CHAPTER – I

Chemical reactions proceed with different rates. Some reactions are too fast and the rate of the chemical change taking place cannot be measured by conventional methods and some are so slow that the rate of the chemical change is almost imperceptible. The initial and final states for a chemical system do not provide us with a complete description of a chemical change in a system. Chemists are always interested in knowing how long a time, does the change require, and why do the times for different changes turn out as they do. According to Henry Eyring "A molecular system" passes from one state of chemical equilibrium to another by all means of possible intermediates but the path most economical of energy will be more often travelled. 

The subject of 'Chemical Kinetics' is concerned with quantitative study of rates of chemical reaction and the factors upon which they depend. A chemical reaction may be thought of as a motion picture of all atoms and their electrons involved in the reaction beginning before the reactants approach each other and ending after the products have been formed. Two kinds of problem arise in any kinetic investigation. The first is the establishment of relationships between the velocity and various factors influencing it and second is an interpretation of stoichiometric equation in terms of mechanism. One important aspect of chemistry is the study of mechanism of chemical reaction i.e. the manner
in which the chemical transformation occurs. A chemical reaction which proceeds at a measurable rate probably takes place in a series of simpler steps. The possible series of such steps is called the reaction mechanism; so a reaction mechanism is a series of reactions which together comprise the steps in the overall change observed. Kinetic statements such as 'That every thing changes is an unescapable fact, which from time immemorial has moved the poets, exercised the metaphysicians, and excited the curiosity of the natural philosopher' is a very apt expression in this context. The most powerful tool for the experimental study of reaction mechanism is chemical kinetics. The most powerful information furnished by the kinetic study of a reaction is its rate equation. This equation expresses the rate of reaction as a function of concentration. In the year 1865 to 1867 Garcourt and Lasson published the results of their investigations on the reaction between potassium permanganate and oxalic acid and the results were analysed mathematically by Lasson. The reaction in which the rate is proportional to concentration of only one reacting substance was called first order by him and the reaction in which the rate was proportional to the product of the two concentrations was second order reaction and so on.

Most of the reactions involve two or more steps. Out of the various steps, the slowest step (or steps) determines the rate of reaction and the nature of the rate equation. Naturally the rate equation may not involve all the
altering materials as such it is not generally possible
to deduce the rate equation from the stoichiometric equation
of the overall reaction. In other words, the molecularity
i.e. (the number of molecules of the reactant on the left
hand side of the balanced overall chemical equation) of a
reaction is not necessarily the same as its kinetic order.

There are various factors which alter the
reaction rate. Some of such factors are, temperature,
solvent, catalyst, ionic concentration, dielectric constant
of medium etc. The effect of solvent was investigated by
Senshutkin in 1892, while studying the reaction between
trimethylamine and ethyl iodide to form the quaternary
ammonium iodide in a variety of solvents at 100° C. He
found that the reaction was slowest in aliphatic hydrocarbons
and fastest in aromatic alcohols. In 1931 Soper made the
study of the reaction between ethyl alcohol and acetic anhydride
to form ethyl acetate in various solvents. Richardson &
Soper suggested that internal pressure of solvent is an
important factor in influencing the reaction rate. The
factor $a/v^2$ of van der Waals equation is roughly equal
to internal pressure of liquid. As a general rule, if the
reaction is one in which the products are of higher
internal pressure than the reactants, it is accelerated by
the solvents of higher internal pressure and vice versa.
Since internal pressure and polarity often run parallel,
a polar solvent might be expected to accelerate a process
in which a polar substance is produced and to retard one in which non polar substance is formed. The activated complex if it interacts with the solvent there may be considerable effect on the reaction rate. The exceptionally high value for Kemeneski reaction in nitrobenzene is accounted for in this manner. Norris suggested that dielectric constant was an important factor in influencing the reaction rate.

