Introduction

“Kinetic” originates from Greek “kinetikos” that, in turn, originates from Greek “kinetos’ which means “moving”. In general, the word “kinetics” is used in physical and life sciences to represent the dependence of something on time. Thermodynamics tells us which direction a reaction will go (e.g. at room temperature and standard pressure, carbon is stable in a form of graphite). Kinetics can tell us how quickly it will get there e.g. a diamond takes a long time, even centuries to convert to graphite.

Chemical Kinetics deals with the rates of chemical reactions and with how the rates depend on factors such as concentration and temperature. Such studies are important in providing essential evidence as to the mechanisms of chemical processes.

Macroscopic kinetics describes the branch of kinetics, which results relate to the behavior of a very large group of molecules in thermal equilibrium. Microscopic kinetics is to investigate the molecules in well-defined states, which will provide information about the dynamic of both reactive and un reactive collisions. (Crossed molecular beams). Chemical kinetics is the study of the rates of chemical reactions. If a reaction is capable of happening, we want to know how far the reaction will proceed, and how fast it will happen. Consider two reactions: the rusting of an iron nail and the combustion of propane. Both reactions will occur, and both will occur to completion. The rusting will take years to complete, but propane will combust in an instant. Furthermore, the nail will rust faster when it's moist, and slower in the presence of less oxygen. Obviously, there are factors that affect the rates of chemical reactions. The study of these factors and rates is chemical kinetics. Consider this generic chemical reaction.

Rate of reaction
Consider a typical chemical reaction:

\[ a \, A + b \, B \rightarrow c \, C + d \, D \]

The lowercase letters \((a, b, c,\) and \(d)\) represent stoichiometric coefficients, while the capital letters represent the reactants \((A\) and \(B)\) and the products \((C\) and \(D)\).

According to IUPAC's Gold Book definition the reaction rate \(r\) for a chemical reaction occurring in a closed system under isochoric conditions, without a build-up of reaction intermediates, is defined as:
The rate of a reaction is always positive. A negative sign is present to indicate the reactant concentration is decreasing. The IUPAC recommends that the unit of time should always be the second. In such a case the rate of reaction differs from the rate of increase of concentration of a product $P$ by a constant factor (the reciprocal of its stoichiometric number) and for a reactant $A$ by minus the reciprocal of the stoichiometric number. Reaction rate usually has the units of mol L$^{-1}$ s$^{-1}$. It is important to bear in mind that the previous definition is only valid for a single reaction, in a closed system of constant volume. This most usually implicit assumption must be stated explicitly, otherwise the definition is incorrect: If water is added to a pot containing salty water, the concentration of salt decreases, although there is no chemical reaction.

For any open system, the full mass balance must be taken into account:

$$F_{A0} - F_A + \int_0^\psi udV = \frac{dN_A}{dt}$$

Where $F_{A0}$ is the inflow rate of $A$ in molecules per second, $F_A$ the outflow, and $\psi$ is the instantaneous reaction rate of $A$ (in number concentration rather than molar) in a given differential volume, integrated over the entire system volume $V$ at a given moment. When applied to the closed system at constant volume considered previously, this equation reduces to:

$$r = \frac{d[A]}{dt}$$

Where

$$[A] = \frac{N_A}{N_0V}$$

Here $N_0$ is the Avogadro constant. For a single reaction in a closed system of varying volume the so-called rate of conversion can be used, in order to avoid handling concentrations. It is defined as the derivative of the extent of reaction with respect to time.

$$\dot{\xi} = \frac{d\xi}{dt} = \frac{1}{v_i} \frac{dn_i}{dt} = \frac{1}{v_i} \frac{d(C_iV)}{dt} = \frac{1}{v_i} \left( v_i \frac{dC_i}{dt} + C_i \frac{dV}{dt} \right)$$
Here is the stoichiometric coefficient for substance i, equal to a, b, p, and q in the typical reaction above. Also $\mathcal{V}$ is the volume of reaction and $C_i$ is the concentration of substance i.

When side products or reaction intermediates are formed, the IUPAC recommends \cite{1} the use of the terms rate of appearance and rate of disappearance for products and reactants, properly.

Reaction rates may also be defined on a basis that is not the volume of the reactor. When a catalyst is used the reaction rate may be stated on a catalyst weight (mol g$^{-1}$ s$^{-1}$) or surface area (mol m$^{-2}$ s$^{-1}$) basis. If the basis is a specific catalyst site that may be rigorously counted by a specified method, the rate is given in units of s$^{-1}$ and is called a turnover frequency.

**Factors influencing rate of reaction**

*The nature of the reaction*: Some reactions are naturally faster than others. The number of reacting species, their physical state the particles that form solids move much more slowly than those of gases or those in solution, the complexity of the reaction and other factors can greatly influence the rate of a reaction.

- **Concentration**: Reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.
- **Pressure**: The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas. The reaction rate increases in the direction where there are fewer moles of gas and decreases in the reverse direction. For condensed-phase reactions, the pressure dependence is weak.
- **Order**: The order of the reaction controls how the reactant concentration (or pressure) affects reaction rate.
- **Temperature**: Usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason that temperature increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants) \cite{1}. The influence of temperature is
described by the Arrhenius equation. As a rule of thumb, reaction rates for many reactions double for every 10 degrees Celsius increase in temperature,[1] though the effect of temperature may be very much larger or smaller than this. For example, coal burns in a fireplace in the presence of oxygen, but it does not when it is stored at room temperature. The reaction is spontaneous at low and high temperatures but at room temperature its rate is so slow that it is negligible. The increase in temperature, as created by a match, allows the reaction to start and then it heats itself, because it is exothermic. That is valid for many other fuels, such as methane, butane, and hydrogen. Reaction rates can be independent of temperature \textit{(non-Arrhenius)} or decrease with increasing temperature \textit{(anti-Arrhenius)}. Reactions without an activation barrier \textit{(e.g., some radical reactions)}, tend to have anti Arrhenius temperature dependence: the rate constant decreases with increasing temperature.

- \textit{Solvent}: Many reactions take place in solution and the properties of the solvent affect the reaction rate. The ionic strength also has an effect on reaction rate.

- \textit{Electromagnetic radiation} and \textit{intensity of light}: Electromagnetic radiation is a form of energy. As such, it may speed up the rate or even make a reaction spontaneous as it provides the particles of the reactants with more energy. This energy is in one way or another stored in the reacting particles \textit{(it may break bonds, promote molecules to electronically or vibrationally excited states)} creating intermediate species that react easily. As the intensity of light increases, the particles absorb more energy and hence the rate of reaction increases. For example, when methane reacts with chlorine in the dark, the reaction rate is very slow. It can be speed up when the mixture is put under diffused light. In bright sunlight, the reaction is explosive.

- \textit{A catalyst}: The presence of a catalyst increases the reaction rate \textit{(in both the forward and reverse reactions)} by providing an alternative pathway with a lower activation energy. For example, platinum catalyzes the combustion of hydrogen with oxygen at room temperature.
• **Isotopes**: The kinetic isotope effect consists in a different reaction rate for the same molecule if it has different isotopes, usually hydrogen isotopes, because of the mass difference between hydrogen and deuterium.

