

CHAPTER I

Introduction

In physical chemistry, kinetics (In Greek kinesis meaning movement) is the study of the rates in chemical reaction. Analyzing what are different factors affect the reaction rate give information about the reaction mechanism and the transition state of a chemical reaction. Knowledge of reaction rates has many practical applications, like in designing an industrial process, in understanding the complex dynamics of the atmosphere. The first quantitative approach, with birth of chemical kinetics in 1850, by German chemist L. F. Wilhelmy who studied the rate of inversion of sucrose [1]. He found that the rate of reaction was proportional to the concentration of sucrose at any instant. The study of chemical kinetics is of wide significance in the physiological processes, reactor design, electrode processes, reaction mechanism, study of drug action etc. indicates its importance.

There are number of types of organic and inorganic reactions studied kinetically like redox reactions, hydrolysis reactions, displacement reactions, addition reactions, substitution reactions, photochemical reactions etc. which find applications in various fields of chemistry. The interest in oxidation-reduction reactions in recent years has been renewed due to their application in catalysis and synthetic organic Chemistry. The classical definition of oxidation and reduction in terms of gain or loss of oxygen has in modern times been abandoned in favor of the concept of electron loss (oxidation) and electron gain (reduction). Oxidation-reduction reactions are also defined as involving changes in the oxidation states or oxidation numbers. The assignment of oxidation numbers is based on the following rules: -

(i) The oxidation number of an atom in an element is zero (ii) the oxidation number of monatomic ion is its charge (iii) the oxidation number of each atom in a covalent compound of known structure is the charge remaining on the atom when each shared electron pair is assigned completely to more electronegative of the two atoms sharing it. An electron pair shared by like atoms is split between them and (iv) the oxidation number of an element in a compound of uncertain structure is usually obtained by assigning reasonable oxidation numbers to the other elements in the compound. Generalizations are also made depending on the position of an element in the periodic table.

Oxidation-reduction in inorganic reactions

Oxidation-reduction reactions may involve one or more electron transfer. On the basis of number of electrons transferred between oxidant and reductant, the reaction may proceed in one or more steps. Transition metal like iron and cobalt usually exhibit stable oxidation states differing by one electron and react with other through one equivalent steps. However, oxidation state in post transition elements such as arsenic, antimony etc. differ by two electrons. Thus on the basis their pattern of reactivity, the reactions of these elements classified into two main categories.

Complementary and non-complementary reactions

Complementary reactions

The oxidant and reductant change their oxidation state by an equal number of units, called complementary electron transfer reactions.

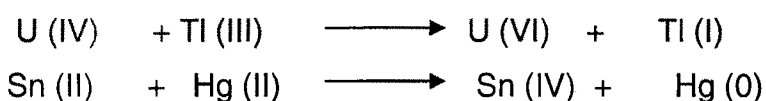
(I) One equivalent- One equivalent reactions

These are reactions in which electron transfer from one species to other. These simple reactions serves as models for more complicated systems and their study has proved invaluable in developing and understanding of the electron transfer reaction in solution.



(II) Two equivalent-Two equivalent reactions

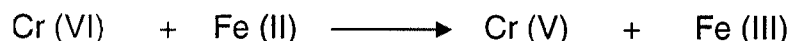
The electron transfer reactions in which occurs with the transfer of two electrons from one species to other.



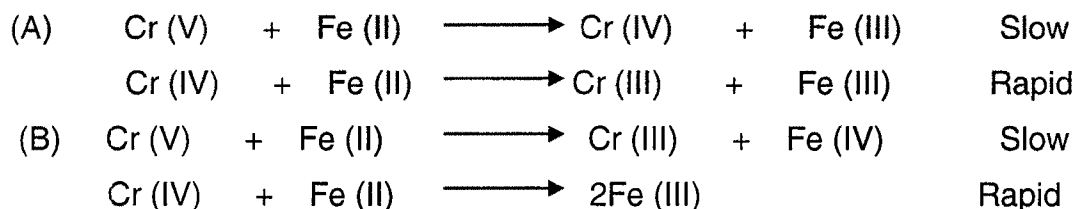
A large number of complementary reactions have been explained on the basis of formation of bridged activated complexes between the oxidants and reductant for easy transfer of electron through the bridging ligand.

Non-complementary reactions

The oxidants and reductants changes their oxidation states by a different number of units, hence name non-complementary electron reactions. Most of such reactions proceeds via elementary steps each involving one electron transfer. The most commonly observed kinetic scheme is



Subsequently, chromium (V) reacts with ferrous ion in a rate determining step one of the following schemes.



The mechanism (A) is more appropriate because step, corresponds to the change in coordination number four of chromium (V) to six of chromium (III).

Electron transfer reactions

These reactions occur by either outer or inner sphere mechanism.

Outer sphere electron transfer reactions

In outer sphere reaction mechanism electron transfer from reductant to oxidant with the coordination sphere of each staying intact. That is one reactant becomes involve in the outer or second coordination sphere of the other reactant and electron flows from reductant to oxidant. Such a mechanism takes place when rapid electron transfer occurs between two substitution inert complexes.

Inner sphere electron transfer reactions

An inner sphere reaction mechanism is one in which the reductant and oxidants share a ligand in their inner or primary coordination sphere electron being transferred across the bridging group.

Multi equivalent reactions

Oxidizing agent like Cr (VI) and Mn (VII) undergo net changes of 3 and 5 units in oxidation numbers respectively during their reactions in acidic solution. Generally these reactions occur by one or two electrons steps, with the necessary intervention of unstable intermediate oxidation states of chromium or manganese. The reactions of Cr(V) with transition metal complexes generally proceed by sequential one-electron step, but with post transition metal ions and with non-metallic compounds, two-electron steps appear to be preferred.

