CHAPTER I:

INTRODUCTION
Chemical kinetics has long been, by its very nature, a quantitative science concerned mainly with measuring the rates of chemical reaction. Reaction rates and reaction efficiency are of great interest to the chemists. One of the basic problems that Chemistry faces in the condition of the scientific and technical revolution is the search of new chemical processes. Often the practicability of a chemical reaction, particularly a commercial process, depends on the reaction rate and reaction efficiency. However, measurements of the reaction rates under a given set of conditions (temperature and pressure, initial composition, presence or absence of an inert diluent) give no indication at all of the rate of the same reaction under arbitrarily prescribed conditions. Yet the main value of kinetic investigation lies both from the theoretical and especially from the practical point of view, in the ability to predict the rate of a given chemical reaction over a wide range of different conditions.

C.N. Hinshelwood\(^1\) would say that the reaction kinetics is the field that borders on chemistry and pure physics, and upon which physicists and chemists live without full agreement. The science of reaction kinetics may be of interest as it tells us how the change in environment changes the rate of a chemical reaction. A knowledge of the reaction mechanism
and of the rate constants of (at least) all the main elementary processes involved is an invariable prerequisite, of a firm understanding of the mechanism has important consequences to such diverse processes as theoretical modelling and design of large scale reactors.

Studies of the mechanism of a variety of chemical reactions, vigorously pursued over a wide front by physical chemists of many countries, are steadily adding to the number of reactions whose mechanism is understood. However we are still at relatively early stage, and a large number of reaction mechanisms still remain to be investigated and more precise.

There has recently been considerable activity in the field of reaction kinetics, especially in the area involving the reactions of metal ions. With the development of fast techniques, it has become possible to examine in detail systems which have previously been outside the scope of investigations. The use of conventional methods on slower reaction has also helped to extend our knowledge in this field.

Most of the reactions encountered in practice take place in solution of one kind or another. The study of kinetics of chemical reactions in gaseous phase is much simpler to deal with but the reactions occurring in solution present many difficulties. The interaction between solvent molecules or other species present must not be ignored. Solvation
activities, dielectric constant, etc. have a great influence on the kinetics of the reaction. The kinetic study of such reactions is likely to be complicated yet such a study really presents one of the interesting problems in Chemistry.

Oxidation and Reduction Reactions:

The term "oxidation" was originally used to represent a process in which a substance acquired oxygen in chemical reaction and the reverse of this is termed as "reduction". According to modern concept, oxidation and reduction are usually conceived in terms of "de-electronation" and "electronation" processes respectively. However it is often convenient to explain certain redox reactions by both electron and hydrogen or oxygen atom transfer. The reason is that the lowering of the energy of the system does not take place simply by electron transfer. In the following example,

\[ \text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-} \]

\[ \text{MnO}_4^- + H \rightarrow \text{H}_2\text{MnO}_4^- \]

\[ \text{MnO}_4^- \rightarrow \text{MnO}_3^- + \text{O} \]

lowering of the potential energy may take place by any of the three processes.

A more consistent definition of oxidation reduction reaction can be profitably discussed in terms of "oxidation
state" of the species involved in a redox reaction. The oxidation state represents a hypothetical charge that an atom would possess, if the ion or molecule were to dissociate. The rules used for assigning oxidation state are arbitrary but reasonable ones. They exclude the transfer of $\text{H}^+$, $\text{O}^{2-}$, $\text{Cl}^-$, etc., ions from the category of those involving oxidation or reduction.

Redox reactions may be classified into two types according to the nature of fission viz., homolytic and heterolytic. Homolytic fission of the bond takes place in such a way that each of the resulting fragments contains an odd electron and may be shown as

$$A \cdot \cdots B \xrightarrow{\text{Homolysis}} A^- + \cdot B$$

In heterolytic fission of the bond, we get a Lewis acid and a Lewis base

$$A - \cdots B \xrightarrow{\text{Heterolysis}} A^- + B^+ \text{ or } A^+ + \cdot B^-$$

When we compare the Lewis acid and base formed with the elemental condition of the atom concerned, we find that there is oxidation and reduction, respectively.

In homolytic oxidation, the removal of electrons from the reductant leads to the formation of an active atom or highly reactive free radical, even though the reductant
molecule may have an unshared pair of electrons. This type of homolytic transfer reactions require very less activation energy and proceed very rapidly. Heterolytic oxidation occurs by the attack of an electrophilic reagent on the exposed electron pair of an atom, for example, O, N, S or the loosely held π electrons of the reductant. These usually require more activation energy and are, therefore, slow.

Redox reactions are sometimes classified as one equivalent or two equivalent reactions depending on the number of electrons transferred. Accordingly reagents are classified as mono- or de- electronators.

