Chapter-I

(a) General Introduction

Kinetic studies are receiving much importance in the recent years since they provide us the most powerful method of investigating the detailed reaction mechanisms. It is one of the most intriguing and challenging areas of chemistry, which deals with the mechanisms of reactions. To many chemists the real heart of chemistry is the study of mechanisms. Thus, chemical kinetics can be defined as that branch of chemistry concerned with the study and prediction of time dependent systems. To understand the mechanism of any reaction we must know a reaction as a function of time, the exact positions of all the atoms as the reactants are converted into product molecules. Virtually all information regarding reaction mechanism comes by inference of indirect evidence. Hence, it is the important job of chemists to device the proper experiments to generate most conclusive evidence.

The kinetic data will be the source of a great deal of detailed insight into the mechanism of a reaction. Although, other types of experimental evidences are also sought for purpose of formulating a reaction mechanism, the study of reaction kinetics generally forms the backbone of a thorough mechanistic investigation. Finally, as an area of pure science in itself, the study of rates and mechanism is one of rich varieties, concerned with the chemistry of every element and full of experimental challenges.
The award of Nobel prize for the year 1992 to Prof. R. A. Marcus on the
"Electron Transfer Reactions" and 1999 Nobel prize to Prof. Ahmed Zewail for
discovery of "Femtochemistry" and 2001 Nobel prize to Profs. William
Knowles, K. Barry Sharpless and Royji Noyori for their work on "Chirally
Catalysed Hydrogenation Reactions" and 2005 Nobel Prize to Profs. Robert
Grubbs, Richard Schrock, and Yves Chauvin on their research achievements on
"Metathesis Catalyst Technology" emphasize the importance of field of
reaction kinetics. Electron transfer reactions play a significant role in physical,
chemical and biological processes. Because of the ubiquity of electron transfer
processes, the study of electron transfer reactions, perhaps more so than that of
any other area of chemistry is characterized by a strong interplay of theory and
experiment\(^1\). Nonetheless the importance of electron transfer in transition metal
redox chemistry has been recognised\(^2\) and more recently it has become
increasingly obvious that many reactions in organic chemistry once thought to
be concerted in nature also occur via sequential one electron steps\(^3\).

The work of Henry Taube\(^4\) 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. As a result, oxidation-reduction
reaction needs at least two reactants, one capable of gaining electrons (oxidant)
and the other capable of losing electrons (reductant), i.e., a reducing agent
(reductant) by losing electrons, gets oxidised and an oxidising agent (oxidant), by gaining the electrons, gets reduced.

**Oxidation–reduction 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 co-ordination 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 co-ordination shells. From 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 a transfer.

**Oxidation–reduction in organic reactions**

The oxidation-reduction concepts, however, are not so clearly applicable in organic chemistry, when carbon compounds are oxidised their component atoms are very seldom deprived of their surrounding complete electron shells. Covalent bond fission is an essential feature of organic reactions and it can be affected 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. Electron removal by these two pathways has clearly distinguishable characteristics.
Multi equivalent reactions

Oxidising agents such as chromium(VI) and manganese(VII) undergo net changes of 3 and 5 units in oxidation number respectively during their reactions in acidic solution. For the most part, these reactions occur by one or two electron steps, with the necessary intervention of unstable intermediate oxidation states of chromium or manganese. The reactions of chromium(VI) with transition metal complexes generally proceed by sequential one-electron step, but with post transition metal ions and with non-metallic compounds, two electron steps appear to be preferred.

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

(a) Michaelis principle of compulsory univalent oxidation steps

(b) Shaffer's principle of equivalent change

Michaelis hypothesis states that an oxidation-reduction reaction takes place in one or more successive single electron transfer steps. 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.

E.g.,

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

The second principle refers to the observation that non-complementary reactions are often slow compared with complementary one's. Examples are the slow reduction of thallium(III) by iron(II) or cerium(IV) by thallium(I) as compared to the rapid reduction of thallium(III) by tin(II) and cerium(IV) by iron(II).
**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. For example, the reductions of thallium(III) by iron(II)\(^{11}\), vanadium(III) or vanadium(IV)\(^{12,13}\) and chromium(VI) by thallium(I)\(^{14}\) can only be explained through the formation of unstable thallium(II) species. Similar unstable oxidation states have been observed in other studies\(^{15,16}\). The interconversions between chromium(III) and chromium(VI) always appear to involve the unstable states, chromium(IV) and chromium(V).

In a classic study, King and Tong\(^{17}\) have worked out the details of the redox reactions between cerium(IV) and chromium(III) in aqueous sulphuric acid. The rate law was found to be as in equation (i), which is very reasonably explained by the mechanism involving steps of equation (ii a) to (ii c).

