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INTRODUCTION

CHEMICAL KINETICS

In general, the word “kinetics” is used in physical and life sciences to represent the dependence of something on time. Adjective “kinetic” originates from Greek “kinetikos” which means “moving”¹.

Chemical kinetics is a branch of science which deals with study of rates of chemical reaction, study of various factors affecting the rate and the study of mechanism of chemical processes. Its two branches i.e. macroscopic and microscopic kinetics are well defined. Macroscopic kinetics is related with the behaviour of very large group of molecules in thermal equilibrium while microscopic kinetics is related to the reacting molecules which are in well defined states².

Chemical kinetics has been widely used in many branches of science. In biology it is used in physiological processes, bacterial growth while in chemical engineering it is used in reactor designing.

In electrochemistry, geology, physics and psychology, kinetics has been used for electrode processes, flow processes, viscosity, diffusion, nuclear processes and subjective to time, memory respectively.

Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions or elementary steps. Elementary reactions usually involve either a single reactive collision between two molecules, which is referred as a bimolecular step, or dissociation / isomerisation of a single reactant molecule, referred as a unimolecular step.

Very rarely, under conditions of extremely high pressure, a termolecular step may occur, which involves simultaneous collision of three reactant molecules. Reactions that are written as a single reaction equation in actual fact consist of a series of elementary steps.

The time scale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron

transfer processes involved in many biological systems or the combustion reactions occurring in flames including neutralization reactions.

Thus a study into the kinetics of a chemical reaction is usually carried out, for the:

1. Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the reaction mechanism and in the,
2. Determination of the absolute rate of the reaction and/or its individual elementary steps.

Rate Law

In chemical kinetics rate law is an important expression. A rate law is a mathematical relation finds how fast the reaction proceeds and how the reaction rate depends on the concentrations of the chemical species involved. A rate law is an equation of the form,

$$-\frac{dx}{dt} = k[A]^x[B]^y[E]^z$$

where x, y, z , are small whole numbers or simple fractions and k is called the "rate constant." The sum of $x + y + z + \dots$ is called the "order" of the reaction³.

The rate law may contain substances which are not in the balanced reaction and may not contain some things that are in the balanced equation even on the reactant side.

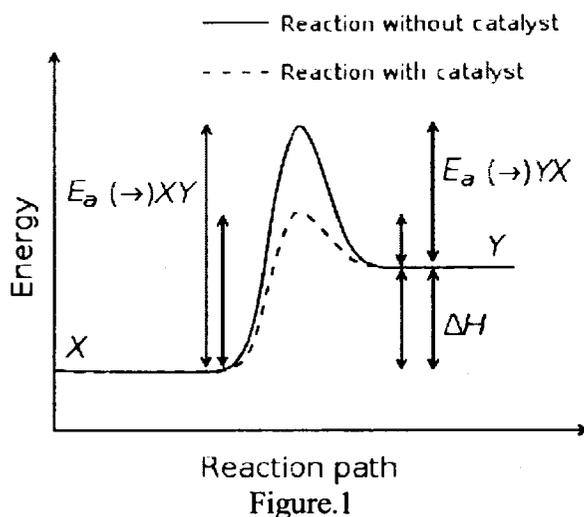
Dependence of rate on Temperature

Temperature has important role in chemical kinetics. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react is significantly higher in terms of the Maxwell-Boltzmann distribution of molecular energies.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower.

The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates.

A reaction's kinetics can also be studied with a temperature jump approach. This involves using a sharp rise in temperature and observing the relaxation time of the return to equilibrium.



It has been suggested that the presence of the catalyst opens a different reaction pathway with a lower activation energy (figure.1) in which the final result and the overall thermodynamics remain the same⁵.