The next important factor is temperature. The speed of practically all reactions are increased by a rise in the temperature. This enhancement of speed is somewhat different for different reactions, but generally the speed increases between two to three fold or slightly higher for a rise of temperature by 10°C. The empirical equation called Arrhenius equation, first suggested by van't Hoff and verified by Arrhenius has been found to represent satisfactorily the variation of rate with temperature for many reactions. Arrhenius equation is

\[ k = A e^{-E/R T} \]

where \( A \) and \( E \) are called frequency factor and energy of activation respectively. The above equation implies that logk of any reaction gives a straight line of slope \( E/2.303 R \) when plotted against reciprocal of absolute temperature. Further it leads to the inference that other things being equal, a large energy of activation signifies a low reaction rate. According to Arrhenius, in every system equilibrium existed between normal and active molecules and
that only the later could take part in a chemical reaction. The reactants which have an energy equal to or greater than a certain minimum value of $E$ are called activated complex. So the energy necessary to transform the reactants into activated complex is called activation energy. The activated complex molecules only can undergo chemical change and other molecules do not. The solution lowers the potential energy of the substance, so, if reactants are solvated the reaction rate will decrease because the necessary energy of activation is increased, but if the activated complex is solvated, the energy of activation is decreased, hence the rate will increase. In the event that both reactant and activated complex are solvated the overall effect on the activation energy and rate may be small. The temperature coefficient gradually decreases at the higher temperatures.

The various theories have been proposed from time to time to explain the mechanism of reactions. Two kinds of the theoretical approaches are made to interpret the kinetics of reactions. They are respectively called collision theory and theory of absolute reaction rate or the transition state theory.

According to collision theory the molecules acquire the energy of activation as a result of collisions between the molecules. It is however well known that all
collisions do not lead to chemical reaction, but only a small fraction of them is effective. Hence the molecular encounters do not necessarily cause chemical reaction. Chemical changes occur only between those molecules of reactants which become activated in the process of collision by acquiring the energy of activation.

According to transition state theory the two reactants, say A B and C, first form a transition complex which then decomposes into products.

\[
AB + C = A \ldots B \ldots C = A + BC
\]

Reactants \quad Transition \; Complex \quad Products

The basic idea is that C comes so close to B and that B becomes undecided as to which partner it belongs to. This state of indecision, as to B being simultaneously attached to A and C, though somewhat loosely than before, is the transition state. One of the important types of reaction in organic chemistry is displacement reaction. When a reagent A having at least one unshared pair of electrons collide with BC, the collision might result in establishment of a bond between A and B and thus liberating C with an unshared pair of electrons. In the reaction the attack of A is directed against the nucleus of B and the process is said to be nucleophilic displacement. The substitution at a carbon atom can occur in either of two ways. Either A can strike BC producing A B and C or B C
can undergo a preliminary slow dissociation into $B^+$ and $C^-$, a carbonium ion, followed by rapid reaction of $A$ with the carbonium ion. Since both paths lead to substitution at the nucleus of carbon atom, they are called nucleophilic substitutions. The electron release or withdrawal will affect a substitution reaction in a different way depending upon whether it is proceeding by preliminary dissociation giving $S_N^1$ type reaction or by direct attack of substituent giving $S_N^2$ type reaction. Concerning the $S_N^2$ type reaction there is now a general agreement that the process proceeds by the attack of $A^-$ at the back side of the carbon to which $C$ is attached, the process is accompanied by Walden inversion, and behaviour of the three other linkages has been described as like the ribs of an umbrella in gale. The mechanism of the process may be shown as follows:

$$A : + B \rightarrow C \rightarrow A \cdots B \cdots C \rightarrow A \cdots B + \rightarrow C$$

The reactants, $A$ and $B$, come together to give rise to an activated complex. During this approach of $A$ towards $B$ there will be electronic interaction between them and during this process the potential energy of system will first increase, then decrease. The activated complex is a transient species passing from initial state to final state. The energy necessary to push $A$ to approach $B$ to form activated complex is energy of activation.