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

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

\[
\begin{align*}
\text{Ce(IV)} + \text{Cr(III)} & \rightleftharpoons \text{Ce(IV)} + \text{Cr(IV)} \quad \text{fast} \quad K \quad (\text{ii a}) \\
\text{Ce(IV)} + \text{Cr(IV)} & \rightarrow \text{Ce(III)} + \text{Cr(V)} \quad \text{slow} \quad k \quad (\text{ii b}) \\
\text{Ce(IV)} + \text{Cr(V)} & \rightarrow \text{Ce(III)} + \text{Cr(VI)} \quad \text{fast} \quad (\text{ii c})
\end{align*}
\]

Excellent support comes from the study of related reactions such as the oxidation of vanadyl ion by acid chromate ion\(^{18}\) (HCrO\(_4\)\(^{-}\)) and the analytical important oxidation of ferrous ion by acid chromate\(^{19}\). It is significant...
the above example the change over from chromium(IV) to chromium(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\textsuperscript{17}. A number of studies of the catalysis by platinum metals of oxidation reactions have been made\textsuperscript{20}. The catalysis by Ag(I)\textsuperscript{21}, Cu(II)\textsuperscript{22}, Mn(III)\textsuperscript{23} and Cr(III)\textsuperscript{24,25} in oxidation–reduction reactions are also found to occur through formation of unstable oxidation 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.

The diperiodatoargentate(III) complex is diamagnetic and exhibits square planar configuration with dsp\textsuperscript{2} hybrid bonds\textsuperscript{26}. Periodate acts as a bidentate ligand and contributes to the stabilization of Ag(III). The structure and cell dimensions of DPA compound resemble those of diperiodatocuprate(III)\textsuperscript{26}. The Ag(III) periodate complex ion can be represented as [Ag(H\textsubscript{2}O)(IO\textsubscript{6})\textsubscript{2}]\textsuperscript{7\textsuperscript{−}} and in solution it can be considered as hydroaquodiperiodatoargentate(III).

To formulate the reaction rate as a function of species concentration, therefore, requires knowledge of the existence of such equilibria and generally speaking, the knowledge of 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 concentration, quite often resemble the equations applicable to different mechanisms.

The study of fast reactions\textsuperscript{27} is on the threshold of exciting developments, since so many of the reactions of complexes, especially of transition series and biological processes are rapid. Muscle action, self reproduction, the combustion of rocket fuel and gasoline, the action of poisons and nerve gases, appearance of colours on addition of indicators etc. complete within a fraction of second and would thus provide a truly formidable challenge to classical kinetics.

Five main components of a kinetic investigation are\textsuperscript{28}

- Product and intermediate detection
- Concentration determination of all species present
- Deciding on a method of following the rate
- The kinetic analysis
- Determination of the mechanism

**Cyclic voltammetry**

Voltammetric technique is widely used by inorganic, physical and biological chemists for non-analytical purpose including fundamental studies of oxidation and reduction processes in various media; adsorption processes on
surfaces and electron transfer mechanism. At one time voltammetry was an important tool used by chemists for the determination of inorganic ions and certain inorganic species in aqueous solutions. In late 1950s and early 1960s, however, these analytical applications were largely supplanted by various atomic spectroscopy methods and voltammetry ceased to be important in analysis.

In mid 1960s several major modifications and classical voltammetric techniques were developed that enhance significantly the sensitivity and selectivity of the method.

In the years after 1960, the further development of electroanalytical methods made it possible to obtain a more detailed understanding of the different steps in the electro-chemical reactions. Both the theory for different types of reactions and the instrumentation were developed, and the introduction of simulation of the various kinds of electroanalytical signals was a great step forward. Cyclic voltammetry being the most widely used technique; publications dealing with the influence of the rate of the heterogeneous electron transfer and the rate of follow up reactions on the shape of the curves were published by Nicholson and Shain. When the electron transfer is followed by a rapid follow up reaction, a high sweep rate is needed to outrun the reaction, and for microelectrodes of conventional diameter about 1 mm the voltage drop caused by the ohmic resistance is difficult to compensate electronically. Higher sweep rates were employed with the help of ultra microelectrodes. Using suitable ohmic-drop compensation it was possible to make an ohmic-drop-free electrochemical investigation in the megavolt per
second range, which correspond to the development of a diffusion layer having only a few nanometers' thickness\textsuperscript{34-37}.

The different problems in molecular electrochemistry that can be solved by ultrafast voltammetric measurements have been discussed by C. Amatore \textit{et al.}\textsuperscript{37} Thus, the investigation at nano seconds time scale will help to characterize reactive intermediates and gain insights into complex mechanism as controlling information transfer to and storage on electronic devices of nanometer dimensions and at gigahertz frequencies is crucial for a wide range of practical applications. Recently, Pt electrodes of nanometer dimensions are synthesized and characterized and their applications in fundamental studies of electron-transfer mechanisms and in analytical chemistry have been reported\textsuperscript{38}.

