One of the most intriguing and challenging areas of chemistry is that which deals with mechanistic study of chemical reactions. To many chemists, the real heart of chemistry is the study of mechanisms. In the ideal case, we consider the mechanism as a mental model devised to explain experimentally observed facts or as a hypothetical motion picture of the behavior of participating atoms in the reaction. To understand the mechanism of an organic reaction we must know as a function of time the exact positions of all the atoms as the reactants are converted into product molecules. This is a goal that can never be realized, fully since many of the changes take place too rapidly for any direct investigation. Virtually all information regarding reaction mechanism comes by inference of indirect evidence. Hence, it is the job of chemist to device the proper experiments to generate most conclusive evidence. A good reaction mechanism must correlate all the known facts about the reaction and will have predictive powers.
The study of rates and mechanism can be undertaken for many reasons. Some of which are as follows.

Reaction rate is of great practical interest in both laboratory and industry. No reaction that takes years to become sensibly complete is particularly useful in making its products, but reactions that are complete in fraction of seconds include hazardous explosions. Therefore, it becomes necessary for a kinetician to understand the factors controlling the rates.

For synthetic purpose, a knowledge of reaction mechanism will often allow the reaction condition to be selected for maximum product yields.

Finally, as an area of pure science in itself, the study of rates and mechanism is one of rich variety, concerned with chemistry of every element and full of experimental challenge. It is an area of chemistry where the practical application of theory lags far behind the realm of experiment, yet at several points theory has had notable successes.

Proposing a reaction mechanism

For most organic reactions, there will be many
conceivable mechanisms. Deciding whether or not a potential mechanism is reasonable and worthy of further consideration and testing is one of the first important steps. Consider the following reaction.

\[ \text{CH}_3\text{I} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{I}^- \]

A conceivable mechanism for this reaction might be the disintegration of the starting molecules into atoms, followed by their reassembly into product molecules.

\[ \text{CH}_3\text{I} + \text{OH}^- \longrightarrow \text{C} + 4\text{H} + \text{O} + \text{I}^- + \text{e}^- \longrightarrow \text{CH}_3\text{OH} + \text{I}^- \]

This is an absurd possibility. A reasonable mechanism that should come to mind quickly would be simple replacement of iodide by hydroxide. Even this simpler replacement is full of ambiguities. Hence, there are number of commonly used methods for determining the mechanism of the reaction. These include product analysis, stoichiometric studies, detection of intermediates, isotopic labelling and finally kinetic evidence.

Rate measurements in solution are conducted for two primary purposes: to measure reactivity and to determine the
mathematical form of the rate law. Once the rate law is known, reactivity can be expressed as the rate constant. The ultimate purposes are often more sophisticated as e.g., to obtain evidence for reaction mechanism, as to characterize transition state or as to factors that determine reactivity.

Rates of chemical reactions in solutions have long been the focus of attention. Yet, the solution kinetics continues to evolve rapidly because, from a molecular point of view, reactions seem to be hopelessly complex. The reason is that, in solution, any particular molecule is at any moment in close contact with a number of nearest neighbours which may vary in number from 4 to 12. In case of reactions involving ionic species, the interactions of the neighbouring molecules are sufficiently large to become a necessary part of the reaction scheme. In fact, in their absence, the reaction may not take place. The study of ionic reactions has been almost completely restricted to solutions for reasons which are quite understandable: ionic processes are virtually nil in the gas phase at temperature below 1000 K.

The modern era of research on the mechanism of electron transfer in solution began when artificially produced radioactive elements became available. The new nuclei made it
possible to measure the rates of many exchange reactions, and these measurements attracted attention not only because of their novelty, but also because of the bearing the results had on the understanding of orthodox chemical reactions.

Electron transfer occurs in many systems\textsuperscript{2} viz., in redox systems, optically induced charge transfer, excited state decay, etc.. But, the theme here is to study the electron transfer in redox systems in condensed state such as solutions.

The work\textsuperscript{3} of Henry Taube in redox systems unequivocally demonstrated the transport of electron from reductant to oxidant. This discovery certainly added many important features in the syntheses of coordination complexes and organometallics. It is such a subject which has manifestations in almost all walks of life.

