorize.

Let us consider general reaction as:

\[
\begin{align*}
\text{A + B} & \quad \rightarrow \quad \bigoplus \quad \text{Primary reaction} \\
\text{A + B} & \quad \rightarrow \quad \bigodot \quad \text{Secondary reaction}
\end{align*}
\]

In both primary and secondary reaction substances A is called an **ACTOR**.

The substance B participating only in the primary reaction of acid its interaction with the actor causes the secondary process is known as **INDUCTOR**.

The substance (C) which participates only in the secondary reaction & receives the effect of the primary reaction is called **ACCEPTOR**.

Kessler introduced the term “Induced oxidation”. He studied the Arsenite induced oxidation of manganous ion by chromic acid.

In any induced oxidation the induction factor is defined as the ratio of the number of equivalence of the reducing agent oxidised to the number of equivalents of the inductor oxidised. However, Induction factor theoretically can be calculated by employing the following relationship.
\[
I. F = \frac{\Delta C_{\text{acceptor}}}{\Delta C_{\text{inductor}}}
\]

\(\Delta C_{\text{acceptor}} = \) Change in number of equivalents of acceptor.

\(\Delta C_{\text{inductor}} = \) Change in number of equivalents of inductor.

It can also be defined as in terms of intermediate product i.e.

\[
I.F = \frac{\text{Reduction in initial product}}{\text{Reduction in intermediate product}}
\]

Induced reaction can be classified into three groups depending upon chemical induction.

1. Where induction factor is infinity (I = \(\alpha\)) in the reaction.
2. Where induction factor is greater than one (I > 1).
3. Where induction factor is less than one (I < 1).

Induced oxidation is very similar to catalysis; the difference is that in catalysis, catalyst is recovered unchanged after the completion of reaction whereas in induced reaction, inductor is consumed in the reaction in stoichiometric relation to the amount of product formed.

Consider a reaction:

\[
3\text{Mn}^{2+} + 2\text{HCrO}_4^- + 2\text{H}^+ \rightarrow 3\text{MnO}_2 + 2\text{Cr}^{3+} + 2\text{H}_2\text{O}
\]

At pH >0

Thermodynamically, the above reaction is impossible but if the same reaction is carried out in the presence of Arsenite, it is represented as follows:
$6H^+ + 2HCrO_4^- + 2H_3AsO_3 + Mn^{+2} \rightarrow 2Cr^{3+} + 2H_3AsO_4 + MnO_2 + 4H_2O$

The free energy liberated in the spontaneous reaction in which the inductor participates may compensate for the expenditure of energy required for the formation of product.

Consider a reaction between Arsenic trioxide by Bromic acid. This reaction is only possible when hydrogen bromide is present in the system. The mixture of HBrO$_3$ & As$_2$O$_3$ is acidified with a weak acid; the reaction practically does not proceed. If the $H^+$ ion concentration is high, formation of HBr is possible.

$$3As_2O_3 + 2HBrO_3 \rightarrow 3As_2O_5 + 2HBr$$ (1)

In the end very small amount of HBr is formed, but then the oxidation of Arsenic trioxide by Bromic acid proceeds with self-acceleration under the influence of the increasing amount of HBr.

The Hydrogen bromide caused the following reactions, which led to the generation of HBr.

$$HBrO_3 + HBr \rightarrow HBrO_2 + HBrO$$ (2)

$$4HBr + HBrO + HBrO_2 \rightarrow 3Br_2 + 3H_2O$$ (3)

$$2Br_2 + As_2O_3 + 2H_2O \rightarrow As_2O_5 + 4HBr$$ (4)

The process as a whole is a self – inductive, since the inductor (HBr) appears in the system as a result of primary reaction (1) and the main reaction (4).
Induced oxidation can be carried out be using Chromic acid. These can be of two types (a) Those where the Chromic acid acts as an oxidizing agent. In these reactions one reducing agent (the inductor), induces the rapid oxidation of the acceptor by Chromic acid, which otherwise (in absence of inductor) could be impossible or very slowly takes place and (b) those where it acts as an inductor. In such reactions Chromic acid induces the rapid oxidation of a reducing agent, by some oxidizing agent, under the conditions where, in the absence of chromic acid, reducing agent is either not attacked or is very slowly attacked by oxidizing agent.

In all induced Chromic acid oxidations induction factor has been found to be either 0.5 or 2. It shows that three oxidation equivalents supplied by each mole of HCrO$_4^-$; either one or two are used for induced oxidation. It suggests that either Cr$^{+4}$ or Cr$^{+5}$ as the oxidation – state of the Chromium atom participate as an intermediate in the reaction.

