ગુજરાત રાજ્યના શિક્ષણવિભાગના પત્ર–ક્રમાંક
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CHEMISTRY

Standard 12

(Semester IV)

PLEDGE

India is my country.
All Indians are my brothers and sisters.
I love my country and I am proud of its rich and varied heritage.
I shall always strive to be worthy of it.
I shall respect my parents, teachers and all my elders and treat everyone with courtesy.
I pledge my devotion to my country and its people.
My happiness lies in their well-being and prosperity.

રાજ્ય સરકારની વિનામૂલ્યે યોજના હેઠળનું પુસ્તક

ગુજરાત રાજ્ય શાળા પાઠ્યપુસ્તક મંડળ
तमसो मा ज्योतिर्गमय

Gujarat State Board of School Textbooks
'Vidyayan', Sector 10-A, Gandhinagar-382010

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PREFACE

The Gujarat State Secondary and Higher Secondary Education Board has prepared new syllabi in accordance with the new national syllabi prepared by N.C.E.R.T. based on N.C.F.-2005 and core-curriculum. These syllabi are sanctioned by the Government of Gujarat.

It is a pleasure for the Gujarat State Board of School Textbooks to present before the students this textbook of **Chemistry** for **Standard 12 (Semester IV)** prepared according to the new syllabus.

Before publishing the textbook, its manuscript has been fully reviewed by experts and teachers teaching at this level. Following the suggestions given by teachers and experts, we have made necessary changes in the manuscript before publishing the textbook.

The Board has taken special care to ensure that this textbook can prove to be interesting, useful and free from errors However, we welcome any suggestions, from people interested in education, to improve the quality of the textbook.

Dr. Bharat Pandit	**Sujit Gulati** IAS
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Date : 05-08-2015	Gandhinagar

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FUNDAMENTAL DUTIES

It shall be the duty of every citizen of India :

(a) to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;

(b) to cherish and follow the noble ideals which inspired our national struggle for freedom;

(c) to uphold and protect the sovereignty, unity and integrity of India;

(d) to defend the country and render national service when called upon to do so;

(e) to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;

(f) to value and preserve the rich heritage of our composite culture;

(g) to protect and improve the natural environment including forests, lakes, rivers and wide life, and to have compassion for living creatures;

(h) to develop the scientific temper, humanism and the spirit of inquiry and reform;

(i) to safeguard public property and to abjure violence;

(j) to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement.

(k) to provide opportunities for education by the parent or the guardian, to his child, or a ward between the age of 6-14 years as the case may be.

* Constitution of India : Section 51-A

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About This Textbook...

It has been decided by the Central Goverment of India, that only one competitive examination will be conducted at national level for the study of higher education. As a result of this planning, the formation of Core-Currilulum took place. The purpose of this was that there must be same syllabus in the subjects of Science stream for national competitive examination. The same syllabus can be possible if the book is prepared according to N.C.F.-2005.

A new syllabus in Chemistry was prepared by experts and teachers on the basis of core-curriculum and N.C.F.-2005, by the Gujarat State Secondary and Higher Secondary Education Board.

'Education Without Burden', an initiative undertaken by the Government of Gujarat will prove beneficial to students in semester system. Gujarat State Board of School Textbooks made positive arrangements for students to have advantage of the expertise of the teachers from Schools and Colleges having their own teaching experience, and experience as paper setters for GUJCET examination as well as Higher Secondary Examination Board. The writers associated with the writing of this book have written units which are reviewed by other teachers, experts and reviewers to make this book useful at national level by carrying out proper additions and alterations.

One important matter has been added. Changes have been incorporated in different words in this new book viz. atomic mass instead of atomic weight, molecular mass instead of molecular weight, enthalpy instead of energy, bar instead of atmosphere as well use of unit pascal. The word like reactivity will appear to be unknown but its inclusion in the modern study was found to be essential. In addition to this, in this existing book, instead of the nomenclature, units etc. the modern SI units, method of nomenclature etc. as in NCERT book are used in the text. This will appear somewhat new but being very useful in competitive examinations and to meet the new challanges and to obtain achievement in present education system, it should be accepted.

Competitive examinations like JEE and NEET are conducted at the national level. SI units are found in question papers. In our GUJCET examination, as SI units were not used, students found it difficult at these competitive examinations but we are sure that the students will shine out bringing glory to the state at national level.

The subject content, presentation, examples are presented in this book in such a way that the students will find easy to understand. Although attempts have been made to ensure quality at each level, we welcome suggestions from teachers and well-wishers. The suggestions, if found relevant, will be incorporated in the revised edition.

'To send proper suggestion is your work and to implement it is ours.' By keeping this goal, the students of Gujarat State may obtain success at national level. We expect you to join us in this pursuit of excellence.

- Authors

UNIT

1

Chemical Kinetics

1.1 Introduction

The chemist tries to find out the following things for any chemical reaction : (i) The feasibility of the reaction which can be predicted on the basis of thermodynamics (As you know that the value of change in free energy must be less than zero i.e. it should be negative and the change in total entropy of the system and surrounding should be positive). (ii) It is necessary for him or her to study the equilibrium of the reaction so as to know to which extent the reaction will be completed (As you know the value of the equilibium constant K should be more than 1). (iii) the rate of chemical reaction i.e. the time required for the reaction to reach to equilibrium (As you know that the reaction can be very slow, slow or fast).

We shall study chemical kinetics in this unit, taking into consideration all these three points. The word kinetics is derived from original Greek word **'Kinesis'** which means velocity or movement.

In industrial field as well as in everyday life, attempts have been made so that the reaction may result. The limitation of thermodynamics is that it does not provide information about the time in which the reaction will be completed. Spontaneous or reaction occurring on its own are completed in as less as possible time. And the equilibrium constants of such reactions are very high as well as the values of change in free energy is as high as possible but negative. Nitrogen and oxygen are present together in the air, from a very long time, even then they do not react. But, under certain circumstances, viz. during the lightening in the sky, both of them combine and form nitric oxide. Thus, the reaction is extremely slow under normal condition. Milk kept in the refrigerator at low temperature does not get spoiled because the biological reaction in it becomes very slow. Thus the rate of reaction like spoilage of milk can be decreased by decreasing temperature and so more time will be required to complete the reaction that is, the milk remains fresh for long time. The liquid or gaseous fuel burns faster than the solid fuel. To cook food, high temperature is required i.e. chemical phenomenon or a reaction is slow at lower temperature but with increase in temperature it becomes very fast. The reactions can be divided into three parts regarding the completion of reaction : (1) very slow reaction, e.g. the radiations emitted from uranium, (2) slow reaction e.g., to carry out reaction by combining dinitrogen and dihydrogen under certain conditions, (3) very fast reaction e.g., the reaction between sodium hydroxide and hydrochloric acid which is completed in only 1 nanosecond (10^{-9} sec.). It is difficult to study very slow reactions. Similary the human being and the apparatus become incapable to measure very fast or instantaneous reaction. Hence, we shall study only slow reactions in this unit.

As studied in chemical equilibrium the reaction occurs both in forward and reverse directions. Suppose, the rate of forward reaction is shown as V_f and the rate of reverse reaction as V_r, then there are three possibilities (1) $V_f > V_r$. i.e. the rate of forward reaction is more than that of reverse reaction. Hence more product will be obtained i.e. more reactant will react. (2) $V_f < V_r$ i.e. the rate of forward reaction is less than that of reverse reaction, less product will be obtained and less amount of reactant will undergo reaction. (3) $V_f = V_r$. If the rates of forward and reverse reactions are same the concentrations of products and reactants will be constant, i.e. equilibrium will be obtained. Thus the rate of reaction shows in which direction the reaction will occur but what will be the proportion (quantity) of the product can not be known. For this, thermodynamics is required. Thus chemical kinetics is completely separate from thermodynamics but both of them are supplementary to each other. In industrial field, the combination of these two is essential and useful.

In chemical kinetics, the rate of reaction and the factors affecting them are studied. The knowledge of chemical kineties is very important in understanding the factors affecting the rate of reaction and the mechanism of the reaction. If the reaction occurs in more than one steps then the slowest step determines the rate of integrated reaction. Generally the rates of reaction are determined from the changes in concentration of reactants or products in unit time.

1.2 Factors Affecting The Rate of Chemical Reaction

The factors affecting rate of chemical reaction are as follows :

(1) The state of substance and the area of surface : If the reactant is in powder form instead of its solid block form the rate of reaction becomes faster. The surface area of contact increases by changing to powder form and so the reaction becomes fast. e.g. iron powder instead of a piece of iron is a better catalyst and so the reaction becomes faster. The area of the surface becomes more by changing to powder form.

(2) Concentration of solution : If the reaction takes place in solution state the rate of forward reaction increases with increase in concentration of reactants. For practical purpose, it is advisable to keep higher concentration of reactants. This is obvious from **LeChatelier's principle.** In industry, the reactant which is cheaper is taken in more proportion. The stoichiometry plays an important role.

(3) Temperature of system : Generally if the temperature is increased, the rate of reaction increases because kinetic energy and the collision of molecules increase with increase in temperature which becomes helpful in increasing the rate, e.g., sugar added in cold water dissolves faster if the temperature of solution is increased and dissolves completely. At equilibrium stage the increase in temperature is advantageous for an endothermic reaction while for exothermic reaction, decrease in temperature is advantageous. The reason for this is that heat reacts as reactant or product.

(4) Pressure of system : If the reaction is in gaseous phase or state, then the rate of reaction will increase or decrease by change in pressure. The increase in pressure will result in increase or decrease of rate depending on the nature of the reactant and stoichiometry. As studied in chemical equilibrium the increase of pressure in certain reactions decreases the rate, while in certain reactions decrease in pressure increases the rate. It is necessary to note that for a gaseous reaction pressure is considered as concentration of gas. Because the pressure and concentration both are associated with the number of molecules of substance. In the reaction, if the number of moles of gaseous products is more than that of gaseous reactants, the decrease in pressure of system is advantageous i.e. more product will be obtained. But if the number of moles of gaseous products is less than that of gaseous reactants then increase of pressure on the system is advantageous and so more product will be obtained.

(5) Effect of Catalyst : With the use of suitable catalyst, the reaction can be made faster i.e. its rate can be increased. The use of catalyst cannot bring change in the proportion (amount) of products. As it increases the rate of reaction, the reaction will be completed in less time. The reason for this is that the energy of activation decreases. We shall study about this later on in this unit. There is no effect of catalyst on equilibrium because it increases uniformly both the rate of forward reaction as well as rate of reverse reaction. If there is any impurity which tries to decrease the rate of reaction then it is called **catalytic poison.** We shall study this in catalysis.

1.3 Rate of Chemical Reaction

The progress of chemical reaction is studied as a function of measuring concentration of reactants / or products and for gaseous reactions measuring pressure instead of concentration i.e. at some definite intervals of time the concentration of any one of the reactants or products can be measured. It can be assumed from the study of general reactions, the proportion (volume) of reactant or product is taken then there is not much change in the total proportion or the concentration remains almost same or remains constant. For this volume of reactant is taken. During the progress of the reaction it is noted that with increase in time the concentration of reactants will decrease and the concentrations of products will increase. Hence the concentration of reactant or product is determined with suitable method of measurement at definite intervals of time.

Suppose, in a reaction one mole of reactant (R) produces one mole of product (P). In the initial concentration of R and P, the decrease and increase remain same respectively. Only the magnitude will change. If the graph of concentration versus time is plotted then, the graph obtained will be as shown in fig. 1.1

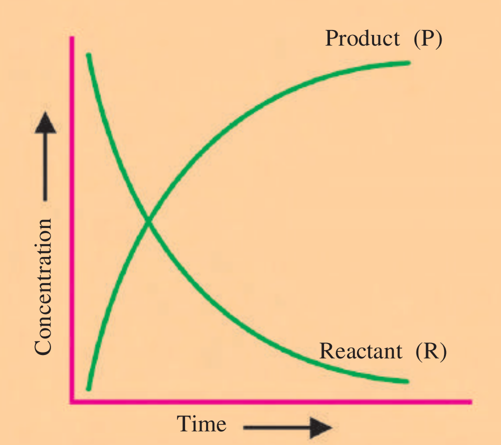


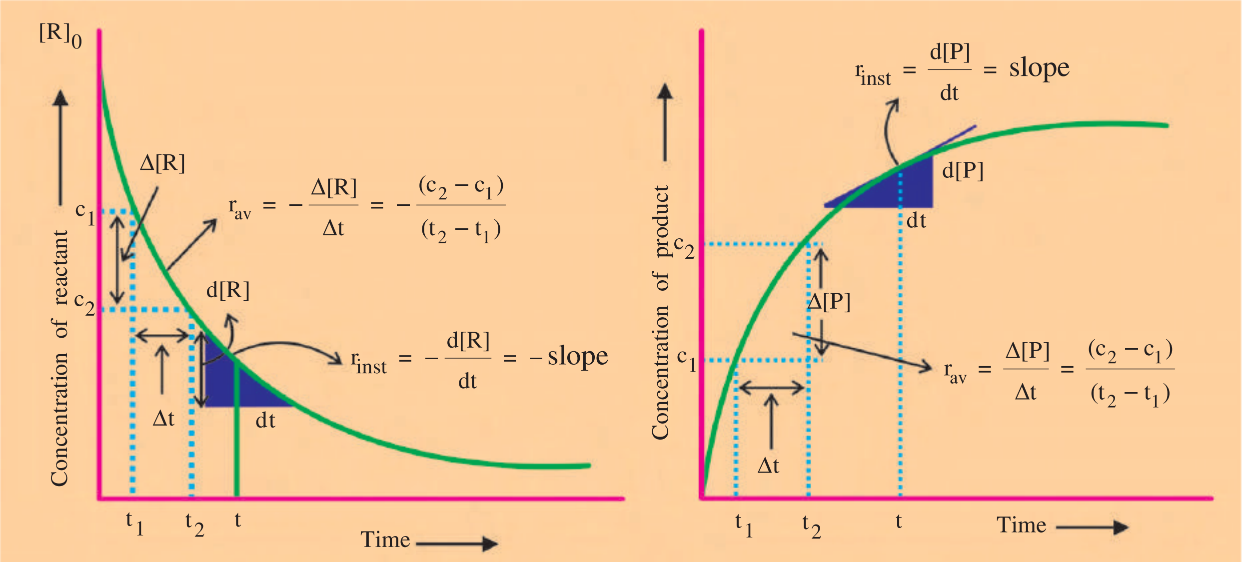
Fig. 1.1 Change in concentration of reactant and product with time

Suppose, at time t_1, the concentrations of reactant and product are $[R]_1$ and $[P]_1$ respectively and at any other time t_2, their concentrations are $[R]_2$ and $[P]_2$ respectivley, then $\Delta t = t_2 - t_1$ and $\Delta[R] = [R]_2 - [R]_1$ and $\Delta[P] = [P]_2 - [P]_1$ where $\Delta[P]$ and $\Delta[R]$ are the changes in concontration of product and reactant respectively. The **average rate** of reaction r_{av} can be expressed as follows :

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t} \qquad ..... (1.1)$$

There is decrease in concentration of reactant and so it is expressed with negative (–) sign and there is increase in concentration of product and so it possesses positive (+) sign which is generally not mentioned. The negative sign is only for mathematical significance. It is apparent from the equation 1.1 that the unit of average rate is concentration time^{-1}, viz. molar second^{-1}, molar minute^{-1}, molar day^{-1}, molar year^{-1}.

To determine the speed of any vehicle, average speed is considered because there is increase and decrease in the speed of the vehicle,. Hence the values determined at any definite time will be different viz. if there is disturbance of traffic then it will be slow and the speed will decrease, but if the road is without traffic, the vehicle will go faster. This is difficult to determine. Hence, all these are integrated and the average is determined and we use it in practice.



[a] [b]

Fig. 1.2 Instantaneous and average rate of reaction

It is clear from the fig 1.2(a) that the rate of reaction decreases rapidly in the begining and becomes less with the increase in time. The instantaneous rate (r_{inst}) changes with the change in instantaneous speed so the instantanteous rate (r_{inst}) is changing. The instantaneous rate (r_{inst}) at any instant of time (t) has definite value. The **instantaneous rate** can be expressed mathematically as follows :

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad \text{OR} \quad r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt} \quad (\text{when } \Delta t \rightarrow 0) \qquad ..... (1.2)$$

To determine **instantaneous rate,** at any time (t) in the graph showing concentration of reactant versus time a tangent (Fig. 1.2) is drawn. The slope of the tangent of the curve is equal to the instantaneous rate at that time.

$$r_{inst} = -\text{ slope (for R)} = -\frac{d[R]}{dt}$$

$$r_{inst} = +\text{slope (for P)} = \frac{d[P]}{dt}$$

Example 1 : The following results are obtained in the hydrolysis of chlorobutane (C_4H_9Cl) :

Time (Sec)	0	100	200	300	400	700	800
Concentation of chlorobutane (mol lit^{-1})	0.100	0.082	0.067	0.055	0.044	0.021	0.017

Find out average rate r_{av} of the reaction during different intervals of time.

Solution : From the given results a table as below can be prepared :

No.	Time (t_1) second	Time(t_2) second	Concentration at time t_1 R_1 (mol lit^{-1})	Concentration at time t_2 R_2 (mol lit^{-1})	$t_2 - t_1 = \Delta t$	$[R]_2 - [R]_1 = \Delta[R]$	Average $r_{av} = \frac{-\Delta[R]}{\Delta t}$ (mol $lit^{-1}sec^{-1}$)
1.	0	100	0.100	0.082	100	– 0.018	1.8×10^{-4}
2.	100	200	0.082	0.067	100	– 0.015	1.5×10^{-4}
3.	200	300	0.067	0.055	100	– 0.012	1.2×10^{-4}
4.	300	400	0.055	0.044	100	– 0.011	1.1×10^{-4}
5.	400	700	0.044	0.021	300	– 0.023	7.7×10^{-5}
6	700	800	0.021	0.017	100	– 0.004	4.0×10^{-5}

It is apparent from the results that the average rate r_{av} decreases from 1.8×10^{-4} to 4.0×10^{-5} mol lit^{-1} sec^{-1}. It is difficult to show instantaneous rate of reaction. To determine reaction rate at any time, the instantaneous rate is to be determined. For which a graph of concentration of reactant versus time is drawn.

The reaction above was resulting from 1mole reactant to one mole product. Thus, the stoichiomentric coefficients were 1. In all the reactions it may not happen like this and so, the stoichiometric coefficients may be different viz. in the following reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Two moles of one reactant NO and one mole of other reactant O_2 react and 2 moles of product NO_2, are obtained. Thus, coefficient becoming different, to calculate the change in concentration they are to be taken into consideration. There will be two times decrease in concentration of NO in comparison to concentration of O_2 which will be equal to the change in concentration of NO_2 but will be opposite. As seen earlier the rate of reaction can be determined by determining concentration of reactant or product but the determination must be consistent. In chemical kinetics, the following method (convention) is accepted.

$$\text{Rate of reaction} = -\frac{1}{\nu_R}\left(\frac{d[R]}{dt}\right)$$

$$= +\frac{1}{\nu_P}\left(\frac{d[P]}{dt}\right) \qquad \text{..... (1.3)}$$

where R is reactant and its stoichiometric coefficient is ν_R and P is any product whose stoichiometric coefficient is ν_P. If we write the above equation in this convention, then

$$\text{Rate} = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} \qquad \text{..... (1.4)}$$

Suppose the reaction is as follows :

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(aq) + 3H_2O\,(l)$$

$$\text{Then rate} = -\frac{1}{5}\frac{d[Br^-]}{dt} = -\frac{d[BrO_3^-]}{dt} = -\frac{1}{6}\frac{d[H^+]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt} \quad ..... (1.5)$$

In aqueous solution, there is negligible change in concentration of water and so the change in its concentration is not expressed.

From the above discussion, for any reaction $n_1A + n_2B = n_3C + n_4D$

$$\text{Rate} = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = +\frac{1}{n_3}\frac{d[C]}{dt} = +\frac{1}{n_4}\frac{d[D]}{dt} \quad ..... (1.6)$$

For gaseous reaction the rate at given temperature will depend on the pressure of reactant or product. Sometime there is effect of external foreign material present, on the concentration.

The presentation of rate of reaction with reference to concentration of reactants is called **rate law.** This rate law in the wide range of concentrations of reactant or product is studied and the law that is established is called differential rate equation or rate expression. This presentation of rate is not easy, because if the same reaction is carried out in different conditions, it changes viz.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Rate = K $[H_2][I_2]$ where K is constant but other reaction of the same type for

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$$\text{rate} = \frac{K_1[H_2][Br_2]^{\frac{1}{2}}}{1 + K_2\ [HBr/Br_2]} \quad ..... (1.7)$$

where K_1 and K_2 are constants

These constants depend on the temperature. In the absence of HBr, the rate of above reaction will be as follows :

$$\text{Rate} = K[H_2][Br_2]^{\frac{1}{2}} \quad ..... (1.8)$$

If the reaction instead of being simple, paralled reactions are occurring then, the terms on the right side will be more than one.

Example 2 : The study of decomposition of N_2O_5 prepared in CCl_4 at 318 K. was carried out. In the begining the concentration of N_2O_5 was 2.33 mol lit^{-1}. After 184 minute it decreases and became 2.08 mol lit^{-1}. The reaction occurs as below :

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Find average rate of reaction.

Solution :

Reaction occurs as : $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

$$\text{Average rate} = -\frac{1}{2}\left\{\frac{\Delta[N_2O_5]}{\Delta t}\right\}$$

$$= -\frac{1}{2}\left\{\frac{(2.08 - 2.33)\text{ mol lit}^{-1}}{184\text{ min}}\right\}$$

$$= 6.79 \times 10^{-4}\text{ mol lit}^{-1}\text{ min}^{-1}$$

1.4 Rate Constant and Order of Reaction

In most of the reactions carried out by taking pure reactant, the simple rate equation can be obtained in which rate is proportional to exponent of the concentration of reactant. In one of the reactions seen above $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the rate is directly proportional to concentration of reactants hydrogen and iodine. While in other reaction it is directly proportional to concentration of hydrogen and square root of concentration of bromine.

Reaction rate $\propto [H_2][I_2]$ and

Reaction rate $\propto [H_2][Br_2]^{\frac{1}{2}}$

Supose we take reaction of decomposition of $N_2O_5(g)$, then,

Reaction rate $= -\frac{1}{2}\frac{d[N_2O_5]}{dt} \; \alpha \; [N_2O_5]$ OR

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = K\,[N_2O_5] \qquad \text{..... (1.9)}$$

where K is **rate constant** and it is called **specific rate constant** when concentration of reactant is 1M. Thus the rate of reaction is proportional to exponent 1 of concentration of N_2O_5. This exponent is called order of reaction in relation to reactant. In this reaction its value is 1. It is necessary to note that the order of reaction has no relation with the stoichiometric cofficient of reactant viz. The stoichlometric coefficient of N_2O_5 is 2 even then the order of reaction is 1.

If we write in a general form, for the reaction $n_1A + n_2B = n_3C + n_4D$

$$\text{Reaction rate} = K\,[A]^x[B]^y \qquad \text{..... (1.10)}$$

The meaning of this is that the order of reaction with reference to reactant A is x and with that of reaction B is y. Hence the total order of reaction is the sum of exponents equal to (x + y), for the reaction as seen earlier

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(aq) + 3H_2O\,(l)$ the reaction rate on the basis of experimental results can be written as follows :

$$\text{Reaction rate} = K[Br^-][BrO_3^-][H^+]^2 \qquad \text{..... (1.11)}$$

i.e. in the above reaction with reference to $[Br^-]$ and $[BrO_3^-]$ it is first order and with reference to $[H^+]$ it is of second order. The total order of reaction will be 1 + 1 + 2 = 4. The total order of reaction can be positive integer, zero or even a fraction.

Thus the **total order of reaction** is equal to the sum of exponents of concentration of all reactants.

As studied earlier, the dimensions of rate is **concentration time^{-1}.** In SI units concentration can be mentioned by mol m^{-3} or mol cm^{-3} but mol lit^{-1} unit is in general use. Generally time is taken in second but it can be in minute, hour, day, year etc. Time is taken in years because of very slow reaction e.g. nuclear reaction of uranium. While many reactions are very fast (neutralisation of strong acid and strong base) and so nanosecond (10^{-9} sec.) or picosecond (10^{-12} sec.) are taken.

As studied earlier.

Rate of reaction = K $[A]^x[B]^y$ ..... (1.12)

$$K = \frac{\text{Reaction rate}}{[A]^x[B]^y} \qquad ..... (1.13)$$

where, x + y will be the total order of reaction. Thus dimension of rate constant depends on order of reaction. The dimensions of $K = \frac{(\text{Concentration})}{(\text{Time})(\text{Concentration})^n} = (\text{Time}^{-1})(\text{Concentration}^{1-n})$. The units of K for reactions of different orders are shown in table 1.1

Table 1.1

Order	Type of reaction	Unit of K (in sec.)	Unit of K (general)
0	Zero order reaction	mol lit^{-1} sec^{-1}	mol lit^{-1} time^{-1}
1	First order reaction	sec^{-1}	time^{-1}
2	Second order reaction	$(\text{mol lit}^{-1})^{-1}$ sec^{-1}	$(\text{mol lit}^{-1})^{-1}$ time^{-1}
n	n order reaction	$(\text{mol lit}^{-1})^{1-n}$ sec^{-1}	$(\text{mol lit}^{-1})^{1-n}$ time^{-1}

The order of reaction can be determined experimentally. The methods for this will be studied later on in this unit.

1.5 Molecularity

The second important term in addition to order of reaction is the **molecularity.** It can be defined for an elementary reaction. There is no meaning of molecularity for complex reaction. The definition of molecularity for an elementary reaction can be given as below :

"The number of atoms, ions or molecules of the reactant that take part in the reaction and which experience collision with each other so that the reaction results, it is called molecularity of the reaction." If one molecule is associated in the reaction it is called monomolecular (unimolecular) reaction. e.g. Decomposition of ammonium nitrite $NH_4NO_2 \rightarrow N_2 + 2H_2O$. In bimolecular reaction two molecules have collision with each other e.g. decomposition of hydrogen iodide $2HI \rightarrow H_2 + I_2$.

In termolecular reaction three molecules collide with one another e.g. reaction of nitric oxide with dioxygen $2NO + O_2 \rightarrow 2NO_2$.

The posssibilty of collision of three or more molecules with one another and to result in the reaction is less. The molecularity more than three is not seen. Hence, the orders of reactions and molecularities of bimolecular, trimolecular elementary reaction are same.

H_2 and I_2 combine and form HI.

$H_2 + I_2 \rightarrow 2HI$

In this, one molecule of hydrogen and one molecule of iodine is used and so its molecularity is 1 + 1 = 2, i.e. it is a bimolecular reaction. Looking to the order of the reaction, the exponents of H_2 and I_2 are 1 and 1. Hence the order of reaction will be 1 + 1 = 2. Thus the order of reaction and molecularity are same i.e. 2. For monomolecular reaction, the order of reaction will be one at high pressure or concentration but at lower pressure or concentration the order will be 2. Under those circumstances, it does not remain elementary reaction. The order of reaction of the following reaction will be 10.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

but, in fact its order of reaction is 2. The reason for this is that in a reaction occurring in more than one steps, the slowest step in the reaction determines order of reaction and so it becomes rate determining step.

The reaction of decomposition of hydrogen peroxide in presence of iodide ion catalyst occurs as follows :

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

In this reaction, it is first order reaction with reference to both H_2O_2 and I^- but this reaction occurs in following two steps.

Step (1) : $H_2O_2 + I^- \rightarrow H_2O + IO^-$

Step (2) : $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

Both the steps are bimolecular elementary reactions; IO^- is called intermediate. It is formed during the reaction but is not found in overall reaction. First step is slow and hence it is rate determining step. Hence the formation of intermediate IO^- decides the rate of reaction. From this type of study following can be concluded.

(1) The order of reaction is an experimental quantity. It can be zero or even a fraction, while molecularity of a reaction cannot be zero or fraction.

