INTRODUCTION
Rates of chemical reactions in solution have long been the focus of attention. Yet, the area of 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 temperatures 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 almost in 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 loss (oxidation) and electron gain (reduction). 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 oxidising 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 oxidation potential of the couple Ce(III)/Ce(IV) 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 stabilising 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, 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 oxidation potential of Co(III) is considerably reduced on complexing with ammonia and it is this reason why the rate of Fe(II) and Co(NH$_3$)$_6^{3+}$ 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 the 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\textsuperscript{1,3,5-9} 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 reactions 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 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 a number of possibilities of electron transfer in non-complementary reactions and these are related to the nature of both oxidant and reductant. The example (i) presents several interesting mechanistic possibilities as follows.

\[ \text{Tl}(\text{III}) + 2\text{Cr}(\text{II}) = \text{Tl}(\text{I}) + 2\text{Cr}(\text{III}) \quad (i) \]
(a) Direct termolecular reactions:
\[ \text{Tl(III)} + 2\text{Cr(II)} \rightarrow \text{Tl(I)} + 2\text{Cr(III)} \]

(b) Initial one electron steps:
\[ \text{Tl(III)} + \text{Cr(II)} \rightarrow \text{Tl(II)} + \text{Cr(III)} \]
\[ \text{Tl(II)} + \text{Cr(II)} \rightarrow \text{Tl(I)} + \text{Cr(III)} \]

(c) Initial two electron steps:
\[ \text{Tl(III)} + \text{Cr(II)} \rightarrow \text{Tl(I)} + \text{Cr(IV)} \]
\[ \text{Cr(II)} + \text{Cr(IV)} \rightarrow 2\text{Cr(III)} \]

(d) Disproportionation of intermediate Tl(II).

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

1) The first of these is the Michaelis principle of compulsory univalent oxidation steps. This hypothesis involves the principle that an oxidation-reduction reaction takes place in one or more successive single electron transfer step. This principle evolved from a consideration of a restricted field of redox reactions, of which the oxidation of hydroquinones to quinones through semiquinone intermediate is typical and is now generally recognised as being without universal validity.
Apart from the reactions involving metal ions, many 2-equivalent redox reactions are now known which proceed in one step through the transfer of a hydride ion or an oxygen atom$^{12,13}$ e.g.,

\[
\text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^-
\]

ii) Shaffer's principle of equivalence change$^{14,15}$ 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 the 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 a concerted 2-equivalent step. This may well be the case for reactions such as the Tl(I)-Tl(III) exchange$^{16-18}$. 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 the unstable valence states as the other possibility$^8$. 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 been now anticipated in a number of such reactions with sufficient proofs. The reactions, for example, 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 redox reaction between Ce(IV) and Cr(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 (ii a) to (ii c).

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

The first step is a rapid equilibrium, and the second step, the interconversion of Cr(IV) and Cr(V), is rate
Ce(IV) + Cr(III) $\rightleftharpoons$ Ce(III) + Cr(IV) fast (ii a)

Ce(IV) + Cr(IV) $\rightleftharpoons$ Ce(III) + Cr(V) slow (ii b)

Ce(IV) + Cr(V) $\rightarrow$ Ce(III) + Cr(VI) fast (ii c)

determining. Excellent support comes from the studies of related reactions such as the oxidation of vanadyl ion by acid chromate ion$^{22}$ (HCrO$_4^-$) and the analytically important oxidation of ferrous ion by acid chromate ion$^{23}$. It is significant that in the above example, the changeover from Cr(IV) to 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 6 to 4 occurs$^{21}$. The stoichiometric examination of the reaction between acid chromate and Fe(II) or VO$^{2+}$ in presence of iodide leads to the conclusion that the rapid oxidation of iodide$^{24}$ is because of its reaction with Cr(V). A related phenomenon is seen in the oxidation of As(III) by peroxodisulphate ion. This slow reaction is accelerated or oxidation is induced by adding Fe(II) and the reaction is postulated$^{25}$ to go by the formation of As(IV) from the reaction (iii a, iii b)

Fe(II) + S$_2$O$_8^{2-}$ $\rightarrow$ Fe(III) + SO$_4^{2-}$ + SO$_4^-$ (iii a)

As(III) + SO$_4^-$ $\rightarrow$ As(IV) + SO$_4^{2-}$ (iii b)
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. The catalysis by Ag(I), Cu(II), Mn(II) and Cr(III) in oxidation-reduction reactions are also found to occur through formation of unstable oxidation states.

