INTRODUCTION

A study of Chemical phenomenon can be made from two fundamental approaches; first of these known as thermodynamics is a rigorous and exact method concerned with equilibrium conditions of initial and final states of chemical changes. The other method known as chemical kinetics, which deals with a more chemical aspect of chemical phenomenon, namely, the rate of change from initial to final state under non-equilibrium conditions.

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 very 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 that how long a time, does the change require, and why do the times for different change 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 with 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 atom 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 problems arise in any kinetic investigation, the first is the establishment of relationship 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 properly 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. The problem of how, and at what rate, a system not initially in equilibrium may change so as to attain equilibrium, is the subject of chemical kinetics.\textsuperscript{[1-3]} Two questions about a chemical reaction are of paramount importance to those engaged in research, design or operation involving chemical reaction.

(i) How far reaction proceed or what is the equilibrium condition?
(ii) How rapidly is it possible to attain some desirable approach to equilibrium condition?

Proper answers are rather complex since many properties and conditions of a chemical system affect both equilibrium and rate. Though the questions are related, as yet no unified quantitative treatment exists and to a large extent they are handled separately by the sciences of thermodynamics and reaction kinetics.

The speed of a chemical reaction is governed by structural and energetic factors not uniquely specified by the thermodynamic quantities, hence study of reaction rates or chemical kinetics provide a complimentary technique for examining the chemistry of reaction. Most of the reactions involve two or more steps, out the various steps, the slowest step determines the 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.

The most powerful tool for the experimental study of reaction 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. There is no obvious correlation between the thermodynamic instability and the speed of a chemical reaction.

Thermodynamics is interested in initial and final states of a system in which, the mechanism where by the system is converted from one state to another and the time required are of no importance. On the other hand, kinetics is concerned fundamentally with the details of the process where by a system gets from one state to another and with the time required for the transition. A reaction rate can not be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more fundamental science than thermodynamics.

Porter, rightly points out is “part of statics and part of dynamics” and “relative immaturity of chemical dynamics or kinetics is to be attributed to its later birth and to be fact that it is a difficult child”. The earlier experiments in the study of the rates of reaction which was made by Wilheny in 1850. He demonstrated with the help of a number of experiments in the case of inversion sucrose and explained that the rate at any instant is proportional to the molecular concentration of sucrose at that instant. In 1862, Berthelot and Gill, and in 1865-1867, Harcourt and Esson concluded the similar results.
Guldberg and Waage\textsuperscript{[14]} in 1863 showed that the rate at which the substance reacts is proportional to the molar concentration of that substance, and Van’t Hoff in 1877 enunciated the principal of mass action applied to heterogeneous systems.\textsuperscript{[15]} In 1999 Arrhenius\textsuperscript{[16]} made an important advancement which deals with large increase in reaction rate due to increase in the temperature.

The usefulness of a particular chemical reaction as a preparative procedure obviously depends upon its rate. As the rate depends upon various factors such as concentration, pressure, temperature dielectric constant of the medium, ionic strength, presence of electrically charged and neutral species, wavelength of light etc. for this reason knowledge of factors which influence reaction velocity has practical consequence\textsuperscript{[17]}, therefore, studies are made generally from such point of view.

Chemical kinetics is concerned not only with the velocity of reactions but also with the intermediate steps by which reactants are ultimately converted into products.\textsuperscript{[18-22]} The science of chemical kinetics may be of interest in itself, the greatest interest to chemists is the fact that kinetics provides the most general method of determining the mechanism of reactions and it is one of the most modern tool in the development and progress of chemistry.\textsuperscript{[23-25]} Kinetics has great importance in fundamental and applied fields. For chemical industry, it gives required conditions which can increase the yield of the products.

1.1 Mechanism of Reaction

Mechanism of a chemical reaction may be considered as a hypothetical motion picture of the behaviour of the participating atoms. Such a picture would begin at some time before the reacting
species approach each other, then go on to record the continuous path of the atoms during reaction, and came to an end after the products have emerged. From a classical point of view, developed chiefly by physical chemists, mechanism of a chemical reaction is understood to mean all the individual collisional or other emanatory processes involving atoms, molecules, radicals, that take place. simultaneously or consecutively in producing the observed overall reaction.

In addition to this classical definition, a new concept of reaction mechanism is developed chiefly by organic chemists. This includes not only a knowledge of all the individual steps in the overall reaction but also a detailed stereo-chemical picture of each step, that occurs.

The methods for determining the reaction mechanism$^{[26-28]}$ can be broadly classified as:

(1) Kinetic studies

(2) Non kinetic studies

Elucidation of the reaction mechanism on the basis of kinetic studies, requires the determination of many kinetic and thermodynamic parameters, such as velocity constant, order of reactions with respect to various reacting species and influencing factors, specific reaction rate, stoichiometry of the reaction, temperature coefficient, energy of activation, entropy of activation etc., study of the effect of catalysts, inhibitors and effect of exposure to radiation also help in interpreting the reaction mechanism.$^{[29-34]}$ Analysis of products obtained helps in confirming the proposed reaction mechanism, studies on primary and secondary salt effect also help in arriving at useful conclusions.
Types of Reaction Mechanism: 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 require 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. 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 AB and C, first form a transition complex which then decomposes into products.