• **Surface Area**: In reactions on surfaces, which take place for example during heterogeneous catalysis, the rate of reaction increases as the surface area does. That is because more particles of the solid are exposed and can be hit by reactant molecules.

• **Stirring**: Stirring can have a strong effect on the rate of reaction for heterogeneous reactions.

All the factors that affect a reaction rate, except for concentration and reaction order, are taken into account in the rate equation of the reaction.

**Rate equation**

For a chemical reaction $a\ A + b\ B \rightarrow c\ C + d\ D$, the rate equation or rate law is a mathematical expression used in chemical kinetics to link the rate of a reaction to the concentration of each reactant. It is of the kind:

$$ r = k(T)[A]^n[B]^m $$

For gas phase reaction the rate is often alternatively expressed by partial pressures.

In the equations $^{(6)}$ $K(T)$ is the reaction rate coefficient or rate constant, although it is not really a constant, because it includes all the parameters that affect reaction rate, except for concentration, which is explicitly taken into account. Of all the parameters influencing reaction rates, temperature is normally the most important one and is accounted for by the Arrhenius equation. The exponents $n$ and $m$ are called reaction orders and depend on the reaction mechanism.

Stoichiometry, molecularity (the actual number of molecules colliding), and reaction order coincide necessarily only in elementary reactions, that is, those reactions that take place in just one step. The reaction equation for elementary reactions coincides with the process taking place at the molecular level, i.e. molecule A collides with molecule B. From collision theory follows that the likelihood of a collision of three molecules is highly unlikely. Therefore molecularity for elementary reactions is either
one or two. Empirically, other values can be assigned to allow mathematical description of the rate. Then, positive rational numbers are not uncommon but should not be assigned physical meaning.

By using the mass balance for the system in which the reaction occurs, an expression for the rate of change in concentration can be derived. For a closed system with constant volume, such an expression can look like

\[
\frac{d[P]}{dt} = k_m [A]^a [B]^b
\]

(7)

Temperature dependence

Arrhenius equation

Each reaction rate coefficient \( k \) has a temperature dependency, which is usually given by the Arrhenius equation:

\[
k = Ae^{-\frac{E_a}{RT}}
\]

(8)

\( E_a \) is the activation energy and \( R \) is the gas constant. Since at temperature \( T \) the molecules have energies given by a Boltzmann distribution, one can expect the number of collisions with energy greater than \( E_a \) to be proportional to \( e^{-\frac{E_a}{RT}} \). \( A \) is the pre-exponential factor or frequency factor.

The values for \( A \) and \( E_a \) are dependent on the reaction. There are also more complex equations possible, which describe temperature dependence of other rate constants that do not follow this pattern. A chemical reaction takes place only when the reacting molecules collide. However, not all collisions are effective in causing the reaction. Products are formed only when the colliding molecules possess a certain minimum energy called threshold energy. Basically, the number of activated molecules nearly doubles for a temperature \( T+10 \) K. The ratio of a reaction at a given temperature to its rate constant at a temperature 10 degree lower is called temperature coefficient.

Pressure dependence

The pressure dependence of the rate constant for condensed-phase reactions i.e., when reactants and products are solids or liquid is usually sufficiently weak in the range of pressures normally encountered in industry that it is neglected in practice.
The pressure dependence of the rate constant is associated with the activation volume. For the reaction proceeding through an activation-state complex

\[ A + B \overset{k^+}{\longrightarrow} [A\ldots B]^+ \rightarrow P \]

the activation volume, \( \Delta V^+ \), is:

\[ \Delta V^+ = \bar{V}_a - \bar{V}_b \]

Where \( \bar{V} \) denote the partial molar volumes of the reactants and products and \( ^+ \) indicates the activation-state complex.

For the above reaction, one can expect the change of the reaction rate constant (based either on mole-fraction or on molar-concentration) with pressure at constant temperature to be

\[ -RT \left( \frac{\partial \ln k}{\partial P} \right)_T = \Delta V^+ \]

In practice, the matter can be complicated because the partial molar volumes and the activation volume can themselves be a function of pressure.

Reactions can increase or decrease their rates with pressure, depending on the value of \( \Delta V^+ \). As an example of the possible magnitude of the pressure effect, some organic reactions were shown to double the reaction rate when the pressure was increased from atmospheric (0.1 MPa) to 50 MPa (which gives \( \Delta V^+ = -0.025 \text{ L/mol} \))

Example: Reaction of hydrogen and nitric oxide

For the reaction

\[ 2\text{H}_2(g) + 2\text{NO}(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \]

The observed rate equation (or rate expression) is:

\[ r = k[\text{H}_2][\text{NO}]^2 \]

As for many reactions, the rate equation does not simply reflect the stoichiometric coefficients in the overall reaction: It is third order overall: first order in \( \text{H}_2 \) and second order in \( \text{NO} \), although the stoichiometric coefficients of both reactants are equal to 2.

In chemical kinetics, the overall reaction rate is often explained using a mechanism consisting of a number of elementary steps. Not all of these steps affect the
rate of reaction; normally the slowest elementary step controls the reaction rate. For this example, a possible mechanism is:

1. \(2\text{NO}(g) \rightleftharpoons \text{N}_2\text{O}_2(g)\) (fast equilibrium)
2. \(\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\) (slow)
3. \(\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}\) (fast)

Reactions 1 and 3 are very rapid compared to the second, so the slow reaction 2 is the rate determining step. This is a bimolecular elementary reaction whose rate is given by the second order equation: \(r = k_2[\text{H}_2][\text{N}_2\text{O}_2]\), where \(k_2\) is the rate constant for the second step.

However \(\text{N}_2\text{O}_2\) is an unstable intermediate whose concentration is determined by the fact that the first step is in equilibrium, so that: \([\text{N}_2\text{O}_2] = K_1[\text{NO}]^2\), where \(K_1\) is the equilibrium constant of the first step. Substitution of this equation in the previous equation leads to a rate equation expressed in terms of the original reactants

\[r = k_2K_1[\text{H}_2][\text{NO}]^2\]

This agrees with the form of the observed rate equation if it is assumed that \(k = k_2K_1\). In practice the rate equation is used to suggest possible mechanisms which predict a rate equation in agreement with experiment.

Order of Reaction:

**Molecularity:** If a chemical reaction proceeds by more than one step or stage, its overall velocity or rate is limited by the slowest step, which is called the rate-determining step. This "bottleneck concept" has analogies in everyday life. For example, if a crowd is leaving a theater through a single exit door, the time it takes to empty the building is a function of the number of people who can move through the door per second. Once a group gathers at the door, the speed at which other people leave their seats and move along the aisles has no influence on the overall exit rate. When we describe the mechanism of a chemical reaction, it is important to identify the rate-determining step and to determine its "molecularity". The molecularity of a reaction is defined as the number of molecules or ions that participate in the rate determining step. A mechanism in which two reacting species combine in the transition state of the rate-determining step is called bimolecular. If a single species makes up the transition state, the reaction would be
called unimolecular. The relatively improbable case of three independent species coming together in the transition state would be called termolecular.