\textbf{Present trend}

At present, the emphasis is moving towards application of the technique for individual systems from the development or refinement of the technique itself. Recent developments such as modified electrodes, conducting polymers and photo electrochemistry also act as catalysts for such developments. With each experimental report, a number of refinements are explored in the experimental approach. Hence, new ideas, new sights and new directions are always noticed in the experimental aspects of voltammetry as well. Some excellent voltammetric techniques are well described as monographs\textsuperscript{39}.

Voltammetric methods used today in analytical laboratories comprise a suite of techniques, the creation of which was made possible by rapid advances in instrumentation by the computerized processing of analytical data and particularly by innovative electrochemists. Advances in microelectronics and in particular the early introduction of operational amplifiers and feedback loops
have led to major changes in electroanalytical instrumentation. Indeed, many functions can be performed now using reliable integrated circuits. Electroanalytical procedures can be fully programmed and can be driven automatically by means of a personal computer with user-friendly software.

Principles used in electrolytic technology

The fundamental principles on which the field of electrolytic technology draws heavily include

- *Thermodynamics* which describes the equilibrium state of an interface, of the species within a given phase, and of the distribution of various possible phases within the cell
- *Kinetics* which relates the rate of passage of current through the interface to the driving forces across the interface
- *Transport* phenomena, which determine the rate at which species and energy can become available for the reaction at the interface region.
- *Current and potential field distribution*, which determines the flow of current between electrodes and the variation of potential along surfaces.

Applications

The voltammetric and polarographic analysis of drugs in pharmaceutical preparations by far the most common use of electrochemistry for analytical pharmaceutical problems. As a rule, many of the active compounds of the formulation can be readily oxidized or reduced. Examples of cyclic voltammetric (CV) and linear sweep voltammetric (LSV) determination of organic compounds in pharmaceuticals include many classes of drugs: antibiotics, diuretics, antineoplastics, antidepressants, muscle relaxants, neuroleptics, analgesics, vitamins, hormones, and others. Differential pulse
voltammetry/polarography (DPV/DPP) has been extremely useful for determination of low amounts of electroactive compound in pharmaceuticals.

Electrode surfaces may be modified in many ways to get better catalytic effects, chiral induction, or some other desirable effect not obtainable at the "classical" electrode materials. Irreversible adsorption\textsuperscript{40}, covalent attachment\textsuperscript{41-43}, polymerization of monomers containing electroactive groups\textsuperscript{44}, and carbon nanotubes\textsuperscript{45} have been used. Voltammetric studies of the kinetics and energetics of coupled electron-transfer reactions in proteins adsorbed at pyrolytic graphite electrodes have been made and it was found that the rates were more likely to be controlled by the chemical reactions coupled to the electron transfer than by the electron transfer. The modified electrodes are usually not stable enough for preparative reactions using high current densities and are mostly employed as sensors\textsuperscript{46}.

The small size of the microelectrodes allows some novel applications such as in vivo electroanalysis\textsuperscript{47,48}. Such electrodes can be used to stimulate or monitor the response of individual nerve cells allowing experimental research into the central nervous system in both the medicine and zoology\textsuperscript{49}.

Recent advances in instrumental techniques, however, promise access to molecular-level information about electrochemical systems that has been unavailable. This exciting development opens up important new opportunities in fundamental and applied science.

In the future, it may become possible to produce organized networks of molecules resembling, in their controlled structure, biological systems, yet having properties different from those of any material known today.
Fundamentals of Cyclic Voltammetry

Voltammetric analysis consists of two circuits: a polarizing circuit that applies the potential to the cell and a measuring circuit that monitors the cell current. The working electrode is potentiostatically controlled. The potential is varied in some systematic manner and resulting current vs potential plot is known as a voltammogram.

Scan rate

A simple potential waveform that is used often in electrochemical experiments is the linear waveform i.e., the potential is continuously changed as a linear function of time. The rate of change of potential with time is called scan rate.

Switching potentials and the excitation signal

Cyclic voltammetry involves the cycling of potential of an electrode between two designated values called the switching potentials in an unstirred solution and measuring the resulting current. The excitation signal is a linear potential scan with a triangular waveform. Single or multiple cycles can be used.

Potential control

The precise control of the external potential is done using a potentiostat and a three electrode system in which the potential of working electrode is controlled relative to the reference electrode, saturated calomel electrode (SCE) or silver-silver chloride (Ag/AgCl) electrode. The current passes between working electrode and the third electrode (the auxiliary electrode).