Consider an example of oxidation of iodide by Chromic acid induced by ferrous ions. Iodide ion is not oxidised either by Chromic acid or by ferric ion alone in weakly acid medium. This indicates that in reaction mixtures there must be formed an oxidizing agent to be more powerful than dichromate. Since the ration of the number of equivalents of iodide oxidised to the
number of equivalents of inductor oxidised is 2:1, this more powerful intermediate oxidizer which reacts with the iodide ion probably Chromium with +5 oxidation states. The mechanism in the skeleton form can be given as follows:

\[
\begin{align*}
\text{Cr}^{6+} + \text{Fe}^{2+} & \xrightarrow{\text{redox}} \text{Cr}^{5+} + \text{Fe}^{3+} \\
\text{Cr}^{5+} + \text{I}^- & \xrightarrow{\text{redox}} \text{Cr}^{3+} + \text{IO}^- \\
2\text{H}^+ + \text{I}^- + \text{IO}^- & \rightarrow \text{I}_2 + \text{H}_2\text{O}
\end{align*}
\]

In the oxidation of manganous salt by Chromic acid induced by arsenite, manganous ions are not oxidised by chromic acid alone. Therefore, in reaction mixtures of arsenite, and manganous salts, some oxidizing agent more powerful than dichromate should be present or produced. The ratio of the number of equivalents of manganous salt oxidised to the number of equivalents of inductor oxidised is 1:2. This suggests that more powerful intermediate oxidizer reacts with manganous salt probably being of +4 oxidation state of Chromium. The probable mechanism is as follows:

\[
\begin{align*}
\text{Cr}^{6+} + \text{As}^{3+} & \rightarrow \text{Cr}^{4+} + \text{As}^{5+} \\
\text{Cr}^{4+} + \text{Mn}^{2+} & \rightarrow \text{Cr}^{3+} + \text{Mn}^{3+} \\
2\text{Mn}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{MnO}_2 + \text{Mn}^{4+} + 4\text{H}^+
\end{align*}
\]

Manchot & Wilhems\textsuperscript{(6)} & Benson\textsuperscript{(7)} studied the induced oxidation of iodide using chromic acid as an oxidizing agent and
Fe$^{2+}$ ion as an inductor. The induction factor has been found to be low.

J. B. Adams and H. M. Brown$^{(8)}$ have studied Discoloration in Raw and Processed Fruits and Vegetables.

Rosalinda Inguanta$^{(9)}$ had studied induced reaction in Preparation of Pd-Coated Anodic Alumina Membranes for Gas Separation Media.

JoeEdington$^{(10)}$ have studied induced reaction in formation of Cerium Oxide/Hydroxide on Copper Substrates by a Spontaneous Immersion Process.

Gerald J Smith$^{(11)}$ had studied photo induced reaction of photo tendering of wool sensitized by naturally occurring polyphenolic dyes. De Lury$^{(12)}$ studied the reaction between chromic acid, iodide and H$_2$AsO$_3$. In which chromic acid acts as oxidizing agent, Iodide acts as acceptor and H$_2$AsO$_3$ as inductor. The induction factor is reported to be 2.

Luther and Rutter$^{(13)}$ studied reactions between chromic acid (oxidizing agent) and iodide (acceptor) using VOSO$_4$, (VO)$_2$ SO$_4$, And (VSO) as inductors. In each case the induction factor was found to be two. They also investigated reactions between chromic acid an oxidizing agent and bromide ion as an acceptor using Fe$^{2+}$, VOSO$_4$ & Ti$^{3+}$ as inductors.
Lang and Zwerina\textsuperscript{(14)} studied reaction between Chromic acid Mn\textsuperscript{+2} and H\textsubscript{2}AsO\textsubscript{3} in which Chromic acid oxidises Mn\textsuperscript{+2} and H\textsubscript{2}AsO\textsubscript{3} acts as an inductor. The induction factor was found to be 0.5.

Kessler\textsuperscript{(15)} studied the induced oxidation of tartaric acid and using Chromic acid as an oxidizer and K\textsubscript{4}Fe (CN)\textsubscript{6}, SO\textsubscript{2}, SbO\textsubscript{3}, SnO and As\textsubscript{2}O\textsubscript{3} as an inductors.

Schonbein\textsuperscript{(16)} studied the reaction between Chromic acid, an oxidizer and Indigo, in which Oxalic acid acts as an inductor.

Manchot and Richter\textsuperscript{(17)} studied the induced oxidation of iodide using Ti\textsuperscript{3+} as an inductor and Chromic acid as an oxidizer. The induction factor was found to be 2, indicating the involvement of more powerful +5 oxidation state of Chromic atom.

**Effect of Salt:**

Ranveer Singh\textsuperscript{(18)} studied the oxidation of P-toluidine and of N, N-diemethyl amine by chromic acid in which he observed negligible salt effect of NaCl, KCl, Na\textsubscript{2}SO\textsubscript{4} on the rate of reaction indicating that the rate-determining step involves are ion and neutral molecule.

The anion effect has been interpreted in terms catalytic effect and a bridge transfer mechanism\textsuperscript{(19)}.  

18
Certain anions, particularly halide ions, catalyze electron exchange reaction for example; it is observed that chloride catalyzes Cuprous-cupric reactions. It also catalyzes ferrous – ferric reaction. Libby demonstrated catalysis by fluoride ion of the Cerous-meric electron exchange \(^{(20)}\). This study reveals that it forms stable ion pairs or halide complexes, the exchange with these ion pair species proceeds with a new path.

