CHAPTER I

GENERAL INTRODUCTION

AND

SCOPE OF WORK.
Chemical kinetics is the part of physical chemistry dealing with rates of chemical reactions. The subject includes both the experimental study of reaction rates and the development of theories to explain experimental results, and to predict the outcome of experiments which have not yet been performed(1). Thus, the aim of chemical kinetics is to predict the rates of chemical reactions and to understand the mechanism of reaction (2).

The study of the different properties of the elements and their compounds, in particular of the structure of atoms and molecules, gives an auxiliary material to chemistry which helps in the solution of its main problem, that of rational direction of chemical change (3).

A chemical reaction mechanism may be thought of as a motion picture of all the atoms (and their electrons) involved in the reaction, beginning before the reactants approach each other, picturing their path during the reaction, and ending after the products have been formed(4).

The creation of a theory of chemical kinetics was one of the chief problems of physical chemistry. The classification of chemical reactions from the kinetic point of view implies the existence of general kinetic laws determining the dynamical behaviour of matter, laws which overshadow the individual properties of different reactions which are generally applicable, if not for all, then at least for a wide class of reactions (5).
The statical properties of substances alone could not develop chemical kinetics. For specifying the kinetics of chemical processes there was imperative need of new dynamical constants.

It will not be out of place to note here that the development of the concept of chemical equilibrium from the kinetic point of view was of some help in the study of the kinetics of chemical reactions. In 1850 Wilhelmy (6) in the course of a study of the inversion of sucrose in presence of acids, showed that the rate of reaction at any instant was proportional to the amount of sucrose remaining unchanged at that instant. The effect of mass on chemical reaction was also brought out clearly by Berthelot and Gilles (1862-63) who studied the reversible formation of ester from ethyl alcohol and acetic acid. They found that the reaction did not go to completion, but the proportion of acid converted into ester increased as the amount of alcohol was increased (7).

In 1850, Williamson concluded from his studies in the esterification of alcohol by concentrated sulphuric acid that in spite of its stationary appearance chemical equilibrium was really dynamic (8).

Thus the problem of chemical kinetics exercised the mind of many chemists. The main object before them was the discovery of dynamical constants to understand the dynamical progress.
Van't Hoff's book "Etudes de dynamique chimique" was published in 1884. The fundamental normal type of reaction kinetics was treated by him in the first part of his book. The laws of mono-, bi-, and multimolecular reactions were studied by him and he also gave them simple kinetical interpretation.

Van't Hoff's (9) studies showed the dependence of the rate constant of a reaction on the absolute temperature of the system. According to him the logarithm of the rate constant was proportional to the reciprocal of the absolute temperature.

The same idea was put forward by Arrhenius. The relationship between the rate constant $K$ and the energy of activation, $\Delta E$ at the absolute temperature, $T$, according to him, was:

$$\log K = -\frac{\Delta E}{RT}$$

$A$ being a constant.

Arrhenius interpreted this equation by suggesting that there existed an equilibrium between normal molecules and what he called "active molecules" and that only the active molecules underwent chemical change.

Van't Hoff laid the foundation of the theory of chemical kinetics. The modern development of the theory (10) of reaction rates can be said to have come from Arrhenius's suggestion about the existence of the temperature dependent equilibrium between the inert and active molecules of reactants.
Van't Hoff's laws were found valid in the case of simple reactions, the number of which was small. Van't Hoff himself realised this. The anomalous behaviour of a reaction was, according to him, due to several "action perturbatrice" (disturbing factors) like autocatalysis due to end products, secondary reactions in the system, catalytic action of the walls. He dealt with such reaction in the second and third part of his book referred to above.

Various theories have been proposed to understand mechanism of reactions. Two of them are (1) collision theory based on the kinetic theory of gases and (2) transition state theory (i.e., activated complex theory).