It is well said that reactions between ions are very rapid. This type of reaction takes place by the diffusion of the ions towards each other and hardly any activation energy is required for their chemical combination. However, there are reactions between ions involving electron transfer and are slow in nature with a normal activation energy.

In recent years, the kinetics and mechanism of redox reactions have been studied in considerable detail. Yatsimirskii classified the oxidant and reductant as follows:

(a) S, P - oxidants and reductants which react, as a rule, slowly even in the presence of catalysts.
(b) d - oxidants and reductants which usually react
quickly and are able to act as catalysts themselves. Redox reactions may be classified as follows:\textsuperscript{13}:

(i) Reactions of various reducing agents with oxidants that belong to group (a) $\text{H}_2\text{O}_2$, $\text{O}_2$, $\text{S}_2\text{O}_8^{2-}$, $\text{ClO}_3^-$, $\text{BrO}_3^-$, $\text{IO}_3^-$, $\text{ClO}_4^-$, $\text{IO}_4^-$, $\text{FeO}_4^{2-}$, $\text{NO}_3^-$, $\text{NO}_2^-$ and organic substances.

(ii) Reactions between various oxidants and reducing agents that belong to group (a) $\text{Hg}_2^{2+}$, $\text{Sn}^{2+}$, $\text{H}_2\text{PO}_4^-$, $\text{AsO}_2^-$, $\text{S}_2\text{O}_3^{2-}$, $\text{I}_2$, $\text{N}_2\text{H}_4$, organic substances such as amines, oxalates, phenols, etc.

(iii) Heterogeneous redox reactions such as $\text{MnO}_2$, silver halogenide, etc.

Reactions of oxidants with reducing agents of group (ii) may also proceed slowly. The reaction rate, in the latter case, may be low owing to like electric charges of the reacting species.

The study of the mechanism of oxidation-reduction reactions has only begun, but the Chemistry involved already has been shown to be astonishingly rich.

\textbf{Redox Reaction and the Acid-Base Reactions}:

It is of some interest to examine the similarity between the redox reactions and acid base behaviour. According to Brønsted and Lowry concept any species capable of
donating a proton is called an acid, while that accepts the proton is called a base. G.N. Lewis proposed a much broader concept of acid base reactions by focussing the attention on the lone pair of electrons present in the molecule. According to this concept a base is an electron pair donor or a nucleophile and an acid is an electron pair acceptor or an electrophile. Usanovich\textsuperscript{14} correlated the acid base reactions with redox reactions according to which all the oxidising agents can act as a Lewis bases whereas the reducing agents can act as Lewis acids. Thus, for the Iron(II)-Iron(III) system, Iron(II) is an electron donor and acts as a base while Iron(III) is an electron acceptor and acts as an acid.

\[
\text{Fe}^{2+} \xrightleftharpoons{} \text{Fe}^{3+} + e
\]

An acid, therefore, resembles a reductant in that both are donors. An acid cannot donate proton unless a base is present. Similarly a reducing agent cannot donate electrons unless an oxidising agent is present as an acceptor. The difference between the two behaviours is that an electron pair is shared by the two reactants in the acid base reaction but gets transferred completely from one reactant to the other in the redox reactions.

Reagents that take part in acid-base and redox reactions may, therefore, be divided into two types as electrophillic reagents and nucleophillic reagents. Some
reagents may be electrophilic under one set of conditions but nucleophilic under another set. Ingold\textsuperscript{15} has tabulated some of the important nucleophiles and electrophiles. An examination of these reagents reveals that nucleophilic and electrophilic character is not simply related to the charges present on them but depends largely on the electronic constitution of the reagent.

Further similarity between two behaviours has been discussed by Michaelis and Schubert\textsuperscript{16}. He points out that electron transfer in polyvalent oxidations can occur successively just like successive dissociation of a polybasic acid. Bradley\textsuperscript{17} has also pointed out the various analogies between the two behaviours.

To summarise it may be said that chemical species, under properly chosen condition, can act as an acid, a base, an oxidant or reductant. It should be clearly noted that the prediction of chemical behaviour of a given species is not possible merely from its chemical identity.

**Hydrogen Peroxide as an Oxidant:**

Hydrogen peroxide has been regularly used as oxidising agents for well over a century both in volumetric analysis and in degradative organic chemistry, yet even today the knowledge of their reaction is only fragmentary. In Baxendale's opinion\textsuperscript{18} it is a measure of complexity and variety of the
chemical reactions in which hydrogen peroxide participates that they have attracted the attention of chemical kineticists for almost a hundred years and that many of the earliest reactions to be investigated still provide matter for further investigations.