The bridge transfer mechanism was studied and deglazed by Taube \(^{(21-22)}\) and his associate. He pointed out that although bridge formation will provide an easier path for an electron transfer, the transfer of the bridging is not an essential feature. Whether groups transfer occurs or not, will depend on the substitution ability of the reactant ions before and after the electron transfer.

The effect of salts in solutions of non-electrolytes is a complex phenomenon \(^{(23)}\).

There have been a number of theories for analysis of the salt effect on the rate of the reaction. Some workers \(^{(24-28)}\) suggested hydrogen theory. According to them, some ions completely tie up a share of water molecules and have no effect on the solvent properties of the rest of the water. Debye P and McAulay \(^{(29)}\) suggested electrostatic theory, they considered heterogeneity of the mixture of water and neutral solute, dielectric constant of solvent.
Kortum\textsuperscript{(30)} suggested that Vander Waals forces might be responsible for decreasing activity coefficient of ion in solution by large ions.

The internal pressure concept of Tammann G\textsuperscript{(31)} was employed by early investigators to relate salt effects to other properties of the salt solutions.

Euler\textsuperscript{(32)} noted a connection between the order of increasing volume contraction on dissolving salts and the order of increasing activity coefficient of ethyl acetate.

There are significant differences between salt effect on acidic and basic non-electrolytes. Acidic non-electrolytes are commonly more sensitive than non polar solutes. The increased salting out (increasing ion activity coefficient) effect is in the order $K < Na < Li$. With basic non-electrolytes there is increased sensitivity to anions and salting out order of the alkali metal cations shifts to the order of $Li < Na < K$.

During the oxidation of aromatic compounds by potassium permanganate, Cullis and Labury\textsuperscript{(33)} observed that, initial rate decreased in the presence of added $\text{Mn}^{+2}$. If intermediate manganese ions are the active oxidizing species, added $\text{Mn}^{+2}$ cause acceleration. Similarly if manganese ions are mainly responsible for oxidations, pyrophosphates and fluoride ions should retard the
oxidation. If MnO$_4^-$ is responsible for oxidation then pyrophosphate and fluoride ions impart no significant change. In general, manganese sulphate has an accelerating influence and the complex forming agents cause retardation. This suggests that Mn$^{+3}$ and associated ions are the principle species responsible for oxidation.

Cullis and Ladbury$^{(33)}$ observed that, the rate of oxidation of ethylbenzene reduces to 60% in presence of large concentration of pyrophosphate ions.

R Gopalan$^{(34)}$ studied kinetics of oxidation of $\alpha$-methyl naphthalene by potassium permanganate. He observed that pyrophosphate, fluoride and sulphate decrease the rate constant.

During the oxidation of antimony (V)$^{(35)}$ with hexacyanoferrate (III), Nandibewoor reported the effect of chloride ion on the rate constant.

K. A. Basheer Ahmed$^{(36)}$ studied oxidation of aliphatic acetylts by N-chlorobenzamide. He observed that sodium nitrate has no effect on rate constant but sodium acetate decreases rate constant.

Puttaswamy$^{(37)}$ observed effect of salt on oxidation of caffeine by sodium - N bromo-p-toulene sulphonamide. He
reported increase in rate by the addition of NaCl but addition of Br- in the form of NaBr had negligible effect on the reaction rate.

Ishwar Bhat\(^{(38)}\) and others reported decrease in rate of reaction with addition of sodium pyrophosphate in the oxidation of pyridoxine by manganese (III).

Bharat Singh\(^{(39)}\) & others reported negative effect of chloride ion concentration on the ruthenium (III) catalysed oxidation of methyl glycol by N-bromosuccinimide.

Valechha\(^{(40-41)}\) and coworkers observed nominal effect of added K\(_2\)SO\(_4\) on the oxidation of acetophenone, allyl, crotyl and cinnamic alcohol by selenium dioxide.

According to Selvaraj\(^{(42)}\) and others, chloride increases the rate of oxidation of substituted piperidin-4-ols and oxan-4-ols by chloramines-T.

**1.4 Nephelometric Analysis:**

In the present work nephelometry is used as a technique for the study of rate of reaction.

Nephelometry and turbidimetry are techniques of analysis that are closely allied to colorimetry. Much of the theory and equipment used in colorimetry apply with little modification to both these techniques.
Both nephelometry and turbidimetry are based on scattering of light by non-transparent particles suspended in a solution. However, the two techniques differ only in the manner of measuring the scattered radiation.

When light is allowed to pass through a suspension, the part of the incident radiant energy is dissipated by absorption, reflection, and refraction while the remainder is transmitted. Measurement of the intensity of the transmitted light as a function of the concentration of the suspended particles forms the basis of turbidimetric analysis.

In nephelometry, the light is also allowed to pass directly through the sample solution having suspended particles. The amount of radiation scattered by the particles is measured at any angle (usually 90°) to the incident beam. The measurement of the intensity of the scattered light as a function of the concentration of the dispersed phase forms the basis of nephelometric analysis.