The classical definition of oxidation and reduction in terms of gain or loss of oxygen has in modern times been abandoned in favour of the concept of electron gain (reduction) and electron loss (oxidation). Oxidation-reduction reactions are also defined as involving changes in oxidation states or oxidation numbers.
The oxidation thus consists of transfer of electrons from a reducing agent to an oxidizing agent, and, as such, there cannot be an oxidation without concomitant reduction. It follows automatically that any oxidation-reduction must involve two redox couples that differ in their affinity for electrons. Generally, a higher negative oxidation potential has higher affinity for electrons. For example, the reduction potential\(^4\) of the couple Ce(IV)/Ce(III) is 1.61V in acid medium which indicates that the Ce(IV) readily undergoes reduction. The redox potentials of couples of metal ions depend upon the solvent media, added ions, some stabilizing agents, etc.. But these thermodynamic potentials do not necessarily decide the kinetic feasibility of chemical reactions. The respective oxidation potentials of peroxodisulphate and peroxodiphosphate redox couples, being appreciably high\(^4\), do not show high reactivity with substrates of low redox potentials. There are many reactions where the rate is sufficiently reduced provided the oxidation potential is appreciably suppressed by the addition of the oxidant complexing reagent. The reduction potential of Co(III)/Co(II) is considerably increased on complexing with ammonia and it is this reason why the rate of Fe(II) and Co(NH\(_2\))\(^{3+}\) complex ion is significantly low.
Probable ways of electron transfer

Oxidation-reduction reactions may involve one or more electron transfers. Depending upon the number of electrons between oxidant and the reductant, the reaction may proceed in one or more steps. Transition metals such as iron, cobalt and several others usually exhibit stable oxidation states differing by one electron and react with each other through one-equivalent steps. However, the stable oxidation states in post transition elements such as arsenic, antimony, etc., differ by two electrons. Thus, on the basis of their pattern of reactivity, the reactions of these elements are classified into two main categories:

1. Complementary reactions and
2. Non-complementary reactions.

Complementary reactions

Complementary reactions are those in which oxidant and reductant both undergo two-equivalent change (or one-equivalent change). Such reaction generally obey a bimolecular rate equation and the electron transfer can take place in a single step or in two steps of one electron each. In Tl(I)-Tl(III) exchange reaction, electrons are transferred in a single step as the formation of the intermediate, Tl(II), is not detected.
The oxidations of As(III) and Sb(III) by Tl(III) are other cases where no evidence for the formation of Tl(II) has been obtained. The evidence obtained for the formation of As(IV) in pulse radiolytic studies indirectly supports one-equivalent steps in As(III) oxidations. However, such an evidence in the reaction of As(III)-Tl(III) has not been obtained.

Non-complementary reactions

Non-complementary reactions are those in which two-equivalent reductant or two-equivalent oxidant interacts with one-equivalent oxidant or one-equivalent reductant. There are number of possibilities of electron transfer in non-complementary reactions and these related to the nature of both oxidant and reductant. The example (i) presents several interesting mechanistic possibilities as follows.

\[
Tl(III) + 2Cr(II) \rightarrow Tl(I) + 2Cr(III) \quad (i)
\]

(a) Direct termolecular reactions

\[
Tl(III) + 2Cr(II) \rightarrow Tl(I) + 2Cr(III)
\]

(b) Initial one electron steps

\[
Tl(III) + Cr(II) \leftrightarrow Tl(II) + Cr(III)
\]
Tl(II) + Cr(II) $\rightarrow$ Tl(I) + Cr(III)

(c) Initial two electron steps

Tl(III) + Cr(II) $\rightleftharpoons$ Tl(I) + Cr(IV)

Cr(II) + Cr(IV) $\rightarrow$ 2Cr(III)

(d) Disproportionation of intermediate Tl(II).