Thus CV can be described as ‘active’ electrochemical method because the experiment drives an electrochemical reaction by incorporating the
chemistry into a circuit and then controlling the reaction by circuit parameter such a voltage.

**Potential Pulse Techniques**

Charging current is minimized using a potential step (pulse) i.e., the potential is stepped from an initial value to a new value and it is held at this new value for a set time period. There is a charging current spike following the initial potential step; however, since there is no further change, the charging current decays experimentally. Since the faradaic current decays more slowly ($1/\sqrt{t}$) for diffusion controlled process, measuring the current after the charging current has decayed can eliminate the charging current. Due to high residual current the application of polarography as an analytical tool is limited up to a concentration of 10 $\mu$M. In order to minimize the charging current, refinements in instrumentation and technique have been made in the form of derivative polarography, ac polarography and pulse polarography. The pulse techniques are divided into normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV).

DPV can be carried out in the presence of more dilute supporting electrolyte than other electroanalytical methods. For trace analysis, it is highly desirable to keep the concentration of the supporting electrolyte as low as possible, in order to avoid any introduction of trace levels of impurity. In an electrochemical reduction process, at potentials well positive of the redox potential, there is no faradaic reaction in response to the pulse, so the difference current is zero. At potential around the redox potential, the difference current reaches a maximum, and decreases to zero as the current becomes diffusion-controlled. The current response is therefore a symmetric peak.
The solvent

A number of physicochemical properties must be considered while choosing a solvent for electrochemical work\textsuperscript{50}

i. it must be a liquid at room temperature,

ii. it must have sufficient solubility for ionic substances to form conducting electrolyte; it must be able to dissolve the electroactive species of interest,

iii. it must have a wide enough potential region for the study of the redox process of interest, that is, solvent itself must not undergo oxidation or reduction in this potential region and

iv. it must possess the required acid-base properties.

The dielectric constant is the most important parameter.

Supporting electrolytes

All ionic salts or ionizable compounds in a solvent are defined as the supporting electrolytes. It is very important to realize that they can influence the electrochemical processes in a number of ways:

i. These electrolytes impart conductivity to the solvent and hence enable the continuous current flow in solution.

ii. They must remain electroinactive in the potential region of interest if any useful voltammetric study is to be conducted.

iii. If the concentration of the supporting electrolyte is very low, they can form a space charge near the surface and the space charge potential can influence the charge transfer kinetics.

iv. If the ions of supporting electrolyte are adsorbed on the surface, they can catalyze or inhibit other reactions.
v. Small cations may form ion pairs with the anion radicals formed in the electrode process and the properties of the ion pairs can be very different from those of the free anion radical.

vi. Some ions may form complexes with the reactants and/or products.

vii. The supporting electrolyte generally control the acidity of the ionic solution.

viii. The liquid electrolyte melts and solid electrolyte acts as the medium for the ionic phase.

H$_2$SO$_4$, HClO$_4$ and HCl are normally employed for studies in acidic aqueous solutions and NaOH or KOH are employed for alkaline media. In neutral region, if buffering is important, acetate, citrate and phosphate buffers are usually employed. Britton-Robinson buffer is used over a wide range of pH. If the redox process does not involve acid-base reactions, no buffers are needed and any electrolyte may be used.

Even today a number of voltammetric results at very positive potentials in KCl media are interpreted without possible influence of Cl$^-$ adsorption. Reductions in Li$^+$ salt solutions are interpreted without consideration of ion-pair effect. One must always consider all possible influence of supporting electrolytes if such pitfalls are to be avoided.

The working electrodes

In electrochemistry, an electrode is the entire assembly of an electronic conductor in intimate contact with an ionic conductor. The working electrode, where the reactions are studied, is usually made of noble metals, carbon, or mercury. Numerous characteristics are required for this kind of electrode: high signal-to-noise and reproducible response, no interfering reactions in a certain range of potential, high electrical conductivity, low surface capacitance.
mechanical and chemical stability, low cost, availability, low toxicity and long
term stability. The electronic conductor can be a metal or a semi conductor or a
mixed electronic and ionic conductor. The ionic conductor is usually an
electrolyte solution; however, solid electrolytes can be used as well. In the
simplest case, the electrode is a metallic conductor immersed in an electrolyte
solution. At the surface of the electrode, dissolved electroactive ions change
their charges by exchanging one or more electrons with the conductor. In
electrochemical reaction both the reduced and oxidizing ions remain in
solution, while the conductor is chemically inert and serves only as a source
and sink of electrons. The technical term "electrode" usually also includes all
mechanical parts supporting the electrode (e.g. a rotating disk electrode or a
static Hg drop electrode). Further more, it includes all chemical and physical
modifications of the conductor or its surface (e.g. A Hg film electrode, an
enzyme electrode, a carbon paste electrode etc.).