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

According to transition state theory the two reactants say, AB & C first form a transition complex A .... B .... C, which then decomposes into A & BC.
\[ AB + C = A \quad B \quad C = A + BC \]

(Reactants) (Transition complex) (Products)

The basic idea is that \( C \) comes so close to \( B \) that the latter becomes undecided as to which atom it now belongs to. This state of indecision as to \( B \) being simultaneously attached both to \( A \), though somewhat loosely than before, and \( C \) is the transition state. This is called the "activated complex". The energy necessary to push \( C \) to approach \( B \) to form this activated complex is the energy of activation. This transition theory helps in calculations of the quantities like enthalpy, entropy and free energy of activation etc. These quantities are extremely useful in mechanism studies. They often indicate the order of reactions. They also give hints on how the transition state is reached.

The idea that the complexities introduced in reactions by disturbing factors could be eliminated in principle at least, made it rather natural for most of the workers in the field of chemical kinetics, to investigate such reactions only as showed normal behaviour. They did not have interest in Van't Hoff's "action perturbatrice". Of course, Bodenstein (11) and Langmuir (12) were exceptions.

Pólya (13) and other expounded the meaning of the energy of activation.

No doubt, much work was done up to about 1930. But it
was mostly connected with improvement and theoretical interpretation of the laws of Van't Hoff and Arrhenius. The introduction of "probability factor" (14) in the Arrhenius equation is an illustration of this. These laws are based on the collision theory of the rate of chemical reactions. This theory is quite satisfactory in explaining the kinetics of simple chemical reactions the number of which is small.

Bodenstein (15), in 1913, was the first to introduce chain mechanism for the reaction between hydrogen and chlorine forming hydrochloric acid. Christiansen and Kramers (16), in 1923, attempted to apply the theory of chain mechanism to thermo reactions.

A paper by Christiansen (17) dealing with the negative catalysis in a series of oxidation processes marked the next step in the development of the chain theory. Further work in this direction was due to Backstrom (18), Bodenstein (19), Haber (20) and others. Hinshelwood and others (21), and Semenoff (22) and others applied this theory to the study of reactions leading to inflammation and explosion.

The discovery of tri-phenyl methyl free radical by Gomberg (23) initiated the study of a most important type of compound of significance in all branches of chemistry (24). One of the several classes of reactions is that which involves
free radicals (25). Free atom or free radical chains (26) are preferred in photochemical and other reactions. The chain theory and free radical concept have done much in explaining the kinetics of several reaction of different types.

The calculations of rates of chemical reactions without a knowledge of the experimentally determined energy of activation, but from such fundamentals as configuration of molecules, dimensions of atoms and molecules, interatomic and intermolecular forces were not possible until the transition state theory was postulated in the fourth decade of the present century (27). In many respects this theory is simpler and more satisfactory than the kinetic theory (28). It was first used in 1932 by Pelzer and Wigner (29) in their calculation of the rate of reaction between hydrogen atoms and molecules which is involved in the thermal homogeneous ortho-para conversion reaction. Eyring and coworkers (30) developed it in general form. The transition state theory is superior to the collision theory. It can be applied where the latter fails.

According to the law of mass action the rate at which a substance reacts is proportional to its active mass. But several cases have been reported where not only the active masses of reactants determined the rate, but the nature of the solvents (containing the reactants) also has a significant role on the rate of the reaction. As an example (31) it may be noted that
the rate constant for the reaction between tri-ethylamine and ethyl iodide in hexane is 0.00018 at 100°C while the corresponding value for the same reactants in benzyl alcohol is 0.133 at the same temperature. It is well known that nitrogen pentoxide decomposes at almost the same rate in several solvents of different dielectric constants. The polar nature of a solvent may generally speaking have an appreciable effect on the reaction rate.

It has already been mentioned that the rate of reaction depends on active masses of the reactants, nature of solvent, and temperature. But these are not the only factors which determine the rate.