Electron transfer reactions are found to be governed by two classical principles.

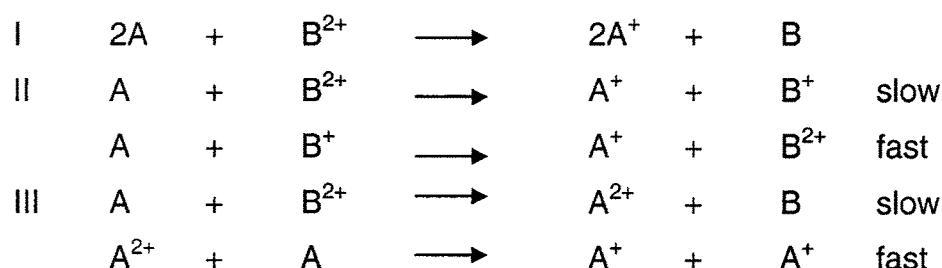
- (a) Michaelis principle of compulsory univalent oxidation steps.

(b) Shaffer's principle of equivalent changes.

(a) The Michaelis principle [1] of "compulsory univalent oxidation steps". This hypothesis involves the principle that oxidation-reduction takes place in one or more successive single electron transfer steps. This principle evolved from the consideration of a restricted field of redox reactions, of which the oxidation of hydroquinones to quinones through semiquinone intermediate is typical and is now generally recognized as being without universal validity. Apart from reactions involving metal ions many two-equivalent redox reactions are now known to proceed in one step through the transfer of a hydride ion or an oxygen atom.

e.g. $(\text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^-)[2,3]$.

(b) Shaffer's principle [4,5] of "equivalence change" refers to the observation that non-complementary reactions (i.e. those between 1-equivalent oxidants and 2-equivalent reductant or vice versa) are often slow compared with complementary ones (those between 1-equivalent reductant and 1-equivalent oxidants or between 2-equivalent reductant and 2-equivalent oxidants). Examples are the slow reduction of Ti^{3+} by Fe^{2+} or Ce^{4+} by Ti^+ compared with the rapid reduction of Ti^{3+} by Sn^{2+} and of Ce^{4+} by Fe^{2+} . This can be interpreted in terms of the following types of mechanisms for a typical non-complementary reaction in which 'A' is oxidized to 'A⁺' and 'B²⁺' is reduced to 'B':

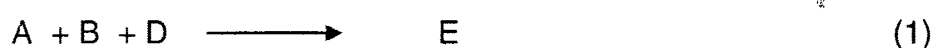


The first of these mechanisms is expected to be slow because it involves a termolecular step and than last two because they involve the formation of unstable intermediates (B^+ or A^{2+}).

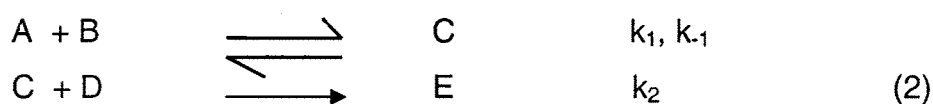
One of the implications of the comparison on which the principle of equivalence change is that reactions between 2-equivalent reductatns and 2-equivalent oxidants occur by concerted 2-equivalent step. This may well be the case for reactions [6] such as the $\text{Ti}^{\text{I}}-\text{Ti}^{\text{III}}$ exchange, $\text{Au}^{\text{III}}-\text{Ti}^{\text{I}}$ reaction and $\text{Au}^{\text{I}}-\text{S}_2\text{O}_8^{2-}$ reaction.

The observation expressed by Shaffer, for non-complementary reactions is based on the law of probability of termolecular mechanisms as one possibility or the formation of unstable valence states as the other possibility [7]. Another expected feature of these reactions will be the frequent occurrence of catalysis since the normal paths will be slow. Reaction rate is of great practical interest in both laboratory and industries. No reaction that takes years to become sensibly complete is particularly useful in making its product but reactions that are complete in fraction of a second include hazardous explosions. It is necessary to understand the factors controlling the rate at least to some extent before a reaction become useful on almost any scale. The rate laws as well as individual rate constants are very useful when complexity is known or suspected. This connection between rate and mechanism can be illustrated with following example. It must be recognized however, that side reactions very often exist. Some times side products are valuable clue to the mechanism of the main reaction but sometimes they form unavoidable but unrelated process.

Consider the following observable reaction,



Which may be composed of the more probable bimolecular simple steps.



If the substance C does not accumulate to significant extent we can write appropriate equation.

$$k_1[A][B] \cong k_{-1}[C] + k_2[C][D] \quad (3)$$

This can be solved for [C] and the values used to express the desired reaction rate.

$$\begin{aligned} d(E) / dt &= k_2 [C] [D] \\ &= k_2 [D] (k_1[A] [B] / k_{-1} + k_2 [D]) \\ &= k_1[A] [B] / (1 + k_{-1} / k_2 [D]) \end{aligned} \quad (4)$$

This equation which contains all three-rate constants is typical equation for complex systems that do not follow simple first or second order rate laws. An observed rate constant can yield, from equation (4), a value of k_1 and only the ratio k_2/k_{-1} but not the individual values of these rate constants. This limitation

is related to the assumption that $[C]$ is small. The evaluation of individual constants and determination of the small steady state concentration of the intermediate, C are different manifestations of the same problem.