A number of carbon electrodes have been introduced into voltammetric
studies. These electrodes have a very wide anodic as well as cathodic potential
region; both in aqueous and non-aqueous solvents. Carbon paste\textsuperscript{51} and vitreous
or glassy carbon electrode introduced into electrochemistry is the most widely
used carbon electrode material today\textsuperscript{52,53}. Carbon epoxy electrodes, carbon
fibre electrodes, graphite and wax impregnated graphite electrodes are also
used. The carbon electrodes have a good positive potential range.

A few other metallic electrodes such as boron nitrides and some carbides
were introduced into electrochemistry\textsuperscript{51}. However, either because of poor
reproducibility or high electrical resistivity, these electrodes were not very
successful. Recently, a variety of chemically modified electrodes (CMEs) have
been studied using CV.
The reference electrode

The general requirement of a reference electrode is very simple. Its potential should not vary when the external potential is applied in the working electrode-reference electrode system of the cell. It must also be chemically stable. There is number of electrode reactions which possess these physicochemical properties\textsuperscript{54-56}.

The most popular reference electrodes, however, are the so-called electrodes of the second kind where the equilibrium electrode potential depends on an ion that does not directly involve in an electrode reaction. In the most widely used saturated calomel electrode (SCE), for example, the Hg is in contact with Hg\textsubscript{2}Cl\textsubscript{2}/KCl paste in contact with saturated KCl solution. The electrode reaction is Hg\textsuperscript{+}/Hg reaction but because of the low solubility of Hg\textsubscript{2}Cl\textsubscript{2}, the electrode potential depends on Cl\textsuperscript{-} concentration. The electrode potentials of such electrodes can be maintained very easily at a constant value. The Hg/Hg\textsubscript{2}SO\textsubscript{4}, Ag/AgCl and Hg/Hg\textsubscript{2}O electrodes also belong to this group.

The metal/metal ion electrodes may also be employed as reference electrodes. Cu/Cu\textsuperscript{2+} reference electrodes are extensively employed. Ag/Ag\textsuperscript{+}(acetonitrile) is used as the reference electrodes in non-aqueous media. Al/Al\textsuperscript{3+} reference electrodes are also employed for measurements in non-polar solvent and in molten salt media\textsuperscript{57}.

The counter/auxiliary electrode

In voltammetric studies, the current flows between the working electrode (WE) and counter electrode (CE). Although the main interest is on the WE, it must be ensured that the CE does not complicate the matters. It must not dissolve in the medium. The reaction product at the CE must reach or react at the WE.
Platinum electrodes fortunately meet most of these requirements and this is the most widely used counter electrode in aqueous, non-aqueous as well as molten salt media. Platinum electrodes in the form of coils or thin foils are normally used. Carbon electrodes are also used in molten salts. The electrode area must be sufficiently larger than the WE area to ensure that the area of the CE does not control the limiting current.50

Electron transfer [ET] or charge transfer

The electron transfer at the interface between the electrode and electrolyte is central to an electrode reaction. Electro active species having moved from the bulk of the solution by either diffusion or under forced convection enters in the electrical double layer, which is under direct influence of the electrode. On entering the double layer the species undergoes a structural orientation so that it can take up or give up electrons from or to the electrode surface respectively with the least activation energy when a suitable potential is applied and macroscopically, we observe a current. This state of the reactant species is known as transition state. Being unstable the species in transit state converts itself to the final product by release of activation energy and gets reduced or oxidized. This final product after undergoing suitable re-orientation either gets deposited on the electrode surface or moves away from the electrode surface into the bulk solution. The transfer of an electron to or from the substrate is an activated process. Three situations of ET arise.

Reversible ET

Here, ET is much faster than the mass transfer (Transport control). An electrochemical experiment is attained at the electrode surface at all times. The
concentration $C_{\text{ox}}$ and $C_{\text{red}}$ of oxidized and reduced forms of the redox couple, respectively follow the Nernst equation

$$
\frac{C_{\text{ox}}}{C_{\text{red}}} = \exp \left[ \frac{nF}{RT} (E - E^0) \right]
$$

where, $n =$ No. of electrons transferred, $F =$ Faraday constant, $R = $ Gas constant and $T = $ Temperature. This type of process is called reversible charge transfer.

By reversible electrochemists means that the reaction is fast enough to maintain the concentration of the oxidized and reduced forms in equals with each other at the electrode surface.

**Diagnostic tests for cyclic voltammograms of Reversible processes at 25°C**

i. $\Delta E_p = E_{pa} - E_{pc} = 59/n \text{ mV}$, where $n$ is number of electron change

ii. $[E_p - E_{p/2}] = 59/n \text{ mV}$, where $n$ is the electron stochiometry

iii. $i_{pc}/i_{pa} = 1$, where $i_{pc}$ and $i_{pa}$ are cathodic and anodic peak currents respectively

iv. $i_p \propto v^{1/2}$, where $i_p$ is peak current and $v$ is the scan rate

v. $E_p$ is independent of $v$, where $E_p$ is peak potential.