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

Reactants Transition Complex 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 & C, though some what loosely than before, is the transition state.

One of the important type of reaction in organic chemistry is displacement reaction. When a reagent A having at least one unshared pair of electron, collides with BC. The collision might result in establishment of a bond between A and B and thus liberating C with an unshared pair of electron. In the reaction the attack of A is directed
against nucleus of B and the process is said to be nucleophilic displacement.

The substitution at the carbon atom can occur in either of two ways. Either A can strike BC producing AB and C or BC 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 leads to substitution at the nucleus of carbon atom, they are called nucleophilic substitution, but there are number of reactions of different types and it is difficult to classify them because they proceed in large number of steps and mechanism in each case is much more complex.

1.2 Kinetic Terms-

(i) Reaction Rate and Rate Law: The rate of a chemical reaction is the rate at which the concentration of reacting substances vary with time. If in a infinitesimally small time dt, the change in concentration of any of the reactants is dc, then the rate is given by \(-\frac{dc}{dt}\). The minus sign is used to denote that the concentration of reactants decreases with time. The dependence of this rate on the concentration of reacting substances is given by the law of mass action also.

A mathematical expression relating reaction rate with concentration is called rate law or rate expression. The rate law expresses the dependance of reaction rate upon concentration.

(ii) Molecularity and Order of Reaction: In the study of chemical kinetics, reaction are expressed either by the "Molecularity" or by the "Order of Reaction". Wiberg \(^{35}\) defines molecularity as the number of individual molecules which react in the slow step of the reaction and points out that "The concept is meaningless when it is applied to any other step", for the ones preceding the slow step would be equilibrium for which the mechanism would usually not be known
and we of course have no knowledge of what happens after the slow step other than what products are ultimately formed unless these subsequent reactions are studied separately.

Since molecularity is concerned with the mechanism of a process and since the formation of a "transition state" or "activated complex" is considered essential for any reaction to take place, it is appropriate to define "molecularity" as the number of molecules involved in the formation of activated complex. The determination of the order of reaction is the first objective of every kinetic study. The order of reaction is strictly an experimental quantity concerned solely with the way in which reaction rate depends on the concentration. The order of the reaction with respect to different reactants indicates how many reactant molecules are involved before the rate determining step.

The molecularity should be distinguished from the total order of reaction, because order of the reaction is derived from kinetic experiments, whereas the molecularity is a theoretical and stoichiometric concept.

(iii) **Expression for rate of reaction**: In the rate of reaction at the given temperature is proportional to the $a^{th}$ power of the concentration of the reactant A; to the $b^{th}$ power of the concentration of the reactant B and so on, then the rate law, can be expressed simply as,

$$\text{Rate} = \frac{dx}{dt} = -\frac{d[A]}{dt} = k \cdot [A]^a \cdot [B]^b \quad ------- \quad (1.1)$$

Where, $x = \text{concentration of given reactant at any instant t}$ and $k = \text{reaction constant or specific reaction rate constant; when concentration of all the reactants are unity.}$
This specific reaction rate is constant for a particular reaction at given temperature. The order of reaction with respect to \( A, B, \ldots \) etc., are respectively \( a, b, \ldots \) etc., The total order of reaction is given by the sum of the orders of reactions with respect to each reactant,

\[
n = a + b + \ldots \quad (1.2)
\]

Where, \( n \) = overall order of the reaction.

Sometimes, the reaction proceeds by two or more than two paths, each with its own rate determining step. In such cases, the rate expression is given by,

\[
\text{Rate} = r = \frac{dx}{dt} = \frac{-d[A]}{dt} = k \cdot [A]^a \cdot [B]^b \cdot \cdots + k' \cdot [A]^a \cdot [B]^b \cdot \cdots \quad (1.3)
\]

In the above equation, the first term gives the contribution from one reaction path, the second term gives that from another reaction path and the sum of all the individual rates is the rate of overall reaction. \(^{[41]}\) For determining the order of the reaction, various methods are used. Ostwald's \(^{[42]}\) isolation method is one of the most common method in use which was suggested by Harcourt and Esson.\(^{[43]}\)

(iv) **Reaction Rate and Solvent**: Solvent may also influence the reaction course in solution by solvating the reactants or by participating as nucleophile or by acting as proton acceptor or donor. The viscosity of the solvent influences the multiple encounters of same two molecules during the time, the solution tends to surround the colliding particles in a 'cage' which traps them for a certain time before each can diffuse out. This process has, however, no effect on the reaction rate for ordinary molecules where most collisions are ineffective.\(^{[44]}\)
1.3 Kinetic and Activation Parameters

[i] Energy of Activation: Primarily a chemical reaction involves collisions between the reacting molecules. The least amount of energy required to cause a molecular collisions so that their constituent atoms are arranged into new product is termed the activation energy. The change that the molecules will collide with at least this amount of energy is given by the following equation,

$$ k = A \cdot e^{-\frac{E_a}{RT}} $$

(1.4)