**Theory:**

Both reflection and scattering phenomena are very important in turbidimetry and nephelometry. If light is allowed to pass through a solution having suspended particles, reflection will take place if the dimensions of suspended particles are larger than the wavelength of incident light. On the other hand, scattering will take
place if the dimensions of suspended particles are of the same order of magnitude or smaller than the incident wavelength. This distinction plays an important role in nephelometry and turbidimetry because it affects the sensitivity of the measurement as well as how the measurement is made. This can be seen from the following discussion:

(i) In nephelometric measurements, the suspended particles should be small with respect to the wavelength used. This is required so that scattering rather than reflection predominates. At the same time, smaller particles undergo scattering to give rise a symmetrical pattern of secondary rays in space having maximum intensity at 90° to the primary incident beam. Due to this reason, most of the instruments used in nephelometry involve measurements at 90°.

If the particles are larger, a small fraction of light gets deviated at right angle to the primary beam whereas the larger fraction gets deviated at angles other than 90°. In such cases, nephelometric measurements are made at angles less than 90° from the primary beam; say in the region 5° to 20°, or even 45°.

In nephelometry, suspended particles should neither be too large nor too small otherwise the scattering efficiency falls off. For measurements to be made in the ultraviolet and visible regions of
spectrum the optimum particles size should be in the range of about 0.1 to 1µm.

(ii) In turbidimetric measurements, particles larger than the wavelength of light do not pose much problem because measurement depends on the total radiation removed from the primary beam irrespective of the mechanism by which it is removed or the angle through which it undergoes deviation. But with larger particles another problem arises, i.e. the relationship between absorbance and concentration does not remain linear. Thus, in such cases measurements cannot be very accurate.

**Factors Affecting Measurements:**

The amount of radiation removed or deviated from the primary radiation beam depends on the following factors:

**Concentration:**

In turbidimetry, one measures the transmittance of a primary beam of radiation which is defined as follows:

\[ T = \text{Transmittance} = \frac{I_0}{I} \]

Where \( I_0 \) denotes the intensity of incident light after passing through comparison cell containing solvent and \( I \), the intensity of the light after passing through the cell containing the sample solution. The transmittance \( T \) is related to the concentration \( c \) of suspended material by an equation similar to Beer’s law, i.e.
\[ S = \log \frac{I_0}{I} = kbc \]

Where \( S \) is called turbidence due to scattering (analogous to the term absorbance), \( b \) is the path length, and \( k \) is proportionality constant known as turbidity coefficient. The value of \( k \) depends on the particle size and shape, wavelength and refractive indices of the suspended and suspending media.

It is important to remark here that the above equation holds good only for such small particles where Rayleigh’s scattering is the main mechanism of attenuation and for dilute suspensions where multiple scattering is unlikely. But the suspension should not be too dilute otherwise the transmitted intensity \( I \) becomes equal to the incident intensity. In such a situation accurate measurement is not possible.

Above equation shows appreciable departures for real cases in analogous to departures from Beer’s law. In turbidimetry, a working curve is prepared by plotting turbidence vs known concentrations of scattering material and then the unknown concentrations are observed from this curve by knowing their turbidence values from the turbidimeter.

In nephelometry, one cannot relate the scattered intensity to the concentration by any simple theoretical equation. The reason
for this is that the scattered intensity in nephelometry depends upon
a number of complicated factors like the properties of the scattering
suspension and the angle and geometry of the measuring
instrument. The best equation will be that one which will relate the
scattered intensity $I$, to the concentration of suspended particles $c$
by the approximate empirical equation such as:

$$I = k_s I_0 c$$

Where $k_s$ denote the empirical constant for a particular
system and $I_0$ is the incident intensity and all measurements are
carried out under identical conditions.

Whenever quantitative analysis is to be carried out in
nephelometry, a working curve is obtained by plotting the
concentration of suspended particles $vs$ $I_s/I_0$ under carefully
controlled conditions. But in the most of the cases $\log (I_0/I_s)$ is
plotted $vs. c$ to conform with the more usual spectrophotometric
and turbidimetric practices.

**Particle geometry:**

In both turbidimetric and nephelometric analysis, the most
critical factor is the control of particle size and shape. The ideal
situation is that when all samples and calibration solutions with
which they are compared should possess the same distribution of
small, medium and large particles. This, in turn, means that one
should prepare samples and standards under identical conditions. But this is not a simple task. The conditions include concentration of reactants, temperature, agitation, $pH$, presence of non-reactants, temperature, the order of mixing of reactants and the time allowed for particle growth. If one does not maintain these conditions, one may get different sized particles which may introduce major error in turbidimetry and nephelometry.

**Wave length of incident light:**

In turbidimetry, the wavelength of incident light is an important factor. The general practice is to select such a wavelength where the sample solution does not absorb strongly. If the sample solution is colourless, one must use the incident light of the same colour. On the other hand, if clear solutions are having dark particles, light in the red or even infrared region must be used where there is maximum absorption.