Electron transfer reactions are found to be governed by two classical principles.

i) The first of these is the Michaelis principle of compulsory univalent oxidation steps\textsuperscript{11}. This hypothesis involves the principle that an oxidation-reduction reaction take place in one or more successive single electron transfer step. This principle evolved from a consideration of restricted field of redox reactions, of which the oxidation of hydroquinones to quinones through semiquinone intermediate is typical and is now generally recognized as being without universal validity. Apart from the reactions involving metal ions, many two-equivalent redox reactions are now known which proceed in one step through the transfer of hydride ion or an oxygen atom\textsuperscript{12,13} e.g.,

\[ \text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^- \]
ii) Shaffer's principle of equivalence change\textsuperscript{14,15} refers to the observation that non-complementary reactions are often slow compared with complementary ones. Examples are the slow reduction of Tl(III) by Fe(II) or Ce(IV) by Tl(I) compared with rapid reduction of Tl(III) by Sn(II) and Ce(IV) by Fe(II).

One of the implications of the comparison on which the principle of equivalence change is based, is that reactions between 2-equivalent oxidants and 2-equivalent reductants occur by concerted 2-equivalent step. This may well be the case for reactions such as the Tl(I)-Tl(III) exchange\textsuperscript{16-18}. The observations expressed by Shaffer, for non-complementary reactions, is based on the low probability of termolecular mechanisms as one possibility or the formation of unstable valence states as the other possibility\textsuperscript{8}. Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow.

Unstable oxidation states

The formation of unstable oxidation states during the course of non-complementary reactions has now been anticipated in a number of such reactions with sufficient proofs. The
reactions, e.g., of Tl(III) by Fe(II)\textsuperscript{19}, V(III) or V(IV)\textsuperscript{20} can only be explained through the formation of unstable Tl(II) species.

The interconversions between Cr(III) and Cr(VI) always appear to involve the unstable states Cr(IV) and Cr(V). In a classic study, King and Tong\textsuperscript{21} have worked out the details of the radox reaction between Ce(IV) and Ce(III) in aqueous sulphuric acid the rate law was found to be as in (ii) which is very reasonably explained by the mechanism involving steps of (iia) to (iic).

\[
\text{Rate} = k \left[\text{Ce(IV)}\right]^2 \left[\text{Cr(III)}\right] / \left[\text{Ce(III)}\right] \quad \text{(ii)}
\]

The first step is a rapid equilibrium, and a second step, the interconversion of Cr(IV) and Cr(V), is rate determining.

\[
\text{Ce(IV)} + \text{Cr(III)} \rightleftharpoons \text{Ce(III)} + \text{Cr(IV)} \quad \text{fast} \quad \text{(iia)}
\]

\[
\text{Ce(IV)} + \text{Cr(IV)} \rightleftharpoons \text{Ce(III)} + \text{Cr(V)} \quad \text{slow} \quad \text{(iib)}
\]

\[
\text{Ce(IV)} + \text{Cr(V)} \rightarrow \text{Ce(III)} + \text{Cr(VI)} \quad \text{fast} \quad \text{(iic)}
\]

Excellent support comes from the study of related reactions
such as the oxidation of vanadyl ion by acid chromate ion \((HCrO_4^-)\) and the analytical important oxidation of ferrous ion by acid chromate \(^{23}\). It is significant that in the above example the change over from \(\text{Cr(IV)}\) to \(\text{Cr(V)}\) or vice-versa, is rate determining. This may be related to the likelihood that, at this stage, a change in coordination number from six to four occurs \(^{21}\). The stoichiometric examination of the reaction between acid chromate and \(\text{Fe(II)}\) or \(\text{VO}^{2+}\) in presence of iodide leads to the conclusion that the rapid oxidation of iodide \(^{24}\) is because of its reaction with \(\text{Cr(V)}\). A related phenomenon is seen in the oxidation of \(\text{As(III)}\) by peroxodisulphate ion. This slow reaction is accelerated or oxidation is induced by adding \(\text{Fe(II)}\) and the reaction is postulated \(^{25}\) to go by the formation of \(\text{As(IV)}\) from the reaction (iiiia, iiib).

\[
\text{Fe(II)} + S_2O_8^{2-} \rightarrow \text{Fe(III)} + SO_4^{2-} + SO_4^- \\
\text{As(III)} + SO_4^- \rightarrow \text{As(IV)} + SO_4^{2-}
\]

(iiiia)  

As mentioned earlier, another feature of these unstable oxidation states is the frequent occurrence of catalysis. A number of studies of the catalysis by platinum metals of oxidation reactions have been made \(^{26}\). The catalysis by \(\text{Ag(I)}^{20}\), \(\text{Cu(II)}\), \(\text{Mn(II)}\) and \(\text{Cr(III)}\) in oxidation reduction
reactions are also found to occur through formation of unstable oxidation states\textsuperscript{27}.