Where, \( R \) = gas constant, \( T \) = absolute temperature,

\( A = \) pre-exponential factor or frequency factor,

\( E_a = \) activation energy

This equation fits many of the available experimental kinetic data, although sometimes the more general equation,

$$ k = AT^n e^{-\frac{E_a}{RT}} $$

(1.5)

is used. Here 'n' can have any value dictated by experiment, expression (1.5) is developed by Arrhenius to explain the variation of the rate constant with the temperature. The logarithmic form of the equation (1.4) is,

$$ \log_{10} k = -\frac{E_a}{2.303 RT} + \log_{10} A $$

(1.6)

The activation energy for a reaction can be calculated directly from values of rate constant measured at two temperatures by the following equation, which has been deduced from equation (1.6),

$$ E_a = \frac{2.303R(T_2-T_1)}{\log \frac{k_2}{k_1}} $$

(1.7)

As it is clear from equation (1.6) that the energy of activation \( E_a \) of any reaction can also be calculated from the slope of the straight line obtained from the plot of \( \log_{10}k_1 \) against reciprocal of absolute temperature. The energy of activation often determine whether a reaction is fast or slow at a given temperature.
[ii] **Temperature Coefficient**: The rate equation and the rate constant for a reaction are determined from kinetic data at a fixed temperature. If experiments are performed at several temperatures, it is generally found that the concentration dependence exhibited in the rate equation is unchanged but the value of the rate constant is much greater at the higher temperatures. In homogeneous process the rate constant is approximately doubled or trebled for each 10°C rise of temperature coefficient, mathematically which can be expressed as,

\[
\text{Temperature Coefficient} = \frac{(k_{t+10})}{k_t}
\]

Where, \( k_t \) = reaction rate constant at \( t \)°C,

\( (k_{t+10}) = \) reaction rate constant at \( (t + 10) \)°C,

It is only an approximate method for indicating the effect of temperature because the coefficient decreases with increasing temperature.

[iii] **Frequency And Probability Factor**: Collision factor A in a bimolecular reaction should be equal to the bimolecular collision frequency \( Z \) which can be calculated from kinetic theory, if the dimensions and masses of molecule are known. Specific rate, \( k \) for a bimolecular reaction can be given by following expression\[^{[46]}\] according to simple collision theory,

\[
k = Z e^{-Ea/RT}
\]

Where, \( Z = \) collision number,

The equation (1.8) has further modified emperically to,

\[
k = P Z e^{-Ea/RT}
\]

Where, \( P = \) 'probability factor' or 'steric factor'. The value of \( P \) varies from unity to about \( 10^8 \) according to the nature of the reaction.
In many cases the value of \( P \) may be smaller than unity. This can be interpreted in many ways. A reaction might be thought to have definite steric requirements, that is, some special, orientation of molecules undergoing collision is necessary. In addition to an energy required for reaction to occur, \( P \) may have lower value, when reaction involves complex molecules because the energy of activation sets concentrated in the particular bond of a molecule undergoing fission. Thus collision theory does not correlate completely the characteristics of the reacting molecules with the value of \( P \). It has no explanation for abnormal fast reactions in which \( P \) is greater than unity.\(^{[47]}\)

**[iv] Enthalpy Of Activation** : On the basis of transition state theory of absolute reaction rates, the rate constant, \( k_r \) is given by,\(^{[48]}\)

\[
k_r = \frac{kT}{h} e^{\frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}} \quad \text{--------} (1.10)
\]

Where, \( k = \) Boltzman constant,  
\( T=\)Absolute temperature,  
\( h = \) Plank’s constant,  
\( S^* \) and \( H^* = \) Standard entropy and enthalpy.  
The linear correlation between the values of the activation enthalpies and entropies of the reaction indicated the operation of a significant compensation effect.\(^{[49-50]}\) in the changes during the activation process. Experimental energy of activation \( E_a \) is related to the enthalpy change, \( \Delta H^* \) by the relation,

\[
E_a = \Delta H^* + RT
\]

or

\[
\Delta H^* = E_a - RT \quad \text{--------} (1.11)
\]

**[v] Entropy of Activation** : If frequency factor \`A` is greater than \( 10^{13} \), then \( \Delta S^* \) will be positive and vice-versa \`A` can be calculated from equation (1.14) by determination of energy of activation, \( E_a \), from Arrhenius equation. If the value of \( \Delta S^* \) is positive, it corresponds to a more probable complex and faction is faster. If the
value of $\Delta S^*$ is negative, the formation of activated complex is less probable and the rate is slower. The utility of the calculation for the increase or the decrease in entropy has been well explained by Frost and Pearson.\textsuperscript{[51]}

For the ordinary cases, energy of activation may be taken as identical with; enthalpy changes.

$$E_{a}^* = \Delta H^* \quad \text{------------------- (1.12)}$$

Comparison of equation (1.9) with equation (1.10) gives,

$$P_z = \frac{kT}{h} e^{\frac{\Delta S^*}{R}} \quad \text{------------------- (1.13)}$$

Compassion of equation (1.9) with equation (1.10) gives,

$$A = \frac{kT}{h} e^{\frac{\Delta S^*}{R}} \quad \text{------------------- (1.14)}$$

Now, $kT/h \approx 10^{13}$ by putting the value of $k$, $T$ and $h$ hence, equation (1.14) can be written as,

$$A = 10^{13} e^{\frac{\Delta S^*}{R}} \quad \text{------------------- (1.15)}$$

The entropy of activation has been calculated with the use of following equation,

$$\Delta S^* = 2.303 R \log A \left( \frac{kT}{h} \right) \quad \text{------------------- (1.16)}$$

and also from the equation

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \quad \text{------------------- (1.17)}$$