Hydrogen peroxide has become an important oxidant for many organic chemical syntheses for example epoxidation, hydroxylations and halogenation, as well as oxidation of sulphur or nitrogen compounds, containing no foreign radicals or metal ions. Hydrogen peroxide gives cleaner oxidations, assuring higher product quality. Today one can control oxidation and reaction better with the use of hydrogen peroxide.

Hydrogen peroxide, in the absence of a catalyst, persists for long periods of time although the reaction

\[ 2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(\text{g}) \]

is accompanied by an enormous decrease in free energy. It is always better to deal with the oxidising power of an oxidising agent in terms of the oxidation potential. The redox chemistry of hydrogen peroxide in aqueous solution may be given by the following potentials:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightleftharpoons 2\text{H}_2\text{O}; \quad E^0 = 1.77 \text{ volt} \]

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2\text{O}_2; \quad E^0 = 0.68 \text{ volt} \]

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2\text{e} \rightleftharpoons 3 \text{OH}^-; \quad E^0 = 0.87 \text{ volt}. \]
This shows that H₂O₂ is a strong oxidising agent in either acid or basic solutions. Only towards very strong oxidants, such as MnO₄⁻ it will behave as reducing agent. In dilute aqueous solutions it has more acidic character than water.

\[ \text{H}_2\text{O}_2 = \text{H}^+ + \text{HO}_2^- \]

In acidic solution oxidations with hydrogen peroxide are said to be slow whereas in basic solutions they are reported to be fast. In basic solutions, however, decomposition of the reagent occurs more rapidly even at low temperature.

The development of both the oxidising and reducing properties of hydrogen peroxide is a fact of great general importance in the use of this chemical\(^{21}\). When dry hydrochloric acid is passed through anhydrous hydrogen peroxide, chlorine is evolved due to high oxidising power of H₂O₂\(^{22}\). On the other hand, powerful oxidants such as chlorine, hypochloride and chlorine dioxide in alkaline solution liberate oxygen from hydrogen peroxide.

Reactions of Hydrogen Peroxide:

Considerable research has been done on the reactions of hydrogen peroxide with various chemical species\(^{23-24}\). From the chemical point of view, the redox reaction of H₂O₂ has been the subject-matter of many investigations. The usefulness of hydrogen peroxide can be appreciated from the fact
that it is still being used extensively. Especially because of its biochemical significance, there has been a good deal of interest in kinetic studies on formation, decomposition, and substrate reaction of peroxy compounds of biologically important metal complexes such as catalase and peroxidase.

Catalysed reactions of hydrogen peroxide may be classified as non-insertion reactions and partial insertion reaction according to cleavage of O-O bond. In the non-insertion reaction, two electron oxidation reaction can be completed either with the disproportionation of $\text{H}_2\text{O}_2$ to oxygen and water (catalase action) or with the retention of the peroxide at the reactive site resulting in the formation of water through the reaction with substrate. Peroxidase enzymes are very similar to catalases in action and are known to involve one electron transfer and free radical intermediate.

Partial insertion reactions may take place by the hydroxylation reactions in which O-O bond is broken or by the entry of one of the oxygen of the peroxide to substrate with the formation of addition compound.

(1) **Non-insertion Reactions**:

Two electron non-insertion reactions with hydrogen peroxide as an oxidant include (a) Catalase models and (b) Catalase enzymes.

A catalase action involves the disproportionation of
the hydrogen peroxide to oxygen and water. Siegel\textsuperscript{29} has discussed the catalase activities of a number of Cu(II) chelates. Involvement of metal ion and two hydroperoxide anions followed by an intramolecular two electron shift and a corresponding transfer of protons through the solvent is suggested in the mechanistic step.

The catalase activities of tetradeionate diethylene-triamine Chelate with Mn(II) and Fe(III) were first described by Wang\textsuperscript{30,31}. In such reaction one peroxide anion is bidentate and occupies two cis-position of the metal ion. A substantial catalase activity has been observed for the product obtained by the oxidation of (CN)\textsubscript{2}Fe(ims)\textsuperscript{3} and (CN)\textsubscript{5}Fe(N-CH\textsubscript{3}imz)\textsuperscript{3} by H\textsubscript{2}O\textsubscript{2}\textsuperscript{32}. Kinetic studies revealed that the thermal pathways are similar to that observed in the oxidation of Fe(CN)\textsubscript{6}\textsuperscript{4-} by H\textsubscript{2}O\textsubscript{2} which is activated by photodissociation of CN\textsuperscript{-}\textsuperscript{33}.