**Irreversible ET**

ET is much slower than the mass transfer (ET control). The current density follows the Butler-Volmer equation

$$
i = \{ \exp[-\alpha nF / RT(E - E^0)] - \exp[(1-\alpha nF / RT(E - E^0))] \}
$$

where, $i_o =$ the exchange current density at $E$=$E^0$ (irreversible ET). This type of process is called irreversible electron transfer.

Butler-Volmer equation reduces to Nernst equation when $i = 0$

The term $\alpha$ is known as the transfer coefficient. It arises because only a fraction of the energy that is put into the system (in the form of the applied potential) lowers the activation energy barrier. Its value varies from...
zero to unity depending on the shape of the free energy surfaces for the reactants and products. For an irreversible electrode process, the peak current is given by

\[ i_p = 2.69 \times 10^5 n (\alpha n)^{1/2} A D_0^{1/2} v^{1/2} C_0^* , \]

where \( A \) is electrode area, \( D_0 \) is diffusion coefficient and \( C_0^* \) is concentration of electroactive species.

Diagnostic tests for cyclic voltammograms of Irreversible processes at 25°C

i. No reverse peak
ii. \( i_p \propto v^{1/2} \)
iii. \( \text{Ep shifts} = 30/\alpha n \text{ mV} \), where \( \alpha \) is charge transfer coefficient
iv. \( [\text{Ep-Ep}_2] = 47.7/\alpha n \text{ mV} \)

Quasi-reversible ET

ET and transport have comparable rates. This mixed control situation is characterized as quasi reversible. Here, both the electron transfer and mass transport control the current. The shape of the cyclic voltammogram is a function of the ratio \( k^0 / [\pi \gamma nFD / RT]^{1/2} \). As the ratio increases, the process approaches the reversible case. Overall, the CV of quasi-reversible system is more drawn out and exhibits a larger separation in peak potentials compared to a reversible system.

Diagnostic tests for cyclic voltammograms of Quasi-reversible processes at 25°C

i. \( i_p \) increases with \( v \) but is not proportional to it.
ii. \( i_{pc}/i_{pa} = 1 \), provided \( \alpha = 0.5 \)
iii. $\Delta E_p$ may approach 59/n mV at a low $v$ but increases as $v$

increases.

iv. $E_{pc}$ shifts negatively with increasing $v$

(b) Summary of present work

In the present thesis, some redox reactions in alkaline medium have been studied. Reactions were followed conveniently by spectrophotometer in the UV-visible region. Also some electro-oxidation reactions were studied by CV. The details of such studies are given below.

I. General introduction

This chapter introduces about the kinetics, mechanism and voltammetry of reactions in general.

Part A: KINETIC STUDIES

II. Kinetic and mechanistic investigations of oxidation of pentoxifylline drug by alkaline permanganate (Stopped Flow Technique)

The kinetics of oxidation of a hemorheologic drug, pentoxifylline by permanganate in alkaline medium at a constant ionic strength of 0.10 mol dm$^{-3}$ was studied spectrophotometrically using a rapid kinetic HI-TECH SFA-12 accessory. The reaction between permanganate and pentoxifylline in alkaline medium exhibits 1:2 stoichiometry (pentoxifylline: permanganate). The products were identified by TLC and spectral studies including LC-MS. The reaction is first order in [permanganate ion] and less than unit order dependence each in [PTX] and [OH$^-$]. However, the order in [PTX] and [OH$^-$]
changes from first order to zero order as their concentration increase. A
decrease in the dielectric constant of the medium increases the rate of the
reaction. The effect of added products and ionic strength of the reaction
medium have been investigated. The oxidation reaction in alkaline medium has
been shown to proceed via a permanganate-pentoxifylline complex, which
decomposes slowly in a rate-determining step followed by a fast step to give
the products. A suitable mechanism is proposed. The reaction constants
involved in the different steps of the mechanism are calculated. The activation
parameters with respect to slow step of the mechanism are computed and
discussed and thermodynamic quantities are also determined.