The rate of reaction increases with raising temperature. Arrhenius equation gives the quantitative relationship between dependence of rate of reaction on temperature. It is given by,

$$k = Ae^{-E_a/RT}$$

Theories of reaction rates

In order to explain the mechanism of reaction various theories have been proposed. Among them the collision theory and activated complex theory have their own importance. The basic requirement for a reaction to occur is that the reacting species must collide with one another. This forms the basis of collision theory⁶ for reaction rates.

The number of collisions are defined in terms of collision frequency (Z). It has been suggested that the value of collision frequency is very high of the order of 10^{25} to 10^{28} .

The collisions that actually produce the product are effective collisions. These effective collisions, which bring chemical change, are few in comparison to the total number of collisions.

Effective molecules possess the, minimum energy i.e Threshold energy.

It is the minimum relative kinetic energy .The fraction of successful collision is equal to $e^{-E_a/RT}$ called Boltzmann factor.

With the threshold energy the molecules must be properly oriented in space for a collision to be successful. With these two factors i.e. collision frequency ZAB and the orientation factor (Steric factor) P, the k from collision theory may be given by,

$$k = PZ AB.e^{-E_a/RT} \text{ and it can be compare with Arrhenius equation i.e.}$$

$$k = Ae^{-E_a/RT}$$

The pre-exponential form in Arrhenius equation is, $A = PZAB$.

The excess energy (Over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy (E_a),

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

In the equation E_a depends upon the nature of chemical bond undergoing rupture and it is independent of enthalpies of reactant and products.

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules.

The reaction with zero activation energy means fraction of effective collision (f) will be very large and the reaction will be very fast reaction (Instantaneous reaction), while reaction with

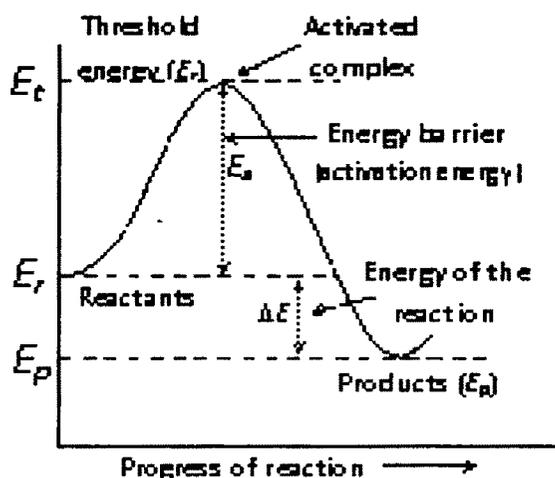


Figure-2

low activation energies i.e. fraction of effective collision (f) will be large, these will be fast reactions. The reaction with high activation energies i.e. fraction of effective collision (f) will

be small and the reaction will be slow reaction. According to the concept of activation energy, the reactants do not change directly into the products. At this state, the molecules must have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as activation energy barrier.

As per the transition state the activated complex is supposed to be in equilibrium with the reactant molecules and the rate is proportional to concentration of transition state.

Rate = Constant \times Transition state

The activation energy for the forward reaction, (E_a^f) and the activation energy for the reverse reaction (E_a^r) are related to the enthalpy (ΔH) of the reaction by the equation $\Delta H = E_a^f - E_a^r$.

(a) For endothermic reactions, $\Delta H > 0$, so that $E_a^r < E_a^f$

(b) For exothermic reaction, $\Delta H < 0$, so that $E_a^r < E_a^f$.

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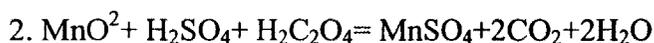
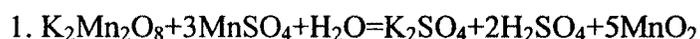
CHAPTER-I-B

LITERATURE REVIEW

Brief History and Philosophy of Chemical Kinetics

It was the German Chemist Ludwig Ferdinand Wilhelmy who introduced the chemical kinetics while studying the rate of inversion of sucrose¹. He had interpreted the rate of reaction with help of differential equation and had reported an empirical equation for temperature dependence of rate. Wenzel² was another one who has noted that rate of reaction changes linearly with the change of acid concentrations. Berthelot and his coworkers³ had observed that the rate of combination of ethanol and acetic acid was proportional to product of the reactant concentration.