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. In the first of these, the inner coordination shells of both the metal ions are intact in the transition state. In the second case, the two metal ions are connected through a bridging ligand common to both the coordination shells. From the Franck-Condon principle, it follows that before electron transfer between two ions 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 a reaction of outer-sphere type, the electron must wait for an 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 $L_XM^{n+1}X_M^{n}W_X$ 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. Delocalisation 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 require other changes in the coordination spheres as well. A feature of the bridged activated complex is that the bridging group may move from the oxidising agent to the reducing agent, that is in the opposite direction to that of the 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 'delocalisation' 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 steps.

Electron transfer in organic reactions

Covalent bond fission is an essential feature of organic reactions 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 particle 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 oxidised in this way, homolytic oxidations usually involve the removal from an organic molecule of one electron together with a hydrogen nucleus, e.g.,

\[ R_3C-H + Cl' \rightarrow R_3C' + H-Cl \]

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 of homolytic oxidations.

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 (α-rays) or electrons (β-rays) 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 atoms such as oxygen, nitrogen or sulphur, or the loosely held π-electrons of olefins, rather than the 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 subject 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 a 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 a consequence 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 catalyst is in the same phase as the 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 catalysts by one of the following paths:

1. The catalyst is first oxidised by the oxidant to its higher oxidation state which in a subsequent step oxidises the substrate;
2. The catalyst forms a complex with oxidant, the complex then oxidises the substrate.
either in the rate determining or in a fast step; (iii) the catalyst itself first oxidises the substrate in a slow step and the reduced form of the catalyst is oxidised by the oxidant in a fast step and (iv) the catalyst traps the radicals produced as intermediates and oxidises them at a faster rate.

Osmium(VIII) is a case in point as it has been utilised\textsuperscript{30} as a catalyst for hexacyanoferrate(III) oxidations 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\textsuperscript{32}.

Often, very small quantities of catalysts (like Os(VIII), Pd(II), I\textsuperscript{-}, Cr(III) etc) cause appreciable rate accelerations of particular reactions\textsuperscript{26,27}. 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 an 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 about two equivalents of I\(^-\) and one of Fe\(^{2+}\) are oxidised 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 existing 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$^{34}$ have reported that three or four species of cerium(IV) exist in sulphuric acid, depending on its strength, and the main active species in dilute solutions is Ce(SO$\text{\textsubscript{4}}$)$^{2+}$ (upto 0.002 mol dm$^{-3}$ H$_2$SO$_4$). Hardwick and Robertson$^{35}$ have given the following equations for the equilibria amongst various species of Ce(IV) in H$_2$SO$_4$ solutions. The concentration of H$^+$, HSO$_4^-$ and SO$_4^{2-}$ would determine the nature of the active species.

$$\ce{Ce^{4+} + HSO_4^- &<--- Ce(SO_4)^{2+} + H^+}$$
$$\ce{CeSO_4^{2+} + HSO_4^- &<--- Ce(SO_4)_2 + H^+}$$
$$\ce{Ce(SO_4)_2 + HSO_4^- &<--- HCe(SO_4)_3}$$ etc.

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 a function of laboratory concentrations, quite often resemble the equations applicable to entirely different mechanisms.

Effect of Ions on the Rate

The rate of redox reactions of complex ions are very 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 reactions between two cations, if the reducing agent is complexed first, it will be more stabilised in the oxidised 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 oxidising agent is complexed first, the anion may stabilise 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 in presence of sulphate. This shows, in agreement with theory, that coulombic repulsions between the reactants do not play a dominant role. The conclusion to be drawn is not that electrostatic factors do not exist, but that other factors (reorganisation 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 ion. 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 product formed, initial molar concentration ratio, pH of solution and solvents etc.