(2) The order of reaction can be applied to elementary as well as complex reaction, while molecularity is applicable only to elementary reaction. Hence there is no meaning of molecularity for a complex reaction.

(3) For complex reaction the slowest step shows the order of reaction and generally the molecularity of the slowest step is equal to the order of the total reaction.

Example 3 : The following are the results of the three experiments carried for determination of differential rate of reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ at definite temperature. (1) Deduce the differential rate law (2) Calculate order of reaction and (3) Find out value of rate constant.

No	**Initial concentration of reactants mol lit^{-1}**		**Initial rate of reaction $-\frac{d[Cl_2]}{dt}$ mol lit^{-1} sec^{-1}**
	[NO]	**[Cl_2]**	
1	0.01	0.02	3.50×10^{-4}
2	0.02	0.02	1.40×10^{-3}
3	0.01	0.04	7.00×10^{-4}

Solution : $-\frac{d[Cl_2]}{dt} = K[NO]^a[Cl_2]^b$

Putting the experimental values in the equation.

(i) $3.50 \times 10^{-4} = K(0.01)^a\ (0.02)^b$ (ii) $1.40 \times 10^{-3} = K(0.02)^a\ (0.02)^b$

(iii) $7.00 \times 10^{-4} = K(0.01)^a\ (0.04)^b$

Dividing equation (ii) by equation (i),

$$\frac{1.40 \times 10^{-3}}{3.50 \times 10^{-4}} = \left(\frac{0.02}{0.01}\right)^{a}$$

$\therefore$ 4 = $(2)^a$ $\therefore$ a = 2

Dividing equation (iii) by equation (i),

$$\frac{7.00 \times 10^{-4}}{3.50 \times 10^{-4}} = \left(\frac{0.04}{0.02}\right)^{b}$$

$\therefore$ 2 = $(2)^b$ $\therefore$ b = 1

$$\therefore \; -\frac{d[Cl_2]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt} = K[NO]^2[Cl_2]^1$$

$\therefore$ Total order of reaction : 2 + 1 = 3

Now, Rate constant $K = -\dfrac{d[Cl_2]/dt}{[NO]^2[Cl_2]^1}$

Putting any of the experimental results in the equation, the value of K can be calculated.

$$K = \frac{3.50 \times 10^{-4} \text{ mol lit}^{-1} \text{ sec}^{-1}}{(0.01)^2 \text{ mol}^2 \text{ lit}^{-2} \times 0.02 \text{ mol lit}^{-1}} = 175 \text{ lit}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

1.6 Integrated Rate Law

We have seen that the change in concentration on rate is the differential rate equation. Always it is not easy to determine instantaneous rate as we have seen for the measurement of instantaneous rate. Thus it is a difficult work to determine rate of reaction from differential rate. Hence, the use of integrated rate law can be made. This law simplifies the determination of concentration at different times. It is also practical in chemical kinetics. We shall understand this integrated rate for zero and first order reaction.

1.7 Zero Order Reaction

The meaning of zero order reaction is that **the rate of the reaction is propotional to zero exponent of the concentration of reactant.** Exponent zero means, the value of term will be 1, that is will be constant. Hence for zero order reaction R → P (R = Reactant and P = Product) :

$$\text{rate} = -\frac{d[R]}{dt} = K[R]^0 = K(1) = K \qquad \text{..... (1.14)}$$

$$\therefore \; -d[R] = Kdt \qquad \text{..... (1.15)}$$

On intergration,

$$[R] = -Kt + C \qquad \text{..... (1.16)}$$

where C is the integration constant and its value can be determined for the concentration at time t = 0 or $[R]_0 = C$

$$\therefore \; [R]_0 = -K \times 0 + C = C \text{ OR } [R]_0 = C \qquad \text{..... (1.17)}$$

Putting this in equation (1.16)

$$[R] = -Kt + [R]_0 \qquad \text{..... (1.18)}$$

Now, if we draw graph of concentration [R] versus time (t) then straight line will be obtained. (Fig 1.3) and the value of the slope will be equal to the negative value of K i.e. –K and the value of the intercept will be $[R]_0$ that is the concentration at zero time or equal to intial concentration $[R]_0$.

Equation 1.18 can be written in this form

$$[R] = -Kt + [R]_0$$

$$-Kt = [R]-[R]_0 \qquad \text{..... (1.19)}$$

$$\therefore\ Kt = [R]_0-[R] \qquad \text{..... (1.20)}$$

$$\therefore\ K = \frac{[R]_0 - [R]}{t} \qquad \text{..... (1.21)}$$

Now, if we write the values of reactant at different times (t) as $[R]_t$ then equation 1.21 can be written as follows :

$$K = \frac{[R]_0 - [R]_t}{t} \qquad \text{..... (1.22)}$$

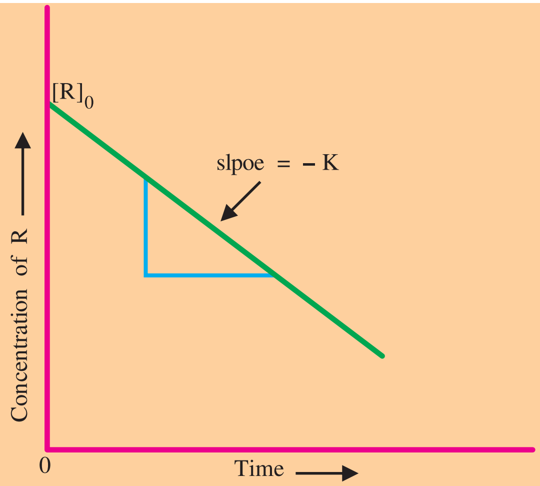


Fig. 1.3 Variation in the concentration vs time plot for a zero order reaction

Half life period of reaction : Half life period of reaction means the time required for the concentration of the reactant in the reaction to be half. The half life period of radioactive elements is definite and it is expressed as $t_{1/2}$. If we put the value of concentration at time $t_{1/2}$ in equation 1.22 then,

$$[R]_t = \frac{1}{2}[R]_0 \quad \text{so}$$

$$t_{1/2} = \frac{[R]_0 - \frac{1}{2}[R]_0}{K} = \frac{[R]_0}{2K} \qquad \text{..... (1.23)}$$

It is apparent from above that the **half life period ($t_{1/2}$) of a zero order reaction is directly proportional to initial concentration $[R]_0$ and inversely proportional to rate constant.**

Zero order reactions are mostly found in heterogeneous reactions viz. adsorption of adsorbent on the surface of the adsorbate. In adsorption reaction the fraction of the surface of the catalyst occupied is proportional to concentration and so it becomes first order reaction but the situation does not change with more and more adsorption and so rate becomes independent of concentration that is it becomes zero order reaction.

The adsorption of ammonia gas on the surface of the finely divided nickel catalyst is proportional to pressure (concentration) of ammonia gas but at high pressure (more concentration) the surface is completely covered and so it becomes zero order reaction. The rate of this reaction can be shown by following equation,

$$\text{rate} = K_1 \bullet \frac{[NH_3]}{1 + K_2[NH_3]}$$

K_1 and K_2 are constants and $[NH_3]$ is concentration of ammonia If $[NH_3]$ is less then $K_2[NH_3]$ can be neglected in comparison to 1 and so rate = $K_1[NH_3]$ and the reaction will be first order reaction. At high concentrations of NH_3, 1 can be neglected in comparison to $[NH_3]$.

Hence, rate $= \dfrac{K_1[NH_3]}{K_2[NH_3]} = \dfrac{K_1}{K_2} = K$

That is the reaction will be of zero order and the specific rate constant K for the reaction can be obtained.

1.8 Rate Equation For First Order Reaction

In the first order reaction **the rate of reaction is proportional to exponent one of concentration of reactant** e.g., For reaction R → P

Rate of reaction $= -\dfrac{d[R]}{dt} = K[R]$ ..... (1.24)

OR

$= -\dfrac{d[R]}{[R]} = Kdt$ ..... (1.25)

Integrating equation (1.25)

$\ln[R] = -Kt + C$ ..... (1.26)

where C is integration constant. Its value can be obtained from the concentration of reactant $[R]_0$ at zero time (t_0). When $t = 0$ then $[R] = [R]_0$. Putting this value in equation (1.26).

$\ln[R]_0 = -K \times 0 + C = 0 + C$

Putting this value in equation (1.26),

$\ln[R] = -Kt + \ln[R]_0$ ..... (1.27)

$\therefore\ Kt = \ln[R]_0 - \ln[R]$ ..... (1.28)

$\therefore\ K = \dfrac{1}{t}\ln\dfrac{[R]_0}{[R]} \quad \therefore\ K = \dfrac{2.303}{t}\log_{10}\dfrac{[R]_0}{[R]_t}$ (Where $[R]_t$ = Concentration at time ‘t’) .... (1.29)

Suppose the concentration $[R]_1$ and $[R]_2$ of the reactants are determined at times t_1 and t_2 and put in the equation (1.29) then,

$K = \dfrac{1}{(t_2 - t_1)} \ln \dfrac{[R]_1}{[R]_2}$ ..... (1.30)

If equation (1.27) is rewritten in the exponential form, it can be written as $[R] = [R]_0 e^{-Kt}$

If we think of equation $\ln [R]_t = -Kt + \ln[R]_0$, then if a graph of values of $\ln[R]_t$ obtained is plotted against different times (t) then a straight line is obtained and the value of slope will be equal to $-K$ and the value of intercept will be equal to $\ln [R]_0$. Writting the above equation to the base 10 of logarithm the above equation $\ln [R]_t = -Kt + \ln[R]_0$ can be written as.

$2.303 \log [R]_t = -Kt + 2.303 \log[R]_0$ ..... (1.31)

Dividing equation 1.31 by 2.303,

$$\log_{10}[R]_t = -\frac{K}{2.303}t + \log_{10}[R]_0 \qquad \text{..... (1.32)}$$

Hence, if a graph of $\log_{10}[R]_t$ against t is plotted a straight line will be obtained and the value of slope will be equal to $-\frac{K}{2.303}$ and the value of intercept will be equal to $\log_{10}[R]_0$ (fig 1.4).

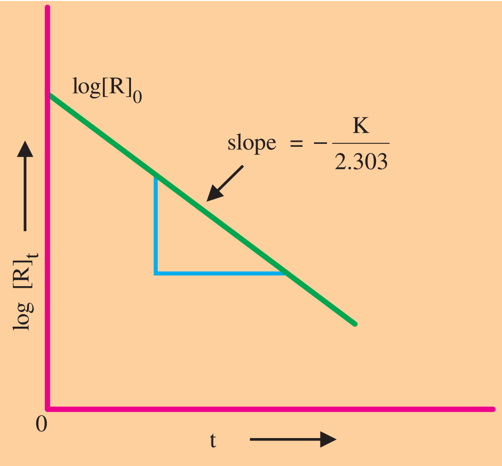


Fig. 1.4 A plot of log$[R]_t$ vs t for a first order reaction.

As seen earlier, if time t is taken such that the initial concentration of the reactant becomes half. i.e. $[R]_t = \frac{1}{2}[R]_0$. This time is called half life period. Putting these values in equation 1.32.

$$\log\frac{1}{2}[R]_0 = -\frac{K}{2.303}t_{1/2} + \log[R]_0 \qquad \text{..... (1.33)}$$

$$\therefore \frac{K}{2.303}t_{1/2} = \frac{\log[R]_0}{\log\frac{1}{2}[R]_0} = \log 2 \qquad \text{..... (1.34)}$$

$$\therefore t_{1/2} = \log 2 \times \frac{2.303}{K} = \frac{0.3010 \times 2.303}{K} = \frac{0.693}{K} \qquad \text{..... (1.35)}$$

$t_{1/2}$ will be constant because 0.693 and K both are constants. **Thus, the half life period of first order reaction is independent of initial concentration of reactant and is inversely proportional to rate constant K.** The study of this is included in subject of nuclear chemistry, where reactions are of first order.

Example 4 : The decomposition of N_2O_5 dissolved in carbon tetrachloride, occurs as follows :

$$N_2O_5 \text{ (solution)} \rightleftharpoons 2NO_2 \text{ (solution)} + \frac{1}{2}O_2(g)$$

This reaction is of first order and its rate constant is 5.0×10^{-4} sec^{-1}. If initial concentration of N_2O_5 for this reaction is 0.30 mole, then (i) What will be the initial reaction rate ? (2) What will be half life period of this reaction ? (iii) What time will it take to complete 80% reaction and what will be concentrations of N_2O_5 and NO_2 at the end of 40 minutes after the starting of reaction ?

Solution :

(1) Reaction rate $-\frac{d[N_2O_5]}{dt} = KC_O = 5.0 \times 10^{-4}\ \text{sec}^{-1} \times 0.30\ \text{mol lit}^{-1}$

$= 1.5 \times 10^{-4}$ mol lit^{-1} sec^{-1}

(2) Half life period $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{5.0 \times 10^{-4}\ \text{sec}^{-1}} = 1386$ sec

(3) When reaction is 80% completed, the concentration of remaining $N_2O_5 = \frac{(100 - 80)}{100} \times 0.30$

$= 6 \times 10^{-2}$ mol lit^{-1}

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\therefore t = \frac{2.303}{5 \times 10^{-4}} \log \frac{0.30}{6 \times 10^{-2}}$$

$$= 3219 \text{ second} = 3.219 \times 10^3 \text{ sec}$$

(4) The concentration of N_2O_5 at the end of 40 minutes : $5 \times 10^{-4} = \frac{2.303}{40 \times 60} \log \frac{0.30}{C}$

$$= 0.0903 \text{ mol lit}^{-1} \approx 0.09 \text{ mol lit}^{-1}$$

At the end of 40 minutes decrease in concentration of N_2O_5 will be decreased by = 0.30 – 0.09 = 0.21 mol lit^{-1}

2 moles N_2O_5 are obtained by decomposition of 1 mole of N_2O_5 and so at the end of 40 minutes concentration of NO_2 = 2.0 × 0.21 = 0.42 mol lit^{-1}.

Example 5 : In a first order reaction, the concentration of reactant decreases from 0.060 to 0.040 mol lit^{-1} and this requires 45 minutes, what will be the half life period of this reaction?

Solution : $K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$

$$K = \frac{2.303}{45} \log_{10} \frac{0.06}{0.04}$$

$$K = 9.01 \times 10^{-3} \text{ min}^{-1}$$

Now, half life period

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{9.01 \times 10^{-3}}$$

$$= 7.69 \times 10^1 = 76.9 \text{ min}$$

1.9 Pseudo First Order Reaction

Some reactions are of first order with reference to two different reactants e.g. the rate of a reaction = K [A][B]; suppose the concentration of reactant A is less in comparison to concentration of reactant B; viz. [A] = 0.01 M and [B] = 55.55 M. (molarity of water), then concentration of water during the reaction decreases to 55.55 – 0.01 = 55.54 M, which can be taken almost as 55.5 M. because 0.01 M can be neglected. Thus, even when the reaction is completed, the concentration of water does not change appreciably. That is if it can be taken as constant then the rate = K_0[A] can be written where K_0 = K[B] will be constant. Now, this reaction will act as first order reaction. Such reactions are called pseudo first order reactions. The hydrolysis of methyl acetate in presence of H^+ gives methanol and ethanoic acid respectively.

$$CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3OH + CH_3COOH$$

In this reaction as seen above, the concentration of water remains almost constant and so this reaction will be considered of first order but this reaction is not really first order reaction, because both the reactants are consumed in this reaction and the exponents of their concentration are 1. Hence this reaction should be 1 + 1 = 2, second order reaction. But considering concentration of water as constant, it becomes first order reaction and it is experimentally proved. **Such reaction is called pseudo first order reaction.** In your practical book this type of experiment is presented as demonstration experiment. If you record the results carefully during the demonstration experiment you will have more information about chemical kinetics, real reaction and pseudo reaction and will be able to understand more about determination of rate constant and the determination of order of reaction experimentally.

Example 6 : Acetic acid obtained by hydrolysis reaction of methyl acetate in presence of HCl is determined by titrating with sodium hydroxide. The concentration of ester (C) at different time (t) were obtained as below :

Time(t) in minutes	0	30	60	90
Concentration (C) of ester M	0.850	0.800	0.754	0.710

The above results show that this reaction is pseudo first order reaction. The concentration of water during the experiment remains constant as 54.2M. Calculate the value of rate constank K

Solution : As the concentration of water remains constant during pseudo first reaction this reactiion will be first order reaction in relation to ester. The calculation values can be shown as follows in the table given below :

Time (t) in minutes	**Concentration of ester (C) M**	$K[H_2O]=\frac{2.303}{t}\log_{10}\frac{C_0}{C}$
0	0.850	–
30	0.800	2.016×10^{-3}
60	0.754	1.996×10^{-3}
90	0.710	1.996×10^{-3}

It is apparent from the table that the value of K $[H_2O]$ is constant and the approximate value obtained is 1.996×10^{-3} min^{-1}. In the calculation of rate constant the equation used is for first order reaction. We got value of K as constant and so this reaction is of first order,

Now $K\ [H_2O] = 1.996 \times 10^{-3}$

$\therefore\ K \times (54.2) = 1.996 \times 10^{-3}$

$$\therefore\ K = \frac{1.996\times10^{-3}}{54.2}$$

$= 3.683 \times 10^{-5}\ mol^{-1}\ lit\ min^{-1}$

The unit of K is for second order reaction. Hence, the hydrolysis reaction of ester is of pseudo first order reaction.

The integrated rate law can be expressed for zero and first order reaction as follows :

Order of reaction	Type of Reaction	Differential rate law	Integrated rate law	Straight line graph	Half life period	Unit of K
0	$R \rightarrow P$	$-d[R]/dt = K$	$Kt = [R]_0 - [R]_t$	[R] vs t	$[R]_0 / 2K$	con. $time^{-1}$ or $mol\ lit^{-1}\ sec^{-1}$
1	$R \rightarrow P$	$-d[R]/dt = K[R]$	$Kt = \ln[R]_0 / [R]_t$	ln [R] vs t	ln 2 / K	$time^{-1}$ or sec^{-1}

1.10 Determination of Order of Reaction

The methods used for determination of order of reaction are as follows :

(i) Initial rate method (2) Use of Integrated rate equation method or Graphical method (3) Half life (reaction time) method and (4) Ostwald's isolation method. From the above methods we shall study only three methods-Integrated rate equation or graphical method, Ostwald's isolation method and half life method in detail.

(1) Integrated Rate Equation Method : The following equations are used for determination of reaction rate constant for zero and first order reactions

For zero order reaction : $K = \dfrac{[R]_0 - [R]_t}{t}$

For first order reaction : $K = \dfrac{2.303}{t} \log_{10} \dfrac{[R]_0}{[R]_t}$

Thus the concentration of reactant $[R]_t$ is determined experimentally at different time (t) and calculated the values of K by substituting the experimental values in the above equation for zero or first order reaction, and values of K can be found out. If the calculation of value of K, is carried out using $K = \dfrac{[R]_0 - [R]_t}{t}$ and the value of K remains almost constant, then the reaction should be of zero order reaction. If the value of K is calculated by putting the values in equation $K = \dfrac{2.303}{t} \log_{10} \dfrac{[R]_0}{[R]_t}$ and the values of K obtained are constant then the reaction should be of first order. In this way for zero and first order reaction, trial and error method for calculation of K is carried out to find whether K obtained is constant or not and from that the order of reaction can be determined.

In addition to calculating as eariler the **graphical method** can also be used. For this the above equation can be transformed to Y = mX + C type straight line graph and graph can be plotted viz.

For zero order reaction $K = \dfrac{[R]_0 - [R]_t}{t}$

This equation can be changed as $Kt = [R]_0 - [R]_t$ or $[R]_t = [R]_0 - Kt$

Now, if concentration $[R]_t$ is plotted on Y-axis and time (t) on X-axis and the graph is drawn for experimental results, the graph obtained will be straight line which proves that the reaction should be of zero order. The value of K can be obtained from the slope and $[R]_0$ from the value of intercept of graph.

For first order reaction, $K = \dfrac{2.303}{t}\log_{10}\dfrac{[R]_0}{[R]_t}$

can be changed as : $\dfrac{Kt}{2.303} = \log_{10}[R]_0 - \log_{10}[R]_t$ or $\log_{10}[R]_t = \log_{10}[R]_0 - \dfrac{K}{2.303}t$

Now if $\log_{10}[R]_t$ on Y-axis and time (t) on X-axis is taken and graph is plotted of the experimental results, then a straight line will be obtained which proves that the reaction is of first order. The value of K can be obtained from the slope of the graph. The value of slope $= \dfrac{-K}{2.303}$ or $-$ slope × 2.303 = K and the value of $\log_{10}[R]$ as the intercept of the graph.

(2) Ostwald's Isolation method : In certain reactions there is involvement of more than one reactants. To determine the order of reaction of such reactions, Ostwald gave a method which is known as Ostwald's isolation method. In this method, the concentration of other reactants in comparison to one reactant is taken in very large proportion. The reaction rate will be indicative with respect to reactant with less concentration because the concentration of other reactants remain almost constant. Including the constant terms, we can write the equation for rate of reaction.

$$\text{Rate} = K[A]^a[B]^b[C]^c = K_0[A]^a \text{ (where } K_0 = [B]^b[C]^c)$$

As [B] and [C] are in very large proportion they are accepted as constant which are included in K_0. The value "a" that is the order of reaction with reference to A can be determined. Thus the order of reaction with reference to B and C can be determined by changing (by increasing) concentrations of A, B and C. The above method will be clear from the example given below :

Example 7 : The reaction $CH_3COF + H_2O \rightleftharpoons CH_3COOH + HF$ was studied under following conditions :

Condition-I	**Condition-II**
$[H_2O]_0 = 1.00$ M	$[H_2O]_0 = 0.02$ M
$[CH_3COF]_0 = 0.01$ M	$[CH_3COF]_0 = 0.80$ M

Condition-I		**Condition-II**	
Time (t) min.	**$[CH_3COF]$ M**	**Time (t) in min.**	**$[H_2O]$ M**
0	0.01000	0	0.0200
10	0.00867	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of reaction and calculate rate constant.

Solution : Suppose, Reaction rate = $K[CH_3COF]^a[H_2O]^b$. Ostwalds' method can be used. In condition-I $[H_2O]_0 >> [CH_3COF]_0$ and in condition-II $[H_2O]_0 << [CH_3COF]_0$.

Hence, in condtion-I the order of reaction can be determined relative to CH_3COF. The reaction is not of zero order because reaction rate changes with time. Hence, the equation for first order can be applied and if we calculate; results as shown below are obtained.

Time (t) min.	**M**	$K[H_2O]^b = \dfrac{\ln\dfrac{[CH_3COF]_0}{[CH_3COF]t}}{t}$
0	0.0100	–
10	0.00857	0.0154
20	0.00735	0.0154
40	0.00540	0.0154

Thus, $K[H_2O]$ = 0.0154 minute is obtained as constant. Hence the order of reaction relative to CH_3COF is 1. Now, applying the equation for first order, for water following values will be obtained.

Time (t) min.	$[H_2O]$ **M**	$K[CH_3COF]^a = \dfrac{\ln\dfrac{[H_2O]_0}{[H_2O]t}}{t}$
0	0.0200	–
10	0.0176	0.0128
20	0.0156	0.0124
40	0.0122	0.0124

$K[CH_3COF] = 0.0124$ is constant Hence, order of reaction with reference to H_2O will be 1.

In condition (I) $K = 0.0154 \text{ min}^{-1} / 1.0 \text{ M}$

$= 0.0154 \text{ min}^{-1} \text{ M}^{-1}$

In condition (II) $K = 0.0124 \text{ min}^{-1} / 0.800$

$= 0.0150 \text{ min}^{-1} \text{ M}^{-1}$

The order of reaction with reference to both the reactants obtained is 1. Hence, total number of order of reaction will be 1 + 1 = 2.

(3) Half life (Half reaction time) method : In addition to the above two methods, the half life or half reaction time method is very simple. As studied earlier the time required to have initial concentration $[R]_0$ to be exactly half i.e. $\frac{1}{2}[R]_0$ is called half life period and it can be determined. The order of reaction can be obtained from following relations.

For zero order reaction $t_{1/2} \propto [R]_0$

For first order reaction $t_{1/2}$ is independent of initial concentration.

For second order reaction $t_{1/2} \propto \dfrac{1}{[R]_0}$

Hence, for n^th order reaction $t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$

Two theories are known for the study of chemical kinetics (1) Transition state theory and (2) Theory of collision. We shall study these theories later on.

1.11 Effect of Temperature on Rate Constant

Mostly the rate constant increases with increase in temperature. It is noted that if the graph (fig. 1.6) of rate constant lnK or $\log_{10}K$ is plotted against inverse of temperature, (T = temperature in Kelvin units) a straight line is obtained. This result is derived from Arrhenius equation.

Arrhenius equation :

Arrhenius equation can be expressed in the following form :

$$K = Ae^{-E_a/RT} \qquad \text{..... (1.36)}$$

where K = rate constant, A = Arrhenius constant, R = Gas constant,

T = Temperature (absolute), E_a = Energy of activation.

Taking logarithm of equation 1.36.

$$\ln K = \ln A - \frac{E_a}{RT} \quad \text{or}$$

$$\ln K = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad \text{..... (1.37)}$$

The values of rate constant K are determined at different temperatures, and a graph of lnK versus $\frac{1}{T}$ is plotted. Thus straight line will be obtained. By changing the equation (1.37) it can be written as

$$2.303 \log_{10}K = 2.303\log_{10}A - \frac{E_a}{RT} \quad \text{or}$$

$$\log_{10}K = \log_{10}A - \frac{E_a}{2.303\ R} \cdot \frac{1}{T} \qquad \text{..... (1.38)}$$

The energy of activation for a reaction being constant, R is gas constant, the above equation can be of straight line type. Hence, if a graph of log K versus $\frac{1}{T}$ is plotted, the value of slope will be $-\frac{E_a}{2.303\ R}$. If the value of R is taken in k cal or k joule then the value of E_a will be also in k cal or k joule. From the value of intercept, the value of log A will be obtained and constant A can be determined.

Arrhenius equation shows that rate constant increases exponentially with temperature. How can this exponential variation be studied ? Is it due to increase in average kinetic energy of molecules ? It is also noted in addition to this that by increasing temperature from 300 to 310 K, the kinetic energy increases only by 3 % because it is proportional to temperature. In addition to this, for most of the reactions the rates have almost **doubled by** increase in temperature by **10 K.** The explanation for this can be given that there must be some pushing energy or threshold energy required for the reaction of molecules. In the fig 1.5 this is shown,

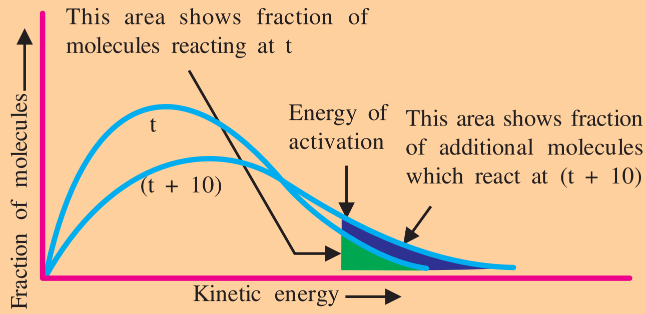


Fig. 1.5 Distribution curve showing temperature dependence of rate of a reaction

The graph of the fraction of the molecules which experience collision possessing different kinetic energy is plotted. It is apparent from this that the average relative kinetic energy increases as expected but the number of molecules (fig. 1.5 portion shown shaded) which possesses threshold relative kinetic energy. It shows increase of E*. Thus the activation energy E_a and such kinetic energy (E*) can be shown by following relation.

$E_a = N_A E^*$ where N_A = Avogadro number.