It may often happen that the value of rate constants and concentrations are such that a complex rate expression will reduce to simpler form. In case of (4) if either of the two terms in the denominator predominates, a much simpler expression results. If k_{-1} predominates i.e., $k_{-1} \gg k_2 [D]$ and we recall that $k_1/k_{-1} = K$, the equilibrium constant for the reaction (2) then equation (4) reduces as,

$$d[E]/dt = k_2 K [A] [B] [D] \quad (5)$$

The expression (5) containing only the rate constants k_2 for the second step. This step then be called a rate determining step and reaction (3) is called a pre-equilibrium unless other information is available, which might be some estimate of k_1 in the absence of reagent D , only the product $k_2 K$ is experimentally determinable. If the second term in the denominator predominates, $k_2 [D] \gg k_{-1}$, then equation (4) reduces to (6) and the first step is rate determining and only k_1 can be determined.

$$d[E] / dt = k_1 [A] [B] \quad (6)$$

This situation can be used to illustrate some of the connection between rate and mechanism. First, if the experimental rate law is (4), we know that there is more than one step, since one step irreversible reaction require only one rate constant to describe the rate and equation (4) has two experimentally distinct rate constants k_1 and k_{-1}/k_2 , if (6) is the rate law it also indicates a complex reaction. Since, the product contains the elements of D , but $[D]$ does not appear in the rate law and therefore the molecule D must be incorporated in the later step, demonstrating the complexity. The limiting form of (5) does not prove complexity although the variety of termolecular reactions strongly suggest, does not rigorously demonstrate, complexity for any kinetically third order reaction. The problem is general, whenever the experimental rate law is of the form predicted by law of mass action for the overall stoichiometric reaction (and order is three or less), the rate law alone will not distinguish between simple and complex mechanisms. We are then forced to look for other evidence of complexity usually by studying the kinetics and products of

analogous reactions and by looking more carefully at structural reactions revealed, for example by stereo chemical or isotopic labeling methods.

Mention should be made of an often stated and often misunderstood principle. A proposed mechanism can be equivocally disproved but never proved. This statement is entirely true but the emphasis on reaction mechanism is misplaced. A reaction mechanism is only one of many models used by the scientists to try to understand and predict experimental results. None of these models are ever 'proved' at best their utility and applicability is extended. At the other extreme a model is disproved or perhaps better discarded when necessary consequence of that model differs essentially from that found experimentally. Thus, the study of mechanism is subject of some restrictions as that of any other area of science and the fact that we often read about a disapproved mechanism gives us encouragement that we are working in an active, growing field rather than a relatively fossilized area where the models have been subject to many decades of scrutiny and thus very seldom questioned.

Oxidation-reduction in organic reactions

The oxidation reduction concepts, however, are not so clearly applicable in organic chemistry, for when carbon compounds are oxidized their components atoms are very seldom deprived of their surrounding complete electron shells. Covalent bond fission is essential feature of an organic reactions and it can be affected by two different pathways, viz., homolytic reactions in which electron pairs are symmetrically disturbed and heterolytic reactions in which electron pairs are transferred from one molecule to another as an undivided entity. Electron removal by these two pathways has clearly distinguishable characteristics.

In homolytic oxidations electrons are removed singly from organic molecules by an active atom such as chlorine, or by active free radicals. Though molecules containing unshared electrons can be oxidized in this way, homolytic oxidation usually involve the removal of an organic molecule of one electron together with hydrogen atom.

Heterolytic oxidation involves the attack on organic compounds of electrophilic reagents, which can by a single process gain control of a further electron pair. Heterolytic oxidation therefore attack the exposed electron pairs

of atom such as oxygen, nitrogen, sulphur or the loosely held electrons of olefins, rather than sigma electron pairs of C-H, O-H, or N-H bonds. Again heterolytic reactions yields molecular or ionic products in one or at least two consecutive stages and very seldom lead to chain reactions. They usually require higher activation energy than homolytic reactions and so tends to be slower processes. When heterolytic reactions are subjected to catalysis, the mechanism of catalysis is largely different from the catalysis involved in the case of homolytic reactions.

Oxidation reaction Involving Trace Metal ions as catalyst

Many transition metal ions such as Ag(I), Mn(II), Cu(II) and complex compounds of Ru(III), Rh(III), Ru(VIII), Ir(II) etc. catalyses a number of redox processes. The catalytic activity is generally due to (a) Exist in more than one oxidation state (b) Form complexes with organic compounds (c) Change their coordination number.

The redox reactions though thermodynamically favorable, are slow because (a) The difficulty in forming a precursor complex between the oxidants and the substrate (b) The symmetry prohibition and (c) Slowness of decomposition of the successor complex formed. Thus substrates like acetic acid and monohydric alcohols that are not oxidized by certain oxidant, get oxidized easily in presence of catalyst.

A metal ions with properties like, the mean value of redox potential is around 0.8 to 1.0 V, the presence of number of vacant d-orbitals acts as good catalysts for redox process.

Working rules for interpretation [8] of rate laws: -

- 1 A multiple term rate law indicates that two or more transition states of different composition are involved in parallel, in the reaction.
- 2 With certain exceptions the rate law indicates the composition and electric charge of transition state. It reports in its numerator all the molecules and ions that must be assembled to form the rate limiting transition state and its denominator the species that are discarded from that assemblage before that transition state is formed.
- 3 If a concentration term appears in the denominator, there is a mobile equilibrium preceding the rate-limiting step that is a prior equilibrium.

- 4 If the concentration term appears in the rate law with non-integral exponent, there is prior equilibrium.
- 5 The summation of terms in the denominator may indicate either a change in the rate-limiting step or that the substrate is split substantially between two forms in a prior equilibrium.
- 6 The rate law itself cannot give any information about the mechanism beyond the rate limiting transition state.
- 7 The rate law itself indicates nothing about the structure or the order of assembly of transition state.
- 8 The rate law cannot give any information about the mechanism of equilibrium step preceding the rate-limiting step.
- 9 The stoichiometric coefficient of a reactant in the balanced equation is greater than the power of its concentration in the rate law, there is at least one step following the rate-limiting step.