**Electron transfer in inorganic reactions**

Two general classes of transition states emerge for redox reactions involving metal complexes, the so called "outer-sphere" and "inner-sphere" types\textsuperscript{28}. In the first of these, the inner coordination shells of both metal ions are intact in the transition state. In the second case, the two metal ions are connected through the bridging ligand common to both the coordination shells. From the Franck-condon principle, it follows that before electron transfer between two ion is possible, the energy of the electron must be the same in the two sites. There must also be sufficient orbital overlap between the two sites to provide for a reasonable probability of transfer.

In the case of reaction of outer-sphere type, the electron must wait for appropriate fluctuation of the ions and their coordination spheres without in any way being able to influence the changes required in the site to which it will be transferred. For reactions of inner-sphere type, an activated complex of the type $L_{x}M_{x}^{n+1}X_{x}M_{x}^{n}W_{x}$ may be formed, where $L$, $X$ and $W$ are ligands. In arriving at a configuration having $X$
as bridging group, either $M^{n+1}$ or $M^n$ (or both) has undergone substitution in the first coordination sphere. Delocalization of an electron over the two sites will lower the energy needed for the formation of the activated complex and the electron will be able to affect the energy required to produce a fluctuation at the site to which it is going to be transferred.

Presumably the reaction is consummated by some fluctuation which causes the separation of $M^{n+1}$ and $M^n$ and may well required other changes in the coordination spheres as well. A feature of the bridged activated complex is that the bridging group may move from the oxidizing agent to the reducing agent, that is in the opposite direction to that of electron.

For outer-sphere reaction there are three factors which play a role in determining the rate of electron transfer. The first is the approach of the reactants to be in sufficiently close proximity to create an electronic interaction which provides a basis for the delocalization of the exchanging electron. The second is a barrier to electron transfer that is created by the equilibrium structural differences between reactants and products. The third is an
additional barrier that is created in the surrounding solvent by the change in charge distribution associated with the electron transfer.

In general, inner-sphere reactions are more difficult to treat theoretically, since they are more complex and involve bond making and bond breaking.

Electron transfer in organic reactions

Covalent bond fission is an essential feature of organic reaction and generally it can take place by two different pathways viz., "homolytic reactions" in which electron pairs are symmetrically disrupted and "heterolytic reactions" in which electron pairs are transferred from one molecule to another as an undivided entity.

In homolytic oxidations, electrons are removed singly from organic molecules by active atoms such as chlorine, or by active free radicals. Though, molecules containing unshared electrons can be oxidized in this way, homolytic oxidations usually involve the removal from an organic molecule of one electron together with a hydrogen nucleus, e.g.,

\[ R_3C-H + Cl^\cdot \longrightarrow R_3C^\cdot + H-Cl \]

The initial organic product necessarily has an unpaired
electron and so must perforce undergo a reaction of similar type, e.g.,

\[ R_3C^* + Cl-Cl \rightarrow R_3C-Cl + Cl^- \]

or must combine with another free radical, before stable entities alone result. Thus, chain reactions, dimerisations or disproportionations, e.g.,

\[ 2C_2H_5^+ \rightarrow C_2H_6 + C_2H_4 \]

are typical homolytic reactions.

All homolytic electron transfer reactions, such as above require very much less activation energy than that needed for direct breakage of a covalence. Hence, homolytic oxidations, when once started, proceed very rapidly indeed. The traces of free radicals required for the initiation of homolytic oxidation may be formed by the thermal dissociation of molecules which have weak covalences, by disruption of molecules by exposure to radiant energy, high energy particles \((\alpha\)-particles) or electrons \((\beta\)-particles) or by single electron transfer from ions of transition elements which can have incomplete inner \(d---\) electron shells.