The catalytic action, i.e., disproportionation of hydrogen peroxide to water and oxygen, also takes place with the catalases\textsuperscript{34} which have iron(III) porphyrin prosthetic group at the active site. George\textsuperscript{35} suggested the reaction sequence of catalase and H\textsubscript{2}O\textsubscript{2} as follows:

\[ E - \text{Fe}^{3+} + \text{H}_2\text{O}-\text{OH} \rightleftharpoons E - \text{Fe}^{3+} \ldots \text{O}^- - \text{O} - \text{H} + \text{H}^+ \]

\[ E - \text{Fe}^{3+} \ldots \text{O}^- - \text{O} - \text{H} \rightarrow E - \text{Fe}^{3+} \ldots \text{O}^0 \leftrightarrow \text{O} \times E - \text{Fe}^{3+} \ldots \text{O}^{2-} + \text{OH}^- \]
O_{2}^{2-} + H_{2}O_{2} \rightleftharpoons O \times E \rightarrow Fe^{3+}O^{2-}O^{-}O^{-}H + H^{+}

Ox - Fe^{3+} + H^{+} \rightleftharpoons Ox - Fe^{3+}O^{-}O^{-}O^{-}H

Ox - Fe^{3+}O^{-}O^{-}H \rightleftharpoons E - Fe^{3+}O^{-}O^{-}H

E - Fe^{3+} + O_{2} + OH^{-}

O_x E represents a two electron oxidised form of the enzymatic active site.

Hamilton described a similar model catalase system which favours the reaction mechanism mentioned above.

Peroxidases, which are very closely related to the catalases, promote the oxidation by hydrogen peroxide of many organic compounds such as aromatic amines and phenols. Chance has extensively studied the relationship between catalase and peroxidase action and the nature of the intermediates.

Partial Insertion Reaction with Hydrogen Peroxide as an Oxidant

Partial insertion reaction is concerned with the cleavage of O-O bond where the oxygen enters the substrate to form hydroxyl groups. Such reactions are termed hydroxylation reactions. One or both of the fragments may then enter
the substrate, depending on the reaction mechanism. It will be of interest to discuss such hydroxylation reactions in which hydrogen peroxide is itself a reactant.

Mechanisms, whatever be the type of reaction under consideration are discussed in terms of geometries and properties of activated complexes and for the purposes of understanding the nature of hydroxylating species in the metal catalyzed reactions of hydrogen peroxide, it is helpful to consider one of the earliest and most widely employed reaction with Fenton's reagent. Let us begin our discussion of metal catalysed reaction of hydrogen peroxide with the oxidation of Fe(II) by $\text{H}_2\text{O}_2$, first studied by Haber and Weiss$^{38}$ and their mechanism is based on the concept of one electron transfer. Barb et al.$^{39}$ studied this reaction in considerable detail. When equimolecular, acidic solutions ($<0.01\text{M}$) of Fe$^{3+2}$ and $\text{H}_2\text{O}_2$ are mixed together, there is nearly quantitative relation

$$\text{H}_2\text{O}_2 + 2\text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$$

with a rate law

$$-\frac{d[\text{Fe}^{3+}]}{dt} = k \left[\text{Fe}^{2+}\right] \left[\text{H}_2\text{O}_2\right]$$

The rate law has been confirmed by Kolthoff and Medalia$^{40}$ by studying this reaction in the absence of organic substrate.

Studies on the kinetics of oxidation of $\text{H}_2\text{O}_2 - \text{Fe}^{3+2} - \text{e}^{+3}$ system have proved the existence of free radicals$^{41}$. They observed that alcohols are very rapidly oxidised to aldehydes
in the presence of Fe$^{+2}$. The mechanism very likely involves abstraction of hydrogen from alcohol by means of a OH radical followed by the oxidation of the radical$^{42}$. For the system Fe$^{+2}$-H$_2$O$_2$-C$_2$H$_5$OH, the reaction can be represented by

$$
\text{H}_2\text{O}_2 + \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{CH}_3\text{CHO}
$$

A chain mechanism can account for all the process occurring including the formation of free radical. Baxendale et al.$^{43}$ also demonstrated the presence of free radicals in the study of oxidation of iron(II) by H$_2$O$_2$. It is found that Fenton’s reagent will rapidly polymerise monomers such as acrylonitrile, styrene and methyl methacrylate in the presence of free radicals. This arises presumably from the addition of OH radical to monomers. There is also competition between iron(II) and the monomer for OH$^-$. 

$$
\text{OH}^- + \text{CH}_2 = \text{CHX} \rightarrow \text{HO-CH}_2-\text{CHX} \rightarrow \text{Polymers}.
$$

A great deal has been done to obtain quantitative estimates for the relevant thermodynamic data for the various steps in the Fe$^{+2}$-Fe$^{3+}$-H$_2$O$_2$ system.