**Kinetics:** One way of investigating the molecularity of a given reaction is to measure changes in the rate at which products are formed or reactants are lost, as reactant concentrations are varied in a systematic fashion. This sort of study is called kinetics, and the goal is to write an equation that correlates the observed results. Such an equation is termed a kinetic expression, and for a general reaction of the type where the rate constant \( k \) is a proportionality constant that reflects the nature of the reaction, \([A]\) is the concentration of reactant A, \([B]\) is the concentration of reactant B, and \( n \) & \( m \) are exponential numbers used to fit the rate equation to the experimental data. Chemists refer to the sum \( n + m \) as the kinetic order of a reaction. In a simple bimolecular reaction \( n \) & \( m \) would both be 1, and the reaction would be termed second order, supporting a mechanism in which a molecule of reactant A and one of B are incorporated in the transition state of the rate-determining step. A bimolecular reaction in which two molecules of reactant A (and no B) are present in the transition state would be expected to give a kinetic equation in which \( n=2 \) and \( m=0 \) (also second order).

It should be noted that the molecularity of a reaction is a theoretical term referring to a specific mechanism. On the other hand, the kinetic order of a reaction is an experimentally derived number. In ideal situations these two should be the same. In nucleophilic hydrolysis of t-alkyl halide, the situation is totally different. It not only shows first order kinetics (only the alkyl halide concentration influences the rate), but the chiral 3º-alkyl bromide reactant undergoes substitution by the modest nucleophile water with extensive racemization. Note that the acetonitrile cosolvent does not function as a nucleophile. It serves only to provide a homogeneous solution, since the alkyl halide is relatively insoluble in pure water.

**Rate Constants:** The rate constant is also known as specific rate or rate coefficient. The value of rate constant is numerically equal to the reaction rate when the reactants are present at unit concentration. In general, its unit depends upon the concentration of
reactants. Thus if the concentration is expressed in moles/liter, the rate constant has units moles/liter/sec. Thus for \( n \)-th order reaction, the unit is mole\(^{(1-n)} \) liter\(^{(n-1)} \) sec\(^{-1} \).

Consider the general reaction

\[
A + 2B \rightarrow 3C
\]

The rate of formation of product C, in mol/lit/sec. is three times the rate of disappearance of A and one half the rate of disappearance of B.

\[
\frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = -\quad -(11)
\]

If the reaction is first order in A, rate constant for the appearance of C is given by

\[
\frac{d[C]}{dt} = k_c[A] = -\quad -(12)
\]

Similarly three times the rate constant for disappearance of A is given by

\[
-\frac{d[A]}{dt} = k_A[A] = -\quad -(13)
\]

*First order rate constant:* Consider a first order reaction, for which rate is directly proportional to the concentration of the reactant i.e.

\[
A \rightarrow B
\]

\[
-\frac{d[A]}{dt} = k[A] = -\quad -(14)
\]

This on integration gives

\[
k = \frac{1}{t} \ln \left[ \frac{[A]_t}{[A]} \right] = -\quad -(15)
\]

For the first order reaction plot of ln [A] or log [A] verses t is a straight line and k can be calculated from the slope.

*Second order rate constant:* In this, rate of reaction is directly proportional to the square of concentration of one of the reactants or the product of the concentration raised to the power unity of two of the reactants. Therefore considering the reaction

\[
2A \rightarrow \text{Product}
\]

\[
-\frac{d[A]}{dt} = k[A]^2 = -\quad -(16)
\]

This on integration gives
\[
\frac{1}{[A]} = \frac{1}{[A_0]} + kt - - - - - - - (17)
\]

Hence \(1/ [A]\) against \(t\) plot give a straight line with slope \(k\)

If the reaction is of the type

\[
a \ A + bB \rightarrow \text{Product}
\]

rate = \(k[A][B] - - - - - - - (18)\)

and the integrated rate equation is

\[
\frac{1}{b[A]_0 - a[B]_0} \ln \left( \frac{[B]_0[A]}{[B][A]_0} \right) = kt - - - - - - - (19)
\]

If \(a=b=1\), the above equation become

\[
\frac{1}{[A]_0 - [B]_0} \ln \left( \frac{[B]_0[A]}{[B][A]_0} \right) = kt - - - - - - - (20)
\]

The plots of left hand sides of above equations against \(t\) will be straight line. Rate constants can be calculated from slopes.

Third order rate constant:-In the third order, three different cases can be considered. In the first case rate is directly proportional to the cube of the concentration of one of the reactant.

\[
3A \rightarrow \text{Product}
\]

rate = \(k[A]^3 - - - - - - - (21)\)

The integration form of equation is

\[
\left[ \frac{1}{2[A]^2} - \frac{1}{2[A]_0^2} \right] = kt - - - - - - - (22)
\]

\[
k = \frac{1}{2t} \left[ \frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right] - - - - - - - (23)
\]

In another case, suppose rate is proportional to the square of the concentration of one of the reactant and first power of concentration of second i. e.

rate = \(k[A]^2[B] - - - - - - - (24)\)

The integrated form of above equation can be given as

\[
\frac{1}{[B]_0 - [A]_0} \left[ \frac{1}{[A]} - \frac{1}{[A]_0} \right] + \frac{1}{([B]_0 - [A]_0)^2} \ln \left( \frac{[A][B]_0}{[A]_0[B]} \right) = kt - - - - - - - (25)
\]
In the third case, rate is proportional to the product of the concentration of the three reactants i.e.

\[ \text{rate} = k[A][B][C] \]  

(26)

This can be integrated to give

\[
\frac{1}{\prod (A)_{0} (B)_{0} (C)_{0} (A)_{0} (B)_{0} (C)_{0} (A)_{0} (B)_{0} (C)_{0} (A)_{0} (B)_{0} (C)_{0} (A)_{0} (B)_{0}}
\]

\[
= k \text{rate}
\]  

(27)

**Oxidation Processes:** There are different ways in which oxidation process is defined. The most common definition of oxidation of an organic compound is “addition of Oxygen, removal of hydrogen or removal of electron/s from that compound” e.g.

Addition of Oxygen:-

\[
\text{RCH}_{2}\text{CHO} \xrightarrow{[O]} \text{RCH}_{2}\text{COOH}
\]

Removal hydrogen:-

\[
\text{RCH}_{2}\text{OH} \xrightarrow{-[2H]} \text{RCHO}
\]

Removal of electrons:-

\[
\text{C}_{6}\text{H}_{5}\text{O}^{-} \xrightarrow{\text{Ce}^{+4}} \text{C}_{6}\text{H}_{5}\text{O}^{-}
\]

There are several modes of Oxidation some of them can be given as under Ferricyanide is capable of removing electrons from carbolic acid
1) In such reaction oxidizing agent should be capable of one electron reduction characterized by suitable redox potential. The requirement of organic compound is that it should give a relatively stable radical on oxidation.