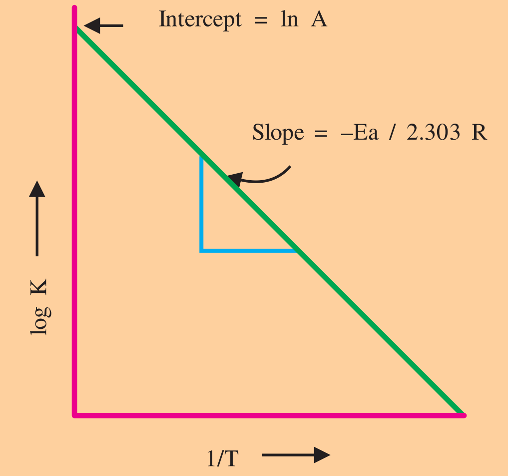


Fig. 1.6 A plot between log K and 1/T

In Arrhenius equation the parameter A is called pre-exponential factor or frequency factor. E_a is called energy of activation. Both of these factors are known as Arrhenius factors. To determine their values a graph of log K versus $\frac{1}{T}$ is plotted and from the value of the slope, E_a can be determined (fig 1.6). But for intercept $\frac{1}{T} = 0$ taken then the value of T should be ∞. The rate constant of a reaction is determined from the change in the limited temperature range and so $\frac{1}{T} = 0$ cannot be taken. Hence, by obtaining value of E_a all the values except A in the equation $\log K = \log A - \frac{E_a}{2.303\,R} \cdot \frac{1}{T}$ are substituted from any result (K and T) and the value of log A will be obtained from which the Arrhenius constant or frequency factor can be determined. In physical chemistry, generally if a graph can be obtained then the results can be transformed in to equation of a straight line and graph is plotted. The values of slope and intercept are determined from the graph. Suppose the Arrhenius equation mentioned earlier is written corresponding to two different temperatures T_1 and T_2, then we can write

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \qquad \text{..... (1.39)}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \qquad \text{..... (1.40)}$$

$$\therefore \ \ln K_2 - \ln K_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2} \quad \text{or}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \qquad \text{..... (1.41)}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{..... (1.42)}$$

When the number of results is less then instead of drawing the graph values of K_1 and K_2 can be determined experimently at temperatures T_1 and T_2 and by putting the values in equation 1.42, the value of E_a can be obtained. In any one of the equations, the values of E_a, K and T are substituted and the value of, logA or A can be obtained. In addition the value of E_a for any reaction is definite and so the rate constant (K) at any other temperature (T) can be evaluated from the value of E_a. This will be clear from the following example :

Example 8 : The rate constant of a reaction at 27^0 C is 2×10^{-3} minute^{-1}. The temperature was increased by 20^0 C and the value of rate constant K increased three times. Calculate the energy of activation of the reaction. What will be value of rate constant at 37^0 C ?

Solution : The value of K at 20^0 C is 2×10^{-3} minute^{-1}. If we increase temperature by 20^0 C, K will be three times. i.e. $3 \times 2 \times 10^{-3} = 6 \times 10^{-3}$ min^{-1}. Now

$T_1 = 27 + 273 = 300$ K, $T_2 = 47 + 273 = 320$ K,

$K_1 = 2 \times 10^{-3}$ min^{-1}, $K_2 = 6 \times 10^{-3}$ min^{-1}

$R = 1.987 \times 10^{-3}$ kcal.

Putting the above values in the following equation,

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{6 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}}\left(\frac{1}{300} - \frac{1}{320}\right)$$

$$\therefore \log 3 = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}}\left(\frac{320 - 300}{300 \times 320}\right)$$

$$\therefore 0.4771 = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}}\left(\frac{20}{300 \times 320}\right)$$

$$\therefore E_a = \frac{0.4771 \times 2.303 \times 1.987 \times 10^{-3} \times 300 \times 320}{20}$$

$$= 10.480 \text{ k cal}$$

Now we want to find out the value of K at 37^0 C then value of $E_a = 10.480$ k cal can be used and any value of K and corresponding T will have to be taken.

$$\therefore \log \frac{K_{37}}{2 \times 10^{-3}} = \frac{10.480}{2.303 \times 1.987 \times 10^{-3}}\left(\frac{310 - 300}{310 \times 300}\right)$$

$$\therefore \log K_{37} - \log 2 \times 10^{-3} = \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$\therefore \log K_{37} - (-2.6990) = \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$\therefore \log K_{37} = -2.6990 + \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$= -2.6990 + 0.2463$$

$$= -2.4527$$

Changing before taking the antilogarithm –2.4537 = $\bar{3}.5473$

Antilog $\bar{3}.5473 = 3.526 \times 10^{-3}$

$\therefore K = 3.526 \times 10^{-3}$ min^{-1}

1.13 Theory of Collision

The theory of collision for chemical reaction was developed by Max Trauz and William Lewis in 1916-18. This principle deals with the energetic and mechanistic matter of the reaction. It is based on the theory of kinetic energy of gases.

According to this theory, it is supposed that the molecules are hard spheres and the reaction occurs only when these molecules collide with each other. In chemical reaction, the number of collision per second per unit volume is called collision frequency (Z).

The other factor affecting rate of chemical reaction is the energy of activation about which you have studied in the Arrhenius equation.

Suppose any bimolecular reaction is as follows

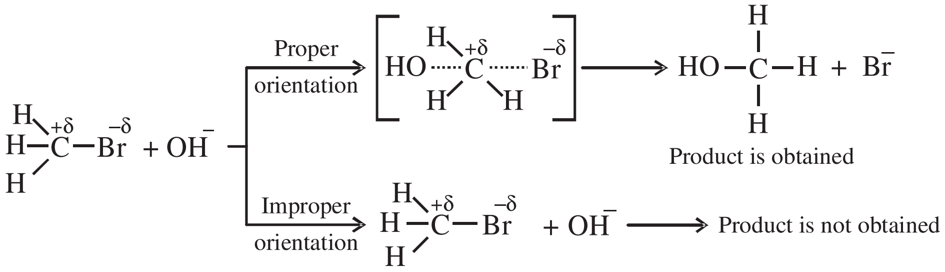
$$A + B \rightarrow \text{Product}$$

The rate of reaction can be shown as below :

$$\text{Rate} = Z_{AB}\, e^{-E_a/RT} \qquad \text{..... (1.43)}$$

where Z_{AB} is the **collision frequency** of reactants, A and B whose energy is equal to or more than e^{-E_a} / RT activation energy. This equation when compared with Arrhenius equation $K = Ae^{-E_a} / RT$ it can be said that Arrhenius constant A is related to collision frequency Z_{AB}. The values of rate constants of reactions having atomic species or simple molecules can be determined accurately using equation (1.43), but there is notable deviation for complex molecules. The reason for this is that all the collisions, do not result into products. Those collisions in which molecules collide with sufficient kinetic energy (which is called threshold energy) and proper direction, then bonds of the reactants break and new bonds are formed resulting into products. Such collisions are called **effective or fruitful collisions.** If we take as an example the preparation of methanol from bromomethane the molecules are oriented as shown below. The reactant molecules having proper orientation lead to bond formation, where as improper direction makes them collide but do not result into product. We shall study the reaction :

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$



For effective collision, another parameter is added which is called **steric factor or probability factor** which takes into consideration the collision from proper direction. Hence ,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT} \qquad \text{..... (1.44)}$$

where, P = probability factor

Thus according to the collision theory, the combinations of activation energy and collision of molecules from proper direction are required for effective collision. Hence, the following points can be concluded :

(1) The collisions between the reactants is essential

(2) There must be certain minimum energy(threshold energy) for the reactant experiencing collision.

(3) The collision of the reactant molecules should be in proper direction(orientations)

(4) The reactants experiencing fruitful collision are converted to products

Many advantages of the phenomenon are found. Had there been no requirements mentioned as above the oxygen of the air will be reacting experiencing fruitful collision with carbon and would burn. The nitrogen and oxygen of the air would have reacted and the oxygen required for life would not have been available. There are certain demerits of collision theory viz. the atoms are assumed to be hard spheres and their structural aspects are not taken into consideration.

Endothermic and Exothermic reactions : To understand the above phenomenon when molecules come nearer to each other, the changes in energy that take place can be studied. When the molecules come nearer to each other, the distance between them is decreasing and their potential energy increases. Such molecules combine with each other and a short lived complex molecule is produced. It possesses maximum potential energy. This short lived molecule is known as **activated complex.** This activated complex possesses very weak bonds. They break due to their oscillation motion. Hence product or original reactant is obtained. As the molecules of resultant product go away from each other, their potential energy decreases. There can be two options for this : (1) If the minimum potential energy of reactant is less than that of product then the reaction will be endothermic (2) If the minimum potential energy of reactants is more than the potential energy of product then the reaction will be exothermic. Thus, in endothermic reaction, the potential energy of products is more than potential energy of reactants. Hence, $H_p - H_r = \Delta H$ will have positive value. In exothermic reaction the potential energy of product is less than the total potential energy of reactants. Hence, the value of $H_p - H_r = \Delta H$ will be negative which can be shown by following fig. 1.7 and 1.8.

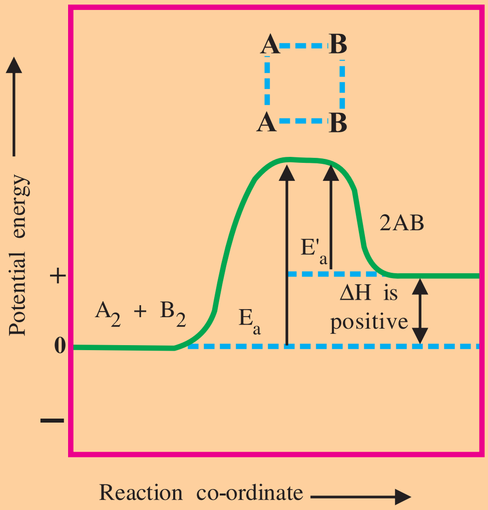


Fig. 1.7 Endothermic reaction

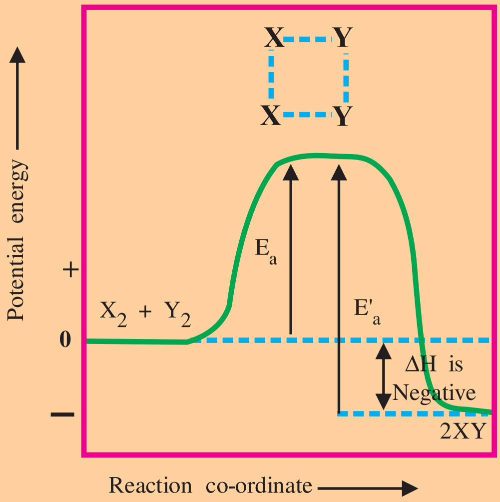


Fig. 1.8 Exothermic reaction

The **energy of activation** is the difference between potential energy of reactant molecules and activated complex. In the above figure if the activation energy of reverse reaction is E'_a and activation energy of forward reaction is E_a, then, $\Delta H = E_a - E'_a$.

Now, if $E_a > E'_a$ the value of ΔH obtained will be positive and so the reaction will be endothermic. If $E_a < E'_a$ then the value of ΔH obtained will be negative and the reaction will be exothermic. It is clear from the above reactions, that there exists an **energy barrier** between molecules of reactant and products. The height of this barrier is the important factor in determining the rate of reaction. If the energy barrier is high, the reaction rate will be low and if the energy barrier is low, the reaction rate will be high. By using proper catalyst the value of reaction rate can be increased. The function of the catalyst is to bring energy barrier down and to decrease the energy of activation so that the path for the reaction to result becomes easy.

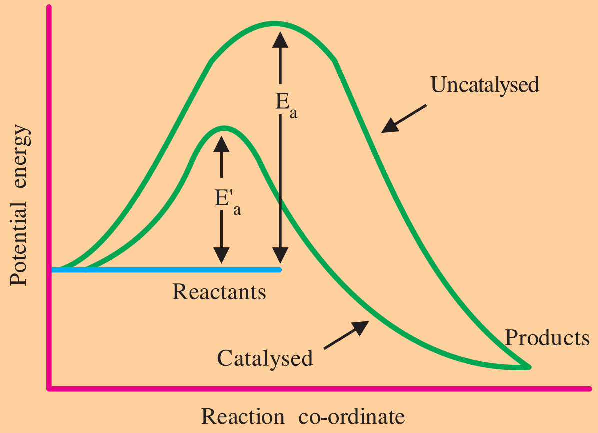


Fig. 1.9

Effect of catalyst on the rate of reaction :

You have studied earlier that oxygen can be obtained by decomposing potassium chlorate ($KClO_3$) by supplying heat. But as the rate of reaction is slow; time required for obtaining oxygen is more; But if manganese dioxide (MnO_2) powder is added and then heated, decomposition becomes fast. Here MnO_2 does not react but increases the rate of reaction. Hence it is called catalyst. We shall study in detail about catalyst in unit 2. The function of catalyst is to combine with the reactant and to form an intermediate complex. This transition state does not last for a longer period and so it decomposes and gives the product as well as the original catalyst is obtained back. The catalyst tries to find out the alternate way so that the activation energy decreases and the height of energy barrier decreases and brings the reaction towards the result. Thus the main function of catalyst is to decrease the activation energy. This phenomenon can be shown in the following fig. 1.9.

It is necessary to remember that the catalyst does not affect the equilibrium constant (K) or free energy change (ΔG). It catalyses the spontaneous reaction. Thus the catalyst has the same impact on the forward and the reverse reaction, with effect that the value of equilibrium constant (K) is not changed but the value of rate of reaction changes, with an increase.

Mechanism of chemical reaction : To understand the mechanism of any complex reaction it is necessary to know its stoichiometry that is the number of moles of each reactant and number of moles of each product.

In certain reactions, so the molecule of intermediate compound is formed in substantial amount in the beginning which then react to give the final product. To determine the mechanism of a reaction is not a simple task. It depends on the experience and expertise of a scientist. The necessary condition for the study of mechanism is that it leads to correct rate law. Even with this it is not sure that we will be able to know correct mechanism. To include in mechanism some methods are necessary to test this study of several steps. We shall study some simple or easy reactions.

(1) Reaction involving two successive first order steps : This type of reaction occurs in two steps in which both the steps are first order reaction viz.

(i) $R \xrightarrow{K_1} I$ (ii) $I \xrightarrow{K_2} P$

In the above reaction in first step : (i) Intermediate compound (I) is formed. (I) Is being collected and becomes maximum as mentioned earlier, then it decomposes and reaches zero concentration and changes in to product. In the fig 1.10 this is shown.

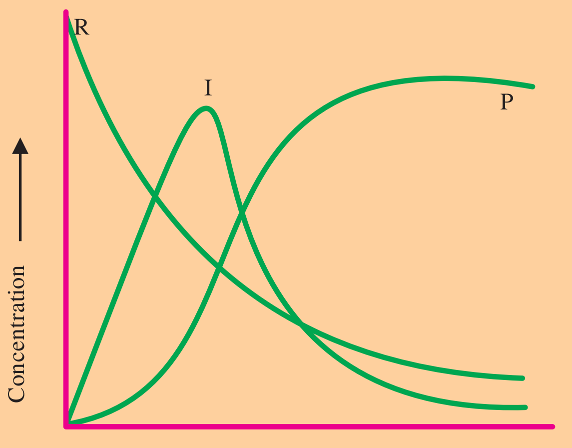


Fig. 1.10 Change in reaction (R), intermediate (I) and product (P) with time.

With the time, the concentration of R decreases and that of I goes towards maximum. After being maximum, at certain time concentration of I decreases and concentration of P increases.

(2) Reaction involving slow step : Suppose any reaction occurs in more than one steps, then the **slowest step becomes rate determining step.** As the rate of this step is slow because the value of its rate constant is low or the concentration of one or more species may be low in elementary reaction. We shall study the following reaction.

$R \xrightarrow{K_1} I \qquad I \xrightarrow{K_2} P$

In the above reaction if $K_1 << K_2$ then the conversion of I into product will be as soon as I is formed. Hence, we can write.

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = K_1[R]$$

To understand this phenomenon, we shall take following illustration. Suppose a message is to be sent from New York to New Delhi. There are two alternatives. In the first alternative the person sending the message (writer) writes a letter in New York and sends it by post. The postman delivers the message to the other person (receiver) in New Delhi. It is clear from the illustration that the time required for the post to reach from New York to New Delhi will be more. Hence, this first step is the slow step.

Hence, the time required in receiving the post, the first step is slow and so more time will be required and so the rate determination for delivery of the post will become rate determining step. Second alternative is that the writer of the message sends the message from New York to New Delhi by telegram and the postman delivers the post to the receiver of the message. In this alternative, the first step is fast but second step will be slow. Hence, the time required for receiving the message will be determined by this step or will become the rate determining step.

The chemical reaction : $3ClO^- \rightarrow ClO_3^- + 2Cl^-$ occurring in certain following steps.

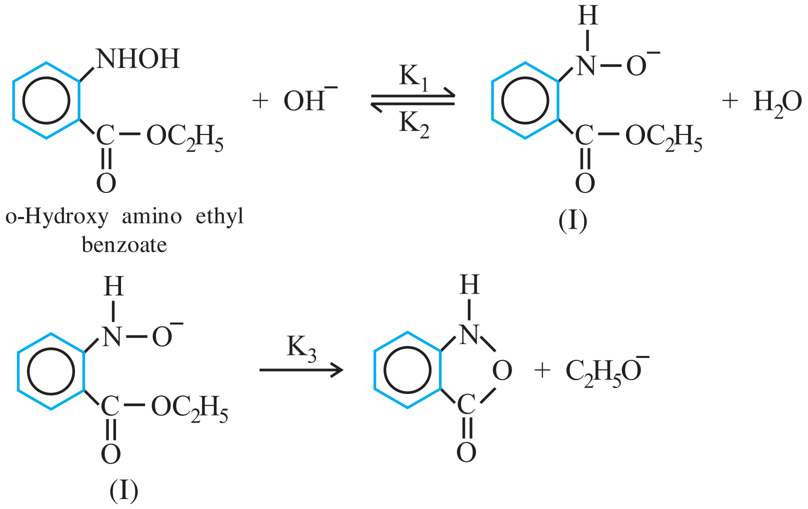
(i) $ClO^- + ClO^- \rightarrow ClO_2^- + Cl^-$ (slow step-Rate determining step.)

(ii) $ClO_2^- + ClO^- \rightarrow ClO_3^- + Cl^-$ (fast step.)

Hence, rate of reaction = $K_1[ClO^-]^2$

(3) The reaction for which steady state hypothesis is valid : Suppose a chemical reaction occurs in more than one steps and certain intermediate compounds of it are possible. In the hypothesis of steady state, we assume that the intermediate compounds carry out reaction in such a way that in the short time at the beginning (which is called induction time) their concentration decreases to some higher value than zero and remains almost constant during the time period of that reaction. Hence, it can be accepted that the concentration of such intermediate compounds (active) which can react is zero. By this hypothesis the equations for the rates of complex reactions can be derived.

(4) Reaction involving intermediate compounds in equilibrium with reactants : Especially in the reactions H^+ and OH^- the rate constants of forward and reverse reactions are very high between them. The intermediate compound that is formed in this way, reacts so slow that there is little change in concentration of intermediate. If we take as an example, the ion $C_2H_5O^-$ obtained from o-hydroxyaminoethylbenzoate, is catalyzed by OH^- ion. The mechanism suggested is as follows :



The value of K_3 is less than the values of K_1 and K_2. Hence, writing the concentration of intermediate compound (I) at equilibrium :

$$[I] = K_1 \frac{[Ester]\,[OH^-]}{K_2}$$

Reaction rate $= K_3[I] = \dfrac{K_3K_1}{K_2}$ [Ester] $[OH^-]$

$= K_0$ [Ester] $[OH^-]$

This is a second order reaction but the over all or the total reaction rate constant includes all the three rate constants. Hence $K_0 = \dfrac{K_3K_1}{K_2}$

Here, K_0 is called overall or total reaction rate constant. Its value depends on the values of all the three rate constants K_1, K_2 and K_3

SUMMARY

- The study of rate of chemical reaction is called chemical kinetics. It is independent of thermodynamics, equilibrium etc. but all the three are associated for the result of the product. Many reactions occur in our every day life in which some of them are very slow viz. Radioactivity of uranium, some medium viz. combination of dinitrogen and dihydrogen and formation of ammonia gas and very fast reaction viz. neutralization reaction between strong acid and strong base. The spoilage of milk, formation of amino acid from urea, etc. are the enzyme catalyzed reactions in everyday life.
- The rate of reaction depends on the rates of their forward and reverse reactions i.e. V_f and V_r. If $V_f > V_r$ then forward reaction (more product) and if $V_f < V_r$ then reverse reaction (less product) and if $V_f = V_r$ then the reactions results in equilibrium.
- Amongst the factors affecting the rate of chemical reaction are (1) state of substance and area of surface (2) concentration of solution (3) pressure of system (for gaseous reactions) (4) temperature (5) effect of catalyst.
- The average rate of reaction $r_{av} = -\dfrac{\Delta[R]}{\Delta t} = \dfrac{\Delta[P]}{\Delta t}$ and its unit is molar sec^{-1}, molar min^{-1} or molar $time^{-1}$. In addition, to this the instantaneous rate determination is difficult. To determine average rate, differential or integration method is used. For the reaction like $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$,

  the rate of reaction $= -\dfrac{1}{2}\dfrac{d[NO]}{dt} = -\dfrac{d[O_2]}{dt} = +\dfrac{1}{2}\dfrac{d[NO_2]}{dt}$

  For a general reaction $n_1A + n_2B = n_3C + n_4D$

  Averge rate $= -\dfrac{1}{n_1}\dfrac{d[A]}{dt} = -\dfrac{1}{n_2}\dfrac{d[B]}{dt} = +\dfrac{1}{n_3}\dfrac{d[C]}{dt} = +\dfrac{1}{n_4}\dfrac{d[D]}{dt}$
- The order of reaction is the exponent of the concentration which determines the rate of any reaction in relation to concentration of reactant. It can be zero, first, second and third order reaction. Reactions having three and more order of reactions are complex and so not included in the study. The second term is molecularity. The number of atoms, ions or molecules of a reactant which takes part in elementary reaction, and experience collision simultaneously

and due to which the reaction results is called molecularity. The order of reaction and their rate constants (K) can be shown as below :

Order of reaction (n)	**Unit of rate constant (K)**
0	mol $lit^{-1}sec^{-1}$
1	sec^{-1}
2	$(mol\ lit^{-1})^{-1}\ sec^{-1}$
n	$(mol\ lit^{-1})^{1-n}\ sec^{-1}$

- The integrated rate law is very simple and useful from experimental study point of view. For zero order reaction rate constant $K = \frac{[R]_0 - [R]_t}{t}$. For first order reaction $K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$. The equations of the rate constants of both these orders can be derived as shown in the unit.

- Pseudo first order reaction is such a reaction in which the concentration of two molecules might change and so it becomes bimolecular but the experimental results satisfy the first order reaction, hence they are called pseudo first order reaction. e.g., the hydrolysis reaction of methyl acetate with water in which methanol and ethanoic acid are obtained. Some characteristics of first and zero order reactions are shown in the following table :

Order	**Type of Reaction**	**Differential rate law**	**Integrated rate law**	**Straight line graph**	**Half life period**	**Unit of K**
0	$R \rightarrow P$	$-d[R]/dt = K$	$Kt = [R]_0 - [R]$	R Vs. t	$[R]_0 / 2K$	Concentration $time^{-1}$ or molar $sec.^{-1}$
1	$R \rightarrow P$	$-d[R]/dt = K[R]$	$[R] = [R]_0\ e^{-Kt}$ **or** $-Kt = \ln[R]_0 / [R]$	ln[R] Vs. t	ln 2/K	$Time^{-1}$ or $sec.^{-1}$

- The methods for determination of order of reaction are (1) Integrated rate equation method or Graphical method (2) Ostwald's isolation method and (3) Half life (reaction time) etc.

- Arrhenius equation combining energy of activation and rate constant is $K = Ae^{-E_a/RT}$ or

$$\log_{10}K = \log_{10}A - \frac{E_a}{2.303\ R} \bullet \frac{1}{T}$$

- In the above equation K = rate constant, A = Arrhenius constant, E_a = energy of activation and T is temperature in Kelvin. According to this equation if a graph of $\log K \rightarrow \frac{1}{T}$ is plotted then the value of E_a from the slope and the value of A from the intercept can be determined. Generally the rate of reaction is doubled during the temperature range 300 to 310 K temperatures.

- According to Arrhenius theory, when the reaction after obtaining sufficient energy increases the value of potential energy, the energy barrier can be crossed and the reaction results into products. To become active, these molecules require the threshold energy and reach the activated state. As it is unstable, it is converted to product.

- In addition to this, there is another theory called the collision theory. In it, the molecules are assumed to be hard spheres. For any molecules to collide and to result in the reaction, the following conditions are necessary :

  (1) There must be collision between reactant molecules.

  (2) Each molecule experiencing collision must have proper energy which is called threshold energy.

  (3) The collision of reactant molecules must be in proper direction (oriented).

  (4) The molecules experiencing fruitful collison change into product molecule.

- In endothermic reaction total potential energy of the reactant molecules is less than the total potential energy of the product molecules and so the value of ΔH obtained is positive. In exothermic reaction, the total potential energy of reactant molecules is more than the total potential energy of product and so the value of ΔH obtained is negative or the heat is released. The collision theory can be expressed as, Rate = $PZ_{AB}\ e^{-E_a/RT}$ where, Z = collision frequency factor and P is the probability of collision. Frequency factor Z and Arrhenius constant A have same meaning. The rate of reaction increases due to the presence of catalyst which can be understood by the principle of adsorption.

- To explain the order of reaction, different alternatives are possible, viz., Intermediate compound, I is formed from reagent A and then product B is formed. Such reaction occurs in more than one-step and so the slowest step becomes rate determining step for the reaction. In addition to this, steady state hypothesis is used in which the reactant in the short time of the beginning of the reaction i.e. in induction period the concentration of product becomes highest. On the basis of such types of explanations the mechanism of reactions can be explained. The examples of which are included in the unit.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which unit of time is selected for fast reactions ?

(A) Day (B) Second (C) Year (D) Nanosecond.

(2) The reaction rate increases with increase in temperature, because .....

(A) Energy barrier decreases

(B) Threshold energy increases

(C) Activation energy increases

(D) The number of molecules undergoing effective collision increases.

(3) For the reaction $n_1A + n_2B \rightarrow$ Products; rate = $K[A]^3[B]^0$ if concentration of A is doubled and concentration of B is halved, then reaction rate....

(A) Increases by four times. (B) Increases by eight times.

(C) Is doubled. (D) Becomes ten times.

(4) Which of the following is indicated by the stoichiometry of the reaction ?

(A) Order of reaction

(B) Mechanism of reaction

(C) The number of intermediate compound

(D) The relative mole number of reactants and products.

(5) What is the SI unit of reaction rate ?

(A) mol sec^{-1} (B) mol $m^{-3}sec^{-1}$ (C) mol dm sec^{-1} (D) mol lit^{-1}

(6) If the order of reaction is 'n', then what will be the unit of its rate constant ?

(A) $lit^{n}\ mol^{-n^{2}}\ sec^{-1}$ (B) $(mol\ lit^{-1})^{n-1}\ sec^{-1}$

(C) $\left(\frac{lit}{mol}\right)^{n-1} sec^{\frac{-1}{n}}$ (D) $mol^{n}\ lit^{-n}\ sec^{-1}$

(7) If the relation between half reaction time and $[R]_0$, is $t_{1/2}\ \alpha\ \frac{1}{[R]_0^{n-1}}$ then what will be the order of reaction ?

(A) $\frac{n-2}{2}$ (B) n–1 (C) $\frac{1}{n-2}$ (D) n

(8) The order of following reactions are respectively .....

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

(A) 2, 2, 2 (B) 0, 2, 2 (C) 0, 1.5, 2 (D) 2, 1.5, 2

(9) If two reactants are taking part in the reaction, then the reaction will never be

(A) First order (B) Second order (C) Monomolecular (D) Bimolecular.

(10) Of which of the following factors, the rate of reaction depends on

(A) Molecular mass of reactant (B) Atomic mass of reactant

(C) Equivalent weight of reactant (D) Active mass of reactant.