The question of one electron or two electron transfer in oxidation reactions of H$_2$O$_2$ has been the subject of much interest. This concept has been successful in many reactions such as photochemical, photosensitised, formation of coloured complex. Electron transfer is subject to the restrictions of Franck-Condon Principle$^{44}$. For a two electron transfer,
a very strong interaction is needed between the donor and acceptor since the electron have to be paired before transfer. The net changes in the dimensions of the reaction partners on electron transfer can have important influence on rates.

**Model Peroxidase Systems:**

The Fe(II) - EDTA complex has been used to catalyse hydroxylation reaction. The reactions of these systems act as a model for peroxidase action because the active site of peroxidase is a porphyrin-bound ferrous ion, which may form an intermediate peroxy complex. Fe(II) Fe(III) couple is a very important one to consider in the present context as the strong interaction of EDTA with ferrous ion is considered necessary to achieve the observed activity. Equimolar amounts of the two electron donor and hydrogen peroxide are needed for the hydroxylation reaction. Thus the sequence of steps in the hydroxylation of salicylic acid as proposed by Grinstead can be represented as follows -

$$\text{Fe(II)} - \text{EDTA} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} - \text{EDTA} + \cdot\text{OH} + \cdot\text{OH}^-$$

$$\text{Fe(III)} - \text{EDTA} + \cdot\text{OH}^- + \text{H}_2\text{A} \rightarrow \text{HA}^- + \text{Fe(II)} - \text{EDTA} + \text{H}_2\text{O}$$

$$\text{Fe(III)} - \text{EDTA} + \cdot\text{OH}^- + \cdot\text{OH}^- \rightarrow \text{A} + \text{Fe(II)} - \text{EDTA} + \text{H}_2\text{O}$$
In the first step HO-... bond cleaves which is followed by reaction of 'OH with the acid to give an acid radical. A second attack of the substrate by the hydroxyl radical yields the hydroxylated product.

Hydroxylation of aromatic hydrocarbons and aliphatic alcohols by a model peroxidase system consisting of H₂O₂ and catalytic amounts of Fe(II) and catechol has been studied by Hamilton et al. Hamilton's mechanism is of special interest in its relationship to the reaction catalyzed by catalase and peroxidase. Excellent reviews on the reactions promoted by peroxidase enzymes are available.

Oxygen Insertion by Peroxides:

Peroxides may react with olefins to produce addition compounds in which only one of the oxygens of the peroxide enters the substrate. Since only one of the oxygen atoms of peroxo group ends up in the reaction product, such reactions fall into the category of partial insertion reactions.

The chemistry of transition metal peroxo compounds has been the subject of a large number of synthetic and mechanistic investigations. For example, Pertungstic acid, formed by the reaction of H₂O₂ and WO₃ catalyzes hydroxylation of olefins in aqueous or mixed solvents to form diols. In this reaction, a peroxide oxygen is transferred from the metal peroxo complex to the substrate. Pertungstic acid-catalyzed hydroxylation
is stereospecific, with trans addition of OH group to the olefin. The ionic mechanism successfully explains the participation of an intermediate hydroperoxide species \( \text{HWO}_3\text{O} - \text{OH} \), as given below:

\[
\begin{align*}
R_2C &= CR_2 + \text{HWO}_3\text{OOH} \quad \rightarrow \quad R_2C \quad \text{OH} \\
\text{OWO}_3H \\
R_2C &= CR_2 + \text{H}_2\text{O} \quad \rightarrow \quad R_2C \quad \text{CR}_2 \quad \text{HWO}_3\text{OH} \\
\text{OWO}_3H \\
\text{OH} \\
\text{HWO}_3\text{OH} + \text{H}_2\text{O}_2 &\quad \rightarrow \quad \text{HWO}_3\text{OOH} + \text{H}_2\text{O}
\end{align*}
\]

Several other studies indicate similar addition of \( \text{H}_2\text{O}_2 \) across olefinic double bonds in the presence of transition metal peroxo compounds. In such reactions remarkable stereo- and regioselectivities are often obtained\(^{53}\).

Under the catalytic action of certain transition metal ions, both alkyl hydroperoxides and hydrogen peroxide become very effective epoxidizing agents. The metal complex catalyzed epoxidation of olefins by organic hydroperoxides has recently been reported by Indicctor and Brill\(^{54}\). It is observed that the presence of methyl group at the site of double bond increases the yield of epoxide. This points that the nucleophilic nature of the substrate is an important factor for the reaction\(^{55,56}\). It seems that the polar mechanism for the
dissociation of the O-O bond operates in the epoxidation reaction.

From the analytical point of view, the reaction of hydrogen peroxide with metallic species has been used for the determination of various metals. The reaction often utilized in the kinetic method of analysis is the oxidation by hydrogen peroxide, the rate of which depends on the concentration of catalyst in solution.\(^57\).