2) During the oxidation of aldehyde auto oxidation takes place and hydrogen atom is removed.
3) In Cannizoro reaction, oxidation takes place due to removal of hydride ion.

\[
\text{PhCHO} + \text{OH}^- \rightarrow \text{PhCOOH}
\]

4) When alkenes are oxidized by peracids, oxygen atom gets inserted to form a epoxide.

\[
\text{HC} = \text{CH} - \overset{\text{O}}{\text{C}_6\text{H}_5\text{COOH}} \rightarrow \text{HC} = \overset{\text{CH}}{\text{CH}} - \overset{\text{R}}{\text{R}} + \overset{\text{C}_6\text{H}_5\text{COOH}}{\text{R}}
\]

5) In the oxidation of diol by lead tetra-acetate oxidizing agent under goes two electron reductions.

\[
\text{R-C} = \overset{\text{OH}}{\text{O}} + \overset{\text{Pb(OAc)}_4}{\text{Pb(OAc)}_2} \rightarrow \text{R-C} = \overset{\text{O}}{\text{O}} \overset{\text{Pb(OAc)}_2}{\text{OAc}} + \overset{\text{O}}{\text{O}} + \overset{\text{Pb(OAc)}_2}{\text{Pb(OAc)}_2}
\]

6) When cyclohexane is heated with palladium/Alumina catalyst, it undergoes dehydrogenation to give benzene.

\[
\text{Cyclohexane} \xrightarrow{\text{Pt/Al}_2\text{O}_3} \text{Benzene} + 3\text{H}_2
\]
**Oxidation Levels:** Oxidation levels cannot be determined by oxidation number for organic compounds. Whether the organic compound is undergoing oxidation or reduction in a given reaction can be known by oxidation levels of the carbon atom of the functional group. To know whether organic compound is undergoing oxidation or reduction, the carbon atom of functional group is classified into five oxidation levels.

1-Level zero: - The lowest oxidation level for carbon is zero. When carbon is bonded to hydrogen or carbon then & only then this state is achieved.

Level One: - The next oxidation level is one i.e. level one is also called alcohols oxidation level. In this category, carbon atoms which have one bond to an electronegative atom such as O, N, S, X, etc.

Level Two: - The oxidation level two contains carbon with two bonds to electronegative atoms ex.
Level Three: Level three contains carbon with three bonds to electronegative atoms

\[
\begin{align*}
\text{H}_3\text{C}=\text{C}-\text{OCH}_3 & \quad \text{H}_3\text{C}=\text{C}-\text{OH} \quad \text{H}_3\text{C}=\text{C} \equiv \text{N} \\
& \quad \text{H}_3\text{C}=\text{C}-\text{N} \\
\end{align*}
\]

Level Four: - When carbon is bonded to four electronegative atoms directly, it is called level four.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{H}_2\text{N} & \quad \text{NH}_2 & \quad \text{H}_2\text{N} & \quad \text{OMe} & \quad \text{MeO} & \quad \text{OMe} & \quad \text{H}_2\text{N} \equiv \text{C} \equiv \text{N} \\
\end{align*}
\]

Theories of Chemical Kinetics: -

The stepwise explanation of a chemical reaction is called as its mechanism. The individual steps which taking place are generally called elementary processes. There are different theories which explain the mechanism of chemical reaction. The most common theories include collision theory and activated complex theory. In this section, a brief discussion of these two theories is given.

**Collision theory:** -

This theory is primarily formulated for bimolecular reactions.

The two reacting particles approach to each other to a sufficiently close distance. It assumes that collision between pair of molecules can lead to a reaction. Further, it is assumed that a reaction will always occur if the initial relative speed \( V_o \) of the two molecules equal or exceed a limit \( V_m \) and if, for a given speed \( V_o \), their centre of mass approach within a distance, \( R \), less than or equal to a limit \( R_m \). The relative motion of the molecule is influenced by a spherically symmetric intermolecular potential \( V(R) \). The rate constant \( k \) for bimolecular reaction is calculated in two steps. First, consider all collisions with same initial velocity \( V_o \) (where \( V_o > V_m \)). The rate at which the projection
A hit their target B is equal to the volume per time $V_oS_o$, multiplied by the projectile A ($V_o$), i.e. concentration $V_oS_oA(Vo)$. The reaction rate is $V_oS_oA(Vo)$, multiplied by the number of targets per unit volume $NB(V_o)$

$$r(V_o) = (V_oS_oN)A(Vo)B(Vo)$$

$$= k A(Vo)B(Vo)$$

Where $k$ is the rate constant and $N$ is Avogadro’s number. Although this is a useful expression for the interpretation of specialized experiments where the relative translation velocity of reactant is selected, in the usual macroscopic reacting system a variety of relative speeds $V_o$ are present. Hence this theory predicts an empirically acceptable form for the rate constant. It is not possible to compare theoretical and experimental activation energies because collision theory does not predict a value for the theoretical equation.

In the solution state, a molecule interacts with its nearest neighbors. These nearest neighbors form a cage around the molecule. The cage creates a potential well within which the molecule can move back and forth. The rate at which the reactant molecules A and B diffuse together to form caged pairs is rate determining step.

The diffusion of B towards A and reaction of the caged AB pair together constitute an elementary bimolecular reaction in solution.

If $k_{d+}$ and $k_{d-}$ are the rate constants for steady state diffusion of B in and out respectively. The elementary rate constant is given as

$$k = \frac{k_{d+}}{1 + \frac{k_{d-}}{k_c}}$$

If $\frac{k_{d-}}{k_c} \ll 1$ then $k = k_{d+}$. The reactions will be diffusion-Limited reaction.

**Activated Complex Theory:**

This theory is also called as absolute rate or transition state theory. This theory is applicable to any rate process which has appreciable activation energy ($E_a>5RT$). Activated Complex Theory can predict rate constants from molecular structure parameters and vibrational frequencies. It gives a detailed calculation of the absolute rate
of a chemical reaction and statistical mechanical derivation and considerable use of the properties of the potential energy surface. Based on transition state theory the following expression can be arrived at for the reaction rate constant and the Arrhenius parameter

\[
k = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \quad \text{(29)}
\]

\[
A = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} \quad \text{(30)}
\]

The equation become

\[
k = Ae^{\frac{-\Delta H^*}{RT}} \quad \text{(31)}
\]

In the transition state theory, the value of A has a different meaning than in the collision theory. It is not simply a frequency factor but also a measure of change in entropy during activation. For gaseous reactions it is observed that entropy of activation is negative. This means that the system becomes more orderly i.e. molecule get properly oriented before going for activated complex.

**Transition State Theory (Absolute Rate Theory) of Chemical Kinetics**

In the following paragraphs, we will outline the derivation of the transition state (Eyring) equation, a fundamental relation between the rate constant for a reaction and the entropy and entropy of activation for that reaction.