There is a stoichiometric equation corresponding with every reaction. But it is well known that there exist substances, having no place in the stoichiometric equation, which on being added to the system, produce a marked effect on the reaction rate. Such substances are classed as catalysts. If the catalyst and the reactants form one phase, the phenomenon is homogeneous catalysis. When the catalyst and the reactants form different phases, heterogeneous catalysis is said to occur.

It is possible to apply Hinshelwood's criteria to ascertain whether one is dealing with homogeneous or heterogeneous catalysis. The theoretical treatment of homogeneous catalysis is
different from that of heterogeneous type. But chemical kinetics has direct application in both of them. Bell's (32) words that "A substance is said to be catalyst for a reaction in homogeneous system when its concentration occurs in the velocity expression to a higher power than it does in the stoichiometric equation" bears out the point in the case of homogeneous catalysis. Absorption and desorption are rate processes and hence the importance of chemical kinetics in heterogeneous catalysis is evinced.

Some of the reactions catalysed by acids and bases were studied by Buria (33). Sodium hydroxide was used by Hjelt (34) in the hydrolysis of ethyl esters of malonic, succinic and several other acids.

Sloubtsky (35) studied the ammonolysis of dimethyl malonate. Datt, Dhar and Bhattacharya (36) studied the hydrolysis of methyl acetate in presence of picric and oxalic acids.

Trevor (37), Cohen (38) and other workers investigated the inversion of sucrose in presence of acids.

In 1901, Ostwald (39) predicted that catalysis would have to be universally recognised in theoretical chemistry. This did happen, consequently the study of catalysis was put on a new footing.

Sabatier (40) and Ipatieff (41) opened up a field of
chemistry and engineering which had enormous industrial consequences.

The value of Haber's work (42) is extraordinary. Other contributors are Langmuir (43), Taylor (44) in heterogeneous catalysis, Bronsted (45), Lowery (46), Dawson (47) etc., in development of acid-base catalysis. The reaction which has been extensively studied from point of view of effects of acids is the mutarotation of dextrose. Those who took interest in this direction, are Lunden (48), Moran (49) and Lewis, Harned and Howkins (50), Shah and Amis (51), Sapozhnikov & Perchenking (52), Pearce & Thomas (53).

Extensive work on catalysis both homogeneous and heterogeneous has been done in India. Prominent work in catalysis in oxidation-reduction reactions is due to Dhar (54).

A number of oxidation-reduction reactions are sensitive to hydrogen ions. As the author is interested in the reaction between malonic acid and chromic acid which involves oxidation-reduction, a reference to this will be made later.

Salts are known to affect the rates of several reactions. Much work has been reported about the effect of salts on reaction rates. However, it is possible to refer to some cases of outstanding work only.

Arrhenius (55) used normal salts in the study of the
inversion of sugar. Ehodan Van Szyskowski (56), appears to have introduced the term neutral salt effect. The study of salt effect is usually, associated with the study of effect of acids. Examples of such cases are hydrolysis of esters, muta-rotation of glucose etc. Intermolecular exchange of aceto-chloro anilide to p-chloro acetaldehyde was studied by Rivett (57) in presence of several chlorides and hydrochloric acid.

The effect of natural salts on the acid dye-bath was reported by Henz and Barracough (58). Loeb (59) observed the effect of neutral salts on the osmotic pressure and other properties of gelatin. A variation on the rate of hydrolysis of copper sulphate by salts was referred by Friedman and Stoker (60). The rate of solution of marble (61) in acetic acid was increased in the presence of different chlorides. Salts are known to influence the optical rotation of gelatin (62) and the rotary power of camphor sulphonate (63) and l-asparagine (64).

Recently isotopic labelling has been introduced in the field of reaction mechanisms and reaction kinetics. An isotopic substitution may give useful information about the mechanism of the reaction. The radio active measurement of acetic catalysed reactions in water and in deuterium oxide are useful in the study of the mechanism of acid catalysis (65).

Reactions involving oxidation and reduction are also known to be sensitive to the presence of neutral salts in the
system. Salt effects on such reactions will be dealt with later.