III. Oxidative degradation and deamination of atenolol by diperiodatocuprate
(III) in aqueous alkaline medium: A mechanistic study

The kinetics of oxidation of atenolol (ATN) by diperiodatocuprate (III)
(DPC) in aqueous alkaline medium at a constant ionic strength of 0.10 mol
dm$^{-3}$ was studied spectrophotometrically. The reaction between DPC and ATN
in alkaline medium exhibits 1:2 stoichiometry (ATN: DPC). The oxidative
products were identified by spot test, IR, NMR and LC-ESI-MS studies. The
reaction is first order in [DPC] and has less than unit order in both [ATN] and
[alkali]. However, the order in [ATN] and [alkali] changes from first order to
zero order as their concentration increase. Intervention of free radicals was
observed in the reaction. Increase in periodate concentration decreases the rate.
The oxidation reaction in alkaline medium has been shown to proceed via a
monoperiodatocuprate (III)–ATN complex, which decomposes slowly in a
rate-determining step followed by other fast steps to give the products. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed, and thermodynamic quantities are also determined.

**Part B: CYCLIC VOLTAMMETRIC STUDIES**

IV. **Electrochemical oxidation of pentoxifylline and its analysis in pure and pharmaceutical formulations at a glassy carbon electrode**

The oxidative behavior of pentoxifylline was studied at a glassy carbon electrode in phosphate buffer solutions using cyclic and differential-pulse voltammetry. The oxidation process was shown to be irreversible over the pH range (3.0-9.0) and was diffusion controlled. The possible mechanism of the oxidation of pentoxifylline was investigated by means of cyclic voltammetry and UV-vis spectroscopy. An analytical method was developed for the determination of pentoxifylline in phosphate buffer solution at pH 3.0 as supporting electrolyte. The anodic peak current varied linearly with pentoxifylline concentration in the range of 0.02 to 0.60 μM pentoxifylline with a limit of detection (LOD) of 0.44 nM. The proposed method was applied to the determination of pentoxifylline in pure and pharmaceutical formulations.

V. **Electro-oxidation and determination of gabapentin at gold electrode**

The electrochemical oxidation of gabapentin has been investigated for the first time by cyclic and differential pulse voltammetry at different pH at gold electrode. Cyclic voltammetric studies were performed in a wide range of
sweep rates and various concentrations of gabapentin. The effect of surfactants was studied. The anodic peak was characterized and process was adsorption-controlled. The oxidation peak corresponds to the amine and probable mechanism was proposed. According to the linear relation between the peak current and the gabapentin concentration, differential pulse voltammetric method for the quantitative determination in pharmaceuticals was developed. The linear response was obtained in the range of 0.3 to 15 μM with a detection limit of 0.13 μM with good selectivity and sensitivity. The proposed method was successfully applied to gabapentin determination in pharmaceutical samples and for the detection of gabapentin in urine as a real sample.

VI. Electro-oxidation and determination of trazodone at multi-walled carbon nanotube modified glassy carbon electrode

A simple and rapid electrochemical method was developed for the determination of trace-level trazodone, based on the excellent properties of multi-walled carbon nanotubes (MWCNTs). The MWCNT-modified glassy carbon electrode was constructed and the electrochemical behavior of trazodone was investigated in detail. The cyclic voltammetric results indicate that MWCNT-modified glassy carbon electrode can remarkably enhance electrocatalytic activity towards the oxidation of trazodone in neutral solutions. It leads to a considerable improvement of the anodic peak current for trazodone, and allows the development of a highly sensitive voltammetric sensor for the determination of trazodone. Trazodone could effectively accumulate at this electrode and produce two anodic peaks at about 0.73 V and
1.00 V. The electrocatalytic behavior was further exploited as a sensitive detection scheme for the trazodone determination by differential-pulse voltammetry. Under optimized conditions, the concentration range and detection limit are 0.2 to 10 μM and 24 nM respectively for trazodone. The proposed method was successfully applied to trazodone determination in pharmaceutical samples. The analytical performance of this sensor has been evaluated for detection of analyte in urine as a real sample.

VII. Voltammetric oxidation and determination of cinnarizine at glassy carbon electrode modified with multi-walled carbon nanotubes

The voltammetric oxidation of cinnarizine was investigated. In pH 2.5 Britton-Robinson buffer, cinnarizine shows an irreversible oxidation peak at about 1.20 V at a multi-walled carbon nanotube (MWCNT)-modified glassy carbon electrode. The cyclic voltammetric results indicate that MWCNT-modified glassy carbon electrode can remarkably enhance electrocatalytic activity towards the oxidation of cinnarizine. The electrocatalytic behavior was further exploited as a sensitive detection scheme for the cinnarizine determination by differential-pulse voltammetry. Under optimized conditions, the concentration range and detection limit are 0.09 to 6.0 μM and 2.58 nM respectively for cinnarizine. The proposed method was successfully applied to cinnarizine determination in pharmaceutical samples. The analytical performance of this sensor has been evaluated for detection of analyte in urine as a real sample.
REFERENCES