Thermodynamic parameters involving formation constant were evaluated as follows. The enthalpy of formation ($\Delta H$) was calculated from the slope of the plot $\log k$ v/s $1/T$ making use of van't Hoff Isochore,

$$\frac{d \ln k}{dt} = \frac{\Delta H^*}{dT^2} \quad \text{------------------- (1.18)}$$

The free energy of formation ($\Delta G_f$) was calculated from van't Hoff Isotherm,

$$\Delta G^* = - R T \ln k \quad \text{------------------- (1.19)}$$

and the entropy of formation ($\Delta S$) was obtained from the expression,

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad \text{------------------- (1.20)}$$
1.4 - Concept of Oxidation and Reduction

Oxidation and reduction are familiar words used to describe a very large number of reactions although the term may be some what difficult to define precisely and comprehensively for organic chemistry.\(^{[52]}\)

The universally used concept of oxidation-reduction is now based on the transfer of electrons during a chemical reaction. Accordingly, a loss of electron is an atomic or ionic species indicated oxidation and a gain of a electron indicated reduction.

Living organisms are all chemically reacting system depending on the continuance of oxidation and reduction. Redox reactions which play an important role in chemical as well as natural life processes are explained in a simple way by the electron loss (oxidation) and electron gain (reduction) and therefore, the essential step in any oxidation-reduction process is transfer of electrons.\(^{[53-54]}\) Mechanism of a given oxidation or reduction reaction often varies greatly with the oxidising or reducing agent employed.\(^{[55-57]}\)

Ross Stewart\(^{[58]}\) has proposed the following general definition: "An oxidation and a reduction has occurred in a chemical reaction if the products differ from the reactants in a way that can not be accounted for simply by an exchange of protons, hydroxide ions, halide ions, ammonium ions, alkali metal ions, amide ions etc. or what is equivalent by an exchange of water, hydrogen, halide, ammonia” etc.

According to Goodstein\(^{[59]}\) "A redox reaction is one in which a change in relative order of electronegativities take place between a given atom and the atom to which it is bonded prior and subsequent to reaction concurrently an opposite change in order of electronegativities take place else where among the reactants.”
The study of mechanism of oxidation of organic compounds according to Waters\textsuperscript{[60]}, is a "subject of major importance to all chemists, for not only does it require consideration of the properties and reactions of both organic and inorganic compounds, above all, it has vast implications in connection with the understanding of the nature of life".\textsuperscript{[61-66]} Organic compounds are essentially covalent and their valency electrons are associated together in pairs. An essential feature of organic reaction is covalent bond fission and organic reactions maybe classified into two types; homolytic and heterolytic.

(1) By homolytic reactions in which electron pair bond is broken symmetrically, so as to form a free, uncharged, compound radical and may be shown as,

\[
A : B \rightarrow A^{\cdot} + B^{\cdot}
\]

(2) By heterolytic fission in which process electron pair is transfered from one atom to another as an undivided entity forming two opposite charged ions, this may be shown as,

\[
A:B \rightarrow A^{+} + B^{-}
\]

or

\[
A:B \rightarrow A^{\cdot} + B^{+}
\]

The homolytic fission provides free radicals which are energetic and highly reactive, hence they require less activation energy. Homolytic oxidation, therefore, when once started, proceeds very rapidly. The heterolytic reactions yields stable molecular or ionic products in one or two consecutive stages and very rarely lead on the chain reactions. They require more activation energy than homolytic reactions and therefore, tend to slower processes. The kinetics of the oxidation of number of inorganic Impounds such as thiourea\textsuperscript{[67]}, antimony\textsuperscript{[68]} and platinum (II)\textsuperscript{[69]} in acidic medium are reported.

The study of oxidation reactions of inorganic and organic compounds \textsuperscript{[70-78]} finds an important role in preparatory chemistry.
The kinetic study of oxidation reactions of inorganic and organic compounds proved an important tool for elucidating the stepwise mechanism of such reactions.

1.5 Acid-Base Equilibria and Catalysis

The field of equilibria and reaction in acidic\[^{79-80}\] and alkaline solution\[^{81}\] has attracted much attention by physical organic chemists both because of the challenging problems encountered, and of the practical interest of water as a reaction solvent. Many chemical reactions take place in aqueous solutions, and most of these have rates that depend on the concentrations of acids and bases. Many such reactions take place on particular relevance as models for biochemical processes. Although the rates of many reactions in aqueous solutions depend on the concentrations of acids in addition to the solvated proton, and bases in addition to the hydroxide ion (so-called acid-base catalysis), catalysis\[^{82-83}\] by the solvent derived species in aqueous solutions always underlies that of the other acids and bases present. Furthermore, some reactions are catalysed only by the proton, or hydroxide ion (specific acid-base catalysis).