In the reaction between the ions, the dielectric
constant of the solvent plays a very important role. Saunder 9 and Koelwyn Hughes 9 modified the collision theory to allow for electrostatic interactions in such reactions. The mathematical expression is as given below:

\[
\frac{D}{D} = \frac{D}{D} - \frac{D}{D} - \frac{D}{D} - \frac{D}{D}
\]

where

\[
\log k_{D=0} = \log k_{D=\infty} - \frac{D_{AB}}{D_{AB} - D_{AB}} - \frac{D_{AB}}{D_{AB} - D_{AB}} - \frac{D_{AB}}{D_{AB} - D_{AB}}
\]

\[
\log k_{D=0} = \text{rate constant of reaction in solvent of dielectric constant } D
\]
\[
\log k_{D=\infty} = \text{rate constant of reaction in solvent of infinite dielectric constant at zero ionic strength.}
\]
\[
Z_A \text{ and } Z_B \text{ are the number of charges on reacting ions, } d \text{ is distance between the reacting ions when they are to interact, } e \text{ is electronic charge, } D \text{ is dielectric constant of the medium, } R = \text{gas constant and } \gamma = \text{Avogadro's number, } T = \text{absolute temperature.}
\]

Wider interest in kinetics developed when rates of reactions were found to change enormously in presence of catalysts. A catalyst is a substance which alters the rate of reaction although it remains usually unchanged at the end of reaction. Actually it does take part in a chemical reaction but it is regenerated and hence the general inference is that it remains chemically unchanged at the end of the reaction. Catalyst can be homogeneous or heterogeneous. The most important examples of homogeneous catalyst in solution are those referred to as acid-base catalyst. The pioneer in the
field was Kircbcrll 0 who in 1812 studied the hydrolysis of starch to glucose in presence of dilute acids. A few years later, Thenard 11 investigated the decomposition of hydrogen peroxide in alkaline solution. Wilhonyme's 12 work on the rate of inversion of sucrose by dilute acid is regarded as classic. It led other investigators to an extensive study of hydrolysis of ester catalysed by both acids and alkalis. Catalytic activity of an acid in hydrolysis of an ester and sucrose was adopted by Arrhenius and Catwale as a measure of strength of the acid in early days of ionisation theory.

Further study of acid base catalysts in the light of modern views on the nature of acid and base 13 species which not only these but their ions and other species present in solution also independently contribute towards catalysis. Thus in case of any acid not only H+ ions but also unionised acid and its anion (which according to modern views is its conjugate base) exert their own catalytic effects. To explain acid or base catalysed reactions the theory of general acid base catalysis is useful.

It will not be out of place to mention here some of the reactions catalysed by acids or bases. Buria 15 studied the effects of hydrochloric, nitric, sulphuric and phosphoric acids on the hydrolysis of ethyl acetate. Sodium hydroxide was used by Hjelt 14 in the hydrolysis of ethyl esters of malonic, succinic
and several other acids. The amphotolysis of
dimethylmalonate was investigated by Slobodsky.\textsuperscript{15}
Datt, Dar and Shattacharya\textsuperscript{16} studied the hydrolysis
of methyl acetate in presence of picric acid and oxalic
acid. Inversion of sucrose in presence of acid was
investigated by Trevor\textsuperscript{17-1} Cohen\textsuperscript{17-2} and other workers.
Mutarotation of dextrose in presence of various acids was
widely studied. Important contributors are Lunden\textsuperscript{18},
Norm and Lewis\textsuperscript{19}, Harne and Hawkins\textsuperscript{20}, Shah and Aris\textsuperscript{21},
Pearce and Thomas\textsuperscript{22}, Sapozhinikov and Percherkina\textsuperscript{23} and
others. Bell and Jones\textsuperscript{24} studied the acid catalysed
inversion of D-xylose. Schoeter and Miguchi\textsuperscript{25} have
reported the racemisation of adrenaline in presence of
hydrogen ions. The effect of hydrochloric and hydrobromic
acids on hydrolysis of hydrogen cyanide has been studied
by Krielle and Serier\textsuperscript{26}. A number of oxidation
reduction reactions are sensitive to hydrogen ions.

Salts are also known to effect the
velocities of several reactions. Arhenius\textsuperscript{27} used
normal salts in the study of inversion of sugar. Bhodan-
Van Szyszowski\textsuperscript{28} appeared to have introduced the
term neutral salt effect. The study of salt effect is
usually associated with study of effects of acids.
Examples of such cases are hydrolysis of esters,
mutarotation of glucose etc. Intramolecular change
of acetochloroaniline to \(\beta\)-chloroaniline was studied
by Rivett\textsuperscript{29} in presence of several chlorides and
hydrochloric acid. Hens and Harradough have reported the salt effect on acid dye baths. A variation in the rate of hydrolysis of copper sulphate by salts was reported by Friedman and Stoker. Thus salt plays an important role in the study of chemical reactions.