1. J. J. Zuckerman,  

2. Sir. G. Wilkinson,  

3. R. A. Sheldon and J. K. Kochi,  

4. H. Taube,  

5. H. Taube,  
D. Banerjee,  

6. W. A. Waters,  

7. H. A. A. Medien,  
Z.Naturforsch., 58b, 1201 (2003);  
R.G.Panari, R.B.Chougale and S.T.Nandibewoor,  

8. L. Michaelis,  
Trans. Electrochem. Soc., 71, 107 (1937);  

9. P. A. Shaffer,  
J. Am. Chem. Soc., 55, 2169 (1933);  
J. Halpern,  

10. M. Anabar and H. Taube,  
J. Am. Chem. Soc., 80, 1073 (1958);
R. Stewart,
*Experimentia.*, **15**, 401 (1959)

11. C. E. Johnson, Jr.,
*J. Am. Chem. Soc.*, **74**, 959 (1952);
K. J. Ashurst and W. C. E. Higginson,
*J. Chem. Soc.*, **3044** (1953);
S. A. Chimbatadar, S.T. Guddalli and S.T. Nandibewoor,

12. W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead and A. G. Sykes,

13. G. A. Hiremath, P. L. Timmanagoudar and S. T. Nandibewoor,

14. S. A. Chimbatadar, S.B. Koujalagi and S. T. Nandibewoor,

15. S. A. Chimbatadar, T. Basavaraj and S. T. Nandibewoor,

16. K. A. Thabaj, D. S. Munavalli, S. A. Chimbatadar and S. T. Nandibewoor,

17. E. L. King and J. Y. Tong,

18. J. H. Espenson,
*J. Am. Chem. Soc.*, **85**, 5101 (1964)

19. J. H. Espenson and E. L. King,

20. K. T. Sirsalmath, C.V. Hiremath and S. T. Nandibewoor,

21. A. T. Gemeay, A. M. Habib and M. A. B. El-Din,

22. V. Sippola and O. Krause,
23. T. K. M. Shing, Y. Y. Yeung and P. L. Su, 

24. D. C. Bilehal, R. M. Kulkarni and S. T. Nnadibewoor, 

25. A. R. Supale and G. S. Gokavi 

26. G. L. Cohen and G. Atkinson, 
Inorg. Chem., 3, 1741 (1964)

27. D. N. Hague, 
"Fast Reactions", Wiley, New York (1971); 
R. Chang, 

28. M. R. Wright, 

29. M. Rudolph, D. P. Reddy and S. W. Feldberg, 

30. D. Britz, 

31. R. S. Nicholson and I. Shain, 
Anal. Chem., 36, 706 (1964)

32. R. S. Nicholson, 
Anal. Chem., 37, 1351 (1965)

33. M. Fleishman, S. Pons, R. Rolison and P. P. Schmidt, 

34. C. P. Andrieux, D. Garreau, P. Hapiot and J. M. Save’ant, 

35. D. O. Wipf and R. M. Wightman, 

36. C. Amatore, E. Maisonhaute and G. Siminneau, 
37. C. Amatore, E. Maisonhaute and G. Siminneau, 

38. B. F. Watkins, J. R. Behling, E. Kariv and L. L. Miller, 

39. J. Wang, 
   "*Analytical Electrochemistry*, 3rd Ed., John Wiley & Sons, Inc., 

40. J. C. Lennox and R. W. Murray, 
   *J. Electroanal. Chem.*, 78, 395 (1977)

41. J. R. Lenhard and R. W. Murray, 
   *J. Am. Chem. Soc.*, 100, 7870 (1978)

42. C. A. Koval and F. C. Anson, 

43. G. Bidan, A. Deronzier and J. C. Moutet, 

44. F. A. Armstrong, R. Camba, H. A. Heering, J. Hirst, L. J. C. 
   Jeuken, A. K. Jones, C. Le'erger and J. P. McEvoy, 

45. A. Merkoci, 

46. E. A. G. Hall, 

47. R. M. Weightman, E. Strope, P. M. Plotsky and R. N. Adams, 
   *Nature*, 262, 145 (1976)

48. J. B. Zimmerman and R. M. Weightman, 

49. J. B. Justice, 
   "*Voltammetry in the Neurosciences*, Humana, Clifton, New Jersey, 
   (1987)

50. M. Noel and K. I. Vasu, 
   "*Cyclic Voltammetry and the Frontiers of Electrochemistry*, 1st Ed., 
51. R. N. Adams,  

52. H. E. Zittel and F. J. Miller,  
*Anal.Chem.*, 37, 200 (1965)

53. W. E. Van Der Linden and J. W. Dieker,  

54. D. J. G. Ives and G. J. Janz,  

55. J. N. Butler,  

56. C. K. Mann and K. K. Barnes,  

57. R. J. Gale and R. A. Osteryong,  

58. B. Speiser,  
PART - A
KINETIC STUDIES