Heterolytic oxidations involve the attack on organic compounds of electrophilic reagents which can, by a single
process gain control of a further electron pair. Heterolytic oxidants therefore attack the exposed electron pairs of atom such as oxygen, nitrogen or sulphur or the loosely held π-electrons of olefins, rather than buried electron pairs of C-H, O-H or N-H bonds. Again, heterolytic reactions yield stable molecular or ionic products in one or at most two consecutive stages and very seldom lead on to chain reactions. On the other hand, they usually require higher activation energy than homolytic reactions and so tend to be slower processes. Use of catalysts lowers the activation energy in such cases. When heterolytic reactions are subjected to catalysis, the mechanism of catalysis is largely different from the catalysis involved in the case of homolytic reactions.

Catalysis

Any substance, other than reactants which influences the rate of chemical reaction but itself remains unchanged chemically at the end, is called a catalyst. The phenomenon of rate alteration is designated as catalysis. Catalysts influence the reactions by changing the reaction path. Such catalytic influence arises as consequences of lowering of the energy of activation.
In solution reactions involving inorganic oxidations, the catalysts are ions having unstable oxidation states. This case is a particular example of homogeneous catalysis where the catalyst is present in the same phase as that of reactants. Though, the mechanism of catalysis depends on the nature of the substrate, oxidant and other experimental conditions, it has been shown that metal ions act as catalyst by one of the following paths.

(i) The catalyst is first oxidized by the oxidant to its higher oxidation state which in a subsequent step oxidizes the substrate.

(ii) The catalyst forms a complex with oxidant, the complex then oxidizes the substrate either in the rate determining or in a fast step.

(iii) The catalyst itself first oxidizes the substrate in a slow step and the reduced form of the catalyst is oxidized by the oxidant in a fast step.

(iv) The catalyst traps the radical produced as intermediates and oxidizes them at faster rate.
Os(VIII) is a case in point as it has been utilized as catalyst for hexacyanoferrate(III) oxidation of organic and inorganic substrates. The catalysis is understood to be due to the intervention of intermediate oxidation states of osmium. The detailed picture of its catalytic action has been reviewed by Agrawal et al. Often, very small quantities of catalysts like Os(VIII), Pd(II), Cr(III), Ru(III), V(V), etc., cause appreciable rate accelerations of particular reactions. The rate increase depends on the catalyst concentration and hence, a kinetic-catalytic method of analysis of the catalytic species becomes available. Thus a method of analysis down to the p.p.m. level is possible in several cases.

Induced reactions

In some cases in which intermediate valence state is produced from a catalyst species, the original state may not be regenerated fast enough compared to continued reaction of the intermediate state. In such cases the catalyst is consumed and the system is referred to as an induced or coupled redox system. An example of such a system is the oxidation of I\(^-\) by HCrO\(_4\)\(^-\) induced by Fe\(^{2+}\). Here I\(^-\) or Fe\(^{2+}\)
and HCrO$_4^-$ react to form an intermediate state presumably Cr(V) and I( or Fe$^{3+}$). In presence of excess Fe$^{2+}$ or I$^-$ the Cr(V) state is further reduced to Cr(IV) or Cr(III). The Cr(IV) goes on to react with another equivalent of I$^-$ to give Cr(III) and I. Depending on the relative concentrations, it is found that two equivalents of I$^-$ and one of Fe$^{2+}$ are oxidized for each Cr(VI) reduced to Cr(III). The study of induced reactions is very valuable in giving information on the reactivity and presence of intermediate valence states.

Active species

If a particular substance (oxidant, reductant or catalyst) is capable of existence in several forms in aqueous solution, all the species existing may not be active. Those species which are involved in a slow step will influence the reaction. The reaction conditions will determine the nature of the active species.