We will be considering the bimolecular reaction of A with B to form P, as shown below, where k is the second order rate constant describing this reaction:

\[
A + B \xrightarrow{k} P
\]

Now, consider the same bimolecular reaction sequence, but in which A and B reversibly react to form an intermediate complex \((AB)^\ddagger\), which irreversibly decomposes to form final product P. The species \((AB)^\ddagger\) is a so-called transition state (or activated complex) whose lifetime is less then \(10^{-13}\) sec.

\[
A + B \xrightarrow[k_1]{k_2} \text{\(AB\)} \xrightarrow{k^1} P \quad \text{---------(32)}
\]

We can now write the rate of reaction of A and B to form P in two ways, as in equation (2):
\[ \frac{d[P]}{dt} = k[A][B] = k' [AB] \]  \hspace{1cm} (33)

In this equation, \( k \) is the bimolecular rate constant for conversion of \( A \) and \( B \) to \( P \) and \( k' \) is the unimolecular rate constant for decomposition of the activated complex \((AB)^\ddagger\) to form \( P \). Now, the Eyring approach assumes that we can assume a thermodynamic quasi-equilibrium to exist between \( A, B \) and \((AB)^\ddagger\). If this is true, we can write an equilibrium constant and an expression for \( \Delta G_0^\ddagger \), the free energy of reaction to form the transition state (normally called the standard free energy of activation); these quantities are expressed as immediately below:

\[
K^\ddagger = \frac{[AB]}{[A][B]} \hspace{1cm} \Delta G_0^\ddagger = -nRT \ln K^\ddagger \]  \hspace{1cm} (34)

This transition state is somewhat similar to a normal molecule with one important difference. It has one degree of vibration that is special. The transition state moves along this special vibrational mode to form product \( P \) (or to reform reactants \( A \) and \( B \)). From the above, we can obtain an expression for \([AB]^\ddagger\) in terms of \( K^\ddagger, [A] \) and \([B] \), and, thus, an expanded expression for the rate of reaction (equation 33) above can be written as equation (35).

\[
d[P]/dt = k[A][B] = k'[AB]^\ddagger = k'K^\ddagger [A][B] \]  \hspace{1cm} (35)

From this equality, we can write that the bimolecular rate constant \( k \) is given by the product \( k'K^\ddagger \). Thus, if we can evaluate \( k' \) and \( K^\ddagger \), we can evaluate \( k \).

\[
\ln K^\ddagger = \frac{\Delta G_0^\ddagger}{RT} = -\Delta H_0^\ddagger /RT + T\Delta S_0^\ddagger /RT = \Delta S_0 /R - \Delta H_0^\ddagger /RT \]  \hspace{1cm} (36)

In this equation, \( \Delta H_0^\ddagger \) is the standard enthalpy of activation and \( \Delta S_0^\ddagger \) is the corresponding standard entropy of activation. From (equation 36) hence, the expression for \( K^\ddagger \) can be given as follows:

\[
K^\ddagger = e^{\Delta S_0^\ddagger /R} e^{-\Delta H_0^\ddagger /RT} \]  \hspace{1cm} (37)

Then we can write the following expression for the rate constant \( k^\ddagger \).

\[
k = k'e^{\Delta S_0^\ddagger /R} e^{-\Delta H_0^\ddagger /RT} \]  \hspace{1cm} (38)

Using statistical mechanical and quantum mechanical reasoning, Henry Eyring calculated the value of \( k' \) was given by \( kRT/Nh \), where \( R \) is the gas constant, \( T \) is the absolute temperature, \( N \) is Avogadro's number and \( h \) is Planck's constant; \( k \) is a constant known as the transmission coefficient and is often taken to have a value of unity. When
the units of the rate constant are in seconds, the value of \( k' \) is given fairly closely by \( 2 \times 10^{10} T \). Thus, the equation for \( k \) can be written as in equation 39.

\[
k = \left( \frac{RT}{Nh} \right) e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} = 2 \times 10^{10} T e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} \quad \ldots \ldots (39)
\]

This equation is known as the transition state equation for bimolecular rate constants; it is often termed the Eyring equation or the absolute rate equation.

**Kinetic Methods:** Different methods used to study chemical kinetics. The methods are used for kinetic investigation depends on the half time period or completion time period. The extreme fast reactions are studied using molecular beam flow, stopped flow etc techniques. While other reactions can be monitored by pH-metry, conductometry and colorimetry titrations etc. The different methods used are summarized in the table.

### Various methods used for kinetic study

<table>
<thead>
<tr>
<th>Method and time scale</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>1) Mix the reactants together in a batch reactor.</td>
</tr>
<tr>
<td></td>
<td>2) Measure conc. Vs time.</td>
</tr>
<tr>
<td>≥10 s</td>
<td></td>
</tr>
<tr>
<td>Stopped flow</td>
<td>1 Set of continuously flow system where reactants are fed into the reactor and flow out again so quickly that there is negligible reaction.</td>
</tr>
<tr>
<td>≥10^{-1} s</td>
<td>2 Stop the flow so that reactant reacts.</td>
</tr>
<tr>
<td></td>
<td>3 Measure the conversion Vs time.</td>
</tr>
<tr>
<td>Pressure Jump and Temperature Jump</td>
<td>Nobel prize was given for this technique to Eigen.</td>
</tr>
<tr>
<td>≥10^{-6} s</td>
<td>1 Mix the reactants at such a low temperature that the reaction rate is negligible.</td>
</tr>
<tr>
<td></td>
<td>2) Use CO(_2) lasers to suddenly heat the reaction.</td>
</tr>
<tr>
<td></td>
<td>3) Measure conc. Vs time.</td>
</tr>
<tr>
<td></td>
<td>4) Measure the reactant conc. Vs time.</td>
</tr>
<tr>
<td>Technique</td>
<td>Duration</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Flash photolysis</td>
<td>$10^{-9} - 10^{-10}$ s</td>
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<tr>
<td>NMR</td>
<td>$10^{-2} - 10^{-9}$ s</td>
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<td></td>
<td></td>
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<tr>
<td>Conventional flow system</td>
<td>$\geq 10^{-3}$ s</td>
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<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular Beam</td>
<td>$10^{-9} - 10^{-13}$ s</td>
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</tr>
<tr>
<td>Femto spectroscopy</td>
<td>$10^{-15}$ s</td>
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</tbody>
</table>

**Oxidizing agents:-**

The species which oxidizes other species give up oxygen or electronegative atom which accept hydrogen or any other electropositive element which gain electron are called oxidizing agents. There are large numbers of compounds which can be used as oxidizing agents in organic chemistry. Classification of these compounds is complicated and difficult. Although the oxidation of medicinal drugs, in the present study is carried out by potassium permanganate, it is necessary to have a look into the different oxidizing agents available. The N-halocompounds are widely used as oxidizing agents for example, N-chloronicotinamide which can be prepared by passing a slow stream of chlorine in the solution of nicotinamide in HCl. It is white precipitate with M.P. 220°C [2]. Kinetics of
oxidation of alpha amino acids by N-Chloronicotinamide in aqueous acetic acid medium in presence of hydrochloric acid has been investigated by Vivekanandan and Nimbi [3]. They reported first order oxidation with respect to [oxidant] and [HCl]. The rate of reaction depend on solvent, it increases with decrease in dielectric constant. They proposed that reaction takes place because of molecular chlorine, which act as strong oxidizing agent. The mechanism of reaction suggested was

\[
\begin{align*}
N-\text{Nicotinamide} + H^+ + Cl^- & \xrightleftharpoons{k_1}{k_1^{-1}} \text{Nicotinamide} + Cl_2 \\
Cl_2 + \text{Amino acid} & \xrightleftharpoons{k_2}{k_2^{-1}} \text{Complex} \\
\text{Complex} & \xrightarrow{k_3} \text{Complex (aldehyde} + \text{NH}_3 + \text{CO}_2) 
\end{align*}
\]

The other N-halo compounds are N-Bromophthalimide [4], N-Bromoacetamide [5], and N-Chlorobenzamide [6].