The reaction between potassium permanganate and oxalic acid was first time studied by Harcourt⁴. Esson⁵ had analysed Harcourt's results with the help of integrated differential equations. Harcourt and co-workers⁶⁻⁸ had also studied the laws of connection between the conditions of a chemical change and its amount, and the variation of the rate of a chemical change with temperature. In the first part of their studies they searched chemical processes those are suitable for kinetics measurements. Harcourt found an initial valid system of the oxidation of oxalic acid with potassium permanganate. He supposed a two step mechanism for first time for this valid reaction as;



King⁹ has experiments with time. The development of the branch was well covered by King & Laidler^{10,11}. Ostwald¹²⁻¹³ studied the verification of the Law of Mass Action on different salts hydrolysis reactions. He later rediscovered also the work of Wilhelmy on the inversion of sugar supposing erroneously that the acids do not react directly but act as accelerator.

A careful survey of the literature reveals that the kinetics and mechanism of oxidation of several organic and inorganic compounds both under catalysed and uncatalysed conditions has been the field of interest for many workers.

Kinetics of glycine oxidation by N-bromophthalimide in the presence of sodium dodecyl sulfate was studied by Joshi et al¹⁴. Role of cetyltrimethylammonium bromide (cationic surfactant) on the tryptophan–MnO₄⁻ reaction was studied by Malik and co-workers¹⁵. Water-soluble colloidal manganese dioxide as an oxidant for L-tyrosine in the absence and presence of non-ionic surfactant TX-100 was studied by Altaf et al¹⁶.

Oxidation of L-Phenylalanine and L-Arginine by Manganese (VII) in concentrated sulfuric acid medium were studied by Iloukhani et al¹⁷ and Moghadasi and coworkers¹⁸. The kinetics of oxidation of amino acids has been studied with many oxidants. Studies in oxidation of alanine and valine by several oxidizing agents have been made by a number of investigators. Garcia et al¹⁹ used chromic acid as oxidant in sulphuric acid medium while Barkat and co-workers²⁰ used manganese dioxide and permanganate in alkaline, neutral and acidic medium to oxidize these amino acids.

Reaction between glycine and permanganate was investigated first by Pokrovskaya²¹ mainly from preparative view point. Cu(II) catalysed oxidation of alkaline glycine by periodate has been studied by Kovates²² while uncatalysed oxidation of acidic and neutral glycine by peroxy-disulphate was studied by Kumar and Saxena²³. Kinetics of oxidation of glycine by Co(III) has been studied by Sthapak and Ghosh²⁴.

Bose²⁵ et al studied the oxidation of glycine, alanine and valine in alkaline media by chloramine-T whereas Govind Chandra et al²⁶ have studied Ag(I) catalysed oxidation of these amino acids by peroxydisulphate. Sethuram and coworkers studied the oxidation of amino acids by Cerium(IV)²⁷ and by Fentons²⁸ reagents. Oxidation of DL- isomers of α -amino acids by permanganate in perchloric acid medium was studied by Verma²⁹ et al. Ag catalysed oxidation of amino acid was studied by Surendra Rao et al³⁰. Kinetics of L-arginine by acid permanganate was studied by Mudaliar³¹. Katre³² has studied the CAT catalysed oxidation of DL-isomers while Nagar³³ has studied the CAT catalysed oxidation of L-isomer of amino acids by permanganate.