This ubiquity of acid-base catalysis by protons and hydroxide ions makes the study of the pH dependence of reaction rates particularly important. Study of the dependence of reaction rate on $\text{H}_3\text{O}^+$ or $\text{OH}^-$ concentration is of special significance because most of the reactants in aqueous media are involved directly or indirectly in equilibria which are influenced in some way by hydrogen or hydroxide ion concentrations. The concentrations of protons and hydroxide ions can be varied, and their concentrations accurately detected, with such immense variation in proton concentration comes the possibility of a rich kinetic and mechanistic diversity.
**Catalysis**: Wider interest in kinetics developed when rates of reactions 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 the reaction. Actually it takes part in a chemical reaction but it is regenerated and hence the general inference is that it remains usually unchanged at the end of the reaction. Catalyst can be homogeneous or heterogeneous. The most important example of homogeneous catalyst in solution are those referred to as acid-base catalyst.\(^{[84-86]}\)

Transition metal ion catalysed reaction have been the subject of scientific study over hundred years. In recent years there has been a renaissance of interest in the study of metal ion catalysis for a variety of reactions.\(^{[87-93]}\)

**Specific Acid-Base Catalysis**: Acid-base catalysis have attracted considerable attention particularly in concentrated acid or base solutions where because of non-ideal conditions the thermodynamic laws show large deviations.

Reaction whose rates depend on the equilibrium proton activity of a system are said to be Objected to specific acid-base catalysis.

**Specific Acid Catalysis**
**General Form**: \[ S + H^+ \rightleftharpoons SH^+ \] \[ (1.21) \]

\[ SH^+ \rightarrow^{(*)} [\text{Transition state}] \] \[ (1.22) \]

**Specific Base Catalysis**
**General Form**: \[ S + OH^- \rightleftharpoons S^- + H_2O \] \[ (1.23) \]

\[ S^- \rightarrow^{(*)} [\text{Transition state}] \] \[ (1.24) \]

\(^{*}\) indicates no proton transfer.
1.6 Reducing Sugar – An Introductory concept

Carbohydrates can be divided into sugars and non-sugars. Sugar can be classified as monosaccharides and disaccharides which are simplest sugars, posses a free aldehydic (CHO) or ketonic (>CO) group and two or more hydroxyl (-OH) groups. Disaccharides consists of two monosaccharides linked by glycosidic linkages.

Carbohydrates are the most abundant class of organic compounds found in living organism. They originate as products of photosynthesis, an endothermic reductive condensation of carbon dioxide requiring energy and the pigment chlorophyll.

\[ n\text{CO}_2 + n\text{H}_2\text{O} + \text{energy} \rightarrow \text{C}_n\text{H}_{2n}\text{O}_n + n\text{O}_2 \]

As noted here, the formulas of many carbohydrates can be written as hydrates of carbon, \( \text{C}_x(\text{H}_2\text{O})_y \), hence their name. Several classifications of carbohydrates have proven useful, and are outlined in the following table:

<table>
<thead>
<tr>
<th>Complexity</th>
<th>Simple carbohydrates</th>
<th>Complex carbohydrates disaccharides, oligosaccharides and polysaccharides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Tetrose</td>
<td>Pentose</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_4 ) sugars</td>
<td>( \text{C}_5 ) sugars</td>
</tr>
<tr>
<td>C=O Function</td>
<td>Aldose- sugars having an aldehyde function or an hemiacetal equivalent</td>
<td>Ketose – Sugars having a ketone function or an hemiketal equivalent</td>
</tr>
<tr>
<td>Reactivity</td>
<td>Reducing – sugars oxidized by Tollen’s reagent (or Benedict’s or Fehling’s reagents)</td>
<td>Non – Reducing – sugars not oxidized by Tollen’s or other reagents.</td>
</tr>
</tbody>
</table>
Sugars that contain CHO groups are oxidized to COOH group and are classified as reducing sugars, common test regents are

1. Benedict’s reagent (CuSO₄/Sodium Citrate)
2. Fehling’s reagent (CuSO₄ / Rochelle Salt)

They are classified as reducing sugars since they reduce the Cu²⁺ to Cu⁺ which forms as a red ppt. of Copper (I) oxide.

In order of oxidation to occur, the cyclic from must open ring to give the reactive aldehyde so any sugar that contains a hemiacetal will be a reducing sugar. But glycosides which are acetal are not reducing sugars.

\[
\text{β - D - glucose (Hemiacetal) reducing sugar}
\]

Sucrose → Non – reducing sugar (Acetal)

Ketose can also be reducing sugar because they can isomerise (tautomerisation) to aldose via enediol,

\[
\begin{align*}
\text{Ketose} & \quad \text{enediol} \quad \text{aldose} \\
& \quad \text{R} \quad \text{OH} \quad \text{OH} \\
\end{align*}
\]

The carbohydrates are widely distributed in both plants and animals tissues. They are a group of universally occurring compounds characterized by having the general formula Cₓ(H₂O)ᵧ. They are the important source of energy required for various metabolic activities of living organisms. Carbohydrates are the most abundant, and among the
most important, of plant products, and also play a vital role in animal metabolism.\textsuperscript{[94-96]} The molecule of a monosaccharide contains an unbroken chain of carbon atom. Oligosaccharides are carbohydrates, the molecule of which consist of two to ten monosaccharide units (which may be the same or different) linked through oxygen, they are subdivided into disaccharides, trisaccharides etc. (according to the number of monosaccharide units in the molecule) and include some of the commonest sugars. The essential feature of oligosaccharides is that they can be hydrolysed by water under the influence of catalyst or enzymes, with formation of the simple monosaccharide molecules from which they are derived: typically, they are soluble sugars, and some of them are not easily distinguished by superficial properties and tests from the structurally simpler monosaccharides.