Effect of temperature on rate of reaction: -

The variation of reaction rate with temperature is usually expressed as Arrhenius equation, which is its integrated form as

$$k = A e^{-E/RT} \quad (7)$$

$$\ln k = \ln A - E / RT \quad (8)$$

$$\log k = \log A - E / 2.303RT \quad (9)$$

The equation is in accordance with empirical fact that for most of reactions plot of $\log k$ versus $1 / T$ is a straight line and slope is $-E / 2.303RT$, E is calculated in this way is called Arrhenius activation energy.

Very careful studies have shown that Arrhenius energy of activation is not completely independent of temperature as given in equation (7). Modified Arrhenius equation of the type

$$k = B T^n \exp (- E / RT) \quad (10)$$

Where n has the particular value depending on the kind of theory and reaction carried. According to transition state theory,

$$k = (kT / h) \exp (-\Delta G^\# / RT) \quad (11)$$

$$k = (kT / h) \exp (-\Delta H^\# / RT) \exp (-\Delta S^\# / R) \quad (12)$$

This has same mathematical form as (10) if $n=1$, $\Delta G^\#$, $\Delta H^\#$ and $\Delta S^\#$ are respectively free energy, the enthalpy and entropy of activation. Most solution

kineticists analyze rate constant into temperature dependent and independent parts in terms of ΔH^\ddagger and ΔS^\ddagger respectively of (12). Equation (12) can be expressed as

$$\ln k = \ln (k / h) + \ln T - \Delta H^\ddagger / RT - \Delta S^\ddagger / R \quad (13)$$

Differentiating

$$d(\ln k) / dT = 1 / T + \Delta H^\ddagger / RT^2 = (RT + \Delta H^\ddagger) / RT^2$$

Comparison with differential form of Arrhenius equation

$$d(\ln k) / dT = E / RT^2$$

This shows that

$$E = (RT + \Delta H^\ddagger) \quad (14)$$

It follows that H^\ddagger can be obtained from Arrhenius activation energy by subtracting RT , in the vicinity of room temperature RT is about 600 cal. The uncertainty in energy of activation is often of this magnitude. Thus there is relatively little difference between Arrhenius activation energy E and ΔH^\ddagger .

Although ΔH^\ddagger is usually reckoned from Arrhenius activation energy by means of equation (14), a more fastidious evaluation makes use of rearranged form of (13). A plot of $\ln (k / T)$ versus $(1 / T)$ has slope $-\Delta H^\ddagger / R$. ΔH^\ddagger is 1.987 times the slope for most solution kinetic data there is little practical difference between two methods of calculation. With reference to (14), (12) can be rewritten as

$$k = (ekT / h) \exp (-E / RT) \exp (\Delta S^\ddagger / R)$$

Taking common logarithms

$$\log k = 2.303 \log (ek / h) + 2.303 \log T - E / RT + \Delta S^\ddagger / R \quad (15)$$

The value of k is 1.3803×10^{-16} erg / deg and h is 6.623×10^{-27} erg-sec / molecule therefore ek / h is 5.664×10^{10} deg⁻¹ sec⁻¹. Hence equation (15) becomes,

$$\begin{aligned} (\Delta S / 2.303R) &= \log k - \log (ek / h) - \log T + (E / 2.303 RT) \\ \Delta S^\ddagger / 4.576 &= \log k - 10.573 - \log T + E / 4.576 T \end{aligned} \quad (16)$$

ΔS^\ddagger has the units of calories per degree per mole, sometimes referred to as entropy unit ' eu ' or in the new usage as gibb's per mole[9]. To calculate ΔS^\ddagger by (16) one inserts a good experimental rate constant, the corresponding

absolute temperature and E , the Arrhenius activation energy calculated as described above.

The enthalpy of activation can be calculated with equal validity from, for example the pseudo-first-order or second-order rate constants for a reaction. This is because it is derived from the rate of change with temperature and not from absolute values of rate constants. In general a different value of ΔS^\ddagger is reckoned from pseudo-first-order rate constant for a reaction than from second-order rate constants for the same reaction. The rate constant used for calculation of ΔS^\ddagger should pertain to the correct rate law as determined experimentally.

It is useful for the kineticist to keep in mind the amount of change in ΔH^\ddagger and in ΔS^\ddagger that bring about ten-fold change in reaction rate. These may be reckoned from (13). A change of ΔS^\ddagger of 4.6 gibb's per mole causes tenfold change in the rate if ΔH^\ddagger remains constant. If ΔS^\ddagger remain constant the rate changes by factor of ten for a change in ΔH^\ddagger of $2.3RT$ which works out as 1.36 kcal per mole at 25°C or 1.71 kcal per mole at 100°C .

Effect of ions on the rate: -

The rates of redox reactions of complex ions are very sensitive to the presence of other ions in the solution. Usually, added anions have the greatest influence on the reaction of two cations with each other and added cations influence the rate of the reaction between two anions. Large effects of anions on the rate are usually anticipated to the formation of bridged species if labile complexes are involved.

In the redox reactions between two cations, if the reducing agents complexed first, it will be more stabilized in the oxidized form and hence the reaction is speeded up in presence of anion. Also a negative ion should enable two ions approach each other more easily. This will be more effective if the negative ion is between the two cations in the transition State.