(11) What is indicated by $-\frac{1}{2}\frac{d[N_2O_5]}{dt}$ term ?

(A) Rate of introduction of N_2O_5 (B) Decomposition rate of N_2O_5

(C) Order of reaction (D) Molecularity of reaction.

(12) Which of the following statements is incorrect for Arrhenius rate constant equation ?

(A) It gives quantitative idea about K and T

(B) As T increases K is increasing and A is decreasing

(C) As E_a increases K is increasing

(D) If $E_a = 0$ then $K = A$.

(13) Which of the following statements is incorrect regarding order of reaction and molecularity ?

(A) Molecularity is the theoretical conclusion while order of reaction is experimental conclusion.

(B) The value of molecularity is positive integer while the value of reaction order may be positive, negative of zero.

(C) Molecularity explains the reaction mechanism while reaction order does not give any information about reaction mechanism.

(D) For elementary reactions, the order of reaction and molecularity are same.

(14) For which elementary reactions, the order of reaction and molecularity will be same ?

(A) Monomolecular and bimolecular (B) Bimolecular and termolecular

(C) Monomolecular and termolecular (D) All the molecular reactions.

(15) Which of the following mathematical relations is correct ?

(A) For zero order $\left(t_{1/2} \times K\right) = \frac{[R]_0}{2}$

(B) For 0.5 order $\left(t_{1/2} \times K\right) \alpha \sqrt{[R]_0}$

(C) For first order $\left(t_{1/2} \times K\right) = 0.693$

(D) All the three relations given here are correct.

(16) What is indicated by negative sign before the term of reaction rate ?

(A) The kinetic energy of the reaction decreases with time

(B) The energy barrier of reaction decreases with time

(C) The energy of activation of reaction decreases with time

(D) The concentration of reactants decreases with time.

(17) If temperature of the reaction is increased from 300 to 310 K, the value of rate constant is almost doubled because.......

(A) Kinetic energy is doubled

(B) The fraction of effective collision of molecules is almost doubled

(C) The number of molecular collision increases

(D) Energy of activation decreases.

(18) The reactions having very high values of energy of activation are generally ……

(A) Very slow (B) Very fast (C) Spontaneous (D) Medium fast.

(19) For a first order reaction $K = 10^{-3}$ min^{-1} its $t_{1/2}$ = ………..

(A) 3300 min (B) 2000 min

(C) 1500 min (D) None of the three.

(20) For which reaction the collision theory is generally more satisfactory ?

(A) First order (B) Second order (C) Zero order (D) Any order.

(21) In the reaction A → B, if the concentration of A is doubled then the reaction rate increases by 1.59 times then what will be the order of reaction ?

(A) $\frac{2}{3}$ (B) $\frac{3}{2}$ (C) $(1.59)^2$ (D) 1.59

(22) Zero order reaction means……

(A) Reaction occurring at zero Kelvin temperature

(B) The value of reaction rate is zero

(C) The reaction in which the reactants do not take part in chemical reaction

(D) Reaction rate and rate constant are equal.

(23) Which of the following reactions will be comparatively the slowest ?

(A) Decomposition of urea in presence of urease enzyme

(B) Formation of rust on iron in presence of inhibitors

(C) The combination of N_2 and O_2 when lightening is there in the sky

(D) The rate of reverse reaction in presence of catalyst.

(24) Which of the following unit of time possessing reaction will be the fastest ?

(A) Femtosecond (B) Nanosecond (C) Picosecond (D) Microsecond.

(25) What is studied in chemical kinetics ?

(A) Structure of molecules

(B) Possibility whether reaction will occur or not

(C) Reactants will transform into which product

(D) The study of reaction rates of chemical and physical changes.

(26) Elementary reaction $2SO_2(g) + O_2(g) \rightarrow$ Products. If pressure is increased by three times then reaction rate …..

(A) Increases by 3 times (B) Increases by 9 times

(C) Increases by 18 times (D) Increases by 27 times.

(27) According to transition state theory, the reaction can be shown passing through which of the following steps ?

(A) Reactants → Products → Activated complex

(B) Reactants → Products

(C) Reactants → Activated complex → Products

(D) Reactants → Activated complex products → Activated complex → Products

(28) For elementary reaction, which of the following is correct ?

(A) Order of reaction $>$ molecularity (B) Order of reaction $\neq$ molecularity

(C) Order of reaction $=$ molecularity (D) Order of reaction $<$ molecularity.

(29) According to molecular collision theory, the reaction is subjected to .....

(A) Number of molecular collisions of reactant

(B) Number of collisions between reactants and activated complex

(C) The collision rate between reactants and product molecules

(D) Number of effective molecular collisions of reactants

(30) Which scientist explained the effect of temperature on the reaction rate constant ?

(A) Faraday (B) Waag and Guldberg

(C) Le-Chatelier (D) Arrhenius

2. Answer the following questions in brief :

(1) Mention limitation of thermodynamics.

(2) Why does the rate of reaction increase with increase in temperature ?

(3) The charcoal powder burns faster than the piece of charcoal. Why ?

(4) What is called chemical reaction rate ?

(5) Mention the mathematical form of instantaneous rate for the reaction $R \rightarrow P$.

(6) What is called specific rate constant ?

(7) Write definition of order of reaction.

(8) The reaction becomes fast by the use of suitable catalyst. Why ?

(9) Write unit of rate constant for zero order reaction.

(10) Write equation of rate constant for first order reaction.

(11) What is called molecularity ?

(12) Write Arrhenius equation.

(13) Mention the value of slope in the graph of log K versus $\frac{1}{T}$.

(14) What is meant by collision theory ? Explain.

(15) Explain half reaction time : Mention its relation with K for the first order reaction.

(16) Write definition of energy of activation.

(17) What is meant by threshold energy ? Why is it required ?

(18) How many times the reaction rate constant increases when temperature of reaction is increased by 10^0 ?

(19) Give examples of very slow and very fast reactions.

(20) For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. write the equation for reaction rate.

3. Answer the following questions in detail :

(1) Mention the factors affecting rate of chemical reaction.

(2) A second order reaction is in respect to some reactant. If the concentration of reactant is (1) doubled and (2) halved, then how will the rate constant be changed ?

(3) Explain the effect of temperature, on the rate of chemical reaction.

(4) Mention Arrhenius equation. Explain the terms involved in it.

(5) Write important points of collision theory.

(6) Give definitions : (i) Reaction order (ii) Molecularity.

(7) Derive the equation of rate constant for the first order reaction.

(8) Explain graphical method to determine the order of reaction.

(9) Give information about energy barrier of chemical reaction and explain its importance.

(10) Describe Ostwald's isolation method for determination of order of reaction.

(11) Explain the terms : Half reaction time and energy of activation.

(12) Explain the effect of concentration of reactant on the rate of reaction.

(13) Explain the effect of catalyst on rate of reaction.

(14) Describe the method to determine instantaneous rate.

(15) What is meant by steady state and intermediate compound ?

4. Calculate the following examples :

(1) The initial concentration of N_2O_5 in the first order reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ is 1.24×10^{-2} mol lit^{-1} at 318 K temperature. The concentration of N_2O_5 decreases to 0.20×10^{-2} mol lit^{-1} after 1 hour. Calculate the rate constant of this reaction at this temperature.

(2) The rate constant of a first order reaction is 1.20×10^{-3} s^{-1}. What time it will take to have reactant 3 gram from 5 gram ?

(3) During decomposition of SO_2Cl_2, its concentration becomes half of its initial concentration in 60 minutes. What will be the rate constant of this reaction ?

(4) The following results are obtained in one pseudo first order reaction :

Time (second)	0	30	60	90
Concentration of reactant mol lit^{-1}	0.551	0.312	0.173	0.085

(i) Calculate average rate of reaction between 30 and 60 seconds (ii) Calculate the rate constant of this first order reaction.

(5) Prove for the first order reaction that the time required for completion of 99% reaction is double than the time required for completion of 90% reaction.

(6) Sucrose is converted to glucose and fructose in presence of acidic solution which is first order reaction. The half reaction time of this reaction is $t_{1/2} = 3.0$ hours. How many times the initial concentration becomes less after 9 hours ?

(7) The decomposition of NH_3 on the platinum surface is zero order reaction. If $K = 2.5 \times 10^{-4}\ Ms^{-1}$, what will be the rate of introduction of N_2 and H_2 ?

(8) If the rate of reaction is doubled by increasing the temperature from 298 K to 308 K, then calculate the energy of activation of the reaction.

(9) The half life period of ^{14}C is 5370 years. In a sample of dead tree, the proportion of ^{14}C is found to be 60% in comparison to living tree. Calculate the age of the sample.

(10) The radioactive ^{90}Sr that is formed due to nuclear explosion has half life period of 28.1 years. In the body of a child born at this time ^{90}Sr is found to be 1μg (10^{-6} gram), then what will be ^{90}Sr left in the body of the child when (a) the age of the child will be 20 years and (b) when the age of child will be 70 years. (^{90}Sr is not lost in any other way).

(11) The rate constant of a reaction is $2 \times 10^{-3}\ min^{-1}$ at 300 K temperature. By increase in temperature by 20 K, its value becomes three time; then calculate the energy of activation of the reaction. What will be its rate constant at 310 K temperature ?

(12) In a reaction R → P the concentration [M] obtained at different times (t) are shown in the following table, calculate the average rate r_{av} of the reaction.

Time (t) (second)	0	5	10	20	30
Concentration [M]	160×10^{-3}	80×10^{-3}	40×10^{-3}	10×10^{-3}	3.5×10^{-3}

(13) The rate constant of a reaction of first order is 70 sec^{-1}. What time will be taken to have the concentration $\frac{1}{18}$ part of the initial concentration ?

(14) The decomposition rate constant of hydrocarbon is $2.428 \times 10^{-5}\ sec^{-1}$ at 550 K and activation energy is 197.7 k joule mol^{-1}, then calculate Arrhenius constant.

(15) In the reaction of decomposition of reactant A into product, the rate constant is $4.5 \times 10^{3}\ sec^{-1}$ at 283 K temperature and energy of activation is 60 k joule mol^{-1}. At which temperature, the value of rate constant K will be $3 \times 10^{4}\ sec^{-1}$?

●

Unit

2

Surface Chemistry

2.1 Introduction

The study of the boundary separating two bulk states or phases is called surface chemistry. This boundary is also known as surface or interface. It is shown by hyphen or slash viz. solid-liquid or solid /liquid. The meaning of this is that the solid and the liquid are two separate states or phases and the interface is between them. As gases mix completely there is no possibility of interface because both of this will be included in one phase. The bulk phase may be pure solid or solution. Interface is a layer of bulk phase consisting of thickness of several molecules. It depends upon the size of the molecules in the bulk phase. In short, surface phenomenon is the phenomenon that keeps the solid and liquid or solid and gas phases in contact even though they are being separate. Such type of phenomena are dissolution, crystallisation, reactions on the electrode, heterogeneous catalysis, corrosion of metals etc. The study of surface phenomenon is useful in industry, analytical chemistry and everyday life.

The surface should be pure and clean. For this $10^{-8} - 10^{-9}$ pascal high vacuum is created and the surfaces of metals can be used. So as to keep them free from the effect of the air they are kept in vacuum. In this unit we shall study the aspects related with surface chemistry such as adsorption, catalysis, colloids, enzymes etc.

2.2 Adsorption

In the solid or liquid state, the molecules experience attraction from all sides but the molecules on the surface experience attraction from below and the sides. Because of this the force on the molecules drawing down is more. Hence, the energy of the molecules on the surface is more. Thus a strain is produced in the surface of the solid or liquid due to the imbalanced or residual forces. If such a surface is brought in contact with any gas or liquid, then it tries to keep it nearer to it by attraction.

For example, suppose in a solution of dye-colour, powder of activated charcoal is added, then in a short time there will be a decrease in the intensity of the colour. The reason for this is that the molecules of the dye colour are attracted towards the solid surface of charcoal. Suppose, such molecules remain on the surface of the solid and do not enter into the solid, then the concentration of the solution on the surface will be more than the concentration of the solution in the inner bulk. Thus change in concentration on the surface is observed. **This phenomenon in which the molecules are maintained on the solid or liquid surface and the concentration of molecules on the surface becomes more than the concentration of the molecules in the bulk, is called adsorption.**

The surface energy decreases due to adsorption. **The solid substance on which adsorption takes place is called adsorbent and the substance which is adsorbed is called adsorbate.** The whole phenomenon is called adsorption. In the earlier example, charcoal is the adsorbent and the molecules or particles of the dye are adsorbate; the whole phenomenon showing adsorption is the surface phenomenon.

Suppose, the adsorbed molecules, for some reason (by decreasing pressure or increasing heat) release from the surface or mix in the gas then it is called desorption. It is reverse or opposite phenomenon. Charcoal, silica gel, chalk, alumina, clay etc. are good adsorbents because they are more porous. Hence, their contact surface is more. If a piece of coal is taken and also powdered coal is taken then as the surface of contact is more in powder; adsorption will be more on powder. Thus, the use of powder state consisting of small particles is more effective in adsorption phenomenon. In many chemical reactions, the catalyst is used in fine powder form. Colloids, which we will study later on in this unit, have very small particles and so the contact surface available is more and so colloids are good adsorbents.

Another phenomenon is called absorption; in which the molecules of the substance are spread in the whole part of the solid or liquid. Hence, it possesses homogeneous (single phase) form. As we have seen, in adsorption, there is heterogeneous (more than one phase) form. Suppose, the light yellow coloured sugar is dissolved in water, we get light yellow coloured sugar solution. As the yellow colour is uniform throughout the solution, the concentration of sugar at all the places will be same. Now, if we add charcoal to this solution, then the yellow colour of solution will decrease and the concentration of solution will be more on the surface of the charcoal than that in the solution. The phenomenon before addition of charcoal is absorption and the phenomenon after addition of charcoal is adsorption. Sometimes, both these phenomena occur simultaneously. It is called sorption. e.g. water is absorbed on the anhydrous calcium chloride while water is adsorbed on silica gel. The dihydrogen gas is first adsorbed on the palladium metal and then it is absorbed. Hence, it experiences phenomenon of sorption.

In the following examples, the phenomenon of adsorption is involved :

(1) If gases like O_2, H_2, CO, Cl_2, NH_3 or SO_2 are filled in closed vessels containing charcoal then their pressures decrease because of the adsorption of gas on the surface of charcoal.

(2) The intensity of the colour of the solution of methylene blue decreases by addition of charcoal because of adsorption of methylene blue on charcoal.

(3) To make yellow sugar colourless, its solution is passed through the layer of charcoal so that the yellow colour is adsorbed on the charcoal and the sugar becomes colourless due to adsorption of yellow colour.

(4) To make the air dry by removing the moisture, it is kept in a closed vessel containing silica gel, so that the moisture (water) is adsorbed on the gel and the air becomes dry.

2.2.1 Mechanism of Adsorption :

The reason for the adsorption is that the molecules on the surface and the molecules in the bulk are not in the same condition. There is attraction force from all the sides on the particles in the bulk and remains balanced but the molecules on the surface do not have attraction from all the sides and so they are not balanced or there are residual forces. These residual forces are responsible for the attraction of the adsorbent on their surface. At the given temperature and pressure the adsorption depends on the area of the surface. More the area of the surface more will be the attraction and more will be the adsorption but if the area of the surface is less then attraction will be less and so adsorption will be less. The second factor in the adsorption mechanism is the heat of adsorption. Adsorption is an exothermic phenomenon or the value of ΔH is negative. The entropy of the molecules decreases due to adsorption. Hence, ΔS also becomes negative. Thus the adsorption phenomenon is associated with the decrease in both ΔH and ΔS. According to second law of the thermodynamics, for any spontaneous reaction, the value of ΔG must be negative. Hence, in equation $\Delta G = \Delta H - T\Delta S$ as the value of ΔS is decreasing the value of $- T\Delta S$ will be positive. Hence, the value of ΔH should be more negative and high. As the phenomenon of adsorption proceeds, the value of ΔH becomes less and less negative; so that the value of ΔH becomes almost that of $T\Delta S$ and the value of ΔG becomes zero. In this situation, the equilibrium is attained.

2.2.2 Types of Adsorption :

There are two types of adsorption (i) Physical adsorption or physisorption and (ii) Chemical adsorption or chemisorption

In physical adsorption, the molecules are adsorbed through van der Waals' forces, while in chemical adsorption, the attraction forces are of chemical bond type. Physical adsorption is a physical process while chemical adsorption is a chemical process. Adsorption is generally an exothermic process. The value of enthalpy of adsorption for chemical adsorption is comparatively more negative than the enthalpy value of physical adsorption.

The comparison of physical and chemical adsorption is given in the following table 2.1.

Table 2.1 Comparison of physical adsorption and chemical adsorption

Physical adsorption	Chemical adsorption
(1) There are van der Waals' forces between adsorbent and adsorbate	(1) There are chemical bond type forces between adsorbent and adsorbate
(2) The value of adsorption enthalpy is about 20 to 40 k Jmol^{-1} i.e. less and negative	(2) The value of adsorption enthalpy is about 80 to 240 k Jmol^{-1} i.e. more and negative
(3) Generally results at low temperature and adsorption decreases with increase in temperature	(3) Generally results at high temperature. There is no special effect of change in temperature
(4) It is not specific i.e. all the gases are adsorbed in a more or less proportion on all solid adsorbents	(4) It is specific. It results if there is possibility of chemical bond formation between adsorbent and adsorbate.
(5) It is instantaneous	(5) It can be slow or fast
(6) Multimolecular layers can be formed on the adsorbent	(6) Generally unimolecular layer is formed on the adsorbent

(7) It is reversible	(7) It is irreversible
(8) Less energy of activation is required	(8) More energy of activation is required
(9) It depends on the nature of the gas. Gases which can be easily liquefied are adsorbed rapidly	(9) It depends on the nature of the gas. The gases which react with adsorbent show more adsorption.

In this unit; we shall study only the adsorption phenomenon of an adsorbate on the solid adsorbent. Some of the illustrations of this are as follows :

(1) Suppose we enter into the atmosphere of chlorine gas by putting on gas mask containing active charcoal, the charcoal will adsorb chlorine and we will be saved from the poisonous effect of chlorine.

(2) To remove moisture from the moist air, silica gel is used as adsorbent. To keep some of the electronic instruments free from moisture, so they may not be damaged by the moisture.

(3) The harmful effect of gaseous pollution in the air can be avoided from their harmful effect by use of charcoal as adsorbent.

(4) Sugar can be made colourless by removing colour (like yellow) from it.

2.2.3 Factors Affecting Adsorption :

The adsorption of gases on the adsorbate depends on the following factors :

(1) Nature of adsorbate (2) Nature of adsorbent (3) The specific area of the adsorbent (4) The pressure on the gas that is adsorbed (5) The temperature (6) Activation of the adsorbent. We shall study some of these factors :

(1) Nature of adsorbate : As studied earlier, physical adsorption being not specific, every gas can be adsorbed on any solid in a more or less proportion. At the given temperature and pressure, the gases like NH_3, HCl, CO_2 etc. which can be easily liquefied are adsorbed in more proportion; while the permanent gases like H_2, O_2, N_2 etc. which cannot be easily liquefied are adsorbed in less proportion. The liquefaction of gas has relation with critical temperature (T_C). Hence, the gases with higher critical temperature are adsorbed more; chemical adsorption being of specific type, if combination is possible, only then adsorption will take place. You have earlier studied about liquefaction of gases, critical temperature, critical pressure and critical volume.

(2) Nature of adsorbent : Generally adsorbents are substances like carbon, animal charcoal, metal oxides, silica gel, alumina and clay. All these adsorbents have their characteristic adsorption properties on the basis of their components and their structure.

(3) Specific area of adsorbent : Specific area means the surface area available for 1 gram adsorbent. More the surface area, more will be the adsorption. More the porosity of the adsorbent more will be the specific area. Hence, in the reactions, porous or powder form of adsorbent adsorbs more gas than blocks of the substance because the available area is more. The iron powder adsorbs more than the iron block. The pores of adsorbent must be big enough so that the adsorbed gas can enter into them.

(4) Adsorption isotherm : Generally the magnitude or the proportion of adsorption of adsorbate gas is expressed as $\frac{x}{m}$ where m is the weight of the adsorbent and x is the concentration or number of moles of adsorbate when dynamic equilibrium is established between free gas and the adsorbed gas. Experimentally $\frac{x}{m}$ is determined and at definite temperature, if we plot a graph of $\frac{x}{m}$ versus p then a curve (isotherm) as shown in fig. 2.1 is obtained. This curve is known as adsorption isotherm curve.

As shown in fig. 2.1 different curves are obtained at different temperatures. In addition, the graphs of isotherms are of different shapes. They are of five different types. We shall study the general isotherm without going into the details of different isotherms. Scientists Freundlich and Langmuir had studied such isotherms and the adsorption isotherm obtained is as shown in fig. 2.1.

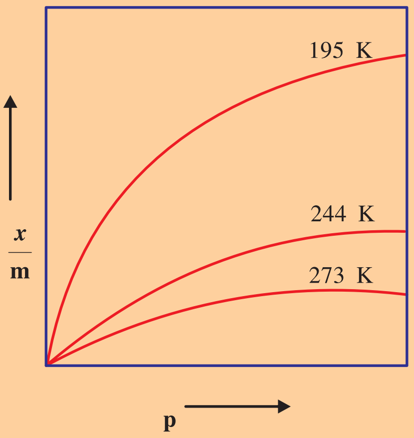


Fig. 2.1 Absorption isotherm

(5) Temperature : There is an effect of increase in temperature on adsorption isotherm. As studied earlier, adsorption is an exothermic reaction, and so according to Le-Chatelier's principle, an increase in temperature will show a decrease in quantity of gas adsorbed. Hence, as shown in fig. 2.1 a decrease in temperature results in an increase in quantity of gas adsorbed.

2.3 Freundlich Adsorption Isotherm

The adsorption of gaseous adsorbate on solid adsorbent at definite temperature is proportional to the pressure of the adsorbed gas. This relation can be shown as below :

$$\frac{x}{m} \propto p^{\frac{1}{n}} \quad \text{OR} \quad \frac{x}{m} = Kp^{\frac{1}{n}} \qquad \text{..... (2.1)}$$

where $\frac{x}{m}$ is the adsorption per gram of absorbent in which m is the weight of adsorbent and x is the pressure (P) of the adsorbed gas. K and n are constants which depend on nature of gas and the temperature. This is called Freundlich adsorption isotherm. The graph shown in fig. 2.2 shows Freundlich adsorption isotherm. The value of specific adsorption $\frac{x}{m}$ increases with increase in pressure; but as n > 1 the value of $\frac{x}{m}$ does not increase so suddenly with increase of p. After certain pressure, the value of adsorption remains almost constant. This isotherm curve is called Freundlich adsorption isotherm. Taking logarithm of equation 2.1

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p \qquad \text{..... (2.2)}$$

As this equation is of the type Y = C + mX if the graph of $\log \frac{x}{m}$ versus log p is plotted a straight line will be obtained which is shown in fig. 2.2.

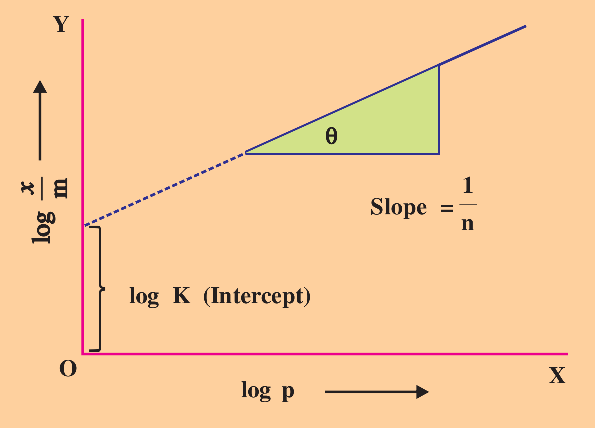


Fig. 2.2 Freundlich isotherm

The value of the slope of the graph will be $\frac{1}{n}$ and the value of intercept will be log K. From this, the values of the constants K and n can be obtained. In addition, whether any adsorption process follows Freundlich equation or not can also be verifed. For this process, if the graph of log $\frac{x}{m}$ versus log p obtained is a straight line, then it satisfies or obeys Freundlich equation.

If you will observe the results carefully in the demonstration experiment on adsorption of methylene blue on charcoal, the explanation will be clear and can be verified.

Limitations of Freundlich adsorption isotherm : In the Freundlich adsorption isotherm, the following deviations and limitations are seen :

(1) This isotherm is applicable in certain limits of pressure but it shows deviation at high pressure so that the curve of the isotherm is changed.

(2) K and n are constants but for the same adsorbent and adsorbate, they change with temperature.

(3) Freundlich adsorption isotherm is empirical; there is no theoretical proof of it.

(4) If the value of $\frac{1}{n}$ is 1 then $\frac{x}{m}$ = Kp so the adsorption will be directly proportional to pressure but if the value of $\frac{1}{n}$ becomes 0, then $\frac{x}{m}$ = constant; so the adsorption will be independent of pressure. Thus, by increasing pressure, the adsorption attains saturation which cannot be explained by Freundlich isotherm i.e. at high pressures it shows deviation.

2.4 Langmuir Adsorption Isotherm

Freundlich adsorption isotherm is empirical. There is no theoretical basis. Langmuir derived a new isotherm on basis of kinetic theory of gases which is called Langmuir adsorption isotherm. It is assumed that all adsorption sites are equal and it is independent of the neighbor sites. He has considered two processes opposite to each other in the isotherm derived by him.

(1) There is adsorption of gas molecules on the surface of solid substance. It is known as condensation.

(2) There is desorption of adsorbed gas molecules from the surface of solid substance. It is called evaporation.

Langmuir assumed that there is dynamic equilibrium established between the above two processes. In addition, he also assumed that adsorbed gas possesses thickness of one molecule or monomolecular layer is formed. Such an aspect is in chemical adsorption. The Langmuir adsorption isotherm can be derived and can be shown in short by the following formula. Langmuir adsorption isotherm can be derived, but it is not in our syllabus. So, it can be written in short as follows :

$$\frac{x}{\mathrm{m}} = \frac{\mathrm{ap}}{1 + \mathrm{bp}} \qquad \text{..... (2.3)}$$

where x/m is the adsorption of gas per gram of adsorbent as seen in Freundlich adsorption isotherm and p is the pressure of the gas; a and b are constants. The above equation can be written in two situations : (1) At low pressure and (2) At high pressure.

(1) At low pressure : In the equation $\frac{x}{\mathrm{m}} = \frac{\mathrm{ap}}{1 + \mathrm{bp}}$ if the value p is taken to be low, then the value of bp can be neglected in comparison to 1. Hence $\frac{x}{\mathrm{m}} = \mathrm{ap}$ i.e. at low pressure, the adsorption of gas is directly proportional to the pressure.

(2) At high pressure : In the equation $\frac{x}{\mathrm{m}} = \frac{\mathrm{ap}}{1 + \mathrm{bp}}$, if the value of p is taken high then, 1 can be neglected in comparison to the value of bp. Hence, $\frac{x}{\mathrm{m}} = \frac{\mathrm{a}}{\mathrm{b}} =$ constant. Thus, at high pressure adsorption will be almost constant which is clear from figure 2.1. To determine the constants a and b the equation $\frac{x}{\mathrm{m}} = \frac{\mathrm{ap}}{1 + \mathrm{bp}}$ can be written by inverting it,

i.e. it will be $\frac{\mathrm{m}}{x} = \frac{1 + \mathrm{bp}}{\mathrm{ap}}$

$$\text{Now } \frac{\mathrm{m}}{x} = \frac{1 + \mathrm{bp}}{\mathrm{ap}} = \frac{1}{\mathrm{ap}} + \frac{\mathrm{bp}}{\mathrm{ap}} = \frac{1}{\mathrm{ap}} + \frac{\mathrm{b}}{\mathrm{a}} \qquad \text{..... (2.4)}$$

This equation is also the equation for straight line and so if a graph of $\frac{\mathrm{m}}{x}$ versus $\frac{1}{\mathrm{p}}$ is plotted, then the value of the slope will be equal to $\frac{1}{\mathrm{a}}$ and the value of intercept will be equal to $\frac{\mathrm{b}}{\mathrm{a}}$. From this, the values of constants a and b can be obtained.