Monosaccharides are classed as aldoses and ketoses. The simplest compound of these classes are,

\[
\begin{align*}
&\text{CHO} \\
&\text{H-C-OH} \\
&\text{CH}_2\text{OH}
\end{align*}
\]

\text{D- glyceraldehydes}

\[
\begin{align*}
&\text{CHO} \\
&\text{HO-C-H} \\
&\text{CH}_2\text{OH}
\end{align*}
\]

\text{L- glyceraldehydes}

\[
\begin{align*}
&\text{CHO} \\
&\text{H-C-OH} \\
&\text{CH}_2\text{OH}
\end{align*}
\]

\text{Dihydroxy Acetone}

\[
\begin{align*}
&\text{CH}_2\text{OH} \\
&\text{C=O} \\
&\text{CH}_2\text{OH}
\end{align*}
\]

\text{The simplest ketose}

The D-and L- forms of a monosaccharides, being mirror image or enantiomorphs, are identical not only in chemical properties but also in most physical properties, except that one form has a specific dextro rotation, and the other a specific leveo rotation, monosaccharides which are optical isomers but not enantiomers may show marked differences in properties, and are known as diastereoisomers.
**D – Glucose, C$_6$H$_{12}$O$_6$**

The general characters of the monosaccharides are well illustrated by reference D-glucose (the most important aldose). It occurs, often associated with D-fructose, in many fruits, and in honey. It is a product of hydrolysis of many common disaccharides, and also of starch and cellulose. It plays a vital in animal carbohydrate metabolism.

D-glucose can be prepared from ‘invert sugar’, which is a mixture of D(+) glucose and D(-) fructose, is fractionally crystallized from alcohol; the glucose separates first, leaving the soluble fructose in solution. D–glucose is made commercially by the completed hydrolysis of starch.

\[
\text{Sucrose} \xrightarrow{\text{inversion}} D\text{- glucose} + D\text{- fructose} \quad \begin{array}{c}
\oplus \text{rotator} \\
\ominus \text{rotatory}
\end{array} \downarrow
\]

‘Invert sugar’

\[
\ominus \text{rotatory}
\]

This hydrolysis or inversion of sucrose is also brought about by the enzyme invertase in yeast.

**Commercial preparation : -**

\[
\text{Starch} \xrightarrow{\text{Acid Hydrolysis}} D\text{- glucose}
\]

D-glucose is a white, crystalline powder. The monohydrate C$_6$H$_{12}$O$_6$·H$_2$O, melts at 86°C, and an anhydrous substance at 146°C. The sugar is freely soluble in water and is sweet, though not so sweet as sucrose (cane–or beet- sugar). It chars readily when heated alone, or when warmed with concentrated sulphuric acid, giving vapours with a characteristic burnt sugar odour. If D-glucose is warmed with
Fehling’s solution the blue colour of copper complex disappears, and a red ppt. of cuprous oxide is formed. Similarly if a solution of glucose is warmed in a test tube with tollen’s reagent, a silver mirror is obtained. The carbon numbering in glucose is,

![Carbon numbering in glucose](image)

Like most sugars D-glucose is a strong reducing agent.

**Structure and Configuration of D-glucose:** Detection of elements (C,H,O) and the determination of molecular weight by depression of the freezing point give the molecular formula C$_6$H$_{12}$O$_6$. The presence of five hydroxyl groups is indicated by the formation of a penta acetyl derivative by the action of acetic anhydride. Further elucidation of the structure results chiefly from studies of the behaviour of the sugar on reduction and oxidation. Reducing agents give a hexahydric alcohol D-sorbitol, C$_6$H$_{14}$O$_6$: a typical behaviour of a carbonyl compound, and that the carbonyl group is aldehydic and not ketonic is shown by the oxidation of D-glucose to an acid containing the same number of carbon atoms (D-gluconic acid).

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CHO} & \quad \text{COOH} \\
\text{(CHOH)}_4 & \quad \text{Reduction} & \quad \text{(CHOH)}_4 & \quad \text{Oxidation} & \quad \text{(CHOH)}_4 \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

D-sorbitol \quad D-glucose \quad D-gluconic acid
**Functions:** Enzyme-regulated addition of glucose to proteins by glycosylation is often essential as below:

- As an energy source - Glucose is a ubiquitous fuel in biology. It is used as an energy source in most organisms, from bacteria to humans. Use of glucose may be by either aerobic or anaerobic respiration. Carbohydrates are the human body's key source of energy, through aerobic respiration, providing approximately 3.75 kilocalories or 16 kilojoules of food energy per gram. Breaking of carbohydrates yields mono- and disaccharides, most of which is glucose. Through glycolysis and later in the reactions of the citric acid cycle, glucose is oxidized to eventually form CO₂ and water, yielding energy, mostly in the form of ATP. The insulin reaction and other mechanisms, regulate the concentration of glucose in the blood.