A brief survey of the progress of chemical kinetics has been made so far.

The author is interested in the reaction between malonic acid and chromic acid. This reaction involves oxidation of malonic acid and reduction of chromic acid. In the following pages a brief review of the properties of malonic acid and chromic acid is given.

Malonic acid is the second member of the aliphatic dicarboxylic acid series. Its primary dissociation constant \((66)\) is \(1.71 \times 10^{-3}\) at \(25^\circ C\) and secondary is \(2.0 \times 10^{-6}\) at the same temperature. It is highly soluble in water. There is no evidence of complex formation between alkaline metals and malonic acid. Malonates of alkali metals are also soluble in water.

Oxidation of malonic acid has been extensively studied by many oxidising agents, such as vanadium \(V\), cerium \(IV\), potassium permanganate, chromic acid, periodate and vanadium oxide.

Oxidation of malonic acid by quinquevalent vanadium was studied by various workers such as Kemp and Waters \((67)\). They have studied the accelerating effect of manganous ions on rate of the reaction.
Yadav and Bhagwat (68) investigated the oxidation of malonic acid by ceric ions.

The reaction between malonic acid and permanganate in alkaline medium was studied by Bengor and Broocock and Randall (69). The oxidation of malonic acid by periodate was reported by Huebner, Ames and Bubl (70).

Chromic acid is known to be an important oxidant for a long time. Westheimer (71) undertook systematic investigation of mechanisms of reactions involving hexavalent chromium as the oxidant.

The known oxidation states of chromium are from 2 to 6. However, Cr VI is normally reduced to Cr III in a redox reaction, as the intermediates Cr IV & Cr V species are unstable under ordinary condition, and as Cr II is an excellent reducing agent.

Further chromic acid is a fairly strong acid. In dilute solutions, it exists largely as HCr\text{O}_4^- (72). In more concentrated solutions, dehydration occurs extensively:

$$2\text{HCrO}_4^- \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

Some investigations on oxidation of organic, and inorganic substances are noted below:

Benson (73) studied the kinetics of oxidation of ferrous
ions by chromic acid.

The reaction between hydrogen peroxide and chromic acid was studied by Bach (74) and Riesenfeld (75). Oxidation of phosphorus acid was studied by Viard (76) and Dhar (77).

Other inorganic substances whose oxidation by chromic acid has been investigated included iodide ion (78), arsenious acid (79), hydriodic acid (80), hydrobromic acid (81) etc.

As regards the oxidation of organic substances by chromic acid, a perusal of the published work shows that various types of them can be oxidised under suitable conditions. The reaction between oxalic acid and chromic acid in aqueous solution were undertaken by Jableynski (82) and Dhar (83).

Dhar & Dey (84) studied the oxidation of tartaric, lactic and maleic acid by chromic acid. Sembert and Carstens (85) reported oxidation of hydrazine by chromic acid.

Mahajani and Bhattacharya (86,87) studied the oxidation of formic acid by chromic acid.

Rai and Mahajani (88) investigated the oxidation of oxalic acid by chromic acid.

Other kinetic studies include oxidation of ortho-substituted cis and trans cyclic alcohols (89), hydroxy and methoxy benzaldehydes (90), glycols, substituted alcohols (91), secondary
alcohols (92, 93), methyl cyclohexane etc.

Studies on the photo-oxidation of quinone (94)\textsuperscript{24},
alcohols (95) by chromic acid have also been published.

It is evident from published work that hexavalent
chromium is effective as an oxidant in acidic medium. Its oxidising
power decreases appreciably with the increase in the pH values
of reaction mixtures.

Having reviewed the occurrence of acid effects and
salt effects in reactions of various types, the reduction
reactions of malonic acid and the oxidation reactions of chromic
acid, it is now appropriate to deal with the reaction between
malonic acid and chromic acid which is the subject of the author's
investigation.

**MALONIC ACID - CHROMIC ACID - REACTION**

Oxidation of malonic acid by chromic acid has been
studied by Snethlage (96).

