CHAPTER I

GENERAL INTRODUCTION
Change is the law of nature. Bacon\(^1\) wrote "It is sufficiently clear that all things are changed and nothing really perishes, and the sum of matter remains absolutely the same". It is well known that right from the time man was gifted with the thinking faculty, he directed it towards the understanding of various natural phenomena. Hinshelwood's\(^2\) statement "That everything changes is an unescapable fact which from time immemorial has moved poets, excercised metaphysicians and excited the curiosity of natural philosophers" stresses this point in a very apt manner.

In the course of evolution man acquired not only the capacity to think and understand but the one to experiment also. The growth of science is a sequel to these two capacities. It is true that it required a very long time for people to acquire the scientific outlook. All kinds of difficulties were created in the path of the development of science. In spite of this it made spectacular progress. Franklin's\(^3\) remark "The rapid progress true science now makes occasions my regretting sometimes that I was born so soon. It is impossible to imagine the height to which may be carried, in a thousand years, the power of man over matter. O that moral science were in as
fair a way of improvement that men would cease to be wolves to one another, and that human beings would at length learn what now they improperly call humanity is very significant in connection with the tremendous progress achieved by science. This remark acquires a special value in the present days of nuclear weapons space-flight.

The limitation of the human mind makes it impossible for any one man to comprehend the accumulated scientific knowledge in its entirety. There is therefore the necessity for dividing science into several branches for the purpose of study and investigation. Science has thus been divided into three principal classes -- abstract, physical and natural. Chemistry is one of the physical sciences.

Chemical change constitutes the main subject of chemistry. Chemical elements and compounds have their own characteristic properties. The study of the properties of elements and their compounds, and of the structure of atoms and molecules supplies auxiliary material which is helpful to chemistry in the solution of its main problem which is the rational direction of chemical change.\(^4\)

Chemical kinetics deals with the rates of chemical
changes. This is of great importance in industry and reaction mechanism.

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, and which are generally applicable, if not for all, then at least for a wide class of reactions. 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 for the study of the kinetics of chemical reactions. In 1850, Williamson concluded from his studies in the etherification of alcohol by concentrated sulphuric acid that in spite of its stationary appearance, chemical equilibrium was really dynamic. This was, later, corroborated by the derivation of the law of mass action from the postulates of the kinetic theory of gases. The history of the law of mass action describes
experiments performed over 100 years ago, dealing with the effect of mass on the velocity of chemical reactions. Wilhelmy's experiment on the rate of inversion of sucrose in the presence of acids is one of them.

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 process.

Van't Hoff's book "Etudes de dynamique chimique" was published in 1884. The fundamental normal type of the reaction kinetics was treated by him in the first part of this book. The laws of mono-, bi-, and multi molecular reactions were stated by him and he also gave them simple kinetical interpretation.

In connection with the effect of temperature on the equilibrium constant \( K \) of a reversible reaction, Van't Hoff deduced, on thermodynamical grounds a relation which in the modern notation is

\[
\frac{d \log k}{dT} = \frac{\Delta E}{R T^2}
\]

It is now simply known as Van't Hoff's equation. Since the equilibrium constants are the ratios of the velocity constants of the forward, and backward reactions,
they are temperature dependent. It was left to Arrhenius to disclose the kinetic meaning of Van't Hoff's equation given above.

According to Arrhenius all molecules of the reactants do not take part in the chemical change. Those which have an energy equal to or greater than a certain minimum value $\Delta E$, undergo chemical change; others do not. The Maxwell's law gives the number of molecules with an energy greater than $\Delta E$ as a fraction $e^{-\Delta E/RT}$ of the total number of molecules. The variation of the velocity constant with temperature is thus expressed as:

$$k = A e^{-\Delta E/RT}$$

and it is called as the Arrhenius law. The quantity $\Delta E$ is not a universal constant. It varies from reaction to reaction. Known as the energy of activation it is a very important dynamic constant which is a characteristic property of the reacting substances in a particular reaction.

Van't Hoff's work in the field of chemical kinetics is that of a genius. He laid the foundation of the theory of chemical kinetics. The modern development of the theory of reaction rates can be said to have some 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 realized this. The anomalous behaviour of a reaction was, according to him, due to several "action perturbatrice" (disturbing factors) like auto-catalysis due to end products, secondary reactions in the system, catalytic action of the walls. He dealt with such reactions in the second and third part of his book referred to above.

The idea that the complexities introduced in reactions by the 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 and Langmuir were exceptions.

Hinshelwood showed that the absolute value of the velocity coefficient could be calculated from the experimentally determined value of the energy of activation and the application of the collision theory. The elucidation of the mechanism of mono- and bi molecular reactions is due to him.
Polanyi\textsuperscript{14} and others 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 the probability factor\textsuperscript{15} 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.