If the oxidizing agent is complexed first, the anion may stabilize it and slow down its rate of reaction. For example, the rates of reactions of Ce^{4+} oxidations are reduced strongly by forming sulfate complexes [10] in presence of sulfate. This shows, in agreement with theory, that coulombic repulsions between the reactants do not play a dominant role. The conclusion to be

drawn is not that electrostatic factors do not exist but that other factors (reorganization energies) are of greater importance. Some significant effects of chloride ion are particularly noticeable in redox reactions, the redox reactions, in which the reductant is able to form complexes with chloride, are found to be accelerated by chloride ion. Among the reductant that can form complexes with chloride are Tl(I), Sn(II) and Sb(III). Presumably because of the complex formation, the oxidation potentials of such redox systems are changed. The oxidation potentials of the complexes Hg(II)/Hg(I), Fe(II)/Fe(II) and Tl(III)/Tl(I) are decreased considerably in presence of chloride ion [11-13]

Influence of solvent dielectric constant

A simple but useful treatment of the influence of the solvent on the rates of reactions between ions is based on electrostatic theory, the solvent being treated as a continuum having a dielectric constant ϵ . This treatment represents a gross oversimplification, but it has proved surprisingly useful because it leads to conclusions that are semiquantitatively correct.

The charges on ions are $z_A e$ and $z_B e$, where z_A and z_B [which may be positive or negative] are the charge numbers and e is the elementary charge (1.602×10^{-19}). Initially, the ions are at infinite distance apart. It is considered that ions are remained to be intact as they approach one another and forms activated complex. The center of ions in activated complex are separated by distance d_{AB} , this particular model is called as double- sphere model.

When a distance x separates the ions, the force acting between them, according to Coulomb's law is,

$$f = z_A z_B e^2 / 4\pi\epsilon_0 \epsilon x^2 \quad (17)$$

Where ϵ is the dielectric constant and ϵ_0 is permittivity of a vacuum ($8.854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2}$). The work done on the system in moving them together a distance dx is

$$dw = (-z_A z_B e^2 / 4\pi\epsilon_0 \epsilon x^2) dx \quad (18)$$

(The negative sign appears because x decreases by dx). The work done on the system in moving the ions calculated by integrating equation (18) within limit $x=\infty$ to $x = d_{AB}$ as,

$$W = z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB} \quad (19)$$

This work is positive if the ionic charges are of the same sign; if they are different, it is negative. This work w is the electrostatic contribution to the Gibbs energy of activation when two ions form an activated complex. Multiplication by the Avogadro constant N gives the molar quantity,

$$\Delta^\ddagger G^\circ_{es} = N z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB} \quad (20)$$

There is also a nonelectrostatic contribution $\Delta^\ddagger G^\circ_{nes}$, and the molar Gibbs energy of activation is thus

$$\Delta^\ddagger G^\circ = \Delta^\ddagger G^\circ_{nes} + (N z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB}) \quad (22)$$

And equation, which relates K to $\Delta^\ddagger G$,

$$K = \frac{kT}{h} e^{-\Delta^\ddagger G^\circ / RT} \quad (23)$$

Introduction of eq. (22) into (23),

$$K = \frac{kT}{h} e^{-\Delta^\ddagger G^\circ / RT} = \frac{kT}{h} e^{-\Delta^\ddagger G^\circ_{nes} / RT} e^{(-z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB} kT)} \quad (24)$$

Since $R/N=k$. Taking natural logarithms, we obtain

$$\ln k = \ln (kT/h) - (\Delta^\ddagger G^\circ_{nes} / RT) - (z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB} kT) \quad (25)$$

This may be written as,

$$\ln k = \ln k_0 - (z_A z_B e^2 / 4\pi\epsilon_0 \epsilon d_{AB} kT) \quad (26)$$

Where k_0 is the value of k in a medium of infinite dielectric constant, in which the electrostatic forces becomes zero. An equation of this form was first obtained by Scatchard[14]. whose method of derivation was quite different. According to this equation, the logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant. This relationship has been tested many times, particularly by causing a reaction to occur in a series of mixed solvents of varying dielectric constant. On the whole, the relationship is obeyed to a reasonable approximation, although there are usually deviations at low dielectric constant.

Catalysis:

The word catalysis (in Greek meaning *to annul*) introduced by Berzelius, is the speed up of the rate of a chemical reaction by means of a substance, called a Catalyst, which remains unchanged chemically in the overall reaction. The opposite of a catalyst is an inhibitor, which slow down

the rate of a chemical reaction. However, a catalyst cannot make a thermodynamically unfavorable reaction proceed. Rather, it can only speed up a reaction that is already thermodynamically favorable. Such a reaction in the absence of a catalyst would proceed, even without the catalyst, although perhaps too slowly to be observed or of use in a given context.

For example, a solution of hydrogen peroxide decomposes very slowly at ordinary temperatures, but in presence of platinum decomposition rate is much greater, even concentration hydrogen peroxide is low. Human body also contains thousands of catalysts, generally called as enzymes, which are more specific and catalyses of reaction essential for life.

So catalysts can provide a different path for reaction with lower activation energy as shown in figure1.

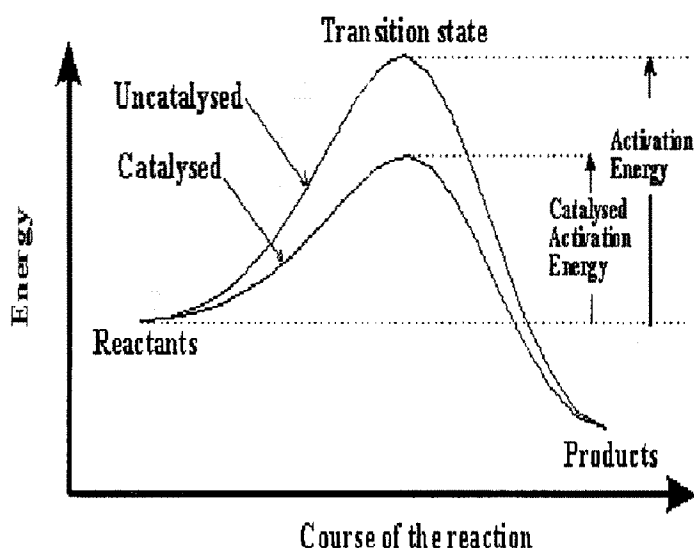


figure1.