The discovery of chain reactions and free radicals have widened the field of chemical kinetics. Bodenstein in 1913 was first to introduce the idea of chain reactions. The formation of hydrochloric acid gas from elements led him to think of chain mechanism. Herst also studied some chain reactions. Christiansen and Krames applied the idea to thermo reactions. Further contributions in this direction were made by Backstorm, Bodenstein, Haber and others. Hinselwood and Semenoff explained the explosion and inflammation in the light of chain mechanism.

Similarly postulation of free radicals gave an impetus to the advances of chemical kinetics. Gomberg was first to discover triphenylmethyl free radical. To explain photochemical and other reactions, free radical mechanism has been very useful. Most of the organic reactions involve free radicals.

Recently isotopic labelling has been introduced in the field of reaction mechanisms and reaction kinetics. An isotopic substitution may cause a meaningful change in the reaction rate. For example, the measurements of acid catalysed reactions in water and in deuterium oxide provides a useful empirical tool for studying the mechanism.
of acid catalysis.

A brief review of oxidation reduction reactions studied by various investigators, majority of them following the method of chemical kinetics, will be useful. The familiar oxidising agents are peroxy disulphate, potassium permanganate, chronic acid, ceric sulphate etc. Oxidation by peroxydisulphate has been studied by various workers such as Saxena, Singh, and Ghosh and Shrivastava etc. The catalysed reaction in presence of Cu²⁺ and Ag⁺ has been studied by King, Ghosh and Gupta, Bhakuni and Shrivastava etc. Saxena and Singh have found the accelerating effects of H⁺ ions on the same reaction. Permanganate oxidation of oxalic acid has been a very favourite reaction for study. S. Senate P. and A. Cancho Cobello, Mercourt, Leuner, Duke, Taube etc. have studied the kinetics of this reaction. R. A. Wassenden and J. C. Redmon have studied the salt effects on the reaction. The salts used were sulphates of potassium, magnesium, aluminium etc. Reaction between oxalic acid and halogens have been studied by A. Berthhoun and H. Belenot, Griffith and R. Kown, Chatterji and Vaishya, Bhagwat and Harwalkar and others and Dhar have followed the reaction between oxalic acid and iodine photochemically. Hydrogen peroxide has been used as an oxidant for oxalic acid by Hatcher, Hatcher and Holden, Walton and Graham etc. A Sobtelsky and A. Glaisher followed the oxidation of oxalic acid by quinquevalent vanadium in presence of mineral acids. J. R. Jonas and Waters confirmed the above
observations. Oxidation of lactic acid by vanadium was investigated by R. L. Yadav and W. V. Bhagwat\(^6\) and malonic acid by ceric sulphate by R. L. Yadav and W. V. Bhagwat\(^6\)

Benzilic acid by ceric sulphate by S. K. Mishra and R. K. Mehrotra\(^6\), malic acid by peroxydisulphate by K. Kumar and L. K. Saxena\(^6\), formic acid by Manganese sulphate by K. Aziz Beg and Firoz Ahmed\(^6\). Benson\(^6\) studied the oxidation of Ferric iron by chronic acid. Dhar\(^7\) and Viard\(^7\) studied the oxidation of phosphorous acid. Kinetics of oxidation of formic acid were studied by Dhar\(^7\), Mahajani and Bhattacharya\(^7\), Mahajani\(^7\), Dhar and Ley\(^7\) studied the oxidation of tartaric acid, lactic acid and maleic acid by chronic acid. Weisbriesser and Watanbe\(^7\) investigated the oxidation of isopropyl alcohol by chronic acid.