Moore and Anderson$^{40}$ have reported that three or four species of Ce(IV) exist in sulphuric acid depending on its strength and the main active species in dilute solutions is Ce(SO$_4$)$_2^{2+}$ (upto 0.002 mol dm$^{-3}$). Hardwick and Robertson$^{41}$ have given the following equilibria amongst various species of Ce(IV) in sulphuric acid solutions. The concentration of H$^+$,
HSO$_4^-$ and SO$_4^{2-}$ would determine the nature of the active species.

\[
\text{Ce}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{CeSO}_4^{2+} + \text{H}^+
\]

\[
\text{CeSO}_4^{2+} + \text{HSO}_4^- \rightleftharpoons \text{Ce(SO}_4\text{)}_2 + \text{H}^+
\]

\[
\text{Ce(SO}_4\text{)}_2 + \text{HSO}_4^- \rightleftharpoons \text{HCE(SO}_4\text{)}_3^-
\]

To formulate the reaction rate as a function of species concentrations, therefore, requires a knowledge of the existence of such equilibria and generally speaking, the knowledge or determination of one or more equilibrium constants. The distinction between the species and laboratory concentrations is particularly critical in the cases of partially displaced equilibria, because the rate equations, if cast in the form of reaction rate as function of laboratory concentrations, quite often resemble the equations applicable to different mechanisms.

Effect of ions on the rate

The rate of redox reactions of complex ions are highly sensitive to the presence of other ions in the solution. Usually, added anions have the greater influence on the
reaction of two cations with each other and added cations influence the rate of two anions with each other. Large effects of anions on the rate are usually attributed to the formation of bridged species if labile complexes are involved.

In the redox reaction between two cations, if the reducing agent is complexed first, it will be more stabilized in the oxidized form and hence the reaction is speeded up in the presence of anion. Also a negative ion should enable two positive ions to approach each other more easily. This will be most effective if the negative ion is between the two cations in the transition state.

If the oxidizing agent is complexed first, the anion may stabilize it and slow down its rate of reaction. For example, the rate of reactions of Ce(IV) oxidations are reduced strongly by forming sulphate complexes\(^{42}\) in presence of sulphate. This shows, in agreement with theory, that coulombic repulsions between reactants do not play a dominant role. The conclusion to be drawn is not that electrostatic factors do not exist, but that other factors (reorganization energies) are of greater importance. Some significant effects of chloride ions are particularly noticeable in redox
reactions. The redox reactions, in which the reductant is able to form complexes with chloride are found to be accelerated by chloride ions. Among the reductants that can form complexes with chloride are Tl(I), Pd(II), Sn(II) and Sb(III).

Stoichiometric ratios in redox reactions

Stoichiometry helps in differentiating certain reactions so far as electron and atom transfer probabilities are concerned. The most significant contribution of the stoichiometry in the reaction dynamics is the detection of intermediates, free radicals or transient species. Stoichiometric ratio depends on number of factors viz., nature of reactants, nature of products formed, initial molar concentration ratio, pH of the solution and solvents.

For example, the reaction between Pu(IV) and NH$_3$OH$^+$ in acid medium, the stoichiometry is owing to the competition between (a) and (b). If the ratio $R$ of $[\text{Pu(IV)}]/[\text{NH}_3\text{OH}]$ is more than one, the product is nitrous oxide. However, nitrogen is formed if this ratio is less than one.

$R > 1; \quad 4\text{Pu(IV)} + 2\text{NH}_3\text{OH} \rightarrow 4\text{Pu(III)} + \text{N}_2\text{O} + \text{H}_2\text{O} + 6\text{H}^+$ (a)

$R < 1; \quad 2\text{Pu(IV)} + 2\text{NH}_3\text{OH} \rightarrow 2\text{Pu(III)} + \text{N}_2 + 2\text{H}_2\text{O} + 4\text{H}^+$ (b)
Although, it is always not true that the rate law conforming to the stoichiometric ratio will define the simplicity or complexity of the reaction events e.g., the oxidation of iodide with hydrogen peroxide in acid medium\textsuperscript{44} is one (reaction (c)) with rate law (d) at constant $H^+$ concentrations. Such type of reactions normally indicate a multistep mechanism in which rate governing step is the interaction of the two reactants in 1:1 ratio as below.