Silver catalysed oxidation of DL-isomers of amino acids was studied by Chourey^{34,35} in acidic medium. Oxidation of L-aspartic acid, L-Glutamic acid and L-asparagine by acidic permanganate was studied by Sahu et al³⁶. Oxidation of L-glutamine by Vanadium(V) was studied by Dubey et al³⁷ while of glycine was studied by Choubey³⁸. Mallama³⁹ has studied the oxidation of cysteine by Bromamine β . Grover et al⁴⁰ studied the oxidation of aspartic and glutamic acid by CAT. Oxidation of L-glutamine by periodatonicelate(IV) was carried out by

Bellakk⁴¹.Farook⁴² et al studied the oxidation reaction of amino acids by new oxidant,i.e. N-chorosaccharine in aqueous medium.

In recent years micelles emerged as attractive reaction media for number of biological and chemical reactions. However,miceller effects on oxidation of amino acids have been much less explored.

Micellar catalysed oxidation of anilines by Chloromine-T and positive cooperativity were explained by Raghvan et al⁴³. A kinetic model analogous to Hill model for the positive cooperativity was suggested by Piszkiwicz⁴⁴. Jursic⁴⁵ introduced miceller in the field of synthetic organic chemistry.Hussain and co-workers⁴⁶ studied the surfactant catalysed oxidation of organic compounds by permanganate.Rodenas et al⁴⁷ investigated the Chromium(VI) oxidation of alkanol components of sodium dodecyl sulphate.

Pandey⁴⁸ has studied the oxidation of L-isomers of amino acids by acidic permanganate volumetrically.Surfactant catalysed oxidation of basic amino acid by acidic permanganate was carried out idometrically by Gour⁴⁹.Kinetics of oxidation of Trans-2 buten-1-ol by quinquivalent Vanadium in presence of sodium lauryl sulphate was studied by Dubey⁵⁰.Kinetic investigation of the oxidation of N-alkyl anilines by peroxomonophosphoric acid in anionic surfactant sodium lauryl sulphate was reported by Panigrahi and co-workers⁵¹.Kinetics of adsorption of anionic, cationic and nonionic surfactants at the cellulose-water interface,was studied by Paria et al⁵².

Sodium Lauryl Sulphate catalysed oxidation of methanone by CAT was studied by Pachori⁵³.Gaur⁵⁴ studied the NDS catalysed oxidation of DL-isomers of amino acids by permanganate ion. Dubey et al studied the CTAB catalysed oxidation of L-glutamine and glycine by Vanadium (V).Kabiruddin⁵⁵ et al studied the CTAB catalysed oxidation of DL-alanine by ninhydrin. Oxidation studies of aspartic acid and glutamic acid, catalysed by SLS, CTAB with CAT oxidant was carried by Pandey et al⁵⁶.

Studies on Mn(II)-catalyzed oxidation of α -amino acids by peroxomonosulphate in alkaline medium was studied by Rani et al⁵⁷.Kinetics of oxidation of L-Valine by a copper (iii) periodate complex in alkaline medium by N-Bromophthalimide by Sharanabasamma et al⁵⁸ while of same in presence of chlorocomplex of Pd(II), Iridium (III) Chloride and by Ruthenium(III) Chloride were carried out by Singh et al⁵⁹⁻⁶¹.

Deamination and decarboxylation in the chromium(III)-catalysed oxidation of L-valine by alkaline permanganate and analysis of chromium(III) in microscopic amounts by a kinetic method was studied by Kulkarni and coworkers⁶².

Kinetic and mechanistic studies of oxidation of glycine and valine by N-bromosuccinimide using chloro complex of Rh(III) in its nano-concentration range as homogeneous catalyst investigated by Singh et al⁶³. Kinetics and mechanisms of the permanganate oxidation of L-valine in neutral aqueous solutions was reported by Perez-Benito and coworkers⁶⁴.

Kinetic study of permanganate oxidation of L-leucine in neutral aqueous solution was studied by Brillas et al⁶⁵. Kini et al⁶⁶ studied the comparative study of ruthenium(III) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate. Kinetics and mechanism of oxidation of Leucine and Alanine by Ag(III) Complex in alkaline medium was observed by Song et al⁶⁷.

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