Homogeneous catalysis:

The reactions in which catalyst and all the participants (reactants and products) are in same state called as homogeneous catalysis. Examples of such reactions are esterification and saponification of esters catalyzed by acids, the decomposition of hydrogen peroxide under the action of ions in the solutions, the inversion of saccharose and the mutarotation of glucose in presence of acids and bases.

Heterogeneous catalysis:

The reactions in which catalyst, reactants and products are in different phases, called as heterogeneous catalysis, and reaction takes place in the boundary layer i. e. at the phase interface. The heterogeneous systems are generally combinations of a solid with a liquid or a gaseous phase that's why the transportation of substance from the bulk of liquid or gas to the solid surface is important for heterogeneous processes, for examples the hydrogenation of carbon -carbon double bonds, in these reactions hydrogen in gaseous state and catalysts Pt, Pd, Ni, Cu in solid state.

Catalysis by Polyoxometalates:

The chemistry of Polyoxometalates (POM: heteropoly acids and heteropoly salt) started by Berzelius back in 1826, have many applications in field like catalysis, material sciences, structural biology and medicine. In last few decades several catalytic processes involving POMs in both homogeneous and heterogeneous modes have been commercialized.

Polyoxometalates are polyoxoanions of the early transition elements, especially vanadium, molybdenum, tungsten and belongs to a large class of nano-sized metal oxygen cluster anions with main two types isopolyanions and heteropolyanions, represented by the general formula $[M_mO_y]^{n-}$ and $[X_xM_mO_r]^{q-}$ (X m) where M is the addenda atom and X is the heteroatom. The most common addenda atoms are molybdenum and tungsten (Mo/W) less frequently vanadium and some other metals or mixture of elements in their highest oxidation states. A much broader range of elements acts as heteroatoms; as such atoms or almost all elements in periodic table can be incorporated in the heteropolyanions.

There are number of applications of POM's, catalysis is by far the most important[15-17]. POM's also useful for clean synthesis of fine and specialty chemicals consequently much current research is centered on various aspects of catalysis by polyoxometalates[18].

Heteropoly compounds are used as catalysts due to their following properties.

1. Different chemical and electrochemical properties.
2. Multifunctionality and structural mobility.
3. Very strong Bronsted Acidity,

4. Efficient oxidants, exhibiting fast reversible multielectron redox transformations under mild conditions.
5. Their acid-base and redox properties can be varied over a wide range by changing the chemical composition.
6. Discrete ionic structural units as Heteropoly anions and counter cations, unlike the network structure of Zeolite, metal alkoxides etc. The structure is frequently preserved upon and it manifest itself to exhibit extremely high proton mobility and a "pseudo liquid phase".
7. Due to very high stability in solid state, heteropoly compounds are the promising acid, redox and bifunctional (acid/redox) catalysts[19].
8. The catalytic reaction can be performed in homogeneous as well as heterogeneous (gas-solid), liquid-solid and biphasic (liquid-liquid) systems.
9. Heteropoly compounds are frequently used as model systems for fundamental research providing unique opportunity for mechanistic studies at molecular level. At the same time they have become increasingly important for applied catalysis.

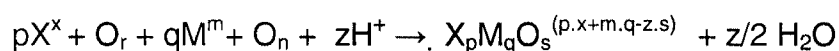
There are more than twenty types of structures, incorporating four to forty metal atoms and from one to nine heteroatoms are known for molybdenum, tungsten, vanadium and niobium heteropolyanions. Some of the commonly known series of heteropolyanions are shown in Table 1.

Table 1: Common Heteropolyacids

X/M	Structure	Formula	Negative charge	X ⁿ⁺
1/12	Keggin (typeA)	XM ₁₂ O ₄₀	8-n	P ⁵⁺ , As ⁵⁺ , Si ⁴⁺ ,
	Silverton (typeB)	XM ₁₂ O ₄₂	8	Ge ⁴⁺ , Ce ⁴⁺ , Th ⁴⁺
1/11	Keggin-Like (lacunary)	XM ₁₁ O ₃₉	12-n	P ⁵⁺ , As ⁵⁺ , Ge ⁴⁺
2/18	Dawson	X ₂ M ₁₈ O ₆₂	6	P ⁵⁺ , As ⁵⁺
1/9	Waugh	XM ₉ O ₃₂	6	Mn ⁴⁺ , Ni ⁴⁺
1/6	Anderson (typeA)	XM ₆ O ₂₄	12-n	Te ⁶⁺ , I ⁷⁺
	Anderson (typeB)	XM ₆ O ₂₄	6-n	Co ³⁺ , Al ³⁺ , Cr ³⁺

M = W⁶⁺, Mo⁶⁺, etc.

The commonest compounds belonging to the 12th series (M:X = 12) are of the greatest importance in catalysis. These Keggin type heteropolyacids are the most stable, more easily available and have been studied in more detail. Heteropolyanions are polymeric oxoanions formed by the condensation of more than two different mononuclear oxoanions in acidic medium as shown in the equation



with M = metal

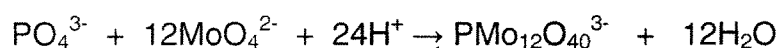
X = hetero-atom

x = valency of hetero-atom

m = valency of the addenda atom

and $s + z/2 = n \cdot q + r \cdot p$ (oxygen balance)

for example,



Although the elements that can function as addenda atoms, M, in heteropoly or isopolyanions, appear to be limited to those with both a favorable combination of ionic radius, charge and the ability to form d-p π M-O bonds and there is no such restriction on the heteroatom X.