\begin{equation}
H_2O_2 + 3I^- \longrightarrow I_3^- + 2H_2O \quad (c)
\end{equation}

\begin{equation}
-d[H_2O_2]/dt = k [H_2O_2] [I^-] \quad (d)
\end{equation}

\begin{equation}
H_2O_2 + I^- \longrightarrow IO^- + H_2O
\end{equation}

However, there are also reactions\textsuperscript{45,46} in which rate laws are compatible with the stoichiometric results, viz.,

\begin{equation}
As(III) + Tl(III) \longrightarrow As(V) + Tl(I)
\end{equation}

\begin{equation}
H_2PO_2^- + 2Fe(CN)_6^{3-} + OH^- \longrightarrow H_3PO_3 + 2Fe(CN)_6^{4-}
\end{equation}

\begin{equation}
PhPO_2H_2 + 2V(V) + 3H_2O \longrightarrow PhPO_3H_2 + 2V(IV) + 2H_2O + 2H^+
\end{equation}
Consequently, a number of conclusions can be drawn from such observations which can help us in formulating reaction mechanism viz.,
i) One can plan the kinetic analysis of the system.
ii) The nature of the products can help in identifying the intermediates which otherwise escape detection.
iii) Significant analytical information is also obtained at this stage for the proper selection of experimental technique to monitor the kinetic analysis.

Permanganate oxidations

From a survey of literature on permanganate oxidations, it is clear that permanganate is reduced to different oxidation states in acidic, alkaline and neutral medium. Furthermore, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the nature of the substrates but also on the medium employed. Permanganate in acidic medium has been extensively used as a potent oxidant for carrying out the kinetic study of various organic substrates. In acidic medium, the reduction product of permanganate is found to be Mn(II) whereas in neutral medium, it is Mn(IV) in almost all the studies. Thus, the process, Mn(VII) → Mn(II) is consisting of several steps and each can be studied separately. MnO₂ appears only at the end of
the reaction i.e., after complete consumption of permanganate. Hence, the reactions can be conveniently followed by using spectrophotometer. Even though, the mechanisms of reactions are not yet clear and in most of the cases doubt persists whether direct oxidation or OH induced. In some cases mechanistic approach has been based on the intermediate complex formation and in other cases the mechanisms are based on free radical intervention even in the absence of kinetic or spectrophotometric evidences. Thus, the mechanisms proposed by various workers are not uniform. This indicates that, a wide varieties of mechanisms are possible for permanganate oxidations of different organic substrates depending on the nature of the reactive species of permanganate and the substrate in acid, alkali and neutral medium. Hence, manganese chemistry involved in these multistep redox reactions permits to draw important conclusions as to the mechanisms of the reaction, since, manganese intermediates are easy to identify. It is well known that permanganate is mainly reduced to Mn(VI) in alkaline medium with evolution of $O_2$. Jaky et al identified the formation of intermediate Mn(V) in one of their studies, but did not provide mechanistic information for two electron reduction.

This prompted us to choose varieties of organic
substrates for oxidation with alkaline permanganate, in order to explore the mechanistic aspects of permanganate in such media.

Present work

In the present investigation some redox reactions in alkaline medium using permanganate as an oxidant, have been studied. Reactions were followed conveniently by spectrophotometry in the uv.-vis. region. The thesis comprises seven chapters with general introduction as a first chapter which gives general idea about the Chemical kinetics.

I. GENERAL INTRODUCTION

II. OXIDATION OF L-PHENYLALANINE BY AQUEOUS ALKALINE PERMANGANATE

The reaction exhibits first order dependence on \( [\text{MnO}_4^-] \), zero order in \([\text{OH}^-]\) and an order of less than unity in \([\text{L-phenylalanine}]\). The reaction has stoichiometry 2:1 (\([\text{MnO}_4^-]:[\text{L-phenylalanine}]\)). Initially added products mangante, corresponding aldehyde and ammonia, have no significant effect on the rate of the reaction. Decrease in dielectric constant increases the rate of the reaction whereas variation of ionic strength of the medium does not affect the
rate. A mechanism consistent with kinetic data is proposed which leads to following rate law.

\[
\frac{d[MnO_4^-]}{dt} = \frac{kK[MnO_4^-][L-phenylalanine]}{(1 + K [L-phenylalanine])}
\]

The activation parameters with respect to slow step of the mechanism have been computed and constants involved in proposed mechanism are evaluated.