In nephelometry, absorption is much less of a problem. In such a case, white light is generally used as a convenience.

**Instrumentation:**

![Instrumentation Diagram]

- Light Source
- Lens
- Sample
- Detector and Readout
Much of the instrumentation used in nephelometry and turbidimetry is very similar to spectrophotometry. Only some special features are described here.

**Sources:**

One may use white light in nephelometer but it is advantageous to use monochromatic radiation. Similarly, monochromatic radiation is used in turbidimeters to minimize absorption. In either case it is necessary to use sources providing high intensity monochromatic radiation and wherever possible short wavelengths are used to increase the efficiency of Rayleigh’s scattering. A mercury arc or a laser, with appropriate filter combinations for isolating one of its emission lines, is undoubtedly the most convenient source. However, if one has to determine the concentration of a particular material, a polychromatic source such as a tungsten lamp may be used. Even in such a case the best results are obtained if we use blue spectral region; a filter may be employed to block other wavelengths.

**Detectors:**

In nephelometer photomultiplier tubes should be used as detectors because the intensity of scattered radiation is usually very small. In most of the nephelometer, detector is generally fixed at 90° to the primary beam but for maximum versatility and
sensitivity it is desirable to vary the detector angle which is generally close to the primary beam. In some nephelometer, the detector is mounted on a circular disc which allows measurement at many angles, i.e., at $0^\circ$ and from $30^\circ$ to $135^\circ$. The outer edge of the disc is usually, graduated in degree and readable from the outside.

In turbidimeter, ordinary detectors such as phototubes may be used.

**Cells:**

Although we can use cylindrical cells, they must have flat faces where the entering and exiting beams are to be passed. This is to minimize reflections and multiple scatterings from the cell walls. In general, a cell with a rectangular cross section is preferred. Where measurements are to be made at angles other than $90^\circ$, semi-octagonal cells are used. The octagonal faces will allow measurements to be made at $0^\circ$, $45^\circ$, $90^\circ$ or $135^\circ$ to the primary beam. Generally, walls through which light beams are not to pass are painted a dull black to absorb unwanted radiation and minimize stray radiation. In experimental cells, a blackened curved horn is frequently affixed to the wall directly opposite the entering beam to trap the entire beam which is not scattered. Alternatively, one can put a light trap for his purpose in the cell of the chamber in which the cell is located.
**Turbidimeter:**

In most of turbidity measurements, ordinary colorimeters or spectrophotometers may be used. Simple visual instruments like the Parr turbidimeter or colorimeter can also be used but the interesting turbidimeter is Du Pont model 430 which is more sensitive to low concentrations of suspended particles than an ordinary turbidimeter. This is a double-beam instrument which depends for its operation on the relative degree of polarization of transmitted and scattered light.

**Application of Nephelometry:**

Nephelometry can be used on gaseous, liquid or even transparent solid samples in greatly varying proportions. The various applications of this technique are as follows:

**Inorganic Analysis:**

In some cases, precipitates are difficult to filter due to small size or a gelatinous nature. In such cases, gravimetric operations cannot be performed. In these cases, nephelometry can be used by converting the precipitates into ideal suspension under rigidly controlled conditions. This is done because the scattering of light depends on the size and number of the particles involved as well as their concentration.
By using nephelometry the results of suspensions of unknown concentration are obtained from the calibration curves.

The important uses of nephelometry are the determination of Barium Sulphate, Carbonate as Barium carbonate, and Chloride as Barium chloride. The determination of Sulphate is of particular importance and serves for the routine determination of total Sulphur in coke, coal, oils, rubbers, plastics and other organic substance. In order to determine Sulphur, it is first of all converted into Sulphate. Then it is shaken with sodium chloride solution and excess of solid barium chloride to get a suspension of Barium Sulphate. Finally, this suspension is subjected to be nephelometer as the case may be and the concentration of suspension may be computed from the calibration curve.

F Jones, Aoliveria, G M Parkinson (43) have studied mechanism for interaction of nitrolotriacetic acid and precipitating Barium sulphats.

Another important application of nephelometry is the determination of carbon dioxide. The method involves the bubbling of the gas through an alkaline solution of a barium salt and then analyzing for the barium carbonate suspension with nephelometry.

The nephelometry methods are more precise and sensitive than colorimetric methods. For example, phosphorus can be
estimated at a concentration of 1 part in more than 300 million parts of water as a precipitate with strychnine-molybdate reagent. Similarly ammonia at a concentration of 1 part in 160 million parts of ammonia can be detected by adding Nessler’s reagent.

**Organic Analysis:**

In food and beverages, turbidimeter is used for analysis of turbidity in sugar products, and clarity of citrus juices. Another interesting application is the determination of benzene in alcohol by dilution with water to make an immiscible suspension.

**Biochemical Analysis:**

An important application of turbidimetry is to measure the amount of growth of a test bacterium in a liquid nutrient medium. It is also used to find out the amount of amino acids, vitamins and antibiotics. Nephelometry has been used for the determination of protein and the determination of yeast, glycogen and of beta and gamma globulin in blood serum and plasma.