Oxidation of quinoline and alcohols by chronic acid have been studied photochemically. The oxidation of oxalic acid by Chromium trioxide or chronic acid have been studied by several workers, some of them are H. Vohl\(^7\), Jansen and L. T. Reicher\(^7\), M. R. Dhar\(^7\), Mukerjee and B. K. Bhattacharya\(^7\), C. Wagner\(^7\) and Snelthage\(^7\) and B. S. Rai\(^7\). N. R. Dhar studied this reaction both in dark and light. He observed that Mn\(^{++}\) markedly accelerated the reaction and when concentration of Manganese sulphate was increased the reaction was found to be independent of chronic acid concentration. In other words it becomes zero order with chronic acid. The temperature coefficient increases in presence of manganese sulphate. This supports the view that reactions of lower orders have higher temperature coefficient. Chow\(^7\) studied the reaction of halogen on oxalic acid.
In study of reaction between the ions the effects of electrostatic attraction or repulsion are obviously important. Various workers particularly Scatchard and Moelwyn Hughes have studied this aspect exhaustively. The first effective treatment of these reactions was provided by J. N. Bronsted and K. Sjerrum in their activity rate theory. If the ions of same sign react the rate constant increases with the ionic strength and if ions of opposite sign react, then the rate constant will decrease with increase in ionic strength. This is called primary kinetic salt effect. The reaction between Cr(H₂O)₆³⁺ and CN⁻ has been studied by C. Postmus and E.L. King, between Co(NH₃)₅Br⁺⁺ and OH⁻ by J. N. Bronsted and R. Livingstone, between Cl⁻ and Br⁻ by Foerster and P. Dolch, between CH₂-COO⁻ and sodium thiosulphate by A. Slaton and A.H. Kappan, between sodium bromoacetate and sodium thiosulphate by Kappan and Patwardhan, V.K. La Mer, C.T. Burries and E.J. Laidler, between sodium methoxide and sodium bromoacetate by George Senter and cod, and Kappan, between S₂O₅²⁻ and S₂O₃ by D.P. Ames and J.R. Willard, between azodicarbonate ion and hydrogen ion by King and Joseph, between persulphate ion and iodide ion by Kiss and Bruckner.

SCOPE OF WORK

The sodium salt of iodoacetic acid is thermodynamically feasible, however the reaction involving replacement of iodine atom of this salt by other substituents like thiosulphate ion, chlorine or methoxy ion can proceed at an observable rate under certain favourable
conditions.

The reactions of sodium salt of chloro or bromo-
acetic acid have been studied for various aspects. The
reaction between potassium salt of iodoacetic acid and
sodium thiosulphate was studied by H.J. Basker and W.H.
Van Nels102. In the literature, only the temperature
coefficient of the reaction between 35° C and 45°C is
available. However, a complete and clear picture of the
reaction under varying conditions such as ionic strength,
dielectric constants and salt effect is not readily
available.

It is, therefore, essential to understand the
factors governing the behaviour of reaction of sodium
iodoacetate towards substituents. Kinetics study of
reaction may provide the means for the quantitative
comparison of its reactions under varying conditions and
from the systematic kinetic studies, the relative importance
of many factors, which may influence reaction rates, can
be assessed. These considerations are specially relevant to
kinetic studies of systems such as the present one. The
kinetic behaviour of sodium salt of iodoacetic acid will
be representative of the behaviour of allied systems
since it is possible to vary at will nearly every factor
which can influence the reaction rate. Present work therfore
undertaken to study the effect of change in ionic concentration,
\( \text{pH} \), temperature, addition of electrolyte, and non electrolytes
to reaction mixture, and dielectric constant etc. on the
rate constant of the reaction and thereby to obtain a reasonable and plausible reaction mechanism. To achieve this object, the reaction was proposed to be studied under the following aspects:

(1) The order of reaction to be found out by various methods. The isolation method would be useful in obtaining the order of reaction with respect to each of the reactants. The order of reaction would furnish a clue to the fact whether in the rate-determining step, the reactants, first form, the activated complex and then split into products, or the reactants first split and then form products.

(2) Second aspect of the study would be to ascertain whether the reaction is homogeneous or heterogeneous. This aspect would be further useful in ascertaining whether the change in reaction rate is due to reactants only or due to change to surface area of the container. The reaction, if studied in dark and in light, could reveal whether the reaction is affected by the radiation of visible region. The study of reaction in medium of various pH would be useful to find out whether it is catalysed by hydrogen ions or by hydroxyl ions and whether it is dependent on their concentrations. The study of the reaction at different temperatures would give us a knowledge about the energy of activation, the entropy of activation, the frequency factor, and the study of change in rate constant with change in ionic concentration would help us in verification of the Debye-Huckel equation.
(3) Third aspect would be the study of reaction under the conditions that is whether neutral or inert electrolytes when added to the reaction mixture affects the reaction kinetics. This might lead us to find out the influence of the inert electrolytes on the order and rate of reaction, and also on the energy of activation of the reaction. This study would also be necessary to find out whether the different electrolytes exhibit the same influence. For this purpose, salts selected were chloride, sulphate and nitrate of sodium, potassium and ammonium, and magnesium sulphate, strontium chloride and barium nitrate, aluminium nitrate, aluminium sulphate, and lanthanum nitrate.