Freundlich adsorption isotherm shown in figure 2.1, shows that in the beginning the values of adsorption $\frac{x}{\mathrm{m}}$ increases with increase in pressure of gas but when the value of pressure increases, the isotherm tends to become constant, that is the adsorption attains saturation and more adsorption will not take place which supports the above two situations.

2.5 Adsorption From Solution

Freundlich adsorption isotherm can be applied to liquid system like that of gaseous system. The adsorption of substance dissolved in solution can be adsorbed on the solid adsorbent. In the practical book, the experiment of adsorption of methylene blue on charcoal is given for demonstration experiment. You should understand this experiment thoroughly by observation and make this study more simple and intensive. Similar to this, other experiments can be carried out. The adsorption of acetic acid from solution of acetic acid on activated charcoal can be carried out. For this, solutions of acetic acid having different concentration can be taken and definite weight of adsorbent - activated charcoal can be added and the concentration of acetic acid not absorbed can be determined. From the difference of concentrations before adsorption and after adsorption the concentration difference of acetic acid can be determined which will be $x \cdot$ m is known because it is taken by weighing adsorbent. Hence, the graph of $\frac{x}{\mathrm{m}}$ versus concentration of acetic acid before adsorption is plotted and Freundlich adsorption isotherm curve will be obtained. By plotting graph of $\log \frac{x}{\mathrm{m}}$ versus log C a straight line will be obtained which is the proof of Freundlich equation. From this, the following can be written for Freundlich and Langmuir adsorption isotherm for physical and chemical adsorption.

Freundlich adsorption isotherm	**Langmuir adsorption isotherm**
(1) Physical adsorption : $\frac{x}{\mathrm{m}} = \mathrm{Kp}^{\frac{1}{\mathrm{n}}}$ OR $\log \frac{x}{\mathrm{m}} = \log \mathrm{K} + \frac{1}{\mathrm{n}} \log \mathrm{p}$	$\frac{x}{\mathrm{m}} = \frac{\mathrm{ap}}{1 + \mathrm{bp}}$ OR $\frac{\mathrm{m}}{x} = \frac{1}{\mathrm{ap}} + \frac{\mathrm{b}}{\mathrm{a}}$
(2) Chemical adsorption : $\frac{x}{\mathrm{m}} = \mathrm{KC}^{\frac{1}{\mathrm{n}}}$ OR $\log \frac{x}{\mathrm{m}} = \log \mathrm{K} + \frac{1}{\mathrm{n}} \log \mathrm{C}$	$\frac{x}{\mathrm{m}} = \frac{\mathrm{aC}}{1 + \mathrm{bC}}$ OR $\frac{\mathrm{m}}{x} = \frac{\mathrm{b}}{\mathrm{a}} + \frac{1}{\mathrm{C}}$

Applications or uses of adsorption : There are many applications of adsorption phenomenon. Some of them are as follows :

(1) Charcoal adsorbent is used to produce high vacuum, in adsorption of small proportion of gases.

(2) While working in the atmosphere of poisonous gas like chlorine, the gas mask that are used contains active charcoal as adsorbent which adsorbs poisonous gas and provides protection.

(3) Silica gel is used as adsorbent for keeping electronic instruments etc. free from moisture.

(4) Activated charcoal is used for removal of impurity of colour from sugar and other substances.

(5) Vanadium pentoxide used as heterogeneous catalyst in production of sulphuric acid and the iron powder used as heterogeneous catalyst in production of ammonia are useful as solid adsorbents.

(6) In separation of inert gases by Dewar's method activated charcoal is used as adsorbent.

(7) Substances used for treatment of certain diseases act as adsorbent and adsorb the microorganism.

(8) In froth floatation method, in concentration of sulphide minerals, turpentine oil or pine oil are used as adsorbents.

(9) In certain titrations eosin or fluorescin is used as an indicator e.g. In the titration of halide with silver nitrate adsorbate like fluorescin is adsorbed on the precipitates of silver halide. Such indicators are called adsorption indicators.

(10) In chromatographic separation, solid substance can be used as adsorbent and separation of inorganic anions, mixture of amino acid, analysis of dyes in the ink can be carried out by adsorption chromatography. In your book of practicals, demonstration experiment of separation of Pb^{2+} and Cd^{2+} by adsorption chromatography is included. In addition, separation of dyes in the ink by adsorption on adsorbent like filter paper is also included in demonstration experiments.

2.6 Catalysis

In the earlier standards you have studied that oxygen gas is obtained by heating potassium chlorate but this reaction is slow. So, if manganese dioxide is added to it, the decomposition of potassium chlorate becomes fast and manganese dioxide remains in the original form. This means that the decomposition rate of potassium chlorate is slow in absence of manganese dioxide but it becomes faster in its presence. Thus, manganese dioxide as a specific substance, without taking part in the reaction affects the reaction rate. Hence, the following can be deduced.

The substance which is not used in the chemical reaction, is obtained back in its original form and increases the rate of reaction or decreases the time required for going towards the product, is called catalyst and thus the phenomenon of increasing rate of reaction with the help of catalyst if called catalysis. As catalyst does not take part in the reaction, its small amount is essential. Many catalysts are used in industry. In the study of adsorption vanadium pentoxide and iron powder are mentioned as catalysts. Nature is also a unique designer of the use of catalysts. The enzymes associated with many biochemical reactions in living beings makes cell reactions fast and sustains the life viz. invertase enzyme forms glucose and fructose from sucrose; urease enzyme transforms urea to ammonia and carbon dioxide as well as pepsin enzyme transforms proteins into amino acids. In obtaining ammonia from dinitrogen and dihydrogen by Haber's process, iron powder is used as catalyst and vanadium pentoxide works as catalyst in obtaining sulphuric acid by contact process.

Even though every catalyst is specific; it normally decreases the activation energy of a reaction. You have studied about activation energy in the unit on chemical kinetics. The decrease in activation energy with the help of catalyst is shown in fig. 1.9 in unit 1.

(1) Catalyst increases equally both the rates of forward and reverse reactions but does not make any effect on equilibrium constant, i.e., is more proportion of product is not obtained.

(2) Catalyst decreases activation energy, i.e., is it lowers the potential energy barrier. Hence, that reaction results in less time.

Types of catalysis : There are two types of catalysis (1) Homogeneous catalysis and (2) Heterogeneous catalysis.

(1) Homogeneous Catalysis : If the catalyst is in the same phase as the reactants are, it is called homogeneous catalyst and this phenomenon is called homogeneous catalysis. It is believed that in this catalysis the catalyst reacts with reactant by undergoing chemical reaction and forms an intermediate compound. This later on decomposes because it is unstable. This is discussed in chemical kinetics and this unstable compound reacts with other reactant and gives the product and the catalyst is obtained back or is recovered. The examples of homogeneous catalysis are as follows :

(1) $O_3(g) + O(g) \xrightarrow{[Cl(g)]} 2O_2(g)$: Decomposition of ozone.

(2) $2CO(g) + O_2(g) \xrightarrow{[NO(g)]} 2CO_2(g)$: Oxidation of carbon monoxide.

(3) $\underset{}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{[H^+(aq)]} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6\,(aq)}$:

This reaction is called inversion of sucrose.

(4) $SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{[NO(g)]} 2SO_3(g)$: Method of preparation of sulphuric acid by Lead Chamber process

(5) $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{[H^+(aq)]} CH_3COOH(l) + CH_3OH(l)$: Hydrolysis of ester

(2) Heterogeneous Catalysis : When the catalyst is in different phase from the phase of the reactant the catalyst is called heterogeneous catalyst and this phenomenon is called heterogeneous catalysis. As studied in adsorption, this phenomenon is also known as surface catalysis. Generally, the catalyst is in solid form and reactants are in liquid or gaseous forms. The reaction occurs on the surface of the solid catalyst because it is a surface phenomenon. We have studied this in detail in adsorption. Some examples of heterogeneous catalysis are as follows :

(1) $2HI(g) \xrightarrow{[Au]} H_2(g) + I_2(g)$: Decomposition of gaseous HI on the surface of gold.

(2) $SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{[V_2O_5(s)]} SO_3(g)$: In oxidation reaction of $SO_2(g)$ use of Vanadium pentoxide (V_2O_5) to obtain sulphuric acid by contact process.

(3) $N_2(g) + 3H_2(g) \xrightarrow{[Fe(s)]} 2NH_3(g)$: To obtain ammonia gas in presence of iron powder by Haber's Process.

(4) $CO(g) + 2H_2(g) \xrightarrow{[Cu / ZnO\text{-}Cr_2O_3]} CH_3OH(l)$: Method of obtaining methanol from carbon monoxide.

(5) By using nickel metal (Raney nickel) in preparing vegetable ghee from vegetable oil (groundnut oil, etc.) saturated fatty acid is obtained by hydrogenation from unsaturated fatty acids. In industry there are many such reactions called catalytic hydrogenation, which depends on such heterogeneous catalysis. Some modern industrial processes based on catalysis are shown in table 2.2.

Table 2.2 Industries based on catalysis

Reactants	Catalyst	Product
Homogeneous :		
(1) Propylene, Oxygen	Mo (VI) complex	Propylene oxide
(2) Methanol, CO	$[Rh(CO)_2I_2]^-$	Acetic acid
(3) Butadiene HCN	Ni, Pd complex compound	Adiponitrile
(4) α-Olefine CO, H_2	Rh/Pd Rhodium palladium complex compound	Aldehyde

Heterogeneous :		
(1) Ethylene O_2	Silver, Cesium chloride on aluminium	Ethylene oxide
(2) Propylene, NH_3, O_2	Bismuth molyblate	Acrylonitrile
(3) Ethylene	Organo chromium and titanium	High density (HDP) polyethylene

2.7 Nature of Solid Catalyst

Solid catalyst can be metals, metal oxides, metal sulphides, clay etc. They can be used in pure form or in mixture form. It is used in crystalline, amorphous or fine particle forms. Their certain characteristics are as follows :

(1) Activity : The basis of activity of catalyst is on the strength of chemical adsorption. The reactant should be adsorbed in proper proportion but not so strongly, that it may not give site to other molecules of the reactant. It is noted that the catalytic activity increases as we move towards metals from group five to group eleven

e.g. $2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$

(2) Selectivity : The selectivity of the catalyst means the reaction should be pushed in such a direction so that the required product can be obtained e.g. In the reaction between $H_2(g)$ and $CO(g)$ different products are obtained in presence of different catalysts viz.

(i) $CO(g) + 3H_2(g) \xrightarrow{[Ni]} CH_4(g) + H_2O(g)$

(ii) $CO(g) + 2H_2(g) \xrightarrow{[Cu / ZnO\text{-}Cr_2O_3]} CH_3OH(g)$

(iii) $CO(g) + H_2(g) \xrightarrow{[Cu]} HCHO(g)$

It is apparent from the above reactions that the selection or selectivity of the catalyst is determined for the reaction which we obtain. The effect of catalyst is specific or selective. Hence, any catalyst can be useful for a certain reaction but it may prove to be useless for other reaction. Thus, the catalyst is selective for certain reactions viz. Pepsin enzyme only will be able to convert amino acid from protein in the deodenum.

2.8 Shape-Selective Catalysis by Zeolite

The catalytic-reaction depends on the pore-structure of catalyst, size of reactant and molecules of product. It is called shape-selective catalysis. Zeolites are good shape-selective catalysts. Their structure is like honey comb. Zeolite are chemically three dimensional network silicates in which silicon atoms are replaced by aluminium atoms. They are naturally available as well as can be prepared artificially. Before using zeolites as catalyst, they are heated in the vacuum so that water of hydration is removed. Hence, zeolite becomes porous. The size of their pores is 260 pm to 740 pm. Hence, the molecules whose size is less than this are adsorbed and can be desorbed. Reactions of zeolite catalyst depend on the size and shape of product and reactant. Hence, they are called shape-selective catalysts.

They are mainly used in petrochemical industries for isomerisation and cracking of hydrocarbons. One important zeolite is ZSM-5 which is used in petrochemicals. It converts alcohol directly to gasoline (petrol) by its dehydration. Hence, mixture of hydrocarbons is formed.

Adsorption theory of Heterogeneous Catalysis : This theory explains the heterogeneous equilibrium. The old theory which is the adsorption theory of catalysis mentions that the reactants which are in gaseous or liquid state are absorbed on the surface of solid catalyst. As the concentration of molecules increase on solid surface, the rate of reaction increases. As adsorption is exothermic, the heat that is released is used in increasing the reaction rate.

The catalytic reaction can be explained on the basis of the formation of intermediate compound. This has been studied in chemical kinetics.

According to modern adsorption theory, there is combination and according to the modern theory, intermediate compound formation, the catalytic activity of the catalyst gets localized on the solid surface of catalyst. Five steps are included in the mechanism.

(1) Diffusion of reactant on the surface of the catalyst.

(2) Adsorption of molecules of reactants on the surface of catalyst.

(3) Occurrence of reaction on the surface of the catalyst by formation of intermediate compound.

(4) Desorption of molecules of product from the surface of the catalyst and to provide surface for more reaction to occur.

(5) The diffusion of product away from the surface of the catalyst.

On the surface of catalyst there are more molecules having free valence than in the inner bulk, which become the sites for chemical attraction forces. When gas comes in contact with such surface, the molecules because of weak chemical combination get filled in the sites. They react with each other and form a new molecule. This new molecule leaves the surface by evaporation and new second molecule of reactant comes on the surface. Thus, this theory explained that the catalyst remains as it was at the end of the completion of reaction and so it is required in less proportion. This theory does not give any explanation for the promoter and catalytic poisoning. Promoter means such substance which helps the catalyst in catalytic action and makes the reaction faster e.g. In the production of ammonia by Haber's process alongwith iron powder as catalyst, molybdenum is used as promoter. In production of sulphuric acid, in the presence of platinum catalyst, the impurity of copper decreases the efficiency of the catalyst. It is called catalytic poison.

2.9 Enzyme Catalysis

In dilute solutions, at normal temperature and pressure, many reactions can be carried out by living microorganisms e.g. They collect small molecules and form complex biopolymer like protein and DNA. They get decomposed and extract necessary energy required for continuing many reactions.

Such reactions are catalysed by biochemical catalyst and such biochemical catalysts are called enzymes. Enzymes are proteins and their molecular masses are in the range of 15,000 to 1,00,000 grammole^{-1}. They increase the rate of reaction by 10^8 to 10^{20} times. They are very effective catalysts and they are very specific-any reaction results with any specific enzyme. As seen earlier, the enzyme named urease hydrolyses urea; but other enzyme present in the body does not work for this reaction

$$\underset{\text{urea}}{NH_2CONH_2} + H_2O(g) \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

The enzyme named zymase converts glucose into ethanol and carbon dioxide. The enzyme named pepsin converts proteins into amino acids. In the animals like cows and buffalos the enzyme called cellulase is present and so they are able to get necessary energy for their body by eating the paper, cloth etc. which are cellulose containing compounds. The notable specificity of enzymes is due to the specific active sites on their surface. The reactant molecule which is called substrate of the reaction binds at that active site and the chemical change starts. In most of the cases, the substrate is combined with intermolecular forces - hydrogen bond, dipole forces and other weak attraction bonds.

2.9.1 Mechanism of enzyme catalysis :

According to lock and key model, the key (enzyme) fits with substrate the lock (active site) so that the lock opens and chemical change starts. Modern X-ray crystal study and spectroscopic methods show that in many cases, when substrate reaches to active site, the enzyme changes its shape. This induced fit model of enzyme shows that the substrate induces the active site and makes it completely fit and not rigid shape like key and lock as per the earlier model. This can be thought as we put our hand in hand gloves, then until the hand glove (active site) attains the functional shape of hand (substrate), the shape of the glove will not be clear.

$$\mathbf{E} + \mathbf{S} \rightleftharpoons \mathbf{[ES]} \longrightarrow \mathbf{E} + \mathbf{P}$$

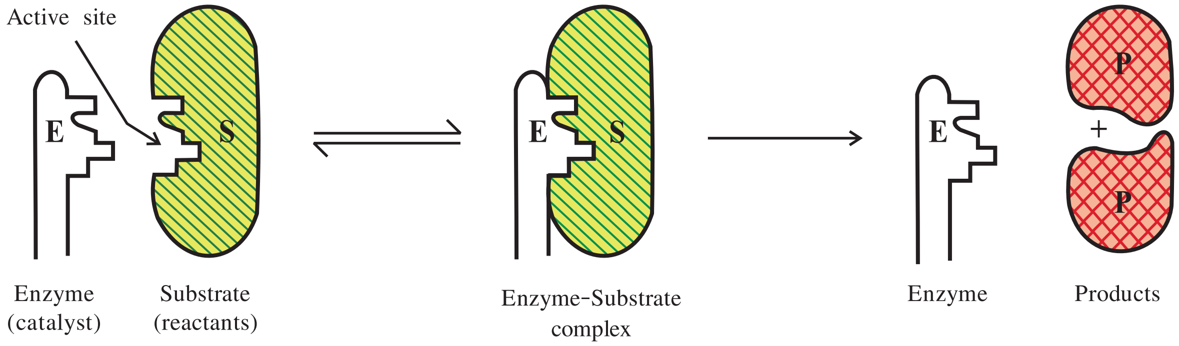


Fig. 2.3 Mechanism of enzyme catalysed reaction

The kinetics of enzyme catalysis is in good agreement with general catalysis. In enzyme catalysed reaction the substrate (S) and the enzyme (E) combine and form intermediate enzyme-substrate complex (ES) whose concentration determines the rate of product (P). In almost all the enzyme reactions, common reactions are as below :

(1) $E + S \rightleftharpoons ES$ (Fast and reversible)

(2) $ES \rightarrow E + P$ (Slow and rate determining)

The rate of enzyme catalysed reactions increases as the concentration of substrate is increased; the change is from first order to zero order. At higher temperature, enzymes cannot survive and so they exhibit failure in the results of the reaction at higher temperature.

2.9.2 Characteristics of Enzyme Catalysis :

Enzyme catalysis possesses unique and high order specificity in its efficiency. The following characteristics are seen in enzymatic production :

(1) One molecule of enzyme can convert ten lacs of reactant molecules to product in one minute.

(2) As the enzyme is specific for every reaction, use of other enzyme is fruitless.

(3) The temperature range of 298-310 K is considered best for the enzyme catalysis. At very high temperature, the enzyme gets destroyed. As the temperature of human body is near 310 K, favourable temperature is available for enzyme catalysed reactions. It is necessary to note that when there is fever the temperature of the body becomes higher than 310 K; there is effect on the enzyme catalyst reactions and there is disturbance in biochemical reactions in human body.

(4) Generally in enzyme catalysed reactions, the rate of reaction is higher in the pH range 5 to 7.

(5) The coenzymes like activators which are with enzymes makes the catalytic reaction of enzyme fast viz. presence of trace amounts of vitamins work as coenzyme for protein in them. Hence, trace amounts of vitamins are essential in body.

(6) Like general catalysis, the inhibition of catalysis or poisoning decreases its activity. Similarly presence of some substances supplies the inhibition or poisoning effect and decreases the activity of the enzyme. Because of certain medicines such effect is produced on enzyme catalyst.

2.9.3 Catalysis in Industries :

The catalysts used in industries and the processes are shown in table 2.3

Table 2.3

Process	Catalyst
(1) Production of ammonia by Haber's process $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Finely powdered form iron, catalyst, molybdenum promoter, 200-atmosphere pressure and 723-773 K temperature
(2) Ostwald's process of production of nitric acid $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos, Temperature 573 K
(3) Production of sulphuric acid by Contact process $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(l)$ and $H_2S_2O_7(l) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5), Temperature 673-723 K.

2.10 Colloids

As studied in earlier standards the true solutions are homogeneous systems viz. solution of common salt or solution of sugar. If we mix sand and water and keep aside for sometime after shaking it, then the sand will settle down. In the earlier homogeneous solution common salt or sugar does not settle down. Thus, the settling down of sand is called suspension. There is a large group of systems in between these two states which is called colloidal dispersion. For simplicity we call them as colloidal solution or colloid or sol. The definition of colloid can be given as below :

"Colloid is a heterogeneous system in which one phase is called the dispering phase and has very fine particles suspended in dispersion medium". The difference between solution and colloid is the size of the particles in them. In solutions particles are ions or small molecules. The dispersion system possesses some macromolecules. Such macromolecules are the protein, synthetic polymer, or aggregate as many atoms, ions or molecules. Colloid molecules are bigger than normal molecules but their sizes are not such that they may get separated but are small and remain suspended in solution. The size of the colloid particles is 1 to 1000 nm. The colloidal particles because of their small size have a large proportion of surface area per gram. Suppose we take a cube of 1 cm length then the total surface of its six sides will be 6 cm^2. If we divide this cube into uniform 10^{12} cubes, then it will be of the size of colloid particle and the total surface area will be 60,000 cm^2 or 6 m^2. Because of this surface area colloid possesses specific property viz. it can act as adsorbent.

Type of colloids : The types of colloids are classified on the basis of the following points :

(a) Physical state of dispersion phase and dispersing medium.

(b) The nature of attraction between dispersing phase and dispersion medium.

(c) Types of particles of dispersed phase

(a) Classification on the basis of the physical states of dispersing phase or dispersion medium : This classification is made on the basis of the dispersing phase and dispersion medium to be solid, liquid or gas. Eight types of colloid systems are included in this classification. This classification is shown in table 2.4.

Table 2.4 Classification of colloid systems

Dispersing phase	Dispersion medium	Type of colloid	Example
(1) Solid	solid	solid sol	Some coloured glass and gemstone
(2) Solid	liquid	sol	Cell fluid
(3) Solid	gas	aerosol	Smoke, dust
(4) Liquid	solid	gel	Cheese, butter jelly,
(5) Liquid	liquid	emulsion	Milk, Hair cream
(6) Liquid	gas	aerosol	Mist, cloud pesticides spray
(7) Gas	solid	solid sol	Pumice stone, Foam rubber
(8) Gas	liquid	foam	Froth, foam

Many natural and artificial things used in everyday life are colloids. Many biological fluids are aqueous sols. Proteins, nucleic acid etc. are aqueous solutions of colloid particles, ions and small molecules. From the systems mentioned in table 2.4 the most common is 'sol' i.e., dispersion of solid in liquid, and emulsion, which means dispersion of liquid in liquid. In this unit we will study dissolution and emulsion. If dispersion medium in colloid is water, then it is called aqua sol or hydrosol and if the dispersion medium is alcohol then it is called alcosol.

(b) Classification on the basis of nature of interaction between dispersing phase and dispersion medium : There are two types of such colloids (a) Lyophilic and (b) Lyophobic. In lyophilic type, the colloid particle attracts solvent and in lyophobic type, repels solvent. If dispersion medium is water then lyophilic is called hydrophilic and the lyophobic is called hydrophobic colloid.

(1) Lyophilic colloid : Lyophilic colloids are liquid-attracting. Their colloid solutions can be directly obtained viz. lyophilic colloid is obtained by mixing gum, gelatin, starch, rubber etc. with suitable liquid (dispersion medium). If the dispersion medium is removed from this type of colloid then dispersing system is obtained back and if the dispersion medium is added again the lyophilic colloid is obtained again. Thus, these colloid solutions are possessing reversible property and so are called reversible sols. They are comparatively very stable and so their coagulation does not occur on its own and so, they are called stable colloids. Coagulation means precipitation of colloid solution. We shall study in detail about this later on.

(2) Lyophobic colloids : Lyophobic colloids are liquid-repelling. If metals, their sulphides are mixed with dispersion medium colloidal sol is not obtained. Special methods are to be used for their preparation which we shall study later on. In such sols, if an electrolyte is added in small proportion and heated or stirred well, precipitates are obtained or get coagulated. Hence, they are not stable. If dispersion medium is separated and then again mixed with dispersion medium then those precipitates do not give sol again. Hence, they are called irreversible sols. Some substances are added to give stability. They are called stabilizers.

(c) Classification on the basis of types of dispersing phases : Colloids can be classified on the basis of types of dispersing phase. For example (1) multimolecular (2) macromolecular and (3) associated colloids. The information about them is as follows :

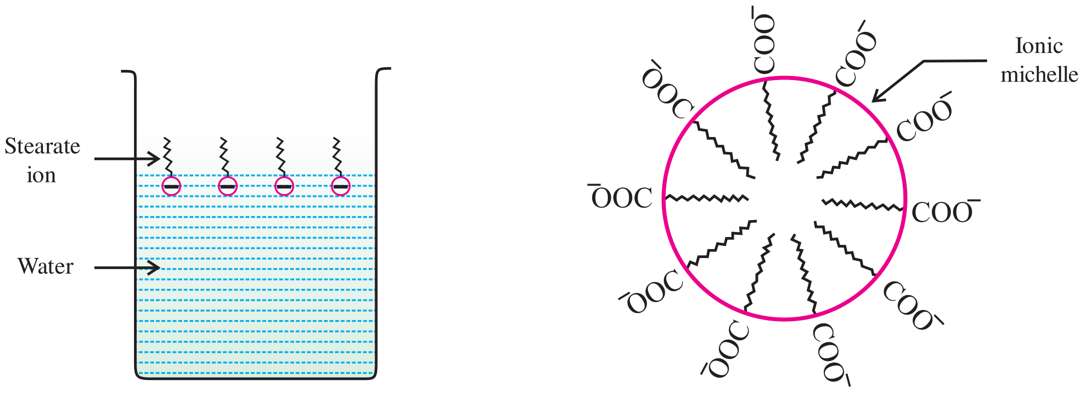
(1) Multimolecular Colloid : When dissolution is carried out, atoms of substances of small particles in very large amount associate with each other and prepare a species whose diameter is more than 1 nm; that is in the range of diameter of colloid particle. Such a species that is formed is called multimolecular colloid e.g. Gold dissolution possesses particles of different sizes having atoms. Similarly dissolution of sulphur possesses thousands or more molecules of sulphur.

(2) Macromolecular Colloid : The molecular masses of macromolecular colloid are very high. When such molecules are dissolved in proper solvent a solution that is obtained in which the small size of macromolecular substance changes into the size of colloidal particles. Such a system is called macromolecular colloid. These colloids are very stable and in many aspects appear like true solutions e.g. starch, cellulose, protein and enzymes. In manmade macromolecular substances like, nylon, polyethylene, polystyrene, artificial rubber etc. are also included.

(3) Associated Colloid : Some substances at lower concentrations show general behaviour but at higher concentration associated particles are formed, which is called micelle. The formation of micelle takes place at temperature higher than certain temperature called Kraft temperature (T_K). At concentration higher than certain value, micelle is formed and this is called critical micelle concentration (CMC). On dilution these colloids change into their original ions. Surface active substances - like soap, artificial detergent are included in this. Such colloids possess both types of lyophilic and lyophobic parts; 100 or more molecules are present in micelle.

Mechanism of micelle formation : We take example of soap solution. Soaps are considered to be salts of fatty acids viz. sodium stearate $CH_3(CH_2)_{16}\ COO^- Na^+$ or $R\ COO^- Na^+$ where $R = CH_3(CH_2)_{16}$ chain. It is main component in most of the soaps. When they are dissolved in water, they dissociate into $R\ COO^-$ and Na^+. There are two parts in the ion $R\ COO^-$. One hydrocarbon chain R is known as nonpolar tail and it is hydrophobic and the polar group COO^- is known as polar ionic head. Head is hydrophilic. Hence, $R\ COO^-$ ions are present on the surface and their COO^- part remains in water and hydrocarbon part R remains away from it on the surface. At high concentration they are dragged in the bulk of solution and they associate in spherical form and attract towards the centre of their hydrocarbon chain. At this time COO^- part remains outside on the surface. This type of formation of association on ions is called micelle. Such micelle contains about 100 such ions.