**Air and water Pollution:**

Turbidimetry and nephelometry are used for the continuous monitoring of air, water pollution. In air, dust and smoke are monitored whereas in water, turbidity is monitored.

A.H. Mahvi, M. Razvi\(^{(44)}\) used this technique and their work is application of poly electrolyte in turbidity removal from surface
water. Here the most important process is the formation of precipitate and coagulation of different types of elements present in water followed by sedimentation.

Telesnicki G. J.Goldberg W. M.\textsuperscript{(45)} have given method for measuring turbidity in coastal water by nephelometric analysis with Formazin calibration. Turbidity generated during a beach restoration project in Florida was compared with Formazin and marl standards.

**Turbidimetric Titrations:**

These titrations may be carried out in a manner analogous to photometric titrations. In these titrations, the absorbance is to be plotted against the volume of titrant added. With the increase in the volume of titrate, the concentration of precipitate increases and hence the absorbance increases. When all the substance gets precipitated, the absorbance become constant. Thus, an abrupt change in the slope indicates the end-point.

**Kinetics Employing Nephelometry:**

Let ‘x’ be the concentration of the compound or precipitate or turbidity. Since ‘x’ is same in each set of experiment it is a constant. If ‘a’ is the original concentrations of the compound (the sodium thiosulphate) the reaction obeys the first order kinetics, then we can write
\[ \frac{d(a-x)}{dt} = -k(a-x) \]

or

\[ \frac{dx}{dt} = k(a-x) \]

Where ‘k’ is the rate constant

On rearranging and integrating, the above equation can be written as

\[ \int_0^x \frac{dx}{a-x} = \int_0^t kdt \]

or

\[ [- \log(a-x)]_0^t = [kt]_0^t + A \]

Where ‘A’ is an integration constant

or

\[ \log \frac{a}{a-x} = kt \]

or

\[ \log \left[ 1 + \frac{x}{a-x} \right] = kt \]

On expansion, the above equation can be written in the following form

\[ \frac{x}{(a-x)} - \frac{x^2}{2(a-x)^2} + \frac{x^3}{3(a-x)^3} - \ldots = kt \]

Of \( x << a \), the higher order terms in the above equation can be ignored and it can be written as
\[
\frac{x}{a} = kt
\]  \hspace{1cm} \ldots \ldots \quad (1)

\text{or}

\[
\frac{1}{a} = \frac{k}{x} \cdot t
\]

This equation (1) suggests that a plot of 1/a vs t (Time) yield a straight line provided ‘x’ is constant.
Chapter – 2
Experimental Details

This chapter deals with chemicals, apparatus, experimental methods utilized for the present investigation of precipitation reaction and induced reaction. The chemicals used were of high purity (AR. Grade) supplied by S D fine chemicals limited. All the solutions were prepared in double distilled water. The volumetric apparatus used were calibrated using the method available in the literature. Following chemicals were used for the present study.

1. Hydrazine sulphate
2. Hexamethylene tetramine
3. Sodium thiosulphate
4. Cerium chloride
5. Strontium chloride
6. Silver nitrate
7. Stannous chloride
8. Cupric chloride
9. Hydrochloric acid
10. Sulphuric acid
11. Oxalic acid
12. Potassium permanganate
**Preparation of Solution:**

1. **Preparation of Hydrochloric acid:**

   The hydrochloric acid of required molarity was prepared by using standard dilution i.e. 8.9ml hydrochloric acid was taken in 100ml volumetric flask and diluted with distilled water. The hydrochloric acid solution was standardized by using Sodium carbonate solution. From this solution 0.1M, 0.05M, and 0.025M solution of hydrochloric acid was prepared and it was used for different experimental readings.

2. **Calibration of Nephelometer:**

   The first part includes the nephelometric analysis of different inorganic compounds. For this, first distilled water was prepared by distilling twice the laboratory water over alkaline permanganate in glass quickfit apparatus, and was always obtained fresh. This is used for setting zero of the instrument.

   For the calibration of nephelometer **formazine solution** was prepared.

   (1) For this preparation, first 5gm of hydrazine Sulphate AR grade was taken in 500ml volumetric flask and it was dissolved in distilled water and this solution was kept for 4hrs.
(2) Then 50 gm of hexamethylene tetramine was taken into 500 ml volumetric flask and dissolved in distilled water then equal volumes of hydrazine Sulphate and hexamethylene tetramine solutions were taken, mixed together and it was kept for 48hrs. It produces insoluble white turbidity corresponding to 4000 NTU.

Then 25ml of this formazine turbidity concentrate was taken in 1 liter volumetric flask and diluted with turbidity free distilled water to obtain 1000NTU formazine standard and this solution is used for setting 100 of the instrument.

(I) Sodium Thiosulphate:

Sodium thiosulphate was taken in increasing amount i.e. 50mg, 100mg, ……500mg. Then to each amount of substance 25ml of distilled water was added and taken in cuvette of nephelometer. Then 5ml of hydrochloric acid was added to it and NTU reading with the increase of time was recorded.