Keggin heteropolyoxometalates:

In 1826 Berzelius[20] described that yellow precipitate is produced when ammonium molybdate is added to phosphoric acid and which is now known as ammonium 12- molybdophosphate $(NH_4)_3(PMo_{12}O_{40})_{aq}$. However it was not until the discovery of tungstosilicic acids and their salts by Marginaç[21] in 1862 that the analytical composition of such heteropolyacids was precisely determined. But he did not propose a structure for the above compound which was later correctly analyzed as $SiO_2 \cdot 12WO_3 \cdot 2H_2O$. The first attempts to understand the composition of heteropolyanions were based on Werner's coordination theory. Structure determination for heteropoly compounds was not possible until the arrival of X-ray diffraction techniques. A hypothesis advanced by Miolati[22] in 1908 was adopted and developed by Rosenheim[23]. During the subsequent 25-30 years, Rosenheim was probably the most productive and influential worker in the field of polyanion chemistry. According to the Miolati- Rosenheim (MR) theory heteropoly acids were based on six coordinate hetero atoms with MO_4^{2-} or $M_2O_7^{2-}$ anions as

ligands or bridging groups. Subsequent isolation of salts such as $\text{Cs}_8[\text{Si}(\text{W}_2\text{O}_7)_6]$ and $(\text{CN}_3\text{H}_6)_7[\text{P}(\text{W}_2\text{O}_7)_8] \cdot 12\text{H}_2\text{O}$ laid an early support to MR theory. The first serious criticism of the theory came from Pauling[24] in 1929. While accepting the Rosenheim structure for 6:1 complex, Pauling noted that molybdenum (VI) and tungsten (VI) had crystal radii appropriate for octahedral coordination by oxygen and proposed a structure for the 12:1 complex based on an arrangement of twelve molybdenum (VI) or tungsten (VI) octahedra surrounding a central XO_4 tetrahedra. The resulting formula were written as $\text{H}_4[\text{SiO}_4\text{W}_{12}(\text{OH})_{36}]$, and these predicted the correct (observed) basicities. The structure was ultimately shown to be wrong in detail, since Pauling considered only the corner sharing between the MO_6 octahedra. After four years, Keggin[25] solved the structure of $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$ by X-ray diffraction and showed that the anion was indeed based on WO_6 octahedra units as suggested, but these octahedra were linked by shared edges as well corners. Anions were confirmed shortly afterwards by Bradley and Illingworth's[26] investigation of $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 29\text{H}_2\text{O}$. Structure determination was based on powder photographs.

Anderson Heteropoloxometalates:

The Anderson structure may be described as an isopolyoxometalate containing a crown of six octahedrons sharing edges. The center may be occupied or not. In the chromium-containing compound structure, there are six hydrogen atoms, the positions of which are considered to be the six OH groups bridging the central atom to the molybdenum-containing crown octahedrons. The oxidation state of chromium may be easily deduced from the charge since it is well known that there usually is molybdenum (VI).

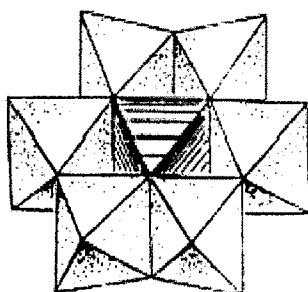


Figure. 1. Structure of the typical Anderson heteropolymolybdate.

The physical and chemical properties of heteropoly compounds are listed below

Heteropolycompounds generally have very high molecular weights ranging over 2000.

Free acids and most salts of heteropolyanions are extraordinarily soluble in water and are often very soluble in a wide range of organic solvents.

The crystalline free acids and salts of heteropolymolybdate and heteropolytungstate anions are almost always highly hydrated.

Many heteropoly compounds are highly colored and the colors ranging through the spectrum and occurring in many shades.

Heteropolytungstates and molybdates are strong acids. The acidity is generally determined by dissociation constants and the Hammett acidity function.

Thermal stability of the free acids of the heteropolymolybdates and heteropolytungstates is quite high.

The transition metal substituted compounds are active as oxidation catalysts with a wide range of organic / inorganic substrates and are operable with a wide variety of oxygen donors in various solvents[27-29]. Oxidation catalysis by polyoxometalates especially by the Keggin type heteropoly oxometalates is a rapidly expanding area due to their unusual versatility and compatibility with environmentally friendly conditions (with oxidants like O₂ and H₂O₂) and operations. Substitution of the addenda atom/s by either d electron transition metal or other addenda atoms increases the oxidation ability of the heteropolyoxometalate.

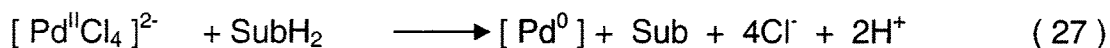
Oxidation of Organic Electron donors by POM Anions :

The polyoxometalate of the Keggin structure have been used as oxidation catalyst for the oxidation of various organic substrates. Since publication of Chester's work in 1970[30], [Co^{III}W₁₂O₄₀]⁵⁻ and related POM anions have been used as well-defined outer-sphere electron-transfer agents. The oxidation of various organic substrates such as halides [31], amines, alcohols, ketones [32] phenols [33], alkyl aromatics [34], dienes [35], alkanes [36] is reported by various workers. The catalytic oxidation of organic sulfides by vanadomolybdophosphates and oxygen was reported by Kozhevnikov, Matveev and co-workers [37]. Ayoko and Olatunji [38] observed that the rates

of oxidations of thiourea and 1,1,3,3-tetramethyl-2-thiourea is independent of $[H^+]$ ions. The oxidation of aliphatic alcohols by $[Co^{III}W_{12}O_{40}]^{5-}$ at very high ionic strength was investigated by Ayoko and Olatunji [39] over a $[H^+]$ range of from 0.75 to 1.75 mol dm^{-3} . In 1994, Hill studied POM catalyzed oxidations of thioethers, R_2S , by t-butyl hydroperoxide in acetonitrile [40].