Similarly, in detergent, e.g. sodium lauryl sulphate- $CH_3(CH_2)_{11}\ SO_4^- Na^+$, its polar group- SO_4^- is with long hydrocarbon chain. So, micelle formation in this is similar to that in the soap. The cleansing action is shown in fig. 2.4.



[a] [b]

Fig. 2.4 Micelle

2.11 Methods of preparing colloid-Sol

The methods to prepare lyophilic and lyophobic sols are as follows :

2.11.1 Preparation of lyophobic sol :

Lyophobic sol can be prepared by the following two methods : (A) Condensation methods (B) Dispersion methods.

(A) Condensation methods : In condensation methods the particles of atomic or molecular sizes are induced to combine, so that the associate having dimensions of colloid, are formed. For this (i) Chemical as well as (ii) Physical methods are taken into use.

(i) Chemical methods : Colloidal solution-Sol can be prepared by process like double decomposition, oxidation-reduction or hydrolysis e.g.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} \underset{\text{(sol)}}{As_2S_3} + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} \underset{\text{(sol)}}{3S} + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} \underset{\text{(sol)}}{2Au} + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{(sol)}}{Fe(OH)_3} + 3HCl$$

(ii) Physical methods :

(a) By exchange of solvent : When any true solution is mixed with other solvent in excess in which the dissolved solute is insoluble and the solvent is soluble, a colloid solution is obtained e.g. colloid of sulphur is obtained when excess of water is added to a solution of sulphur prepared in alcohol.

(b) Excessive cooling : To obtain colloid solution of ice in organic solvent like chloroform or ether the solution in water is cooled. The molecules of water which cannot remain separate, associate and form particles of the size of colloid particles and sol is obtained.

(B) Dispersion methods : In dispersion methods, big particles of the substance are broken in the presence of dispersion medium and changed to smaller particles. Some suitable stabilising agent is added to make them stable. Some known methods among the dispersion methods are as follows :

(i) Mechanical dispersion : In mechanical dispersion method the original suspension of the substance are made smaller in dispersion medium by grinding with colloid mill and brought to colloidal state. Such mills are ball mill, ultrasonic disperser and colloid mill used for grinding. Colloid mill is shown in Fig. 2.5.

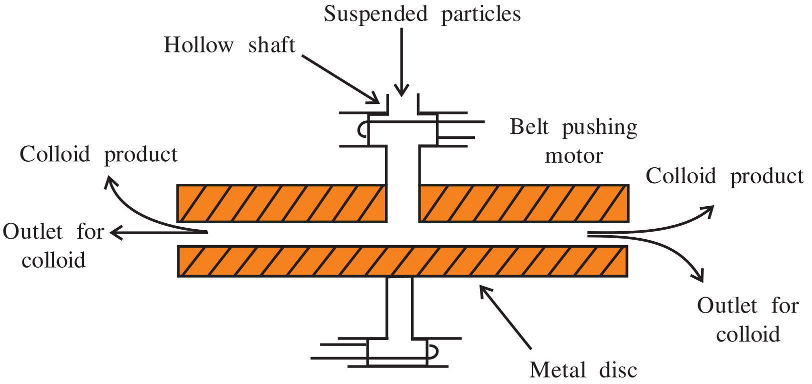


Fig. 2.5 Colloid mill

As shown in the fig. 2.5 there are two layers in the colloid mill. At very high velocity about 7000 revolutions per minute, the two layers are rotated in direction opposite to each other. The suspended particles get grinded and change to small colloidal size and the sol is obtained.

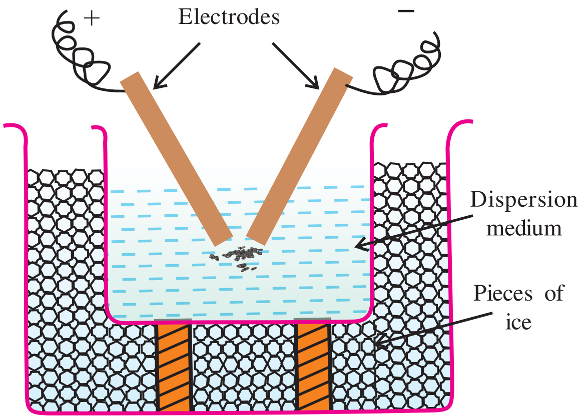


Fig. 2.6 Bredig's Arc Method

(ii) Electric dispersion or Bredig's Arc method : In Bredig's Arc method, dispersion and condensation both are involved. Colloidal solutions of metals like gold, silver, platinum etc. are obtained by this method. As shown in figure 2.6 electric spark is applied between the electrodes of the metal kept in dispersion medium. High degree of heat is produced due to the spark which evaporates the metal. Hence, particles of the size of the colloids of the metals are obtained in the medium. Ice is filled in the outer vessel to cool this system.

(iii) Peptization : Suitable precipitates of electrolyte are obtained. The precipitates are stirred in the dispersion medium in presence of electrolyte, taken in small proportion and the precipitates are converted to colloidal particles and sol is obtained. This transformation method is called peptization. The cations and the anions used in this reaction; any one of them is present in the solution are common. Because of this, positive or negative electric charge is produced on the precipitates. As a result of this it breaks into small pieces and the size of the particles is in the range of colloid particles e.g. Freshly prepared ferric hydroxide ($Fe(OH)_3$) precipitates are mixed with aqueous ferric chloride ($FeCl_3$) solution which is called peptizing agent and is stirred. Hence, Fe^{3+} ions are adsorbed on the surface of the precipitates. As a result particles are changed to the size of colloid particles and sol is obtained.

2.11.2 Preparation of Lyophilic Sols :

As lyophilic sols are very stable, they can be prepared by mixing lyophilic substance with dispersion medium and stirring it e.g. the sols of gelatin, gum, starch, egg albumin etc. can be obtained by adding water and then stirring. Some sols being reversible, if the solvent has evaporated, they can be again prepared by adding solvent. You are familiar regarding this with colloid of gum.

2.12 Purification of Colloidal Solution-sol

There are impurities in the sols prepared by different methods. This is because of the presence of electrolytes, other soluble substances which are also present as impurity. These impurities can make the sol unstable. Hence their purification is necessary.

In the very important method of purification, semipermeable membrane is used and the soluble impurities from the sol are removed. This is called dialysis.

(1) Dialysis : Across the semipermeable membranes like parchment paper, butter paper, cellophane membranes, the particles of the true solutions can pass through but the particles of colloid which are larger in size are not able to pass through. You have studied earlier about this in osmosis. A bag of such semipermeable membrane is prepared and sol is filled in. As shown in fig. 2.7 it is dipped in a vessel filled with distilled water. The particles of the electrolyte can come out but the colloid particles are not able to come out. Fresh distilled water should be added to the vessel and a siphon system can be arranged so that continuous purification can be carried out by dialysis. In the above method, if two electrodes are kept outside the bag and electric current is passed, the cation and the anion of the electrolyte will be attracted rapidly to the electrodes of opposite charge and the impurity will be removed very fast. Hence, this method is faster than general dialysis. This method is called electrodialysis. By this method better purification can be carried out.

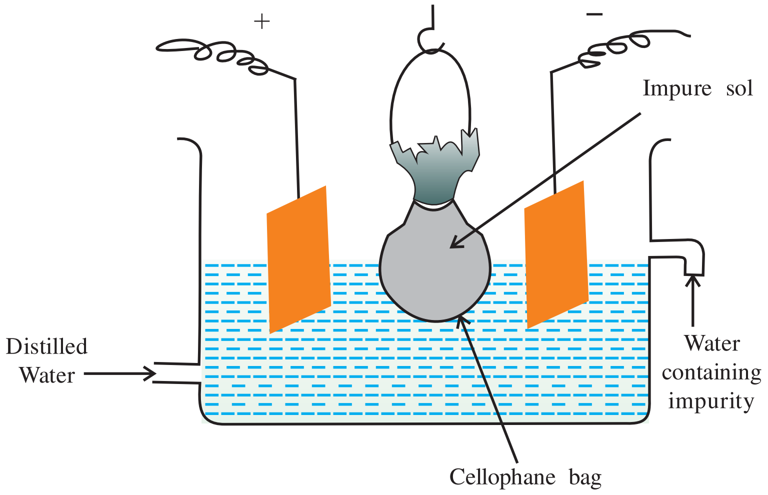


Fig. 2.7 Electrodialysis

When the kidney of a person is not functioning properly and becomes incapable of throwing out unnecessary waste, then an artificial machine is used for the function of kidney. This is called kidney dialysis in common practice. It is used in hospitals and is based on such a principle.

(2) Ultrafiltration : In ultrafiltration method, colloidal solution, special type of filter paper which is known ultrafilters is used for filtration. Such filter papers allow only the electrolyte to pass through. Such filter papers are prepared by impregnation of colloidal particles on ordinary filter paper. To make the filtration fast, external pressure is increased and it is sucked so that the rate of filtration becomes faster.

(3) Ultracentrifugation : In ultracentrifugation method, colloidal solution is taken into a hard glass tube and is placed in the ultracentrifuge machine. When ultracentrifuge is started the inner tube performs rotational motion with very high speed. As a result the colloidal particles are collected at the bottom of the glass tube because of centrifugal force. Impurities remain dissolved in the upper solution. It is called centrifugate. The colloidal particles which have settled down in the tube are mixed with suitable dispersing medium so that sol is regenerated and the upper impure solution is thrown away.

2.13 Important Properties of Colloidal Solution-sol

The important properties of colloidal sol are of four types : (1) Colligative properties (2) Optical properties (3) Mechanical properties and (4) Electrical properties.

(1) Colligative properties : The colligative properties are proportional to the concentration of substance or the concentration of the particles inside it. Colloidal solution-sol shows colligative properties like decrease in vapour pressure, elevation in boiling point, depression in freezing point, osmotic pressure. As the average molecular mass of colloidal particles is very high, the mole fraction of dispersed phase is very low. Hence, notable change is not observed in the results of colligative properties. Only osmotic pressure method is used to determine the molecular masses of polymer molecules like colloid.

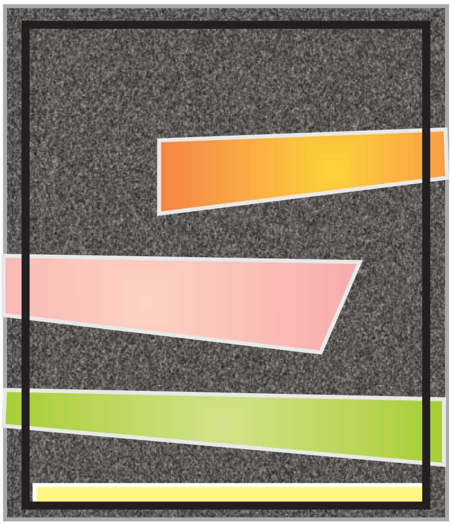


Fig 2.8

(Three beams of white light passing through a colloid of sulphur particles in water change from orange to pink and bluish green. The colours produced depend on the size of the particles and also on the position of viewers. The smaller the particles, the shorter (blue) the wavelength.)

(2) Optical properties : Scientist Tyndall mentioned in 1869, that if a ray of light is passed through colloidal solution placed in the dark, then its path is illuminated. This phenomenon is called Tyndall effect. It is due to scattering of rays of light by colloid particles. The illuminated path is called Tyndall cone. You must have observed a similar phenomenon. If there is hole in the ceiling of a closed room, and if sunlight enters into the room through the hole, then the dust particles (like colloid particles) scatter this light and you will see an illuminating path. When the head lights of vehicles are on at night, you will find an illuminated path on the road at night. True solutions do not show Tyndall effect because the particles are very small so that they are not able to scatter the rays of light.

If three rays of light are passed through colloidal sulphur, they are changed from orange to pink, and from bluish to green colour. These colours depend on the size of the colloid particles and the position of the observer. If the size of the particles is small then wavelength is less (bluish).

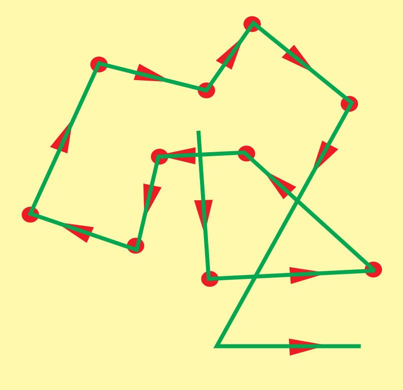


Fig. 2.9 Brownian movement

(3) Mechanical properties : Brownian movement : Botanist Robert Brown suggested in 1827 that if the pollen grains of the flower are placed in water, then they do not remain stationary but continuously and randomly move. Phenomenon similar to this was noted later on for the colloidal particles when the colloidal particles were observed under the instrument like ultramicroscope, they were moving continuously in zigzag directions as shown in fig. 2.9.

If there is an increase in the size of the particles, then the effect (collision) becomes average and the Brownian movement becomes slow. At last if the dispersed particles become so big that their dimensions are such that the medium particles of smaller dimension of the particles are not able to move them by pushing- that is, Brownian movement cannot be observed. Two important results are obtained from this property.

(1) According to kinetic theory, on the basis of this hypothesis, the molecules are in continuous motion, and straight way are demonstrated by this observation.

(2) Brownian movement attacks against the gravitation force existing on the particles and as a result they do not allow colloidal particles to settle down at the bottom and does not make the colloid unstable. Hence, the colloidal solution-sol attains stability.

(4) Electrical properties : Electrophoresis : A colloidal particle possesses positive or negative electric charge. The polarity of the sol not only depends on the dispersing phase but also on dispersion medium which has equal but of opposite positive or negative charge. Hence, colloidal system is neutral. Colloidal particles possess similar electric charge and so experience repulsion. Hence, they are not able to form big molecule by combination. So, the sol remains stable and the particles do not settle down. Arsenious sulphide, gold, silver and platinum possess negative electric charge in their colloidal solutions;

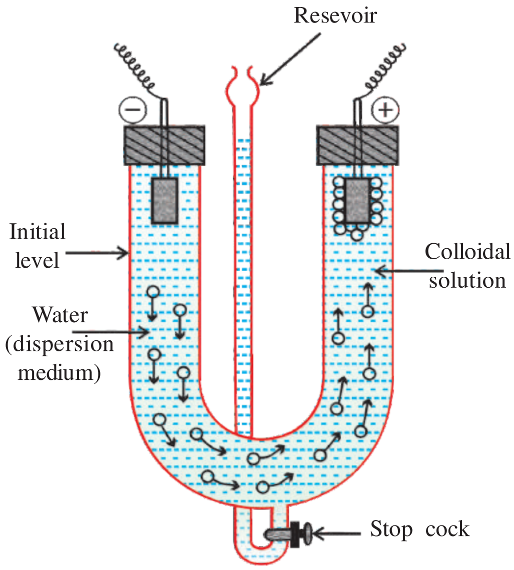


Fig. 2.10 Electrophoresis

while the colloids of ferric hydroxide, aluminum hydroxide, zirconium hydroxide possess positive electric charge. The existence of positive or negative electric charge of the colloid can be determined by the phenomenon like electrophoresis. In this the colloid particles according to their electric charge are attracted towards positive or negative electrode under the effect of electric field. The electrophoresis instrument is shown in fig. 2.10.

Colloidal solution is filled in U-shaped tube. Platinum electrodes are fixed on the two ends of the tube. On passing electric current the colloidal particles are moving towards the electrode of opposite charge. Suppose we take arsenious sulphide sol then the colloidal particles will move towards anode because arsenious sulphide colloid possesses negative electric charge. Iron hydroxide colloid possesses positive charge and so will get attracted towards negative electrode.

2.14 Coagulation of Colloids

For the stability of the colloids presence of electrolyte in small proportion is essential but if the concentration of electrolyte is increased then the colloid particles in the solution attract the ions of opposite electric charge and become neutral. Neutral particles combine with each other and start forming associated and become larger in size. As a result they get precipitated and separate from colloidal solution. **The formation of association of colloid particles by addition of electrolyte to form an insoluble precipitate is called coagulation. If concentration of electrolyte is less, then association of particles occurs but they do not get precipitated and can go back to the form of colloid. This phenomenon is known as flocculation.** If concentration of electrolyte gets increased, they result in coagulation. When the water of a river containing colloidal clay enters the water of the sea, it gets induced for coagulation because of the salts present in sea water and the layers of the clay are formed. It is necessary to note that the coagulation of colloidal solution does not occur until certain amount of electrolyte is not available to coagulate by the electrolyte. The minimum amount (in milli-moles) of the electrolyte required for complete coagulation of colloidal solution or sol is called the coagulation or precipitation value of the electrolyte.

The coagulation values of different electrolytes are different. Scientists Hardy and Schulze studied the behaviour of different electrolytes. The two laws that they have noted are as follows :

(1) The effective ion for the coagulation of sol is that which possesses opposite electric charge compared to electric charge of colloidal particles.

(2) The coagulating power of the electrolyte is in the fourth power of the valency of the coagulating ions.

It can be said from the above rules that for negatively charged sol like As_2S_3, positive ions (cations) can have coagulation and if the positively charged sol like $Fe(OH)_3$, negative ions (anions) can have coagulation. The order of different coagulating ion for negatively charged As_2S_3 is monovalent ion (Na^+) < divalent ion (Ba^{2+}) < trivalent ion (Fe^{3+}) i.e. $Fe^{3+} > Ba^{2+} > Na^+$. Similarly, for sol like $Fe(OH)_3$ having positive charge trivalent $PO_4^{3-} > SO_4^{2-} > Cl^-$. From this it can be said that the concentration of ions necessary for coagulation will be concentration of trivalent ion < concentration of divalent ion < concentration of monovalent ion. Both the above observations are known as Schulze-Hardy rules.

These observations show that necessary precaution should be taken for keeping the colloidal solution having small proportion of electrolyte, separated from the atmosphere; otherwise coagulation will result and the colloid solution will become useless.

2.15 Emulsion

Emulsions are colloids but the dispersion medium and dispersed phase both are in liquid form. There are two main types of emulsion (1) Oil in water (oil / water) emulsion and (2) Water in oil (water /oil) emulsion.

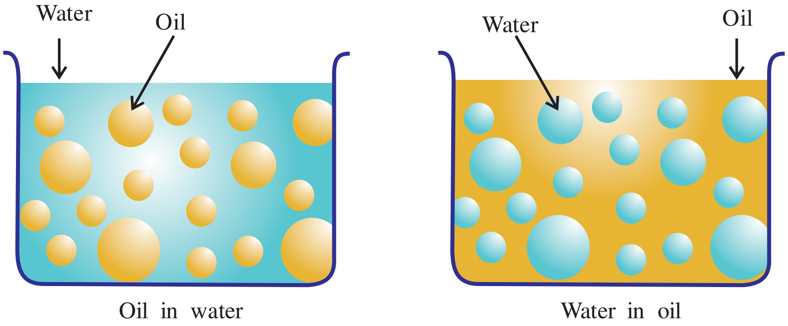


Fig. 2.11 Types of emulsions

(1) Oil /water emulsion : In this type of emulsion, oil (organic solvent) acts as dispersed phase and water acts as dispersion medium. The examples of this type of emulsions are milk, vanishing cream etc.

(2) Water /oil emulsion : In this type of emulsion, water is dispersed phase and oil (organic solvent) acts as dispersion medium. Cold-cream, butter, cod-liver oil etc are this type of emulsions.

2.15.1 Test of Emulsion :

The methods to test both the types of emulsion as described above are as follows :

(i) Dye test : Certain dyes soluble in oil are added to emulsion and if the background becomes coloured then emulsion is water in oil. If coloured droplets or small particles are formed then it can be said that the emulsion is oil in water.

(ii) Dilution test : If dilution of emulsion with water is possible then it can be said that dispersion medium is water and so the emulsion is oil in water type. If the added water makes a separate layer then it can be said that the emulsion is of water in oil type.

2.15.2 Preparation of Emulsions :

(1) Emulsification : The method of preparation of emulsion is called emulsification. Emulsion can be obtained by forcibly mixing the two liquids. Hence, unstable emulsion will be obtained. Dispersed drops will immediately come nearer and will form a separate layer. For stabilization of emulsion, some third substance is added in small proportion which is called emulsifier. it is always required; Soap and detergents are mostly used as emulsifiers. They form a layer on the drops and stop them from coming near to each other. Hence, emulsion becomes stable. Other stabilizing substances are protein, gum, agar etc.

The type of emulsion depends on the relative proportion of both the liquids. If water is more, then oil in water type and if oil is more, then water in oil type emulsion is formed. This type of emulsion depends on the nature of emulsifying substance. For example, in presence of soluble salt (alkali metal atom containing soap) like emulsifier, the oil in water type emulsion is favoured; while in insoluble soap (soap containing non-alkali metal) water in oil type emulsion is favoured.

2.15.3 Demulsification :

Separation of two components of emulsion is called demulsification. The techniques used for demulsification are freezing, boiling, centrifugation, electrostatic precipitator or chemical methods to destroy emulsifier.

2.16 Uses of Colloids

Colloids and emulsions have many uses in our everyday life and industries. Some of them are as follows :

(1) Rubber plating : The negatively charged particles of rubber colloid are deposited on the handles of vessels and other wares. Rubber gloves are prepared by depositing colloids like this on suitable thing.

(2) Sewage disposal : Electrically charged colloidal particles of dirt are there in the sewage water which do not settle easily. They are removed by making them electrically discharged near the electrodes. Dirty water is passed from one tunnel in which metal electrodes are fixed.

Because of high electric potential (30,000 volt or more) the colloidal particles are attracted towards the electrode of charge opposite to their own and the electric charge is neutralized so that coagulation takes place. The displaced matter can be used as fertilizer and the water can be used for irrigation purpose.

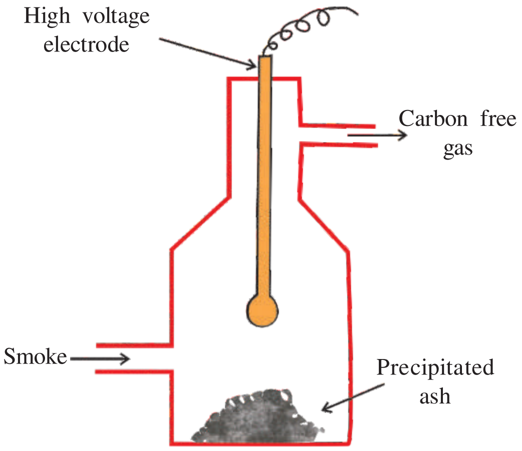


Fig. 2.12 Cottrell Smoke Precipitator

(3) Cottrell Smoke Precipitator : Smoke is the dispersion of negatively charged colloidal particles of carbon in air. It is passed through Cottrell precipitator at high voltage. Hence, carbon separates from the particles.

Such precipitators are set in the chimney of industrial plant. There are two plates of metal which are electrically charged by high electric voltage. The carbon particles become chargeless and get precipitated, while gases go out through the chimney.

(4) In preparation of nano products : By using reversible micelle as catalyst such substances are prepared.

(5) In medicines : Most of the medicinal and pharmaceutical preparations are emulsions. It is believed that medicines in this form are more effective, and mixes or gets absorbed easily.

(6) Germicides : Germicides like Dettol, Lysol when mixed with water oil in water type emulsions are obtained.

(7) In metallurgy : Emulsions play an important role in industries. The concentration of ore containing sulphide is carried out by froth floatation method. Finely grinded ore is concentrated by emulsion formed between pine oil and water

(8) Construction of roads : An emulsion is pepared of alsphalt (without melting it) in water and used for construction of roads.

SUMMARY

- The study of chemistry regarding the boundary separating two bulk states or phases is called surface chemistry. This boundary surface is known as interface. It is expressed as hyphen (–) or slash (/). Dissolution, crystallization, catalysis, metallic corrosion are surface phenomena.
- The surface should be completely pure which can be obtained by vacuum generating method and can be stored also.
- In this unit, surface phenomena like adsorption, catalysis, colloid and emulsion are studied.
- In adsorption, the substance which is in solid form and on which other gas or liquid is adsorbed is called adsorbent. The substance that is adsorbed is called adsorbate and the whole phenomenon is called adsorption. The phenomenon opposite to adsorption is called desorption.
- Absorption is such a phenomenon in which there is homogeneous system viz. any coloured solution but if solid adsorbent like charcoal is added to it then there is decrease in intensity of the colour which is adsorption. The combined phenomenon of adsorption and absorption is called sorption. In adsorption the concentration of adsorbate is more than that in the bulk. More porous the adsorbent more will be adsorption. Adsorption is an exothermic phenomenon.
- In adsorption, the residual particles on the surface are responsible for the adsorption that is due to difference in forces of attraction.
- Adsorption is of two types– Physical and Chemical. The points of difference between them are given in the unit.
- Adsorption is used in many fields as well as in everyday life viz. To wear gas mask in which there is adsorbent to save from the poisonous gas like chlorine. Silica gel is used as adsorbent for keeping the electronic instruments moisture free. In the removal of yellow colour from sugar, the phenomenon of adsorption is used.
- The factors affecting adsorption are (1) nature of adsorbate (2) nature of adsorbent (3) specific area of adsorbent surface (4) pressure of adsorbed gas (5) temperature. The detailed discussion about each one is included in the unit.
- At constant temperature the graph of pressure of gas adsorbed or concentration is called adsorption isotherm. There are five different types of isotherms. The study of adsorption isotherm was done by scientist Freundlich and gave the equation $\frac{x}{m} = Kp^{\frac{1}{n}}$ or $\log \frac{x}{m} = \log K + \frac{1}{n} \log p$ (for pressure (p)) and $\frac{x}{m} = KC^{\frac{1}{n}}$ or $1 \log \frac{x}{m} = \log K + \frac{1}{n} \log C$ (for concentration (C)) where K and n are constants. This was an empirical isotherm and had no scientific base.
- Langmuir on the basis of kinetic theory of gases gave isotherm equation.

  $\frac{x}{m} = \frac{ap}{1 + bp}$, $\frac{x}{m} = \frac{aC}{1 + bC}$ (where a and b are constants)

- The study of Freundlich isotherm can be understood by the study of demonstration experiment in practicals book. There are many uses of adsorption which are described in the unit.
- Catalysis is also a surface phenomenon. Some chemical reactions are slow. To increase their rates, the substance used in small proportion is called catalyst. This phenomenon is called catalysis. The catalyst is obtained back in original form at the end of the reaction.
- There are two types of catalysis (1) Homogeneous and (2) Heterogeneous. In homogeneous catalysis, catalyst and the reactant are in one phase e.g. hydrolysis of methyl acetate in presence of H^+ (2) In heterogeneous catalysis the catalyst and the reactants are in different phases e.g. Production of sulphuric acid in presence of V_2O_5 by contact process. There are many uses of homogeneous and heterogeneous catalysis as shown in the unit.
- The characteristics of catalysis are activity, selectivity that is specific reaction; selection of specific catalyst e.g. zeolite. The zeolite named ZSM-5 is used to obtain gasoline from alcohol. Catalyst increases the rate of reaction but does not affect the equilibrium because it affects equally both the forward and the reverse reaction. Hence, more product is not obtained.
- Enzymes are proteins and are necessary for biochemical reaction. For every reaction separate and specific enzyme works viz. invertase can transform sugar into glucose and fructose. Urease can decompose urea into ammonia and carbon dioxide.
- For enzyme catalysis the lock and key model or induced fit model are proposed. As the lock can be opened by suitable key, similarly for a particular reaction suitable enzyme will be required. The enzymes work at the temperature of the body i.e. 298-310 K temperature is considered the best.
- Colloid chemistry is also a surface phenomenon. The colloidal solution is called sol. There are two components called dispersing phase and dispersion medium in it. The particles are of some particular size so this is a heterogeneous system. Colloids are of two types-Lyophilic and Lyophobic. The colloid which has attraction for solvent (dispersion medium) is used called lyophilic colloid e.g. gum. The colloid which has repulsion towards the solvent (dispersion medium is called lyophobic colloid. If water is as a medium then they are respectively called hydrophilic and hydrophobic. Colloids are of eight types which depend on the dispersing phase and dispersion medium. This is shown in the unit. Multimolecular, macromolecular and associated colloids are also known. In associated colloids molecules come nearer and form an association which is called micelle.
- The certain temperature, at which the micelle is formed is called Kraft's temperature (T_K). Below the critical micelle concentration (CMC), it remains in colloidal state and at higher than that concentration it is changed to solid in the form of precipitates. The formation micelle is obtained in the cleansing action of soap. Molecules like soap are shown as RCOONa, and their ionization form will be $RCOO^-Na^+$. From this $RCOO^-$, R part combines with organic impurity and drags inside. It is called tail. The upper charged part COO^- attracts dust etc. and removes the dirt. It is called head.
- The methods of preparation of colloids are as follows :
- **Condensation method :** In these methods, oxidation, reduction, decomposition etc. types of reactions are associated. In physical methods, excessive cooling is used, and in dispersion

methods-mechanical dispersion (use of colloid mill), electrical dispersion (Bredig arc method) and peptization are used.