(1) In the same way the increasing concentrations of Sodium thiosulphate was taken and 25ml distilled water was added and 5ml of different concentration of acid i.e. 0.1M, 0.05M and 0.025M, concentrations were taken and NTU readings were recorded for each concentration of acid.
**Studying The salt effect OR The ionic Strength:**

To study the salt effect on the reaction, Potassium chloride solution was prepared by weighing 74.55mg of it in 100ml volumetric flask and diluted by distilled water, 2.5ml, 5ml, 7.5ml, 10ml and 12.5ml of KCl was added to the 25ml distilled water, to this 5ml of acid solution was added for getting the effect of salt on reaction with Sodium thiosulphate and Hydrochloric acid.

**Radiation effect:**

Effect of radiation was studied, for this reaction, varying amount of Sodium thiosulphate was taken in 500ml distilled water and this solution was taken in brown coloured bottle covered with black coloured paper and acid of respective normality was added and NTU readings were recorded with the increasing time.

**Effect of temperature:**

For the study of this effect, varying amount of Sodium thiosulphate were taken in 500ml beaker and diluted with distilled water. This beaker was kept in another beaker containing water for maintaining the temperature of reaction mixture. The water in the outer beaker was replaced so as to maintain the temperature of reaction mixture and NTU readings at different temperatures i.e. $288^{0}\text{K}$, $298^{0}\text{K}$, $303^{0}\text{K}$, were recorded.
(IV) Cerium Chloride:

1. Cerium chloride salt was taken in varying amount i.e. 50mg, 100mg, 150mg, …….. 500mg and taken in 25ml diluted with distilled water and it was transferred in cuvette of Nephelometer and 5ml of hydrochloric acid was added to it and NTU readings were recorded.

2. In the same way as above i.e. varying amount of Cerium chloride was treated with 0.1M, 0.05M and 0.025M Hydrochloric acid and readings were recorded.

Salt Effect:

By taking one concentration of acid and varying amount of Cerium chloride it was treated with 0.1M, 0.2M, 0.3M, 0.4M and 0.5M of Potassium chloride to have the reading of salt effect and ionic strength on the reaction of Cerium chloride with hydrochloric acid.

Effect of Radiation:

Varying amount of Cerium chloride and any one concentration of acid were taken in 500ml brown coloured bottle covered with black coloured paper and diluted by distilled water and respective amount of acid was added and NTU readings were recorded with the increase of time.
**Effect of temperature:**

For the study of this effect, varying amount of Cerium chloride were taken in 500ml beaker and diluted with distilled water. This beaker was kept in another beaker containing the water for maintaining the temperature of reaction mixture. Water of outer beaker was replaced so as to maintain the temperature of reaction mixture and NTU readings at different temperatures i.e. 288°K, 298°K, 303°K, were recorded.

**(III) Strontium chloride:**

1. Strontium chloride salt was taken in varying amount i.e. 50mg, 100mg, 150mg, ……. 500mg and diluted in 25ml distilled water and it was transferred in cuvette of Nephelometer and 5ml of hydrochloric acid was added to it and NTU readings were recorded.

2. In the same way as above i.e. varying amount of Strontium chloride was treated with 0.1M, 0.05M and 0.025M Hydrochloric acid and readings were recorded.

**Salt Effect:**

By taking one concentration of acid and varying amount of Strontium chloride, was treated with 0.1M, 0.2M, 0.3M, 0.4M and 0.5 M of Potassium Chloride to have the reading of salt effect and
ionic strength on the reaction of Strontium chloride with hydrochloric acid.

**Effect of Radiation:**

Varying amount of Strontium chloride and any one concentration of acid were taken in a 500ml brown coloured bottle covered with black coloured paper and diluted by distilled water and respective amount of acid was added and NTU readings were recorded with the increase of time.

**Effect of temperature:**

For the study of this effect, varying amount of Strontium chloride were taken in 500ml beaker and diluted with distilled water. This beaker was kept in another beaker containing the water. For maintaining the temperature of reaction mixture water of outer beaker was replaced so as to maintain the temperature of reaction mixture and NTU readings at different temperatures i.e. $288^0\text{K}$, $298^0\text{K}$, $303^0\text{K}$, were recorded.
(II) Silver Nitrate:

(1) Silver nitrate salt was taken in varying amount i.e. 50mg, 100mg, 150mg, ……. 500mg and diluted with in 25ml distilled water and it was transferred in cuvette of Nephelometer and 5ml of Hydrochloric acid was added to it and NTU readings were recorded.

(2) In the same way as above i.e. varying amount of AgNO₃ was treated with 0.1M, 0.05M and 0.025M hydrochloric acid and readings were recorded.

Salt Effect:

By taking one concentration of acid and varying amount of Silver nitrate it was treated with 0.1M, 0.2M 0.3M, 0.4M and 0.5M of Potassium Chloride to have the reading of salt effect and ionic strength on the reaction of Silver nitrate with Hydrochloric acid.