The inadequacy of the simple laws to explain the behaviour of a large number of reactions posed a new problem and efforts had to be made to solve it.

Bodenstein\textsuperscript{11}, in 1913, was the first to moot the idea of chain reactions. His studies in connection with the formation of hydrochloric acid from the elements led him to think of the chain mechanism of the reaction. It was also implicit in the work of Nernst\textsuperscript{16}. The first attempt to apply the concept of chains to thermo reactions was due to Christiansen and Kramers\textsuperscript{17}. This they did, in 1923, while trying to clear up the difficulties in the kinetic investigation of the decomposition of nitrogen pentoxide. Their work, although interesting, did not draw
much attention.

A paper by Christiansen\textsuperscript{18} dealing with 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\textsuperscript{19}, Bodenstein\textsuperscript{20}, Haber\textsuperscript{21} and others. Hinshelwood and others\textsuperscript{22} and Semenoff\textsuperscript{23} and others applied this theory to the study of reactions leading to inflammation and explosion.

The discovery of triphenyl-methyl free radical by Gomberg\textsuperscript{24} initiated the study of a most important type of compound of significance in all branches of chemistry.\textsuperscript{25} One of the several classes of reactions is that which involves free radicals.\textsuperscript{26} Free atom or free radical chains\textsuperscript{27} are preferred in photochemical and other reactions. The chain theory and free radical concept have done much in explaining the kinetics of several reactions of different types.

The calculations of the 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, inter atomic and inter molecular forces was not possible until the
transition state theory was postulated in the fourth decade of the present century. In many respects this theory is simpler and more satisfactory than the kinetic theory. It was first used in 1932 by Pelzer and Wigner 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 co-workers developed it in general form.

The transition state theory is superior to the collision theory. It can be applied where the latter fails. However, when both the theories can be applied to the same situation, they agree as far as the order of magnitude is concerned, e.g., the case of hydrogen - iodine reaction.

The rate of a chemical reaction can be affected by a number of factors. Concentrations of the reactants, temperature, absorption of radiation, nature of the medium, and foreign substances are some of them. Chemical kinetics can be applied to the study of effects produced not only by the first two factors but by others also.

It is definitely known that the effect of foreign substances on the rate of reactions has been known even in the alchemy era. Several cases were known in the 18th century e.g., the manufacture of sulphuric acid by the chamber process,
the saccharification of starch by acids, etc. As a result of his study of such phenomena, Berzelius\textsuperscript{34}, in 1836, introduced the term catalysis to coordinate these observations of chemical changes of diverse character. In 1901, Ostwald\textsuperscript{35} predicted that catalysis would have to be universally recognised in theoretical chemistry. This did happen.

The field of catalysis is very wide. It covers phenomena of inhibition, promotion, induced reactions, salt effects, medium effects.

The theoretical treatment of homogeneous catalysis is different from that of heterogeneous type. But chemical kinetics has direct application in both of them. Hall's\textsuperscript{36} words that "A substance is said to be catalyst for a reaction in a homogeneous system when its concentration occurs in the velocity expression to a higher power than it does in the stoichiometric equation." bears out the above 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.

Important work was done in catalysis in the last century. It is difficult to comprehend a fraction of the work in this field in the present century. In this brief review very outstanding work alone can be mentioned. Ostwald\textsuperscript{35} gave a
new definition of catalysis. The works of Sabatier\textsuperscript{37} and Ipatieff\textsuperscript{38} opened up a field of chemistry and engineering which had enormous industrial consequences. The value of Haber's\textsuperscript{39} work can never be exaggerated. It will ever be remembered. The contributions of Langmuir\textsuperscript{12} and Taylor\textsuperscript{40} in heterogeneous catalysis are fundamental. Bronsted\textsuperscript{41}, Lowry\textsuperscript{42}, Dawson\textsuperscript{43}, etc., contributed much in the development of acid-base catalysis. India's notable contribution in the field of catalysis is mostly due to Dhar.\textsuperscript{44}

There is no doubt that chemical kinetics provides the most general method of determining the mechanism of chemical reactions. Chemical kinetics with its dynamic viewpoint may be regarded as a more fundamental science than thermodynamics with its static viewpoint. However, each of the two schools of thought is important in its own way. Chemists\textsuperscript{45} find them naturally helpful and supplementary.

Before concluding this general introduction, it is worthwhile to mention here that the author has studied certain aspects of the reaction between formic acid and chromic acid in aqueous solution, following mostly the method of chemical kinetics. The kinetics of the reaction were first investigated by Dhar\textsuperscript{44(11)}. The reaction is homogeneous and its rate is affected by acids and salts. Details of the scope of study are given in the next chapter.
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