Hydrogen peroxide is known to react with a variety of inorganic species. A kinetic investigation on the reaction between nitrous acid and hydrogen peroxide has been carried out in HClO\(_4\) medium under different conditions spectrophotometrically by Bhattacharya et al.\(^58\). The results are interpreted on the basis of the following mechanism:

\[
\begin{align*}
\text{HNO}_2 + H^+ & \rightleftharpoons_{K_{eq}} \text{H}_2\text{NO}_2^+ \\
\text{H}_2\text{NO}_2^+ + \text{H}_2\text{O}_2 & \rightarrow_{K_4} \text{HOCNO} + \text{H}_3^+ \\
\text{HOCNO} & \rightarrow_{\text{fast}} \text{NO}_3^- + H^+
\end{align*}
\]

The reaction between U(IV) by H\(_2\)O\(_2\) in H\(_2\)SO\(_4\) medium has been investigated by the same author\(^59\) and the conversion of U(IV) to U(VI) is presumed to take place through the possible formation of hydroxo complex of U(IV). A large number of metal ion oxidations involving Ce(IV) induced reduction of Thallium (III)\(^60\), Mo(IV)\(^61,62\), Cr(II)\(^63\), etc. by H\(_2\)O\(_2\) are also reported.
Siridhar suggests that kinetics of conversion of ferrocyanide to ferricyanide in the presence of hydrogen peroxide follows a compensating oxidation reduction mechanism involving free radical.

Apart from these inorganic systems, there have been many investigations of organic reaction in aqueous as well as in non-aqueous media. These include studies of auto oxidation of thiols promoted by bifunctional polymer bonded Cobalt phthalocyanine Catalyst, 2,4-diaminophenol, p-aminophenol, tri-hydroxy benzene by $H_2O_2$ in presence of Cu(II), aldehydes in alcohols containing $SO_2$, tartaric acid in presence of $Cu^{2+}$, glutathione, butyric acid in aqueous dioxane medium in presence of KU-2 ion exchange resin by hydrogen peroxide.

**Sodium Tungstate and Sodium Molybdate as Catalyst**

In recent years compounds containing two or more metal ions have been extensively used as catalysts. Numerous reduction reactions of hydrogen peroxide in acidic medium are efficiently catalysed by tungstate and molybdate. It is found that oxygen deficient compounds possess trapped electron in the vacant lattice sites. Positive holes are also present in some metal ions in higher oxidation state. Thus the catalytic activity in a number of chemical reactions emerges from the presence of anionic species with trapped electrons and positive holes.
In the course of reaction, ions or molecules can interact directly with hydrogen peroxide to form complexes. In such complex compounds, a hydrogen peroxide molecule is activated, its geometry and the distribution of electric charges are changed, and even heterolytic decomposition to $\text{OH}^+$ and $\text{OH}^-$ becomes possible. It should be noted that hydroxy complexes show higher catalytic activity compared to that of simple ions. This finding has wide application of tungstate and molybdate as catalysts.

The oxidation of iodide with $\text{H}_2\text{O}_2$ was one of the first reactions investigated in acid medium in the presence of these catalysts. This reaction is still under investigation. The rate of oxidation of thiosulphate to sulphate by hydrogen peroxide in the presence of catalysts consisting of compounds of Mo(VI) and W(IV) is obtained by Yatsimirskii and Maryshkina. Apart from these inorganic systems, a large number of organic molecules like allyl alcohol, allyl chloride, and bromide, crotonaldehyde, sulphides and alkenes, phenols, amines, and unsaturated acids have been oxidised by $\text{H}_2\text{O}_2$ in presence of tungstate or molybdate as catalyst. The oxidation of maleic and fumaric acid and diphenyl sulphide with hydrogen peroxide - Catalysed by vanadate is also reported.

Sodium tungstate and molybdates contain discrete regular tetrahedral ions, $\text{WO}_4^{2-}$ and $\text{MoO}_4^{2-}$ in crystals. However it is not certain that $\text{WO}_4^{2-}$ and $\text{MoO}_4^{2-}$ are tetrahedral in aqueous
solutions also. Although tungstate and molybdate ions exist as \( \text{WO}_4^{2-} \) and \( \text{MoO}_4^{2-} \) at pH 6 in aqueous solution\(^{93}\), it undergoes acid hydrolysis and polymerization\(^{94}\). In aqueous solutions, tungstate and molybdate ion hydrolyse into the acid anion as in Eq. (1) and (2).

\[
\begin{align*}
\text{MO}_4^{2-} + H^+ & \rightleftharpoons H\text{MO}_4^- \\
H\text{MO}_4^- + H^+ & \rightleftharpoons H_2\text{MO}_4
\end{align*}
\] ... (1) ... (2)

where, M is Mo or W.