(4) Similar study could be done by adding different non-electrolytes to reaction mixture i.e., in the medium of different mixed solvents. This would tell us whether there is change in the order or rate of the reaction or energy of activation of the reaction because when non-electrolytes are added to the reaction mixture, the dielectric constant of the medium changes and the effect of change of rate constant with change in dielectric constant of medium would enable us to calculate the value of the parameter i.e., the distance between two reacting ions when they form activated complex.

(5) The study of the reaction of iodoacetate with ethoxy or methoxy ions when done in non-aqueous medium i.e., in ethanol or methanol, the value of \( \frac{dHk}{dJ\mu} \) could be
determined and compared with theoretical value. The values of energy and entropy of activation and frequency factor could then be calculated and the effect of addition of electrolyte on the rate of the reaction could be investigated.

(6) Lastly, attempts could be made to establish a correlation between salts of halogen substituted acids and sodium thiosulphate and finally a reasonable reaction mechanism could be evolved based upon the observations as detailed above.

**Methods of Measurements**

Chemicals and glass wares:

All chemicals used were either BDH Analytical reagents or E Merck, guaranteed reagents. Except where especially mentioned, Pyrex glass wares were used in experiments for storing the solutions of various salts or reaction mixtures. E. Miller's burettes and pipettes were used. All solutions were prepared in conductivity water. The solutions of various salts at different concentrations were prepared by dissolving exact quantities of salts. The conductivity water was prepared using Dalgastat ion exchanger and stored in Pyrex flasks. As the aqueous solution of iodine and thiosulphate change their strength on keeping for a long time, fresh solutions were prepared for each set of experiments from salt which had been twice crystallised from water below 60°C. This was done to remove sulphate which was slowly produced from solid thiosulphate on standing. The solution of sodium thiosulphate was
standardised against N/10 potassium dichromate solution and in this manner the sodium thiosulphate solution of required concentration was prepared. Iodine solution was standardised against this standard thiosulphate solution.

**Instruments:**

Electrically regulated thermostat was used. The temperature of the thermostat hardly varied by ± 0.1°C from the desired temperature.

For determination of pH Philip's pH meter was used. The glass saturated calomel electrodes were kept immersed in water bath maintained at 30°C in a thermostat. The reactants were mixed at 30°C in the usual manner and reaction mixture was transferred immediately to an empty beaker placed in a thermostat and then the electrodes were dipped and pH was measured.

**Preparation of iodoacetic acid:**

5 Merek Chloroacetic acid dried over phosphorous pentoxide now known to be P₂O₅ was dissolved in pure and dry acetone to make fairly concentrated solutions. 28 gms. of chloroacetic acid was dissolved in 20 ml acetone. 50 gms. of powdered potassium iodide was dissolved in 120 ml acetone. Both the solutions were stirred thoroughly for two hours and then mixed and kept for 25 hours at 30°C. The mixed solution was vacuum distilled and thus the solution was concentrated to 100 ml. To this solution 60 ml pure benzene was added, shaken and then filtered. The process was repeated and the
residue was washed with benzene each time. The filterate was vacuum distilled, iodoacetic acid thus prepared was dissolved in pure and dry ether and ether was removed by evaporation in vacuum. The yield was found to be 26 grams. Its melting point was determined and was found to be 82°C.