In the chemical literature there are a few references
to the oxidation of malonic acid by chromic acid. The reaction
is known to be very very slow at ordinary temperature. Snethlage
investigated the reaction in presence of sulphuric acid at high
temperature.

The velocity of oxidation of malonic acid by chromic acid
in 10 - 96.55 % sulphuric acid was measured between 273 and 353° K. The rate increases with the sulphuric acid concentration to a maximum between 70 and 96 % (293° K). No strict proportionality between the acidity of the medium and the rate of oxidation could be observed; this is in contrast to observations on formic acid. The temperature coefficient of the reaction is reported to depend on both the temperature of the system and the concentration of sulphuric acid present in it.

**SCOPE OF WORK**

The reported investigations on the reaction between malonic acid and chromic acid appear to imply that it is homogeneous. It is well known that some of the apparently homogeneous reactions i.e., the formation of quaternary ammonium salts, (97), the interaction of acetic anhydride and ethyl alcohol, the interaction of methyl alcohol and acetic acid (98), take place predominantly on the wall of the vessel.

It has been pointed out above that the reaction between malonic acid and chromic acid is catalysed by sulphuric acid. The rates of reactions of different types are affected by acids and that the nature of an acid has some thing to do with its role in varying the rate of reactions. Sulphuric acid is the only acid whose use in this reaction has been reported by Snethlage. The author has thought of studying the effect of other acids in this
reaction in order to determine whether their catalytic effect in these cases varies from acid to acid, and if so, whether it depends on the nature of the acid.

The selection of acids for this purpose requires that there is no interaction of the added acid with either malonic acid or chromic acid. After preliminary experiments the author has found that up to certain concentration limits acetic, phosphoric, hydrochloric and sulphuric acids do not act either with malonic acid or chromic acid.

Acetic acid is a weak, phosphoric acid moderately strong and hydrochloric and sulphuric acid strong. A comparative study of their effects on the rate of the reaction would be expected to bring out whether their effect on governing the rate of the reaction depends (as in the case of hydrolysis of esters, inversion of sugar, etc.) on their nature.

Salts are known to affect the rates of reaction catalysed by acids, with a view to determining the salt effects on the acid catalysed malonic acid - chromic acid, the author has undertaken this investigation. The effects of the chlorides of lithium, sodium and potassium on the hydrochloric acid catalysed reaction and those of the sulphates of lithium, sodium and potassium on the sulphuric acid catalysed reaction have been planned for investigation.

Manganese sulphate is known to exhibit interesting effect
(99) on same reactions. In view of this, the author has investigated its effect on the reaction between malonic acid and chromic acid, both in the presence and absence of few catalysing acids.

The pH value of the reaction medium is the true measure of its hydrogen ion concentration. In the presence of any added acid in the medium, the rate of the reaction is expected to depend on its pH value and not on the total acid concentration. In view of this, pH values of reaction mixtures, immediately after the start of the reaction have been measured.

The oxidation potential of any oxidising - reducing system is a measure of its capacity to bring about oxidation. The greater the oxidation potential the greater is the power to oxidise. It follows, therefore, that the rate of oxidation should increase with the oxidation potential of the system.

In the reaction between malonic acid and chromic acid, acids enhance the rate. An increase in the oxidation potential of the system in presence of acids is expected.

The author has planned to measure the oxidation potential of the system in the presence of different acids, salts and mixtures of acids and salts to see if any correspondence exists between the oxidation potential of the system and the rate of the reaction.
Measurement of electrical conductivities of the reactants, and of the reaction mixture just after the start of the reaction have been made in order to see whether formation of complex ions is indicated.

Potassium dichromate and potassium chromate oxidise malonic acid. The rates of oxidation of malonic acid by them at the same concentration as that of chromic acid have been planned for measurement to know how the oxidation by potassium dichromate solution and by potassium chromate solution compares with that by chromic acid.

The experimental details are given in the next chapter.
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