- For purification of prepared colloidal solution, a method like dialysis and better method like electrodialysis can be used. On addition of certain electrolytes to colloid solutions, precipitation occurs which is called coagulation. The order of concentration for coagulation for iron sol having positive charge is trivalent > divalent > monovalent for negative ions (anions). Similarly for arsenious sulphide colloid having negative charge, the order of coagulation remains the same but positive ions (cations) are used. Amongst the other methods used for purification of colloids are ultrafiltration and ultracentrifugation.
- The properties of colloidal solutions-sol are as follows : (1) Colligative properties (2) Optical properties (3) Mechanical and (4) Electrical properties.
- In colligative properties determination of molecular masses is by osmosis method. In optical properties- Tyndall effect and in mechanical properties Brownian movement and in electrical properties, instrument called electrophoresis is used for determination of electrical charge of colloid. There are two laws given by Hardy and Schulze for the study of coagulation of colloids. The electrolytes having electric charge opposite to that on the colloid are required for coagulation of colloid. For colloid having positive or negative electric charge negative or positive ions of the electrolyte respectively are useful. In concentration, highest concentration of monovalent and less than that concentration of divalent ion and the least concentration of trivalent produces coagulation.
- Emulsions are also colloids, in which both the dispersion medium and the dispersed phase are in liquid form. They are of two types- Oil / water and water/oil. The examples of water/oil emulsion are cold cream, butter etc; while in oil/water emulsion the examples are milk, vanishing cream etc. There are two methods for the test of emulsions (1) Dye test and (2) Dilution test. Demulsification is the opposite phenomenon of emulisification.
- There are many uses of colloids. Its specific uses are rubber plating, sewage disposal, Cottrell smoke precipitator, preparation of nano-substances, medicines, as germicides in metallurgy, construction of roads etc. which are described in detail in the unit.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) What is called the boundary that separates the phases in two bulks ?

(A) Line (B) Point (C) Slash (D) Interface.

(2) On which does the interface depend ?

(A) on the volume of molecules in the bulk-phase

(B) on the weight of molecules in the bulk phase

(C) on the number of molecules in the bulk phase

(D) on the physical state of molecules in the bulk phase

(3) Which of the following is not an example of surface phenomenon ?

(A) Dissolution (B) Corrosion

(C) Electrode reaction (D) Homogeneous catalysis

(4) How many Pascal high vacuum is required for obtaining completely pure surface of metals ?

(A) 10^{-8} to 10^{-9} (B) 10^{-8} to 10^{-10} (C) 10^{-6} to 10^{-9} (D) 10^{-8} to 10^{-7}

(5) What is the phenomenon called when the molecules adsorbed on the surface are released by any reason ?

(A) Sorption (B) Desorption (C) Adsorption (D) Precipitation

(6) Because of adsorption............

(A) Surface energy decreases

(B) Surface energy increases

(C) The value of surface energy becomes zero

(D) No change takes place.

(7) By which other name the adsorption of gases on the solid surface is known ?

(A) Evaporation (B) Surface tension

(C) Condensation (D) Sorption

(8) What is the substance that is adsorbed called ?

(A) Adsorbent (B) Adsorbate (C) Absorsent (D) Absorbite

(9) Which of the following substances is not an adsorbent ?

(A) Sugar (B) Clay (C) Silica gel (D) Alumina

(10) What type of attraction forces are present between adsorbent and adsorbate in physisorption ?

(A) van der Waals (B) Strong chemical (C) Gravitation (D) Metallic bond.

(11) Which statement is correct for physical adsorption ?

(A) It is slow or fast process

(B) The value of adsorption enthalpy is low

(C) Unimolecalar layer is formed on the adsorbent

(D) Generally results at high temperature.

(12) What is used for the electronic instruments so that they may not be spoiled by moisture ?

(A) Alumina (B) Silica gel (C) Iron powder (D) Animal charcoal.

(13) Which of the following gaseous molecule has maximum physical adsorption enthalpy ?

(A) Ne (B) H_2O (C) H_2 (D) C_2H_6

(14) Mention the Freundlich adsorption isotherm.

(A) $\frac{x}{m} = Kp^{n}$ (B) $\frac{x}{m} = Kp^{n^2}$ (C) $\frac{x}{m} = Kp^{\frac{1}{n}}$ (D) $\frac{m}{x} = pK^{n}$

(15) Which equation is applicable to Langmuir adsorption isotherm at low pressures ?

(A) $\frac{x}{m} = \frac{b}{a}$ (B) $\frac{x}{m} = ap$ (C) $\frac{x}{m} = \frac{1}{n}p$ (D) $\frac{x}{m} = \frac{a}{b}$

(16) Which of the following is applicable to Langmuir adsorption isotherm when derived ?

(A) The random motion of molecules of gas

(B) Kinetic theory of gases

(C) Magnitude of adsorption of gas

(D) All the given

(17) What is called the substance which increases the rate of chemical reaction but does not take part in the reaction ?

(A) Adsorbent (B) Catalyst (C) Adsorbate (D) Reactant

(18) Which type of catalyst is used in obtaining SO_3 gas required in obtaining sulphuric acid by Lead chamber process ?

(A) Homogeneous catalyst (B) Heterogeneous catalyst
(C) Catalyst is not used (D) Vanadium pentoxide

(19) Which catalyst is used in the reaction of preparing vegetable ghee from vegetable oil ?

(A) Iron powder (B) Zinc powder
(C) Raney nickel (D) Vanadium pentoxide

(20) On what does the shape-selective catalytic reaction depend ?

(A) Molecules of product (B) Size of reactant
(C) Porosity of catalyst (D) All the given.

(21) What are enzymes made up of ?

(A) Carbohydrates (B) Lipids (C) Vitamin (D) Proteins

(22) If sand is dissolved in water, shaken and kept for some time, the sand settles down. The phenomenon is called :

(A) Colloid solution (B) True solution (C) Suspension (D) Dispersion

(23) What is the colloid in which both dispersion medium and dispersed phase are in solid state called ?

(A) Emulsion (B) Gel (C) Aerosol (D) Solid sol.

(24) Which of the following colloid is reversible ?

(A) Lyophilic (B) Lyophobic (C) Hydrophilic (D) Both (A) and (C)

(25) What type of colloid is sulphur (S_8) dissolution ?

(A) Associated colloid (B) Micelle
(C) Multimolecular colloid (D) Macromolecular colloid

(26) Which choice is correct for micelle ?

(A) Is a combination of emulsion and gel
(B) Is an adsorbate catalyst
(C) Is an ideal solution
(D) Is an associate of colloids.

(27) At critical micelle concentration, the molecules on the surface…

(A) Decompose (B) Associate
(C) Dissociate (D) Completely soluble.

(28) What is the correct effective coagulating order of ions for positively charged colloid of $Fe(OH)_3$?

(A) $PO_4^{3-} > Cl^- > SO_4^{2-}$ (B) $PO_4^{3-} > SO_4^{2-} > Cl^-$
(C) $Cl^- > SO_4^{2-} > PO_4^{3-}$ (D) $SO_4^{2-} > PO_4^{3-} > Cl^-$

(29) Which of the following colloidal sol can not be prepared by Bredig's arc method ?

(A) Sulphur (B) Silver (C) Gold (D) Platinum

(30) With which property of colloid Tyndall effect is associated ?
(A) Mechanical (B) Colligative (C) Optical (D) Electrical

(31) By which name the zigzag motion of colloidal particle in the dispersion medium is known ?
(A) Brownian movement (B) Tyndall motion
(C) Vibrational motion (D) Mechanical motion.

(32) By which instrument the existence of positive or negative electric charge of colloid is determined ?
(A) Electrophoresis (B) Microscope
(C) Ultrasonic dispersant (D) Voltmeter.

(33) Which of the following is oil/water (oil in water) emulsion ?
(A) Cold cream (B) Vanishing cream
(C) Butter (D) Cod liver oil

(34) Which of the following is water/oil (water in oil) emulsion ?
(A) Cold cream (B) Butter milk (C) Milk (D) Vanishing cream

(35) Which of the following substances is an emulsifier ?
(A) Common salt (B) Urea (C) Oil (D) Soap

(36) Which of the following is a multimolecular colloid ?
(A) Wax (B) Latex-rubber (C) Silicones (D) All the given

(37) From which of the following effects the colloidal system is free ?
(A) Gravitational effect (B) Effect of added electrolyte
(C) Effect of heat (D) Effect of applied electrical field.

(38) At isoelectric point the colloid...
(A) Stabilizes (B) Peptizises
(C) Does not possess electrical charge (D) Can not be coagulated

(39) By which method ferric hydroxide colloid is prepared ?
(A) Hydrolysis (B) Peptization
(C) Double decomposition (D) Oxidation

(40) The dimension of colloid particles is.........
(A) Less than that of true solution
(B) Between true solution and suspension
(C) More than that of suspended particles
(D) Can be of any dimension

2. Answer the following questions is brief :

(1) Give definition of adsorption
(2) Give definition of colloid. Give one example.
(3) Write the name of any one enzyme and its function.
(4) What is meant by emulsion ? Give example.
(5) Give three examples of reversible colloids.

(6) Write formula of Langmuir adsorption isotherm.
(7) What is micelle ? Explain its formation.
(8) Give names of three factors that affect adsorption.
(9) Give name of purification method for colloid.
(10) How adsorption is useful for protection against effect of poisonous gases ?

3. Answer the following questions :

(1) Explain giving suitable example : adsorption, adsorbate, adsorbent.
(2) Mention three differences between physical and chemical adsorption.
(3) Why the granular or powder form substance is considered good adsorbent ?
(4) Explain the factors affecting adsorption of gaseous adsorbate on solid adsorbent.
(5) What is meant by adsorption isotherm ? Explain.
(6) Explain giving examples homogeneous and heterogeneous catalysis.
(7) Give explanation of micelle. Explain critical micelle concentration.
(8) Write Freundlich adsorption isotherm and explain the terms involved in it .
(9) Write two chemical methods for preparation of colloids.
(10) Explain the difference amongst true solution, suspension and colloid.
(11) Write types of colloid and give one example of each.
(12) What is meant by emulsion ? Explain its types giving examples.
(13) Explain the terms : (i) Peptization (ii) Emulsification
(14) Explain the terms : (i) Tyndall effect (ii) Brownian movement.
(15) What is meant by shape selective catalysis ? Explain.

4. Answer the following questions in detail :

(1) Explain giving examples the terms : dispersion medium, dispersing phase.
(2) How are colloids classified on the basis of dispersing phase ?
(3) How catalysis occurs by zeolite ?
(4) Explain Hardy-Schulze rules.
(5) "Colloid is not a substance but a state of substance." Discuss.
(6) Write five examples of the biochemical reactions occurring by use of specific enzymes.
(7) Write short notes : (i) Coagulation (ii) Electrophoresis
(8) Mention types of emulsion and describe the tests for their identification.
(9) Describe the methods to prepare colloids of sulphur and gold.
(10) Write short notes : (i) Tyndall effect (ii) Brownian movement
(11) Explain the working of enzyme catalyst by lock-key model.
(12) Explain purification of colloid by electrodialysis.
(13) Write short note on Cottrell smoke precipitator.
(14) Mention uses of colloids in different fields.
(15) Write short notes : (i) Bredig's arc method (ii) Colloid mill.

●

UNIT

3

d- and f-Block Elements

3.1 Introduction

We have obtained the information about modern periodic table for classification of elements in standard 11 (semester I). In addition to this, we have also studied in detail the s- and p-block elements during semesters I to III. We know, the elements in modern periodic table are classified into s-, p-, d- and f-blocks and 1 to 18 groups. The elements of groups 1 and 2 and the groups 13 to 18 are known as s-block and p-block elements respectively; while elements of rest of the ten groups, group no 3 to 12 are called d-block elements because the last electron of the elements, enter into the available d-orbital. The position of these elements is between s-block and p-block elements. The properties of d-block elements show transition between the properties of representative elements of periodic table i.e. most electropositive elements of s-block (metal elements) and least electropositive elements of p-block (nonmetals, metalloids and metals). Hence, they are known as **transition elements.** This means that those elements have their properties which intermediate between those of s- and p-block elements. The two horizontal rows at the bottom of the modern periodic table are called f-block elements because the last electron enters into the available f-orbitals. Th (Z= 90) has got the electronic structure [Rn] $5f^0 6d^2 7s^2$. In Th, the last electron is not filled in f-orbital although the experimental results support the elements as f-block elements. Thus, it is included in f-block elements. These elements being part of the transition series of transition elements of periods 6 and 7; are called **innertransition elements.**

3.2 Transition Elements – Elements of d-Block

The elements which in their ground state or any one of its oxidation state, have incompletely filled d-orbitals with electrons are called the transition elements. The elements whose ground state or any of its oxidation state have vacant 3d-orbitals are called **first transition series elements,** if 4d-orbitals are incompletely filled then **second transition series elements** and

5d-orbitals incompletely filled with electrons then they are called **third transition series elements.** In each of these series there are ten elements. Fourth transition series corresponding to the filling of 6d-orbital begins with actinium (Z = 89) followed by element with atomic number 104 (Rf) onwards. Regarding fourth transition series, the research is continuing at present.

3.2.1 Electronic Configuration and Oxidation States of Transition Elements :

The general electronic configuration of transition elements is $(n-1)d^{1-10}ns^{1-2}$. Generally the stability of half filled or completely filled orbital is relatively more. Because of this the electronic configuration of Cr is considered $[Ar]3d^54s^1$ instead of $[Ar]3d^44s^2$. In the same way the electronic configuration of Cu is considered $[Ar]3d^{10}4s^1$ instead of $[Ar]3d^94s^2$. It is necessary here to note that the difference between energies of 3d and 4s orbital, is very less, hence this becomes possible.

When ions are formed from first transition series elements, the electron entering last in 3d-orbital is not removed first but both the electrons of 4s orbital are removed first and then the electrons of 3d-orbital are removed; because the electrons in the outermost orbital have relatively less attraction towards the nucleus in comparison to the electrons in the inner orbital. It is important to note here that the orbit having higher value of principal quantum number is considered as the outermost orbital. Thus, between the 3d-orbital (n = 3) and 4s-orbital (n = 4), 4s-orbital will be outermost orbital. Similarly, when ions are formed from the elements of second transition series, the electron of 5s-orbital is removed first and then the electron of 4d-orbital when ions of third transition elements, the electron is removed first from 6s-orbital and then the electron from 5d-orbital is removed; the electronic configuration of elements of first transition series in the ground state and their oxidation states are shown in table 3.1.

Table 3.1. The electronic configuration of first transition series in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
Sc	21	$[Ar]3d^14s^2$	(+3)
Ti	22	$[Ar]3d^24s^2$	+2, +3, (+4)
V	23	$[Ar]3d^34s^2$	+2, +3, (+4), +5
Cr	24	$[Ar]3d^54s^1$	(+2), (+3), +4, +5, (+6)
Mn	25	$[Ar]3d^54s^2$	(+2), +3, +4, +5, +6, (+7)
Fe	26	$[Ar]3d^64s^2$	(+2), (+3), +4, +5, +6
Co	27	$[Ar]3d^74s^2$	(+2), (+3), +4
Ni	28	$[Ar]3d^84s^2$	(+2), +3, +4
Cu	29	$[Ar]3d^{10}4s^1$	+1, (+2)
Zn	30	$[Ar]3d^{10}4s^2$	(+2)

Note: Stable oxidation state is shown in parenthesis.

The electronic configuration of Cu in ground state in first transition series is $[Ar]3d^{10}4s^1$. In it 3d-orbital is completely filled with electrons but electronic configuration of Cu^{2+} is $[Ar]3d^9$. Here, 3d-orbitals are incompletely filled with electrons and so Cu is considered transition element. The electronic configuration of Zn in ground state is $[Ar]3d^{10}4s^2$. In it, 3d-orbital is completely filled with electrons. In addition, the electronic configuration of Zn^{2+} is $[Ar]3d^{10}$. Here, also, the 3d-orbital is completely filled. Hence **Zn is not considered as a transition element.** The electronic configuration of elements of second transition series in the ground state and their oxidation states are shown in table 3.2.

Table 3.2. Electronic configuration of elements of second transition series in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
Y	39	$[Kr]4d^1 5s^2$	(+3)
Zr	40	$[Kr]4d^2 5s^2$	+2, +3, (+4)
Nb	41	$[Kr]4d^4 5s^1$	+3, (+5)
Mo	42	$[Kr]4d^5 5s^1$	+1, +3, +4, +5, (+6)
Tc	43	$[Kr]4d^5 5s^2$	(+4), +5, (+6)
Ru	44	$[Kr]4d^7 5s^1$	+2, (+3), +4, +6
Rh	45	$[Kr]4d^8 5s^1$	+2, (+3), +4
Pd	46	$[Kr]4d^{10} 5s^0$	(+2), +4
Ag	47	$[Kr]4d^{10} 5s^1$	(+1), +2, +3
Cd	48	$[Kr]4d^{10} 5s^2$	(+2)

Note: Stable Oxidation state is shown in parenthesis.

On the basis of the table 3.2, it can be said that in this transition series the electronic configuration of Pd, Ag and Cd in ground state have $4d^{10}$ that is 4d-orbital is completely filled with electrons; but in +2 of Pd and +2 of Ag, oxidation states, the electronic configurations, 4d-orbital is incompletely filled and so they are considered as transition elements but in the electronic configuration of Cd^{2+}, 4d-orbital is completely filled ($4d^{10}$). Hence **Cd is not considered as a transition element.** The electronic configuration of elements of third transition series in ground state and their oxidation states are shown in table 3.3.

Table 3.3. Electronic configuration of third transition elements in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	$[Xe]5d^1 6s^2$	(+3)
Hf	72	$[Xe]4f^{14} 5d^2 6s^2$	+2, +3, (+4)
Ta	73	$[Xe]4f^{14} 5d^3 6s^2$	+3, (+5)
W	74	$[Xe]4f^{14} 5d^4 6s^2$	+1, +4, +5, (+6)
Re	75	$[Xe]4f^{14} 5d^5 6s^2$	(+3), (+4), +5, (+6)
Os	76	$[Xe]4f^{14} 5d^6 6s^2$	(+4), +5, +6
Ir	77	$[Xe]4f^{14} 5d^7 6s^2$	(+3), (+4)
Pt	78	$[Xe]4f^{14} 5d^9 6s^1$	(+2), (+4)
Au	79	$[Xe]4f^{14} 5d^{10} 6s^1$	+1, (+3), +5
Hg	80	$[Xe]4f^{14} 5d^{10} 6s^2$	+1, (+2)

Note: Stable oxidation state is shown in parenthesis.

On the basis of table 3.3, it can be said that in the electronic configuration of Au and Hg in ground state there is $5d^{10}$ that is 5d-orbital is completely filled but in the electronic configuration of Au^{3+}, 5d-orbital is incompletely filled ($5d^8$) and so Au is considered transition element while in electronic configuration of Hg, 5d orbital is completely filled ($5d^{10}$) and so **Hg is not considered transition element.**

3.2.3 Occurrence of Transition Elements :

Definite transition metal is obtained from its definite mineral and a definite method is used for obtaining pure metal from the mineral. You have studied in unit 4 of semester III about the methods for the extraction of Cu, Fe and Zn from their minerals.

3.2.4 General Characteristics of Transition Elements :

- All the transition elements are metallic elements.
- These elements are hard and strong.
- Their melting points are high.
- These elements can form alloys with each other.
- Most of these elements dissolve in acid, but acid has no effect on certain noble elements.
- These elements possess various valencies.
- They possess property of malleability and ductility.
- They are good conductors of electricity and heat.
- Some of their ions possess paramagnetic property.

3.3 Periodic Trends in Properties of Elements of First Transition Series

(1) Metallic property : All the elements of first transition series possess metallic property. This point can be understood from the study of general characteristics of transition elements (see point 3.2.4)

(2) Atomic radii and Ionic radii : Generally in the periodic table, moving from left to right, there is decrease in atomic radii. This trend is observed in the transition elements, but this decrease in atomic radii is less. The tendency of ionic radii in transition elements is found to be similar to atomic radii. The atomic radii and ionic radii of first transition series elements are shown in tables 3.4 and 3.5 respectively.

Table 3.4 Atomic radii of first transition series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radius (pm)	144	132	122	117	117	117	116	115	117	125

Table 3.5 Ionic radii of first transition series elements

Element	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic Radius (pm)	-	90	79	82	82	77	74	70	73	75

As shown in table 3.4, the atomic radius decreases from Sc to V while the atomic radii from Cr to Cu is almost similar. In addition to this, instead of decreasing the atomic radius of Zn is found to be increasing. The reason for this is that, as we move from left side to right side in period, the positive electric charge of nucleus increases and the entering electron is added to 3d-orbital. This electron, increases the shielding effect for attraction of electron present in 4s-orbital due to increase in positive electric charge in the nucleus. As a result, the electrons present in 4s-orbital are not attracted more towards the nucleus (Relative to neighbouring transition element). Thus, the orbit does not contract hence the atomic radii remain same. 3d-orbital of Zn atom is completely filled. Hence, it decreases the attraction towards electron of 4s-orbital of positive electric charge of nucleus due to its shielding effect. Also repulsion between electron-electron in 3d orbital increases more than the value of attraction of electrons of 4s-orbital and nucleus. Hence, there is expansion of orbit; so the value of atomic radius of Zn is seen to be increasing.

(3) Ionisation enthalpy : Moving from left side to right side in first transition series elements, the nuclear electric charge increases and so the value of ionization enthalpy increases but the increase in this value, is not equal to the increase in enthalpy in the elements of the main group. Thus, there is not much change in the first ionization enthalpies of two neighbouring transition elements (table 3.6). The values of first, second and third ionization enthalpies are shown in table 3.6.

Table 3.6 First, second and third ionization enthalpies (kJ mol^{-1}) of first transition series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_i H_1$	631	656	650	653	717	762	758	736	745	906
$\Delta_i H_2$	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H_3$	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

As shown in table 3.6, there is not much difference seen in the values of second ionization enthalpies like the changes in the first ionization enthalpies of first transition series elements. But chromium and copper are found to be exceptions. The values of second ionization enthalpy of these two elements are more than those of their neighbouring elements, because both these elements attain the electronic configuration Cr^+ : $[Ar]3d^5$ and Cu^+ : $[Ar]3d^{10}$ after loss of one-one electron from these two elements. From Cr and Cu, the second electron is removed from half filled or completely fill 3d orbitals respectively having more stability. It is natural that more energy will be required for removal of such electrons.

(4) Electrode potential : Thermodynamic stability of transition metals depends on their magnitude of ionization enthalpy. The compounds of metals having less ionization enthalpy are more stable, while the stability of compounds in solution is more dependent on relative electrode potentials.

The value of electrode potential is determined on the basis of the sum of the enthalpy changes (ΔH_T) of different reactions. The stabilities of different oxidation states of transition metal ions are determined on the basis of the electrode potentials. More negative the values of standard reduction potientials more will be the stabillity of ions in aqueous medium.

3.4 Characteristic Properties of Elements of First Transition Series

(1) Colour : Most of the ionic and covalent compounds of transition elements are coloured. It is due to the presence of incompletely filled d-orbitals. When visible light falls on transition metal ions, they absorb light of definite wavelength and emit the remaining light. Our eye catches the colour of this emitted light as the colour of those ions. Hence, ions appear coloured. For example, when visible light passes through the aqueous solution of $[Ni(H_2O)_6]^{2+}$, green colour is emitted and other colours are absorbed. Hence, the colour of this aqueous solution appears to be green. In the similar, when visible light passes through aqueous solution of $[Co(NH_3)_6]^{3+}$, then red and green colours are emitted and other colours are absorbed. Because of the mixing of the emitted red and green colour, the colour of this solution appears to be yellowish orange. During absorption of light the electrons in d-orbital of ions receive energy and go to the d-orbital having higher energy. This transition of electrons is called **d-d transition.** It is necessary to note here, that generally the energy of all five d-orbitals is equal but according to crystal field theory, there is splitting of d-orbitals in different energy levels. The splitting of d-orbitals of different energy levels in transition compounds having tetrahedral and octahedral geometry are shown in figure 3.1.

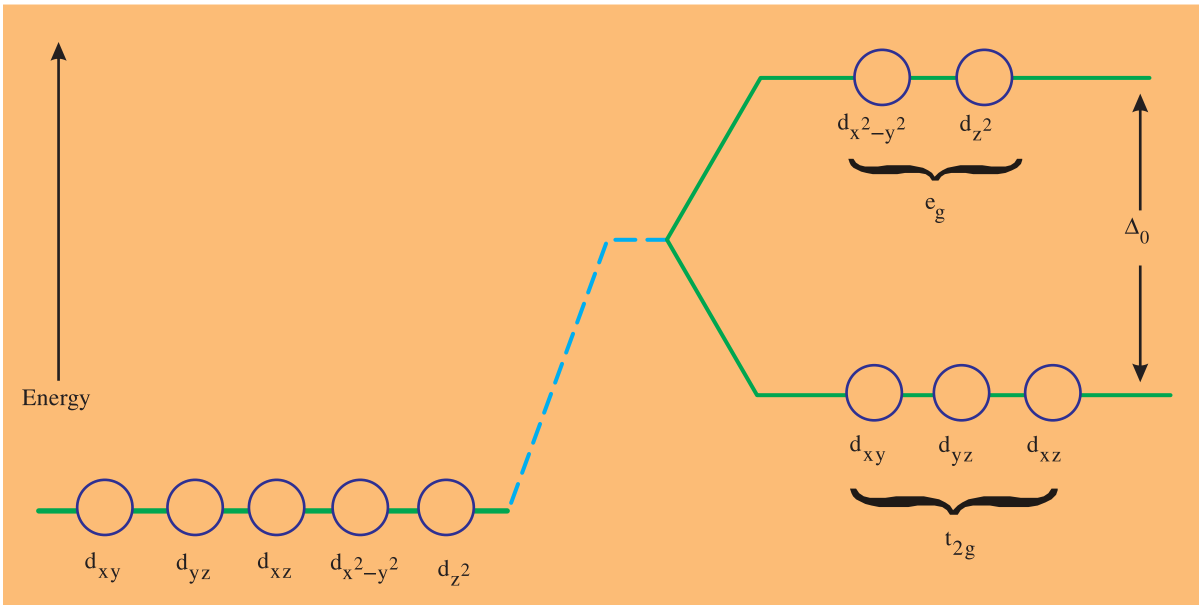


Fig.3.1(a) Splitting of d-orbitals in octahedral complex compounds

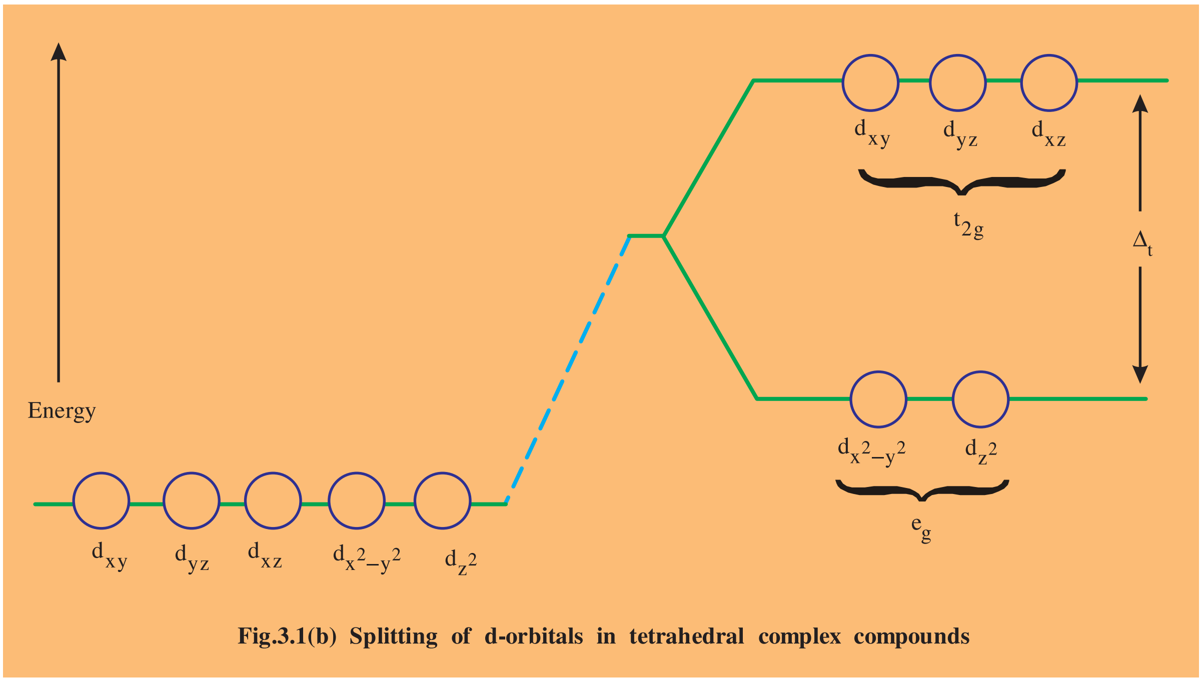


Fig.3.1(b) Splitting of d-orbitals in tetrahedral complex compounds

The colours of some metal ions are mentioned in table 3.7

Table 3.7 Colours of some of the hydrated metal ions of first transition series

Metal ions	Colour
Cu^{2+}, Cr^{2+}, Co^{3+}, V^{4+}	Blue
Ni^{2+}, Fe^{2+}, V^{3+}	Green
V^{2+}, Cr^{3+}, Mn^{3+}	Violet
Co^{2+}, Mn^{2+}	Pink
Fe^{3+}	Yellow
Ti^{3+}	Purple
Zn^{2+}, Sc^{3+}, Ti^{4+}, Cu^{+}	Colourless

Student friends, the verfication of colour of certain metal ions mentioned in table 3.7 can be done in chemistry laboratory by observing easily the colours from the chemicals available- $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_3$ and $ZnCl_2$.