The following discussion will throw light on the nature of the catalytic species and the multifarious mechanism that operates in the tungstate and molybdate catalyzed oxidations.

Let us consider one of the most significant, though rather simple reaction catalysed by tungstate and molybdate ion viz. the oxidation of iodide by \( \text{H}_2\text{O}_2 \).

It has long been known that molybdate catalyses the oxidation of iodide by \( \text{H}_2\text{O}_2 \) in acid medium.

\[
\text{H}_2\text{O}_2 + 3I^- + 2H^+ \rightarrow 2\text{H}_2\text{O} + I_3^- \quad .... (3)
\]

and this method has often been used for analysis. Molybdate forms several different peroxo complexes depending upon conditions\(^{95}\). The investigation of this reaction by Smith and Kilford (Loc.Cit.) shows that significant proportion of molybdate in the solution will be present as peroxo complexes.
and the reaction proceeds as follows:

\[ \text{H}_2\text{MoO}_4 + \text{H}_2\text{O}_2 \xrightleftharpoons{k_1} \text{H}_2\text{MoO}_4(\text{H}_2\text{O}_2) \]

\[ \text{H}_2\text{MoO}_4(\text{H}_2\text{O}_2) + \text{H}_2\text{O}_2 \xrightleftharpoons{k_4} \text{H}_2\text{MoO}_4(\text{H}_2\text{O}_2)_2 \]

\[ \text{H}_2\text{MoO}_4 + I^- \xrightarrow{k_3} \text{H}_2\text{MoO}_4 \cdot I^- \]

\[ \text{H}_2\text{MoO}_4(\text{H}_2\text{O}_2)_2 + I^- \rightarrow \text{products} \]

The rate law implied by this sequence is:

\[ -\frac{[\text{H}_2\text{O}_2]}{dt} = k_4 \left[ \text{H}_2\text{MoO}_4(\text{H}_2\text{O}_2)_2 \right] [I^-] \]

The kinetics of iodide oxidation by \( \text{H}_2\text{O}_2 \) catalysed by tungstate ion has also been investigated\(^96\). Both the mechanisms suggest the view that the first stage of the catalytic oxidation involves the formation of a complex between hydrogen peroxide and a catalyst fragment.

\[ \text{M} + \text{H}_2\text{O}_2 \xrightleftharpoons{} \text{M} \cdot \text{H}_2\text{O}_2 \]

where \( \text{M} \) = catalyst fragment predominant in the solution.

Further the mode of dependency on the \( \phi \) in acid media suggests that there is a maximal accumulation of the species which catalyse the reaction. There is no reason to assume the polymeric forms of tungstic acid to act as catalyst because it has been shown\(^97\)
that at low concentration of catalyst, polymerisation is slight and $\text{VMO}_4^-$ and $\text{H}_2\text{Mo}_4$ ($\text{M} = \text{W}$ or Mo) are predominant. The presence of these species is also confirmed by the polarographic method\textsuperscript{98}.

Beg and Ahmad\textsuperscript{99} have reported that the formation of $\text{HMO}_4^-$ is maximum around pH 4.7 compared to $\text{HMoO}_4^-$ around pH 3.6. According to them peroxo acids are the main attacking species in the epoxidation of maleic acid (Loc.Cit.) as shown below:

$$\text{HMO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{HMO}_5^- + \text{H}_2\text{O}$$

$$\text{H}_2\text{A} + \text{HMO}_5^- \rightleftharpoons [\text{Intermediate complex}]$$

$$[\text{Intermediate complex}] \rightarrow \text{H}_2\text{E} + \text{HMO}_4^-$$

with epoxidation rate as

$$\text{Epoxidation rate} = k' \left[ \text{H}_2\text{A} \right] \left[ \text{HMO}_5^- \right]$$

Specific mechanism are observed in the sodium tungstate catalysed oxidation of allyl chloride\textsuperscript{100} and acrylic acid\textsuperscript{101}. All these reactions show a zero order dependence on $\text{H}_2\text{O}_2$ and first order each in catalyst and substrate.

Ogata and Tanaka\textsuperscript{102} have studied the oxidation of dimethyl sulfoxide with aqueous $\text{H}_2\text{O}_2$ catalysed by sodium tungstate. The authors think that both $\text{H}_2\text{Mo}_5$ and $\text{H}_2\text{Mo}_6$ may be the main attacking species. On the basis of polarographic study they
claim that $\text{Na}_2\text{WO}_5$, $\text{Na}_2\text{WO}_8$ and peroxy polytungstates are formed immediately after mixing $\text{Na}_2\text{WO}_4$ and aqueous $\text{H}_2\text{O}_2$ at pH 4.00 and peroxypoly-tungstates are gradually converted into $\text{Na}_2\text{WO}_5$ and $\text{Na}_2\text{WO}_8$. The oxidation rate of $\text{Na}_2\text{WO}_8$ is presumably higher than that of $\text{Na}_2\text{WO}_5$ because of the higher electrophilicity of $\text{Na}_2\text{WO}_8$.