The oxidation of alpha amino acids by ethyl N-Chlorocarbamate (ECC) in aqueous acetic acid leads to the formation of the corresponding aldehydes [7]. The reaction is first order with respect to ECC. It was observed that reaction rate increases with an increase in the polarity of the medium. The reaction was susceptible to the both polar and sterric effects of the substituents. The mechanism proposed is

\[
\begin{align*}
\text{RCH(N}^+\text{H}_3\text{)COO}^- + \text{Cl} & \xrightarrow{k_3} \text{Complex} \\
\text{Complex} & \xrightarrow{k_4} \text{R} \xrightarrow{H^+} \text{NH}^+ + CO_2 + HCl + EtCOONH^- \\
\text{R} \xrightarrow{2H_2O} \text{RCHO} + NH_4^+ 
\end{align*}
\]

The N haloamine has diverse nature of its ability to furnish halonium cations, hypo species, an N anion which acts as both bases and nucleophile. These compounds contain positive halogen and are mild oxidants [8]. The various compounds of which
oxidation kinetics was investigated in the literature include. N-Chloronicotinamide which is reported to oxidized cyclohexanol [9].

N- Bromosuccinimide oxidation [10] of L-arginine in aqueous acidic medium is first order in [NBS], fractional order in [L-arginine] and of inverse fractional order in [H+] The suggested mechanism was

\[
\begin{align*}
\text{H}_2\text{C} & \text{CO} \quad \text{NHBr}^+ \quad \text{H}_2\text{C} \quad \text{CO} \\
\text{H}_2\text{C} & \text{CO} \quad \text{NBr}^+ + \text{H}^+ \\
\end{align*}
\]

N- Bromosuccinamide is successfully used to study kinetics and mechanism of oxidation of aliphatic Ketone [11], 5-aminopyrazoles [12], 1-2 diaols [13]. Polyhydric alcohols [14], Lysozyme [15], norephedrine [16], D-arabinose [17], D- xylose and D-galactose [18], secondary alcohols [19]. Amines [20], acid red due [21], diamine [22], silicone [23], vanillin [24], caffeine [25] and thiols [26] are oxidized by N- chlorobenzene sulphonamide.

Oxidation of L- arginine by diperiodato nickelate (IV) (DPN), in aqueous alkaline medium was studied by Kembhavi et al [27], methyl t-butyl ether [28], 4-Hydroxycumasin [29], substituted benzaldehyde [30], Etophylline [31], l-leucine and l-isoleucine [32], atenolol [33], 2-5-diamino-1,2,3-thiadiazole [34], Quinolinium
chlorochromate (QCC) [35], lactic acid [36], glycine / L-alanine & L-Lencince [37], methylene blue [38], ruthenium III [39], chromium III [40], black B dye [41], ethylacetate [42], D-arabinose and D-xylose [43], supercritical water oxidation of acidic acid [44], pentaaminecobalt (III) [45], L-valine [46], Chalcones [47]. They reported that reaction is first order with respect to [DPN], fractional order in [L-arginine] and [OH\(^{-}\)]. The rate of reaction decreases with decrease in the dielectric constant. The suggested mechanism is

\[
\begin{align*}
[\text{Ni} (\text{H}_3\text{IO}_6) (\text{H}_2\text{IO}_6) (\text{OH})_2]^3- & \rightleftharpoons [\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)]^+ + \text{H}_3\text{IO}_6^{-2} \\
[\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)]^- + \text{R} & \rightarrow \text{Complex} \\
\text{Complex} & \rightarrow \text{R} - \text{C} = \text{NH}^+ \text{Ni(OH)}_2 + \text{H}_3\text{IO}_6^{2-}
\end{align*}
\]

Quinolinium chlorochromate is an orange/brown crystalline solid. It is a selective oxidizing agent for the oxidation of primary alcohol in presence of secondary alcohol.

The kinetics of oxidation of aliphatic primary alcohol by quinolinium chlorochromate (QCC) to the corresponding aldehydes has been studied by Abdul Jameel. He observed that the reaction is first order in [QCC], [alcohol] and [H\(^{+}\)]. Based on kinetic measurement the proposed mechanism is

\[
\begin{align*}
\text{Alcohol} + \text{QCC} & \rightarrow \text{Complex} \\
\text{Complex} & \rightarrow \text{Product}
\end{align*}
\]

Quinolinium dichromate (QDC) is also used as oxidant for organic and inorganic compounds [48]. It is prepared by adding a known quantity of quinoline to cold solution of chromium trioxide in water with stirring. After 30 minutes, the solution is diluted with acetone and cooled to -20°C for about 15 hours. A orange solid is obtained (melting point-160°C). It is recrystallised from water.

Similar oxidants used are zinc chlorochromate, pyridinium chlorochromate, magnesium and potassium chlorochromate [49]. Tetraethyl ammonium chlorochromate is
a mild and selective oxidizing reagents used for the oxidation of primary aliphatic alcohols [50].

The potassium nitrosodisulphonate (PNDS) (Fremy’s radical) can be used as oxidizing agent, Baloji Kawale et al [51] studied oxidation of alpha amino acids by Fremy’s radical in aqueous borate buffer medium. They reported that oxidation is first order in [PNDS] and [alpha amino acid]

\[
\begin{align*}
RCH(N^+H_3)COOH & \overset{OH^-}{\underset{H^+}{\rightleftharpoons}} RCH(N^+H_3)COO^- \\
& \overset{OH^-}{\underset{H^+}{\rightleftharpoons}} RCH(NH_2)COO^-
\end{align*}
\]

H S Singh et al [52] reported that the rate of oxidation of ethyl glycol, n- mannitol and n-sorbitol by hexacyanoferrate (III) ion in aqueous alkaline medium is directly proportional to [substrate] and [OH\(^-\)]. The dependence of rate on hexacyanoferrate ion is nearly first order at lower concentration and tends towards zero order at high concentration. The mechanism involved is

\[
S + OH^- \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} S^- + H_2O
\]

\[
S^- + [Fe(CN)_6]^{3-} \rightleftharpoons C \text{ (complex)}
\]
The kinetics of oxidation of Disaccharides such as lactose, maltose, cellobiose and melibiose has been studied by hexacyanoferrate in the presence of ammonia [53]. The other compounds for which oxidation by hexacyanoferrate is studied includes aromatic amines [54], glutathione [55], trithanolamine [56], diol [57], thiols [58] and phenylhydrazinium chloride [59].

K K Banerji et al [60] reported that oxidation of alpha amino acids by pyridinium hydrobromide perbromide (PHPB) in aqueous acetic acid leads to the formation of the corresponding aldehydes. The reaction is first order with respect to PHPB. The proposed mechanism was

\[
2RCH (N^+H_3)COO^- + \text{PyH}^+\text{Br}_3^- \rightarrow \text{Complex} \\
\text{Complex} \rightarrow RCH=\text{N}^+\text{H}_2 + \text{CO}_2 + \text{Br}^- + \text{HBr} + \text{PyHBr} + \text{RCH} (N^+\text{H}_3)\text{COO}^- \\
RCH=\text{N}^+\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{RCHO} + \text{NH}_4^+ 
\]

Chloramine-T: The IUPAC name of chloramines T is 4-chloro-4 methyl benzenesulfonamide. Its molar mass is 227.64. In water it breaks to yield a hypochlorite. It can be used as a source of electrophilic chlorine in organic synthesis.