Oxidation of Inorganic Electron donors by POM Anions :

Experimental rate laws have been determined for reactions of $[Co^{II}W_{12}O_{40}]^{6-}$ and other POM's with wide variety of inorganic electron donors. In addition numerous examples of homogeneous oxidations catalyzed by multicomponent systems consisting of Pd(II) salts, substrates, vanadomolybdophosphate complexes ($H_{3+n}[PV_nMo_{12-n}O_{40}]^{(3+n)-}$) and oxygen have been reported [41]. Generally, the POM anions play a role analogous to that of Cu salts in the Wacker process. During the catalytic cycle, Pd (II) is reduced by the substrate ($SubH_2$) (equation 27) and the POM anion catalyzes reoxidation of the reduced Pd(II) species. After electron transfer from the reduced-Pd species to the POM anion (equation 28), the resultant heteropolyblue is oxidized by O_2 (equation 29). These reactions sum to the net oxidation of the substrate by O_2 (equation 30).



The kinetics of these multicomponent systems and the effects of specific variables on overall reaction rates have been studied in detail [41]. However, little if any detailed information concerning oxidation of reduced Pd-species by POM anions is available. One reason may be that the reduced Pd-species formed during the catalyst-turnover conditions, usually written as Pd(0) are unstable and poorly defined [41].

The potentially commercially useful POM catalyzed oxidation of hydrogen sulfide to elemental sulfur was first explored using vanadomolybdophosphate complexes, $H_{3+n}[PV_nMo_{12-n}O_{40}]^{(3+n)-}$, where $n = 1$ to 6. In later studies, oxidations of hydrogen sulfide by well-defined heteropolytungstate anions were investigated. Oxidations of inorganic

substrates by various POM anions and their corresponding rate laws have been included in a review by M. Sadakane and E. Steckha [42].

Present Work:

Heteropolyoxometalate have received particular attention mainly because of their use as homogeneous, heterogeneous, redox and acid catalysis. The nature of these heteropolyoxoanions can be varied by changing the co-coordinated oxoanion or by the central transition metal cation. The properties that can be altered by such variation leads to change in redox potential and solubility in organic solvents which are required for their use in catalytic applications. On the other hand, oxidations by peroxocompounds like hydrogen peroxide, peroxydisulphate, peroxomonosulphate, perborate and bromates are slow and require the presence of a catalyst. The present investigation is combination of the oxidizing power of the bromate and catalyzing properties of the heteropolyoxometalate to oxidize organic hydrazides.

Chapter-I includes literature survey and detailed procedure for the treatment of kinetic data to arrive at mechanism of reactions. The chapter also includes survey of polyoxometalate-mediated reactions and their mechanism.

Chapter-II covers experimental technique of present work i.e. experimental conditions, preparation of standard solutions and their standardization, catalyst preparation, characterization, with example run.

In chapter-III the reaction between benzoic acid hydrazide and potassium bromate catalyzed by Anderson type hexamolybdochromate(III) under pseudo-first-order condition keeping large excess of hydrazide concentration over that of the oxidant was studied. The reaction is accelerated by the hydrogen ion concentration due to the involvement of the prior protonation equilibria of both catalyst and the hydrazide. The protonated forms of the catalyst and the substrate are the active species in the reaction. The initiation of the reaction occurs through oxidation of the catalyst $\text{H}[\text{CrMo}_6\text{O}_{24}\text{H}_6]^{2-}$ to $\text{H}[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{2-}$ which then reacts with the hydrazide to give products without any intervention of free radicals. The oxidized form of the catalyst $\text{H}[\text{O}=\text{Cr}^{\text{V}}\text{Mo}_6\text{O}_{24}\text{H}_6]^{2-}$ was isolated and characterized by its FTIR spectra. The rate of the reaction also increases with increase in ionic strength and the decrease in the relative permittivity of the medium. Along with the

effect of ionic strength and relative permittivity the activation parameters determined also support the mechanism. The detailed mechanism and the rate equation are proposed for the reaction.

In chapter IV deals with oxidation of benzoic acid hydrazide by potassium bromate catalyzed by octamolybdomanganate (II) under pseudo-first-order condition keeping benzoic acid hydrazide concentration excess in aqueous acidic medium. The order with respect to both substrate and oxidant was unity. The accelerating effect of hydrogen ion concentration is due to the prior protonation of the substrate, benzoic acid hydrazide. This protonated form of substrate is the active species during the reaction. Also the order of more than unity in catalyst concentration is due to autocatalytic nature of its oxidation by bromate as reported in earlier studies. Hence the protonated form of the catalyst and the bromate ion are also found to be active species and the initiation of the reaction takes place by the oxidation of protonated catalyst, $H_4[Mn^{II}Mo_8O_{27}]$, to its higher oxidation state $H_2[Mn^{IV}Mo_8O_{27}]$. The oxidized form of the catalyst $H_2[Mn^{IV}Mo_8O_{27}]$ forms a complex with the free catalyst in a prior equilibria. The oxidized form of the catalyst oxidize the substrate in slow step to give the product. The ionic strength effect, solvent polarity effect and determined activation parameters support the proposed mechanism for the reaction. ✓

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