The sodium iodoacetate was prepared as follows. The prepared iodoacetic acid was dried over phosphorous pentoxide. It was dissolved in pure and dry ether so as to make a concentrated solution. To this a drop of phenolphthalein solution was added and then, an almost saturated solution of sodium ethoxide in absolute alcohol was added drop by drop, the mixture being well stirred until the liquid turned faint pink. Most of the sodium salt, as formed, appeared as precipitate. Next, the mixture was treated with a drop or two of acid solution so that the pink colour of solution just disappeared and then precipitate was filtered rapidly under a suction pump and washed with pure and dry ether. Considerable amount of salt thus obtained was purified by recrystallisation. (The salt was dissolved in absolute alcohol and to this was added dry ether. The salt, being less soluble in ether could be precipitated). It was preserved in a dish over fused calcium chloride in a desiccator. The purity of the salt was tested by estimation of iodine obtained from a definite amount of salt. Then 0.2060 gm. of salt was heated in a closed vessel, iodine was liberated and the entire amount of the liberated iodine was found to be deposited on the wall of vessel on cooling. So this potassium
solution was added for dissolving out the liberated iodine. The solution in the vessel was titrated against standard 7/10 hypo solution using starch as indicator. The titre value in this case was found to be 10.0 ml. which corresponded to 0.2080 g. of sodium iodide acetate salt.
INDEX TO REFERENCES .. CHAPTER - 1

1. Hinselwood, The Kinetics of Chemical Change, Oxford 1949 P. 1
3. Herschutkin, Z. Phys. Chem. 1. 629 (1887)
8. G. Scottard, Chem. Rev. 10, 229 (1932)
10. Kirchoff; Schweigert's, Journal 4, 108 (1812)
18. J. Cohen; Z. Physik. Chem. 21, 442 (1897)
19. Lamben; Med. K. Vatensk. Tidsskr. Inst. 2 (No. 3), 1, 1911
26. Schroeter & Miguchi, J. Am. Pharm. Assoc. 47. 426 (1958)
27. Krieele and Geriker, J. Am. Chem. Soc. 55, 2326 (1933)
30. Rivett, Z. Physik. Chem. 85, 113 (1913)
32. Friedman and Storer, J. Am. Chem. Soc. 61, 118, 1939
37. Haber, Naturwiss 19, 450 (1931)
40. Gomberg, Ber 33, 3150 (1900) J. Am. Chem. Soc. 22, 752 (1900)
43. Singhal, Journ. Indian. Chem. Soc. 27, 405 (1960)
45. King, J. Am. Chem. Soc. 49, 2697 (1927) 50, 2089 (1928)
47. Saxena and Singhal, J. Physik. Chem. 221, 178 (1959)
48. Senate Cabello, Annales. Real. Sociedad Española. 177 (1951)
49. Harcort, Phil. Trans. Roy. Soc. London. 156, 193 (1866)
50. Launer, J. Am. Chem. Soc. 54, 2597 (1932)
52. Taube, J. Am. Chem. Soc. 70, 1218, 1948
61. Walton and Graham, J. Am. Chem. Soc. 50, 1641 (1928)
64. R. L. Yadava and V. Bhatkawat, Jour. Indian Chem. Soc. 41, No. 1, 25 (1964)
65. R. L. Yadava and V. Bhatkawat, Jour. Indian Chem. Soc. 41, 5, 389 (1964)
69. Jenson, J. Phys. Chem. 7, 1, 356 (1903)
70. Dhar, Ann. Chim. (9) 11, 130 (1919)
71. Viard, Compt. rend. 124, 148 (1897)
74. Mahajani, Ph.D. Thesis, Saugor University (1952)
75. Dhar and Day, J. Electrochem. 32, 586 (1926)
76. Weisthemeier & Satanbe J. Chem. Phys. 17, 61 (1926)
77. H. Vohl., Liebig's. Ann. 53, 398 (1847)
80. Mukerjee and J. N. Bhattacharya, J. Hy. Chem. 32, 1824 (1928)
81. C. Wagner, Z. anorg. Chem. 152, 279 (1928)
82. Snethlage, Rec. Trav. Chim. 57, 1347 (1938)
85. Scatchard, Chem. Revs. 10, 229 (1932)
89. S. L. King, J. Phys. Chem., 59, 1216 (1955)
91. Poerster and Dolch, Z. Elektrochem., 23, 137 (1917)
94. Kappanna, J. Indian Chem. Soc., 6, 45 (1929)
95. V. K. La For, J. Am. Chem. Soc., 51, 334 (1929)