Chloramine-T is another oxidant; literature shows oxidation of methyl vinyl ketone and isopropyl methyl ketone [61], ketoglutaric acids [62], formic acids [63], substituted trans cinnamic acids [64], methionine [65], substituted and unsubstituted imidazole and benzimidazoles [66].

The kinetics of oxidation of ascorbic acid has been reported by using Octacyanomolybdate (V) [67]. Periodate ion is also used as oxidizing agent, the substrate used was Crotonic acid [68], Hexamethylenediamine tetraacetatocobaltate (II) complex [69]. T-butyl hydro peroxide is reported to study kinetics and mechanism of oxidation of anisole [70]. Solvent free oxidation of primary alcohol [71] by potassium dichromate and oxidation of arsenius acid [72] by persulphate is also reported.

The other oxidants used in for the kinetic and mechanistic study of organic and inorganic compounds include hydrogen peroxide [73], N-Chlorosaccharin [74], Pyridiniumchlorochromate [75], Tris(benzhydroxamato) iron (III) [76],...
Benzimidazdiumfluorochromate [77], Benzimidazdiumbromochromate [78], Diperiodatoargentate (III) [79], Imidazoliumdichromate [80], methyleneblue [81], diperiodatocuprate (III) [82], tetrakis (pyridine) silver dichromate [83], benzyl trimethylammonium chlorobromate [84], morpholinium chlorochromate [85], trichloro isocyanuric acid [86], Cetyl trimethylammonium dichromate [87].

Permanganic oxidation:

MnO₄⁻ with Mn (VII) oxidation state is the inorganic oxidant. Formerly known as permanganate of potash or condy’s crystals, it is a strong oxidizing agent. It dissolves in water to give intense purple solutions, the evaporation of which gives prismatic purplish – black, glistening crystals, potassium permanganate decomposes when exposed to light:

$$2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$

It forms orthorhombic crystals with constants: a=910.5 pm, b=572.0 pm, c=742.5 pm.

The MnO₂ is fused with KOH and heated in air or with KNO₃ (a source of oxygen). This process gives potassium manganate, which upon electrolytic oxidation in alkaline solution gives potassium Permanganate, permanganates can also be generated by treating a solution of Mn²⁺ ions with strong oxidants such as PbO₂ (lead oxide), or sodium bismuthate (NaBiO₃). These reactions used the vivid violet colors of permanganate as a test for the presence of manganese. Almost all applications of KMnO₄ exploit its oxidizing properties. As a strong oxidant that does not generate toxic byproducts, KMnO₄ has many niche uses. KMnO₄ is one of the principal chemicals utilized in the film and television industries to ‘age’ props and set dressing. The Mn-containing products from redox reactions depend on the pH. Acidic solutions of permanganate are reduced to the faintly pink manganese (II) ion (Mn²⁺) and water. In neutral solution, permanganate is only reduced by three electrons to give MnO₂, wherein Mn is in a 4+ oxidation state. Mn shows variable oxidation state from 7+ to 2+. The most stable oxidation state for Mn are 2+, 4+, and 7+.

Manganese (III) ions exist in strong concentration acidic media. It undergoes disproportionation to give Mn²⁺ & Mn⁴⁺. Trivalent manganese is known as mangenic ion. The Mn is stable in 4+ forms as MnO₂. It is grey to grey white black solid. In fuming
sulphuric acid, it dissolves to give clear blue solution. In potassium hypomanganate (K₃MnO₄) manganese is in 5+ states which is unstable and decomposes to give Mn⁴⁺ or Mn³⁺. It slowly decomposes to MnO₂. The Mn in +6 states exists only in basic solution as deep green manganese ion. The permanganate i.e. Mn in 7+ oxidation state and Intense purple colour.

In Visible range, the solution of potassium permanganate shows different λ_{max} which indicates mostly Mn⁷⁺, Mn⁶⁺ & Mn⁵⁺. The absorption maxima data for these species is given in the following table. The visible spectrum of permanganate is unaltered by changes in solvents and temperature.

**Spectrophotometric absorbance of Mn species**

<table>
<thead>
<tr>
<th>Species</th>
<th>Maximum wavelength (Mµ) &amp; molar extinction coefficientsx10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₄⁻</td>
<td>546(ε = 2.38);526(ε = 2.40);311(ε = 1.80)</td>
</tr>
<tr>
<td>MnO₄²⁻</td>
<td>606(ε = 1.71);439(ε = 1.38);347(ε = 1.83);299(ε = 1.66)</td>
</tr>
<tr>
<td>MnO₄³⁻</td>
<td>667(ε = 0.90);313(ε = 3.90)</td>
</tr>
</tbody>
</table>

Some examples of kinetics and mechanistic study of oxidation reaction are given in the table.

Alkaline KMnO₄ is also used [88] to oxidize simultaneously Pb²⁺ and Ti⁺. The other inorganic species which are studied by acid or alkaline KMnO₄ includes sulphite [89], arsenic (III) [90].

KMnO₄ is used for the oxidation of methylated humic acids [91], thymidine and thymidylic acids [92], DNA [93], 4-thiouracil derivatives [94], primary alcohol [95], aldehydes [96], catechol [97], silymarin [98], L-valine [99], mandelic acid [100], pyrimidines [101], 3 and 5 formylsalicyclic [102], L-valin [103], substituted mandelic acids [104] and pyrimidines [105].

Potassium permanganate is also used to carry out induced oxidation of carboxylic acid. There are several reactions which can be carried out simultaneously. Some of them are spontaneous and others nonspontaneous. When a system consists of two reactions one is spontaneous and another nonspontaneous, the spontaneous reactions cause a
nonspontaneous processes. This is called chemical induction. The induced oxidation of various carboxylic acids indicates involvement of Mn (VII) species [106].

\[
\begin{align*}
\text{Mn (VII)} + \text{As (III)} & \rightarrow \text{As (V)} + \text{Mn (V)} \\
\text{Mn (V)} + \text{As (III)} & \rightarrow \text{As (V)} + \text{Mn (III)} \\
\text{Mn (III)} + \text{CH}_2(\text{COOH})_2 & \rightarrow \text{Mn (II)} + \text{oxidation product}
\end{align*}
\]

**Oxidation of some Medicinal drugs and substituted benzaldehyde:**

Since in the present study, oxidation of some medicinal drug and important benzaldehyde derivatives is carried out, a literature survey regarding oxidation of various drugs and substituted benzaldehyde by different oxidizing agents has been carried out. The following researchers studied the oxidation of medicinal drugs and their importance in metabolism.

The gabapentin is a potent drug used for the prevention of seizure. It is prescribed for the management of neuralgia, mood disorder, anxiety and tardive dyskinesia. Mohan and Jagdeesh [107] studied kinetics of oxidation of gabapentin by chloramines–T and by N- Bromosuccinimide in perchloric acid medium [108]. Chloramines–T is considered to be antiseptic has been used in the oxidation of vitamin B$_1$ and B$_6$ [109]. Metronidazole and tinidazole are antibacterial and anti-protozoal drugs. They are used in the treatment of amoebiasis. In the presence of an anaerobic electron transport system, the nitrogen group of these compounds is reduced to a series of transiently reactive intermediates that are thought to cause DNA damage. N- Bromosuccinimide in acid medium is also reported for the oxidation of these drugs [110]. The oxidation of Sulfacetamide, a Sulfonamide drug by alkaline diperiodatocuprate (III) has been studied by Naik et al [111]. They reported that, the reaction is first order in oxidant and has less than unit order in drug concentration. They also observed that rate constants increase with increase in alkali concentration and decrease with increase in periodate concentration.