Thus the study of kinetics and mechanism of tungstate and molybdate catalysed reactions by hydrogen peroxide are of interest because of crucial importance of defining the nature of oxygen transfer process from a mechanistic point of view.

**Oxidation of Unsaturated Acids:**

Lapworth and Mottran\textsuperscript{103} have examined the conversion of oelic acid to dehydroxy stearic acid by permanganate as early as 1925.

The cis-hydroxylation of oleic acid to the diol at low $\left[\text{MnO}_4^-\right]$ and high pH has been studied by Wiberg and Saegbarth\textsuperscript{104}. A cyclic ester has been postulated. The mode of addition of the hydroxyl group is cis and has been shown by the conversion of maleic acid to meso tartaric acid and fumaric acid to dl tartaric acid\textsuperscript{105}. The proposed cyclic mechanism is confirmed by the observation that the oxygen introduced to the substrate arises from the permanganate.
The oxidation of olate, crotonate and cinnamate by \( \text{MnO}_4^- \) has revealed that the reaction follows a first order dependence on the substrate and oxidant. The products were found to be pH dependent. The reactions were mostly insensitive to electronic effects. Phenyl conjugation with the double bond produced a small increase in the rate of reaction.

Wiberg et al.\(^ {107} \) have also detected a cyclic intermediate in the \( \text{KMnO}_4 \) oxidation of crotonic acid. The observations and the analysis of the rate data suggests the following mechanism.

\[
\text{CH}_3\text{CH} = \text{CHCOO}^- + \text{MnO}_4^- \xrightarrow{k_1} \text{A} \\
\text{A} + \text{OH}^- \xrightarrow{k_2} \text{B}
\]

In neutral media, the intermediate was highly stable.

Recently Lee et al.\(^ {108,109} \) have re-examined the oxidation of substituted cinnamic acids by \( \text{MnO}_4^- \). The kinetic isotope effect points to a cyclic intermediate. Rates of substituted cinnamic acids showed that the formation of the cyclic intermediates is relatively insensitive to the electronic effects.

The most interesting observations were made in the oxidation of maleic and fumaric acids by \( \text{MnO}_4^- \). The formation of hydroxy malonic, glyoxylic and oxalic acid is reported.

Jimandi and Jaky\(^ {111} \) have also investigated the differential
reactivity of maleic and fumaric acid in their oxidation by MnO₄⁻. The results of this investigation show that the difference between the reactivity of undissociated acids arises due to steric hindrance to the cis- approach of the MnO₄⁻ in maleic acid. The unsaturated reactions are still being investigated by these authors¹¹²-¹¹⁴.

Lee and Spitzer have studied the oxidation of unsaturated acids by RuO₄¹¹⁵. The oxidation of unsaturated acids by sodium per ruthenate¹¹⁶ shows second order kinetics. The oxidation is very similar to that of MnO₄⁻ oxidation and also cleaves C = C double bond¹¹⁷.

Several reactions involving oxidation of unsaturated acids by phenyl iodosyl acetate¹¹⁸, chromic acid¹¹⁹, acid bromate¹²⁰ and Ce(IV)¹²¹. The mechanism of Ag⁺ Catalyzed oxidation of acrylic acid¹²² and maleic acid¹²³ by peroxo disulphate has also been investigated.

Present work:

Epoxides have shown a growing industrial importance, particularly in the polymer field. Under the catalytic action of certain transition metal ions, both alkyl hydroperoxides and hydrogen peroxide become very effective epoxidizing agents of allylic alcohols¹²⁴,¹²⁵. The mechanism of such reactions
are often explained by invoking the formation in the ground state, of a peroxy metal complex which makes possible an intramolecular peroxide oxygen transfer to the double bond of the metal-bound substrate.

Because of the crucial importance of defining the nature of oxygen transfer process from mechanistic point of view, the comparative kinetic studies of the tungstate and molybdate catalysed epoxidation of some unsaturated organic acids by hydrogen peroxide have been following and the effect of -

i. hydrogen ion concentration,

ii. variation of substrate, oxidant and catalyst concentration,

iii. variation of ionic strength and dielectric constant and

iv. temperature variation and the thermodynamic parameters

are reported. The range of investigation extends from fixation of order with respect to oxidant, substrate and catalyst to stoichiometry, and product study and evaluation of thermodynamic parameters.

To a good extent the present work has contributed in confirming the electrophillic characters of the oxygen transfer process as is reported and discussed in subsequent chapters.