III. OXIDATION OF MANDELIC ACID BY AQUEOUS ALKALINE PERMANGANATE

The third chapter involves the detailed kinetic study of title reaction. The reaction has 2:1 ([MnO_4^-]:[MA]) stoichiometry. The reaction shows first order kinetics in [permanganate ion] and less than unity in both mandelic acid (MA) and alkali concentrations. Added products have no significant effect on the rate, increase in ionic strength and decrease in dielectric constant increases the rate of the reaction. On the basis of the observed kinetics a suitable mechanism has been proposed which leads to the rate law:

\[
\text{Rate} = - \frac{d[MnO_4^-]}{dt} = \frac{k K_1 K_2 [MnO_4^-] [MA] [OH^-]}{1 + K_1 [OH^-] + K_1 K_2 [MA][OH^-]}
\]

The constants involved in the mechanism are evaluated and
activation parameters with respect to slow step of the mechanism are calculated.

IV. OXIDATION OF L-ARGININE BY ALKALINE PERMANGANATE

The fourth chapter deals with the kinetic study of a basic amino acid. In this, the stoichiometric studies reveal that two moles of permanganate consumes one mole of L-arginine. Decrease in dielectric constant and increase in ionic strength increases the rate of the reaction. Added products have no effect on the reaction rate. Under the conditions employed, reaction seems to proceed via two paths; one substrate dependent and another substrate independent, the mechanism with two paths has been proposed and arrived at following combined rate law.

\[
\frac{d[MnO_4^-]}{dt} = \frac{k_1 K [MnO_4^-] [L-Arg] [OH^-]}{1 + K [OH^-]} + k_2 [MnO_4^-][OH^-]
\]

The reaction has been studied at different temperatures and the activation parameters with respect to rate determining steps for the two paths have been computed.

V. OXIDATION OF 1,10-PHENANTHROLINE BY ALKALINE PERMANGANATE

The reaction exhibits first order dependence on \([MnO_4^-]\),
zero order in $[\text{OH}^-]$ and an order of less than unity in 1,10-phenanthroline (1,10-phen.) concentration. The reaction has a stoichiometry $4:1$ ($[\text{MnO}_4^-]:[1,10\text{-phen.}]$). Initially added products have no significant effect on the rate of the reaction. Decrease in dielectric constant increases the rate of the reaction whereas variation of ionic strength of the medium does not affect the rate. A mechanism consistent with kinetic data is proposed which leads to the following rate law.

$$\frac{d[\text{MnO}_4^-]}{dt} = \frac{k K [\text{MnO}_4^-][1,10\text{-phen.}]}{1 + K [1,10\text{-phen.}]}$$

The activation parameters with respect to slow step of the mechanism have been computed and constants involved in proposed mechanism are evaluated.

VI. OXIDATION OF DMF BY AQUEOUS ALKALINE PERMANGANATE

Kinetics of oxidation of dimethylformamide follows first order dependence each in permanganate ion and alkali concentrations and fractional order in $[\text{DMF}]$. Stoichiometric studies reveal that eight moles of $\text{MnO}_4^-$ consumed one mole of DMF. Added products have no significant effect on the rate of reaction and effect of variation of ionic strength and
dielectric constant was studied. Based on the kinetic observations, a two pathway mechanism is proposed which leads to the following rate law.

\[
\text{Rate} = \frac{\text{d}[\text{MnO}_4^-]}{\text{dt}} = k_1K_1[\text{MnO}_4^-][\text{DMF}][\text{OH}^-] + k_2[\text{MnO}_4^-][\text{OH}^-]
\]

The constants involved in the mechanism are evaluated and activation parameters are computed.

VII. OXIDATION OF DIMEDONE BY ALKALINE PERMANGANATE

Oxidation of dimedone (5,5-dimethyl-1,3-cyclohexane-dione) (DM) by alkaline permanganate has been carried out at lower and higher [alkali]. At higher [alkali], reaction is independent of [OH\(^-\)] and at lower concentration reaction is fractional order in [OH\(^-\)]. The orders in [MnO\(_4^-\)] and [DM] are unity and less than unity in both lower and higher concentrations of alkali, respectively. Based on kinetic observations the two different mechanisms are proposed which are applicable at both the [OH\(^-\)].
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