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 [Pu(IV)] / [NH$_3$OH] is more than one, the product is nitrous oxide. However, nitrogen is formed if this ratio is less than one.

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

Although it is not always 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 is one (reaction(c)) with rate law(d) at constant H$^+$ concentrations. Such type of reactions normally indicate a multistep mechanism in which rate

\[
\text{H}_2\text{O}_2 + 3\text{I}^- \rightarrow \text{I}_3^- + 2\text{H}_2\text{O} \quad (c)
\]
\[
-d \left[\text{H}_2\text{O}_2\right]/dt = k\left[\text{H}_2\text{O}_2\right]\left[\text{I}^-\right] \quad (d)
\]
The governing step is the interaction of the two reactants in 1:1 ratio as below:

$$H_2O_2 + I^- \rightarrow IO^- + H_2O$$

However, there are also reactions$^{39,40}$ in which rate laws are compatible with the stoichiometric results, viz.,

$$As(III) + Tl(III) \rightarrow As(V) + Tl(I)$$

$$H_2PO_2^- + 2Fe(CN)_6^{3-} + OH^- \rightarrow H_3PO_3 + 2Fe(CN)_6^{4-}$$

$$phPO_2H_2 + 2V(V) + 3H_2O \rightarrow phPO_3H_2 + 2V(IV) + 2H_2O + 2H^+$$

Consequently, a number of conclusions can be drawn from such observations which can help us in formulating a 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 or identification.
Significant analytical information is also obtained at this stage for the proper selection of experimental technique to monitor the kinetic analysis.

**Present Work**

The work undertaken in the present thesis entitled "A study of kinetics and mechanism of some electron transfer reactions" comprises the following:

**I. PALLADIUM(II) CATALYSED OXIDATION**

**IA - Oxidation of mercury(I) by cerium(IV) in aqueous perchloric acid media**

This reaction has the stoichiometry of 1:2 ([Hg\(^{2+}\): [Ce\(^{4+}\)]), the catalyst (Pd\(^{2+}\)) being effective in as little as 1% of that of oxidant/reductant. The approximate rate law under the conditions studied is given by

\[
\text{Rate} = \frac{k[\text{Ce(IV)}][\text{Pd(II)}][\text{Hg(I)}]^{0.3}[\text{Cl}^-]^{0.5}[\text{H}^+]^x}{[\text{Ce(III)}]^{0.3}}
\]

(as \text{H}^+ increases, \text{x which is initially nearly +0.5 decreases to nearly -0.5 after going through a maximum}).
The likely active species are $\text{H Ce(SO}_4)_3$, $\text{Hg}_2\text{ClO}_4^+$ and $\text{PdCl}^+$. A mechanism in agreement with experimental data is proposed and the resulting rate law verified.

**II. Analysis of palladium(II) by kinetic method and mercury(I) by volumetric/spectrophotometric method**

Palladium(II) catalysed cerium(IV) oxidation of mercury(I)/allyl alcohol in acid medium has been utilised to propose a kinetic method of analysis of palladium(II). The analysis, which is carried out by spectrophotometry, enables analysis of palladium(II) in the range of $4.0 \times 10^{-2}$ to 6.5 µgm/cm$^3$. The palladium(II) catalysed Ce(IV) -Hg(I) reaction is also found to be useful as an analytical method for microamounts of mercury(I), where titrimetry or spectrophotometry can be used. Some interferences in both analyses are given.