Effect of Radiation:

Varying amount of AgNO₃ and any one concentration of acid were taken in 500ml brown coloured bottle covered with black coloured paper and diluted by distilled water and respective amount of acid was added and NTU readings were recorded with the increase of time.
**Effect of temperature:**

For the study of this effect, varying amount of Silver nitrate were taken in 500ml beaker and diluted with distilled water. This beaker was kept in another beaker containing water for maintaining the temperature of reaction mixture. Water of outer beaker was replaced so as to maintain the temperature of reaction mixture and NTU readings at different temperatures i.e. 288°K, 298°K, 303°K, were recorded.

**Induced reaction**

**Preparation of Solution:**

All the solutions required during the course of study were prepared and standardized using suitable method.

1 M solution of Cerium chloride was prepared by weighing 24.650 mg dissolved in distilled water taken in a 100ml volumetric flask and diluted with distilled water, from this solution different Cerium chloride solutions of varying molarity were prepared i.e. 0.01, 0.02, 0.03, 0.04, 0.05M Solution.

**Preparation of Potassium Permanganate:** Solution 3.950gm of KMnO₄ was dissolved in 250ml of distilled water to prepare 0.1M solution from this solution required Molarity of this solution were prepared and standardized by using Oxalate solution in the
presence of $\text{H}_2\text{SO}_4$. Some times the purity of $\text{KMnO}_4$ is not up to the mark therefore, it is standardized by using Oxalic acid.

**Standardization of Potassium Permanganate:**

For the standardization of Potassium permanganate, for a number of years analyst employed the procedure recommended by M.C. Bridge.\(^{46}\)

He suggested the titration of Oxalic acid against $\text{KMnO}_4$ to be carried out at elevated temperature with vigorous stirring Later, Fowler and Bright \(^{47}\), thoroughly investigated the reaction and recommended that almost all of the permanganate be added rapidly to the acidified solution at room temperature after the reaction is complete, the solution is heated to $60^\circ\text{C}$ and titration completed at this temperature. This procedure eliminates any error caused by the formation of hydrogen peroxides. This latter method was employed for reproducible result.

When acidified Potassium Permanganate is titrated against Oxalate Ions, $\text{MnSO}_4$ is one of the products of reaction, which act as a catalytic agent. Hence, the reaction which is slow in the beginning gets accelerated. A brown turbidity is some times observed due to the formation of hydrated manganese Oxide in such titrations. This is purely due to the lesser concentration of the acid ($\text{H}_2\text{SO}_4$) present in the titrating solution.
2KMnO₄ + 3H₂SO₄ → K₂SO₄ + 2MnSO₄ + 3H₂O + 5O.

2KMnO₄ + 3MnSO₄ → K₂SO₄ + 2MnSO₄ + 3MnO₂ + H₂O

2KMnO₄ + 2H₂O → K₂O + 2MnO₂. H₂O + 3O

Hydrochloric acid cannot be used in place of dilute H₂SO₄ Because of reducing behavior of Cl⁻. Also Cl⁻ sometimes induces air Oxidation of Oxalic acid. Therefore, it is this reason of excess consumption of KMnO₄ in such reactions.

Nitric acid cannot be used in place of dilute H₂SO₄, because it is a self oxidizing agent and the volume of KMnO₄ used will be less.

Procedure:

Burette was cleaned repeatedly with distilled water and finally with KMnO₄ Solution to be used for titration and to the titration mixture, KMnO₄ Solution was added from the burette till the end point is reached.

Variation of Cerium Solution:

Several numbers of conical flasks were initially washed with chromic acid and finally with distilled water to check the presence of any trace impurity. Each flask was having different concentration of Oxalic acid in water and to it 5ml of 2M Solution of Sulphuric acid was added, to it 10 ml of Cerium chloride was
added and this solution was titrated with KMnO₄ i.e. 0.01M Solution. Readings were recorded similarly by changing the concentration of Cerium chloride solution.

**Variation of Oxalic Acid:**

Several conical flasks were initially washed with chromic acid and distilled water. Different concentration of Cerium chloride solution with different amount of it was taken in the conical flask and to this solution 5ml of 2M Sulphuric acid was added and 10 ml of Oxalic acid having concentration 0.01M was added. Then this mixture of solution was titrated against 0.01 M KMnO₄ Solution. Similarly, by variation of Oxalic acid concentration i.e. 0.01M, 0.02M …..0.05M, of it. In different sets of conical flask and different mixture of solution as above were taken and was titrated against KMnO₄ Solution and the readings were recorded.

**Variation of Sulphuric acid:**

Several conical flasks were cleaned and dried. Then different amount of H₂SO₄ were taken and to this Solution water was added then, to this solution 10ml of Oxalic acid and 10ml of Cerium chloride was added and the final mixture solution was titrated against KMnO₄ 0.01M Solution.
Similarly, by changing the concentration of H$_2$SO$_4$ the different sets of conical flask were prepared and readings were recorded.