- Use of glucose as an energy source in cells is via aerobic or anaerobic respiration. Both of them start with the early steps of the glycolysis metabolic pathway. The first step is phosphorylation of glucose by hexokinase to prepare it and later provide energy.

**D-Galactose, C₆H₁₂O₆**
Galactose is less sweet than glucose and it is sparingly soluble in water. It is more commonly found in the disaccharide, lactose or milk sugar.

![D-Galactose structure](image)

It is classified as a monosaccharide, an aldose, a hexose, and reducing sugar. It is considered a nutritive sweetener because it has food energy. A genetic defect of not being able to utilize galactose is
called Galactosemia. The disorder is caused by a deficiency in one or more enzymes required to metabolize galactose. Since galactose is in milk as part of lactose, it builds up in the blood and urine. Undiagnosed it may lead to mental retardation, failure to grow, formation of cataracts, and in severe cases death by liver damage.

**D-Ribose, C$_5$H$_{10}$O$_5$**

D-ribose, is an aldopentose — a monosaccharide containing five carbon atoms, and including an aldehyde functional group in its linear form.

![D-Ribose Structure](image)

As a component of the RNA that is used for genetic transcription, ribose is critical to living creatures. It is related to deoxyribose, which is a component of DNA. It is also a component of ATP, NADH, and several other chemicals that are critical to metabolism.

**2-Deoxyribose, C$_5$H$_{10}$O$_4$**

Deoxyribose, is an aldopentose — a monosaccharide containing five carbon atoms, and including an aldehyde functional group in its linear structure. It is a deoxy sugar derived from the pentose sugar ribose by the replacement of the hydroxyl group at the 2-position with hydrogen, leading to the net loss of an oxygen atom.

![2-Deoxyribose Structure](image)
Ribose forms a five-member ring composed of four carbon atoms and one oxygen. Hydroxyl groups are attached to three of the carbons. The other carbon and a hydroxyl group are attached to one of the carbon atoms adjacent to the oxygen. In deoxyribose, the carbon furthest from the attached carbon is stripped of the oxygen atom in what would be a hydroxyl group in ribose.

**Lactose, \( \text{C}_{12} \text{H}_{22} \text{O}_{11} \)**

Lactose (milk sugar) is a disaccharide, occurs to the extent of about 4.8% in milk, from which it can be obtained by adding rennet to precipitate caseinogens and fat, filtering and evaporating the filtrate to small bulk. The sugar separates in crystals when the liquid is cooled, and can be recrystallized from water. Lactose is a disaccharide that consists of \( \beta \)-D-galactose and \( \beta \)-D-glucose fragments bonded through a \( \beta \) \((1\rightarrow4)\) glycosidic linkage.

Lactose is a comparatively sparingly soluble sugar, and is not very sweet. It reduces Fehling’s solution, but does not ferment readily with yeast. When hydrolysed by hot, dilute acid, or by the action of the lactase, it yield a mixture of D-glucose and sugar, D-galactose, which is a stereoisomer of glucose.

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6
\]

Lactose    D-glucose  D-galactose
Metabolic pathway of the oxidative degradation:

Conversion of glucose to glycogen in the presence of insulin and converting liver glycogen back to glucose in the presence of glucagon. These changes are important regulators of the blood glucose level.[97-98] After meal the blood in the portal vein has a high glucose content and insulin converts some to glycogen for storage. Glucagon converts this glycogen back to glucose as required, to maintain the blood glucose level within relatively limits.

Insulin

Glucose ⇌ Glycogen

Glucagon

Further oxidation of glucose produce pyruvic acid and ATP. This oxidation takes place via glycolysis in which one mole of glucose aerobically changes into two moles of pyruvic acid and eight moles of ATP, which is a source of energy and anaerobic glycolysis produces pyruvic acid, which is converted into lactic acid. This enzyme catalysed process is called as Embden-Meyerh of pathway.

The oxidation of pyruvic acid to acetyl Co-A is a necessary step before the products of glycolysis could enter into the citric acid cycle. These yield 6 ATP molecule. The final common pathway for the oxidation of carbohydrate is citric acid cycle, which accounts for the oxidation of acetyl residue to two CO$_2$ and H$_2$O. This pathway is commonly known as Kreb’s cycle which produces 12 moles of ATP in one cycle.

An alternate pathway of oxidation of glucose with the production of CO$_2$ and pentose. This provides ribose - 5 phosphate.
Glucose is broken down in the body giving energy, CO$_2$ and metabolic water. The total number of ATP molecule, which may be generated from the complete breakdown of one molecule of glucose is 38.
## Factors affecting metabolic rate

<table>
<thead>
<tr>
<th>Factors</th>
<th>Effect on metabolic rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age</td>
<td>Gradually reduced with age</td>
</tr>
<tr>
<td>Gender</td>
<td>Higher in man than woman</td>
</tr>
<tr>
<td>Height &amp; weight</td>
<td>Relatively higher in small people</td>
</tr>
<tr>
<td>Ingestion of food</td>
<td>Increased</td>
</tr>
<tr>
<td>Elevated body temperature</td>
<td>Increased</td>
</tr>
<tr>
<td>Muscular activity</td>
<td>Increased</td>
</tr>
<tr>
<td>Starvation</td>
<td>Decreased</td>
</tr>
<tr>
<td>Excess thyroid hormones</td>
<td>Increased</td>
</tr>
</tbody>
</table>

### 1.7 Cerium(IV)- As an Oxidant

Cerium, a versatile and well known rare earth metal was first discovered by M.K.Lapworth, J. Berjelius and W. H. Hisinger. Cerium is a well known oxidant in acidic media having reduction potential of the couple Ce(IV)/Ce(III) at 1.70 V and is stable only in higher acidic medium.