**II CHROMIUM(III) CHEMISTRY IN ALKALINE MEDIA**

**IIA Oxidation of chromium(III) by hexacyanoferrate(III)**

In view of the known amphoterism of chromium(III) and its not too well understood chemistry in alkaline medium, the study of oxidation of chromium(III) by
alkaline Fe(CN)$_6^{3-}$ is of interest. The 3:1 redox system of Cr(III) - Fe(CN)$_6^{3-}$ has the approximate rate law under the conditions studied:

$$\text{Rate} = k[\text{Fe(CN)}_6^{3-}][\text{Cr(III)}]^{0.92} [\text{OH}^-]^{0.94}$$

The likely active species are Na$^+$Fe(CN)$_6^{3-}$ and Cr(OH)$_4^{-}$. Fresh solutions of chromium(III) in alkali gave satisfactory results. However, on 36 hr. standing the chromium(III) solution leads to slower kinetics and this aspect is also looked into. A plausible mechanism has been suggested and some constants involved in the mechanism are derived.

IIB Oxidation of chromium(III) by osmium(VIII)

The noncomplementary Os(VIII)-Cr(III) redox reaction has been studied in aqueous alkali. The reaction is followed by measuring the absorbances of different species at three wavelengths, since no single $\lambda_{\text{max}}$ was available for any one of them. The concentrations are calculated by using a set of triple simultaneous equations. The reaction is approximately first order in chromium(III) and of fractional orders in osmium(VIII) and OH$^-$ concentrations. The likely active species are Cr(OH)$_4^{-}$.
and $\text{OsO}_5(\text{OH})^3^-$. The formation constant, $K$, of $\text{OsO}_5(\text{OH})^3^-$ and rate constant, $k$, of $\text{Cr(OH)}_4^-\cdot\text{OsO}_5(\text{OH})^3^-$ interaction, are obtained.

III OSMIUM(VIII)/OSMIUM(VI) OXIDATION OF ARSENIC(III) IN AQUEOUS SULPHURIC ACID

Studies of osmium(VIII)/osmium(VI) oxidations in acid medium are scanty. Osmium(VIII) and osmium(VI) involve multi-oxidation states and several possibilities exist for their oxidation mechanisms. In both oxidations, the products are osmium(IV) and arsenic(V). The experimental rate law under the reaction conditions studied is

$$\text{Rate} = k[\text{Ox}][\text{As(III)}]^{0.9} [\text{Os(IV)}]^{0.5}$$

where $\text{Ox} = \text{Os(VIII)}$ or $\text{Os(VI)}$.

A multistep mechanism is suggested in order to explain the autocatalysis which occurs in both the reactions. Some constants involved in the mechanism are computed. Rates calculated using these constants are in reasonable agreement with the experimental rates.
IV KINETICS OF OXIDATION OF ALLYL ALCOHOL

IVA Osmium(VIII) catalysed cerium(IV) oxidation of allyl alcohol in aqueous sulphuric acid

Allyl alcohol is important in industry. Osmium(VIII) seems to have found little application as a catalyst in the oxidation of allyl alcohol. Here, cerium(IV) oxidation of allyl alcohol is studied in acid medium with osmium(VIII) as a catalyst. The stoichiometry is as follows:

\[
\text{Os(VIII)} + 2\text{Ce(IV)} + \text{CH}_2=\text{CH}-\text{CH}_2\text{OH} \rightarrow 2\text{Ce(III)} + \text{CH}_2=\text{CH}-\text{CHO} + 2\text{H}^+ + \text{H}_2\text{SO}_4
\]

The reaction is first order in catalyst, oxidant and acid and fractional order in reductant under the reaction conditions used. Free radical intervention is shown in experiments in the presence of acrylamide. A mechanism in agreement with the experimental results is proposed.

IVB Oxidation of allyl alcohol by diperiodatonicelate(IV) in alkaline medium

In view of the fact that a comparatively small number of oxidations involving nickel(IV) are available,
a study of the title reaction was undertaken. The reaction is understood to be complementary, since the main product is identified as acrolein and the test for free radicals is negative. The following approximate rate law is observed:

$$\text{Rate} = k[Ni(IV)][AA]^{0.5} [OH^-]^{0.5} /[IO_4^-]^{0.5}$$

The likely active species of oxidant is $[Ni(OH)_2(H_2IO_6)]^-$. A possible mechanism is discussed.
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