Atenolol is a drug used to monitor blood pressure because of its cardio selective action as a beta blocker. Puttaswamy and Suresha [112] studied oxidation of Atenolol by chloramine-T in aqueous perchloric acid medium. They reported that reaction is first order with respect to [oxidant], a zero order with respect to [drug] and an inverse fractional order with respect to [H$^+$]. They also used N-chloro-p-toulene sulfonamide
(chloramines-T) for the oxidation of Atenolol in Alkaline medium [113]. Sulfamethozole (SMZ) is a antibacterial drug. Its removal from waste water by environmental friendly oxidant, potassium ferrate (VI) was studied by Sharma and other [114]. They observed that the oxidation is first order with respect to SMZ and Fe (VI) respectively. The second order rate constant decreases non linearly with increase in pH. The results of their study reveal that $K_2FeO_4$ has the potential to sence as an oxidative treatment for removing SMZ from water. Williams [115] has also included SMZ in the list of essential drugs. Chloroamphenicol is a antibiotic drug. It is reported that, the kinetics of oxidation of chloroamphenicol by 1- chlorobenzotriazole (CBT) in $HClO_4$ medium over the temperature range 293-323 K exhibits first order with respect to [oxidant]$_0$ and zero order with respect [substrate]$_0$ respectively. The fractional order dependence on [$H^+$] indicates formation of protonated complex between oxidant and [$H^+$] [116]. Mephenesin and Guaifenesin are used for the relief of skeletal muscle spasm and have mild sedative property. Puttaswamy and Sukhdev [117] studied oxidation of these drugs using chloramine-B in hydrochloric acid medium. The oxidation behavior is similar for both the drugs. The rate shows a first order dependence on both [CAB]$_0$ and [HCl]$_0$ respectively and is fractional in [sub]$_0$.

The researchers who studied the oxidation of substituted benzaldehyde are A plausible mechanism of oxidation of aldehydes using Oxone is reminiscent of Baeyer–Villiger oxidation and is, thus, instructive and conceptually comprehensible to an average. The energetically favored scission of the weak O – O bond is accompanied by a hydride migration as shown to produce the oxonium ion intermediate $1C$, which subsequently loses a proton to give the final carboxylic acid product. The preferential migration of H over the phenyl group from $1B$ can be justified if one considers the resonance stabilization of $1C$ versus $1C^-$, which would be the oxonium ion intermediate obtained upon phenyl migration. The benzylic stabilization available for $1D$, the less stable resonance contributor of $1C$, with an incomplete octet is not a viable stabilization feature for $1D^-$ as the involvement of $\pi$ electrons will result in even less stable charge-separated resonance contributors with the negative charge on carbon, a non-electronegative atom [118].
Oxidation of thirty six monosubstituted benzaldehydes by quinolinium bromochromate (QBC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to both QBC and aldehydes. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form \( k_{\text{obs}} = a + b [\text{H}^+] \). The oxidation of [2H] benzaldehyde (PhCD\( \text{O} \)) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the oxidation of para-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of ortho- and meta-substituted compounds, which display a greater dependence on the field effect. It suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the ortho-substituents.

The kinetics of oxidation of benzaldehyde (BA) by Benzyltrimethyl ammonium fluorochromate (BTMAFC) in protic solvent system has been reported at 303K. A unit order dependence of the reaction with respect to [BTMAFC], [BA] and [H+] ions has been observed. The reaction is catalysed by \( \text{H}^+ \) ions. To study the effect of structure reactivity relationships, some para-substituted benzaldehydes were subjected to oxidation by BTMAFC at four different temperatures and thermodynamic parameters were calculated. The Exner plot showed that all the para-substituted benzaldehydes are oxidized by the same mechanism. The Hammett plot is linear with positive \( \rho \) values. The products of the oxidation are the corresponding acids.

During the synthesis of 4-fluorobenzaldehyde via the SN\( \text{Ar} \) reaction of 4-nitrobenzaldehyde with TBAF, it was found that an equivalent amount of TBAF could oxidize benzaldehyde to benzoic acid. The reaction of 4- nitrobenzaldehyde with tetrabutylammonium fluoride (TBAF) gave 4-nitrobenzoic acid in high yield. Depending on the reaction conditions, other aromatic aldehydes produced acids with fewer amounts of alcohols. However, this type of oxidation has limited practical applications. Nevertheless, the mechanism is quite different from the Cannizzaro reaction because the amounts of the acid salt and alcohol formed were different [119].

The oxidation of thirty-six ortho-, meta- and para-substituted benzaldehydes by Bis (pyridine)silver permanganate (BPSP) resulted in the formation of the corresponding benzoic acids. The reaction is first order with respect to both BPSP and aldehydes. The
reaction is catalyzed by hydrogen ions. The rate of reaction increases with an increase in the amount of acetic acid in the solvent. The rates of ortho-compounds showed excellent correlation with LDRS equation. The oxidation of para-compounds is more susceptible to the delocalization effect. The oxidation of ortho- and meta-compounds exhibited a greater dependence on the field effect. The polar reaction constants are negative indicating an electron-deficient centre in the rate-determining step. A mechanism involving a rate-determining hydride transfer from the aldehyde to the protonated BPSP has been proposed [120].

The oxidation kinetics of aromatic aldehydes by 1-bromobenzimidazole (BBI) has been studied in 80% (v/v) acetic acid – water mixture in presence of mercuric acetate. The reaction exhibits first order dependence each in [BBI], [Aldehyde] and [H+] ions. Increase in acetic acid content of the solvent medium increases the rate of reaction. The rate of reaction is not influenced by the addition of electrolyte like sodium perchlorate. Thermodynamic parameters have been calculated. Electron donating groups increase the rate while electron-withdrawing groups decrease the rate. (H2OBr)+ has been postulated as the reactive oxidizing species. Suitable mechanism consistent with the observed kinetic data is proposed [121].

Oxidation of meta-substituted and para-substituted benzylamines by cetyltrimethylammonium permanganate (CTAP) to the corresponding aldimines is first order with respect to both the amine and CTAP. Oxidation of deuteriated benzylamine (PhCD2NH2) exhibited the presence of a substantial kinetic isotope effect ($kH/kD = 5\times60$ at 293 K). This confirmed the cleavage of an $\alpha$-C–H bond in the rate-determining step. Correlation analyses of the rates of oxidation of 19 monosubstituted benzylamines were performed with various single and multiparametric equations. The rates of the oxidation showed excellent correlations in terms of Yukawa–Tsuno and Brown’s equations. The polar reaction constants are negative. The oxidation exhibited an extensive cross-conjugation, in the transition state, between the electron-donating substituents and the reaction centre. A mechanism involving a hydride-ion transfer from the amine to CTAP in the rate-determining step has been proposed [122].
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