In sulphuric acid and acidic media, several sulphate complexes of cerium(IV) form, but their role has not received much attention so far. The oxidizing potentialities of cerium (IV) in H$_2$SO$_4$ medium have conclusively been established and the oxidant exists in the form of sulphato species.

From the previous work on cerium oxidation it has been seen that cerium is strong oxidizing agent and it can oxidize various organic and inorganic substances such as amino acids, antimony(III),...
peridone\textsuperscript{[112]}, formic acid\textsuperscript{[113]}, phenethyl alcohols\textsuperscript{[114]}, glycols\textsuperscript{[115]}, dialkyl sulphoxides\textsuperscript{[116]}, tellurium(IV)\textsuperscript{[117]} etc.

Various investigations on oxidation; kinetics involving cerium(IV) and amino acids, glycols, malonic acid\textsuperscript{[118]}, aliphatic aldehydes and ketones\textsuperscript{[119]}, isobutyric and 3-bromopropanoic acid\textsuperscript{[120]} have been reported in which oxalic acid\textsuperscript{[121]} is much revealed.

Cerium carry a wide range of application in synthesis,\textsuperscript{[122-123]} as analytical reagent\textsuperscript{[124]} and catalyst.\textsuperscript{[125-126]} Analytically cerium in its tetravalent state differs from the rest of the lanthanide due to its immense oxidizing power in acid solutions. This property of Ce(IV) stands for offering a promising area for research in oxidation reactions. It is evident that metal ion\textsuperscript{[127-128]} oxidants have been widely employed in Chemistry of carbohydrate but very few literature\textsuperscript{[129-132]} is available on carbohydrate oxidation by cerium(IV).

\textbf{1.8 Importance and Scope of the Study}

The appraisal of the scientific literature cited earlier emphasizes on the importance of the oxidation-reduction reactions taking place in the nature, and their close relationship with human life, health, vegetation and agriculture. The basic infrastructure of natural processes is now showing up sings of increasing interferences resulting from the rapid growth of industrialisation and urbanization, particularly in the Chhattisgarh region. It was found useful to take up some areas of this region, and undertake in depth studies of selected categories of oxidation-reduction reactions which were closely related to the human life of these area.

The study of kinetics is of vital importance as it gives information about particular reaction and its rate. The data of chemical kinetics of oxidation reactions provide a judicious and rational basis for the search of the new analytical reagent. The oxidation studies are important in
analytical as well as in synthetic chemistry. A large number of oxidants have been used by different workers for the kinetic studies of the oxidation of various organic substances.

Carbohydrates have unique biological activity with serve as store and source of energy of the different carbohydrates. The monosaccharides are of vast biological importance, as they are known to be involved in carbohydrate metabolism. They are reported to exist in acyclic and cyclic forms and posses a higher density of functional group than any other class of organic compounds. The mechanisms of the oxidation reaction involving monosaccharides are of immence importance. Beside from the sugars and starches that meet this vital nutritional role, carbohydrates also serve as a structural material (cellulose), a component of the energy transport compound ATP, recognition sites on cell surfaces, and one of three essential components of DNA and RNA.

The main purpose of the study of their oxidation is to see whether they give oxidative degradation or simply the oxidation of one of the functional groups, i.e. aldehydic or primary alcoholic groups, so that we could arise on a result which well be helpful in simulating simple and easy oxidation of carbohydrate.

Ribose and 2-deoxy ribose is a component of RNA and DNA respectively. Hence, the reactions involving these sugars are considerable interest. Reducing sugar exhibits metabolic oxidative degradation by means of some chemical oxidants. Sugar oxidation also plays wide spectrum of activities in various field of organic, analytical medicinal and food chemistry. It has been therefore, worthwhile to study the kinetics of the oxidation of sugar to understand the stepwise mechanism of the reaction. Kinetic study of reaction may provide the means for the quantitative comparison of its reaction under verying
condition and from the systematic kinetic studies the relative importance of many factors, which may influence reaction rates can be assessed.

Oxidation is probably the most active research topic in the field of saccharides for industrial application. The sodium salt of gluconic acid is used as a sequestering agent in industrial cleaning agents for the purification of metal surfaces or for the cleaning of bottles. Glucouronic-6, 3-lactone, the internal ester of gluconic acid, can also be found in several gums of plants and is used as a detoxifying agent during treatment of hepatitis and arthritis.

Finally, we want to establish a correlation between reducing sugar and oxidant, lastly a plausible reaction mechanism could be evolved based upon the observations.

1.9 Objectives of the Study

1. To study the kinetics of uncatalysed and catalysed reaction in acidic medium.
2. To identify the oxidative products and reactive species.
3. To elucidate a plausible mechanism.
4. To deduce an appropriate rate laws and
5. To calculate the activation parameters.
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