(2) Catalytic property : Transition metals and their certain compounds increase the rate of chemical reaction. Hence, they are useful catalysts. These substances used as catalyst are in solid state. The random and pointed peak points on the surface at the ends of the edges of their particles are responsible centres for catalysis work. The molecule-atom in the depth in the matter of solid substance are surrounded by similar other atoms. Hence, the magnetic field of their unpaired electrons is destroyed by the effect on each other, while atoms of the ends of the edges or the peak points, get affected by the magnetic field which are active centres for catalysis. The molecules of reactant are attracted by the magnetic field and so the required activation energy of the reaction decreases. As a result, the reaction rate increases viz. Ni in hydrogenation of vegetable oil, Fe in industrial production of NH_3 by Haber process, V_2O_5 catalyst is used in obtaining SO_3 from SO_2 in contact process for manufacturing of H_2SO_4. You have studied in detail the point on catalysis in unit 2 : Surface Chemistry.

(3) Magnetic property : When a substance is placed in the magnetic field, then they possess two types of magnetic properties (i) Paramagnetism and (ii) Diamagnetism.

The molecule, atom or ion of a substances in which there are unpaired electrons, such substances possess paramagnetism, so they are called **paramagnetic substances;** while molecule, atom or ion in which all the electrons are paired, possesses diamagnetism. Hence, they are called **diamagnetic substances.** In the electronic configuration of transition elements, the (n–1)d-orbitals are incompletely filled; hence they possess unpaired electrons and so the atoms of these elements are paramagnetic. Because of paramagnetism they possess magnetic moment. Magnetic moment is produced due to rotation of unpaired electron on its axis and orbital rotation. In transition metal ions the unpaired electrons are present in the outermost orbit. Hence, in such cases axial rotation contribution is much more important than the orbit contribution. The value of magnetic moment based on only rotation on axis, can be calculated with the help of following formula :

$$\mu = \sqrt{n\,(n+2)}\ \text{BM}$$

where μ = Magnetic moment, n = Number of unpaired electrons, BM = Bohr Magneton (unit)

The value of magnetic moment increases with increase in number of unpaired electrons. Thus, through the measurement of magnetic moment we come to know about the number of unpaired electrons in atom, molecule or ion. Maximum five unpaired electrons can be in d-orbitals, so the theoretical values of magnetic moments are shown in table 3.8.

Table 3.8 Theoretical Value of Magnetic Moment

Number of unpaired electrons (n)	Magnetic moment μ (BM)
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

The magnetic moments of ions of transion elements or their compounds, are based on the axial rotation; so sometimes their values obtained experimentally are slightly more or less than the theoretical values. The reason for this is the rotation-orbital combination. This type of combination being directional, the value obtained is slightly more or less i.e. it depends on how these directional combinations occur. Earlier you have studied about diamagnetic or paramagnetic properties in semester III in unit 1 on Solid State.

Example : 1 Calculate magnetic moment of $Co^{2+}(aq)$

Solution :

			3d			4s
Co (Z = 27) : [Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Co^{2+} : [Ar]	↑↓	↑↓	↑	↑	↑	

Here number of unpaired electrons n=3

Now, magnetic moment $\mu = \sqrt{n(n+2)}$ BM

$= \sqrt{3(3+2)}$ BM

$= \sqrt{15}$ BM = 3.87 BM

Thus, the value of magnetic moment of $Co^{2+}(aq)$ will be 3.87 BM

(4) Capacity of transition metal ions to form complex compounds : Transition metal ions combine with one or more anion or neutral molecule (ligand) and form complex species by co-ordinate covalent bond having definite characteristics which are called complex compounds. In depth, study of such **complex compounds** will be done in Unit 4 : complex compounds. The capacity of transition elements to form complex compounds is more than that with other elements; the reason of which is the below mentioned characteristics of transition metal ions.

- The size of transition metal ions is small.
- The nuclear electric charge and ionic electric charge of transition metal ions is comparatively more.
- The electronic configurations of transition metal ions is favourable for formation of complexes. In these metal ions, d-orbitals are vacant and so the electron pairs coming from the ligand can be accommodated.

- As very less difference is there between energy values of 3d, 4s, 4p or 4d orbitals, hybridization of different types can be possible with these orbitals. Thus, the different hybrid orbitals produced are helpful in formation of complex compounds.
- Due to formation of various types of hybridization and because of co-ordinate covalent bonds are directional, different types of geometrical shapes containing complex compound can be formed.
- Transition metal ions exhibit various oxidation states. Thus, varieties of complex compounds can be formed.

3.5 Interstitial Compounds

The atoms in solid state of transition metals are arranged in definite crystal structure. There are definite voids between atoms in such an arrangement. Hence, non-metallic atoms of smaller size viz. H, C, N and B can be easily arranged in the voids of crystal structure. The compounds formed in such a manner are called **interstitial compounds;** in which chemical bond is not formed between non-metal elements of smaller size arranged in the voids and the metal atom, hence the proportion of components in such compound is not definite. So interstitial compounds are not detinite. In fact interstitial compounds are nonstoichiometric or non-proportionate compounds, e.g., $TiH_{1.7}$, $VH_{0.56}$ etc. On the basis of the non-metal arranged in the interstitial void, they can be classified as hydrides, carbides, nitrides and borides, because elements like hydrogen, carbon, nitrogen and boron can be arranged in interstitial positions.

A notable change is observed in the characteristic properties of metals due to presence of non-metal elements like H,C,N and B in the voids of crystal structure. The small size of non-metal atoms present here in the void attract free electrons of metallic bond, hence free electrons of metallic bond are localised and so the strength of the bond increases. Hence, the properties of the metals like hardness, melting point resistance to wear, resistance to corrosion etc. are notably increased. Therefore, interstitial compounds are used in preparation of tools, machinery parts, vehicles etc. This type of compounds have not definite molecular formula. VN, Fe_3N, Fe_3C, Cr_3C_2, Mn_3C, TiC, VB, CrB_2 etc. are interstitial compounds.

3.6 Alloys

The characteristic properties like hardness, conductance, malleability, resistance to corrosion are essential for machineries, tools, vehicles and vessels of house-hold usages. There is no combination of all these properties and is not together found in any pure metal. Hence, instead of using pure metals in practice, alloys prepared from two or more metal-elements are used frequently..

Scientists **Hume** and **Rothery** presented rules as follows to obtain alloys of combination of useful properties :

(1) The atomic size of two metals forming the alloy must be the same. There must not be more than 15 % difference in their atomic radii.

(2) The chemical properties of the metals used for preparation of alloys must be same, that is, their electronic configurations of valence shell must be the same.

(3) The crystal structures of pure metallic elements used for alloys must be similar.

22 carat gold ornaments is the best example of alloy. It is the alloy of Au and Cu. The difference between atomic size of Au (atomic size = 134 pm) and Cu (atomic size = 117 pm) is about 14.5 %. Both of them possess cubic close pack structure. Both of them being members of group-11 the electronic configuration of their valence shells is same. Thus best alloy can be prepared according to laws

suggested by Hume and Rothery. The difference in atomic sizes between Cr, Mn, Fe, Co, Ni, Cu metals, is less than 2%. There is much less difference in the electronic configuration of valence shell of these elements. Hence, these elements form number of alloys having different proportions which are very useful in practice. Certain important alloys, their components, properties and uses are shown in table 3.9.

Table 3.9 Alloys, their components, properties and uses

Alloy	Components	Properties	Uses
Stainless steel	Fe (70%), Cr (20%) Ni (10%)	No effect of air, water and alkali and does not get rusted	In preparation of utensils, blades, surgical instruments.
Brass	Cu (70%), Zn (30%)	Ductile, hard, corrosion resistant and can be shaped easily	In preparation of cooking vessels, parts of machine and musical instruments.
Bronze	Cu (90%), Sn (10%)	Very strong and possessing more corrosion resistance	In preparation of statues, currency coins and medals.
Nitinol	Ti (45%), Ni (55%)	Light in weight and strong and resists corrosion. It has marvellous property of memory.	Rivetting and useful in space research.
Cupronickel	Cu (75-85%), Ni (15-25%)	Strong and corrosion resistant.	In preparation of currency coins.
	Cu (50-55%), Ni (45-50%)	Electrical resistance is more.	In preparation of electric resistant wires.
German-silver	Ni (40-50%), Zn (25-30%) Cu (25-30%)	Possesses shining as silver	In preparation of household vessels,art models and resistant wires.
Nichrome	Ni (60%), Cr (40%)	Electrical resistance is very high	As electric resistant wire in electric furnaces and electric heaters.

In addition, amalgam with mercury - alloy is also well known. In this alloy there are Hg (50%), Ag (35%), Sn (12%), Cu (3%) and Zn (0.2%). This alloy is, used in filling the cavity in the tooth. When this alloy is to be filled in cavity in the tooth, all these metals are mixed, some time before filling. This alloy is soft. By the time the dentist can fill in the cavity of tooth, it remains soft so that it becomes convenient for dentist to fill in the cavity. After filling in this alloy in cavity, it becomes hard and it does not expand.

3.7 Some Important Compounds of 3d-Transition Elements

Many compounds of 3d-transition elements are familiar. We shall study here, preparation, properties and uses of only potassium dichromate $(K_2Cr_2O_7)$ and potassium permanganate $(KMnO_4)$.

(1) Potassium dichromate $(K_2Cr_2O_7)$:

Perparation : Sodium chromate (Na_2CrO_4) and ferric oxide (Fe_2O_3) are formed by fusion of chromite mineral ($FeCr_2O_4$) with sodium carbonate and quick lime in presence of air. After the reaction, the roasted mass is extracted with water when Na_2CrO_4 is completely dissolved while Fe_2O_3 is left insoluble in presence of air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Filtering the yellow coloured solution of sodium chromate, it is acidified with H_2SO_4; so that sodium dichromate $(Na_2Cr_2O_7)$ is formed, which reacts with potassium chloride and forms potassium dichromate and sodium chloride. $K_2Cr_2O_7$ being much less soluble than NaCl it crystallizes out on cooling.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Properties :

- Potassium dichromate is orange coloured crystalline substance.
- It is soluble in water.
- It acts as a strong oxidizing agent in acidic medium.
- When an alkali is added to an orange coloured solution of potassium dicromate a yellow coloured solution results due to the formation of potassium chromate and on acidifying it, the colour again changes to orange due to the reformation of potassium dichromate.

Chromate and dichromate ions are interconvertible in aqueous solution; which depends on the pH of the aqueous solution; because the oxidation state of chromium in chromate and dichromate is the same.

$$\underset{\text{Yellow colour}}{2CrO_4^{2-}} + 2H^+ \rightarrow \underset{\text{Orange colour}}{Cr_2O_7^{2-}} + H_2O$$

$$\underset{\text{Orange colour}}{Cr_2O_7^{2-}} + 2OH^- \rightarrow \underset{\text{Yellow colour}}{2CrO_4^{2-}} + H_2O$$

Uses :

- Potassium dichromate is mainly useful in leather industry and formation of azo compounds.
- As oxidizing agent used in synthesis of organic compounds, used as a reagent in chemical oxygen demand (COD) measurement in polluted water. In addition, the mixture of potassium dichromate with concentrated sulphuric acid which is known as chromic acid, is used for cleaning of glasswares in laboratory. It is corrosion inhibitant.
- It is used as titrant in redox titrations to determine the amount of metal ions like iron (II).

(2) Potassium permanganate $(KMnO_4)$:

Preparation : Dark green coloured potassium manganate (K_2MnO_4) is formed by fusion of manganese dioxide (MnO_2) with KOH in presence of air or oxidizing agent like KNO_3. Potassium permanganate is formed when sulphuric acid is added to this solution and made acidic.

$$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{(Green colour)}}{2K_2MnO_4} + 2H_2O$$

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O$$

Properties :

- Potassium permanganate is dark purple coloured crystalline substance.
- It is soluble in water.
- It acts as oxidising agent in acidic, basic and neutral medium.

Uses :

- Potassium permanganate is used as strong oxdising agent in synthesis of organic compounds.
- It is used as bleaching agent for cotton cloth, silk and wood and in textile industries.
- An aqueous solution of potassium permanganate is used for gargling to keep mouth germfree as it is antiseptic.
- It is useful as titrant in redox titrations to know the proportion of metal ions like iron (II) and organic compounds like oxalic acid.

3.8 Applications of d-Block Elements

- The alloys-stainless steel, brass, bronze, nitinol, cupronickel, german silver and nichrome prepared from elements of d-block elements are used for preparation of household utensils, currency coins, statues, and machinery.
- Some elements and compounds of these elements act as catalyst in chemical reaction e.g., Ni in hydrogenation of vegetable oil, Fe in Haber process of industrial production of NH_3, V_2O_5 catalyst for obtaining SO_3 from SO_2 in contact process for production of H_2SO_4.
- Alloy like mercury-amalgam is useful for filling in tooth cavity.
- Alloy of gold and copper is more appropriate for preparation of ornaments.
- Mercury is used in thermometer.
- The use of inert metal like platinum is made as electrodes in the experiments of electro-chemistry.
- Some compounds like $KMnO_4$ and $K_2Cr_2O_7$, of d-block elements act as strong oxidizing agents in synthesis of organic compounds. They are used as titrant in redox titrations.
- MnO_2 is used in dry cell.
- To prevent water pipes and the roof on the house from corrosion they are changed in to galvanized form with the help of zinc metal.

3.9 Innertransition Elements (Elements of f-Block)

The f-block elements are distributed into two series : (A) Lanthanide series and (B) Actinide series. The series of fourteen elements immediately after lanthanum- Ce(Z = 58) to Lu (Z = 71) is called **lanthanide series.** The elements of this series are known as **lanthanoids.** Lanthanoids are expressed by general symbol Ln. As lanthanum has more similarity with lanthanoids, it is included in the lanthanide series, during discussion. In the periodic table, series of fourteen elements immediately after actinium-Th (Z = 90) to Lr (Z = 103) is called **actinide series.** The elements of this series are known as **actinoids.** As actinium possesses more similarity with actinoids, it is included in the discussion of actinide series. **The general electronic structure of outermost electrons of elements of f-block is $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$.**

3.10 Lanthanide Series

To understand the lanthanide series, we shall study here, its electronic configuration, oxidation state, atomic size, chemical reactivity and lanthanide contraction.

3.10.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of lanthanide series, $6s^2$ is common in all the elements but the electrons in 4f-orbital keep changing. **All the lanthanoids and lanthanum element possess stable oxidation state + 3.** The electronic configuration and oxidation states of lanthanum and lanthanoids are shown in table 3.10.

Table 3.10 Electronic configuration and oxidation states of lanthanum and lanthanoids

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	$[Xe]5d^1 6s^2$	(+3)
Ce	58	$[Xe]4f^1 5d^1 6s^2$	(+3), +4
Pr	59	$[Xe]4f^3 6s^2$	(+3)
Nd	60	$[Xe]4f^4 6s^2$	+2, (+3)
Pm	61	$[Xe]4f^5 6s^2$	(+3)
Sm	62	$[Xe]4f^6 6s^2$	+2, (+3)
Eu	63	$[Xe]4f^7 6s^2$	+2, (+3)
Gd	64	$[Xe]4f^7 5d^1 6s^2$	(+3)
Tb	65	$[Xe]4f^9 6s^2$	(+3), +4
Dy	66	$[Xe]4f^{10} 6s^2$	(+3), +4
Ho	67	$[Xe]4f^{11} 6s^2$	(+3)
Er	68	$[Xe]4f^{12} 6s^2$	(+3)
Tm	69	$[Xe]4f^{13} 6s^2$	+2, (+3)
Yb	70	$[Xe]4f^{14} 6s^2$	+2, (+3)
Lu	71	$[Xe]4f^{14} 5d^1 6s^2$	(+3)

Note : Stable oxidation state is shown in parenthesis

It is apparent from the study of electronic configuration shown in table 3.10, that only in the lanthanoids like Ce, Gd and Lu electrons are filled in 5d orbital. In Gd, because of half filled orbital like $4f^7$, stability may be obtained and so newly added electron enters into 5d orbital, while in Lu, 4f orbital being completely filled, the added new electron enters into the 5d orbital. The filling of electron of Ce in 5d-orbital is accepted at present as an exception. Thus, **the general electronic configuration of lanthanoids is [Xe]$4f^{1-14}5d^{0-1}6s^2$.** Amongst lanthanoids, promethium (Pm) is a radioactive element.

3.10.2 Atomic Size and Lanthanide Contraction :

Like the elements in any period of periodic table, in elements of lanthanide series going from cerium(Ce) to lutetium (Lu), the atomic radii and ionic radii go on decreasing, In the elements of this series, with the increase in atomic number the addition of new electron is in inner orbit 4f(n = 4) instead of last orbit (n = 6). Hence, with the increase in positive electric charge, the electrons in 4f-orbital possess more attraction towards it. Hence, there is contraction of atom. i.e. atomic radius decreases. This contraction occurring in lanthanide elements, is called **lanthanide contraction.** The effect of this lanthanide contraction is observed on the atomic radii of the elements after lanthanide series. The atomic radii of some of the elements of third transition series after lanthanide series are equal to the atomic radii of some elements of second transition series earlier to this, which can be understood from table 3.11.

Table 3.11 Atomic radii (pm) of elements of second and third transition series

Second Transition Series	Y 162	Zr 145	Nb 134	Mo 129	Tc -	Ru 124	Rh 125	Pd 128
Third Transition Series	Lanthanoids	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 126	Pt 129

3.10.3 Chemical Reactivity :

As lanthanoids possess (+3) oxidation state they form hydroxides of the type $Ln(OH)_3$. These hydroxides are less basic than $Ca(OH)_2$ but more basic than $Al(OH)_3$. The carbonates and nitrates of these elements decompose faster into their oxide by heating. The size of ion decreases on going from Ce^{3+} to Lu^{3+}, hence their basicity decreases, that is $Ce(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. These elements possess similarity in physical and chemical properties so their separation is carried out on the basis of the difference in their basicity. Ln_2O_3 type oxides of these elements are ionic and basic. The property of basicity decreases with ionic size. Some ions of these elements possess paramagnetic property because of unpaired electrons in f-orbital. Their certain ions are coloured and give coloured solution. The general chemical reactions of lanthanoids are shown below :

$$Ln \xrightarrow{H_2O} Ln(OH)_3 + H_2$$

$$Ln \xrightarrow{C / 2773\ K} LnC_2$$

$$Ln \xrightarrow[\Delta]{N} LnN$$

$$Ln \xrightarrow[\Delta]{S} Ln_2S_3$$

$$Ln \xrightarrow{\text{Combusting in } O_2} Ln_2O_3$$

$$Ln \xrightarrow{\text{Acid}} Ln^{3+} + H_2$$

$$Ln \xrightarrow{X_2} LnX_3$$

3.11 Actinide Series

We shall study electronic configuration and oxidation states to understand the actinide series.

3.11.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of actinide series, $7s^2$ is common in all the elements but electrons keep on changing in 5f orbital. Irregularity is found more in the electronic configuration of actinoids. Actinoids possess more than one oxidation states. The electronic configuration and the oxidation states of actinium and actinoids are shown in table 3.12.

Table 3.12 Electronic configuration and oxidation states of actinium and actinoids

Element	Atomic Number	Electronic configuration	Oxidation state
Ac	89	$[Rn]6d^17s^2$	(+3)
Th	90	$[Rn]6d^27s^2$	(+4)
Pa	91	$[Rn]5f^26d^17s^2$	+3, +4, (+5)
U	92	$[Rn]5f^36d^17s^2$	+3, +4, +5, (+6)
Np	93	$[Rn]5f^46d^17s^2$	+3, +4, (+5), +6, +7
Pu	94	$[Rn]5f^67s^2$	+3, (+4), +5, +6, +7
Am	95	$[Rn]5f^77s^2$	(+3), +4, +5, +6
Cm	96	$[Rn]5f^76d^17s^2$	(+3), +4
Bk	97	$[Rn]5f^97s^2$	(+3), +4
Cf	98	$[Rn]5f^{10}7s^2$	(+3)
Es	99	$[Rn]5f^{11}7s^2$	(+3)
Fm	100	$[Rn]5f^{12}7s^2$	(+3)
Md	101	$[Rn]5f^{13}7s^2$	(+3)
No	102	$[Rn]5f^{14}7s^2$	(+2), +3
Lr	103	$[Rn]5f^{14}6d^17s^2$	(+3)

Note : Stable oxidation state is shown in parenthesis

In the electronic configuration of elements Th to Np as shown in table 3.12, irregularity is found to be more in comparison to other elements which is at present accepted as an exception, while in Cm and Lr, the half filled 5f-orbital and completely filled 5f-orbitals respectively, to attain stability, the new added electron is filled in 6d-orbital.

Thus **general electronic configuration is $[Rn]5f^{0-14}6d^{0-2}7s^2$.** All the actinoids are radioactive.

3.12 Comparison of Actinoids with Lanthanoids

- Actinoids are like silver in appearance. More irregularity is observed in the metallic radii in actinoids than lanthanoids. Hence, diversity is found in the structures of actinoids.
- As the outermost orbit in actinoids is far from the nucleus in comparison to lanthanoids, their electron can be easily removed. Hence, the values of ionization enthalpy of actinoids are less than the values of ionisation enthalpies of lanthanoids.

- The stable oxidation state of all the lathanoids is (+3). In actinoids, oxidation states (+2) to (+6) are seen.
- In lanthanoids only promethium is radioactive but all the actinoids are radioactive.

3.13 Applications of f-Block Elements

- Pyrophoric Misch metal (50 % Ce +40 % La + 7 % Fe + 3 % other metals) is used as reducing agent and as stones in gas lighters.
- CeO_2 is useful in pigments.
- Ceric compounds are used as oxidizing agent in volumetric analysis.
- Oxides of lanthanoids are useful in preparation of optical glass of camera having high refractive index.
- Gadolinium sulphate is used to produce very low temperature by magnetic effect.
- Metals like, uranium, plutonium, and thorium are useful in production of atomic energy. Electrical energy can be obtained from nuclear energy.

SUMMARY

Position in periodic table	Block
Groups 1 to 2	s-Block
Groups 13 to 18	p-Block
Groups 3 to 12	d-Block
Two horizontal rows at the bottom of the periodic table	f-Block

- d-block elements are in periods 4 to 7.
- f-block elements are in periods 6 and 7.

Elements of d-block (Transition metal elements)

- The elements which in their ground state or any one of their oxidation states, d-orbital is incompletely filled are called transition elements.
- Amongst the d-block elements Zn, Cd and Hg do not act as transition elements.
- All the transition elements are metallic elements.
- In the first transition series, atomic radii decrease from Sc to V, while atomic radius remains same in elements Cr to Cu and the atomic radius of Zn is found increasing instead of decreasing.
- Not much difference is observed in first and second ionization enthalpies of two neighbouring transition elements but the value of second ionization enthalpy of Cr and Cu are more than those of their neighbouring elements.
- Most of the ionic and covalent compounds of transition elements are coloured.

- Compounds of transition elements act as catalysts in certain chemical reactions.
- The magnetic moment of transition element compounds,

  $\mu = \sqrt{n\,(n+2)}$ where μ = magnetic moment. n = number of unpaired element

  The unit of magnetic moment is BM (Bohr Magneton)
- The capacity to form complex compounds is much more than other elements because of definite characteristics of transition elements.
- In the formation of crystals of transition metals, the voids are there in which non-metal elements (H, C, N, B) arrange and form interstitial compounds.
- Scientists Hume and Rothery suggested the rules for the alloys and accordingly alloys having useful properties are obtained from transition metal elements.
- The compounds of transition element- $KMnO_4$ and $K_2Cr_2O_7$ are very useful in laboratory and in synthesis of organic compounds.

f-Block elements (Innertransition elements)

- f-Block elements are divided in to (1) Lanthanide series and (2) Actinide series.

Lanthanide series

- Lanthanide series : In period-6 Ce (Z = 58) to Lu (Z = 71)
- Elements of lanthanide series are called lanthanoids which are shown by symbol Ln.
- All the lanthanoids possess stable oxidation state (+3).
- The general electronic configuration of lanthanoids : $[Xe]4f^{1-14}5d^{0-1}6s^2$
- Amongst lanthanoids, promethium (Pm) is radioactive.

Actinide series

- Actinide series : In period-7 Th (Z = 90) to Lr (Z = 103).
- Elements of actinide series are called actinoids.
- The stable oxidation state in actioids is found to be from (+2) to (+6).
- The general electronic configuration of actinoids is : $[Rn]5f^{0-14}6d^{0-2}7s^2$
- All the actinoids are radioactive.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Elements of which groups are called d-block elements ?

(A) Groups 1 to 2 (B) Groups 3 to 12

(C) Groups 13 to 18 (D) Groups 13 to 17

(2) Which of the following elements is of d-block even then it is not transition element ?

(A) Cu (b) Ca (C) Fe (D) Hg

(3) The aqueous solution of which of the following ions is green coloured ?

(A) Co^{2+} (B) Zn^{2+} (C) Ni^{2+} (D) Cr^{2+}

(4) What will be the order of energy of d-orbitals during their division in tetrahedral complex compounds ?

(A) $d_{xy} \cong d_{yz} \cong d_{xz} < d_{x^2-y^2} \cong d_{z^2}$ (B) $d_{x^2-y^2} \cong d_{z^2} < d_{xy} \cong d_{yz} \cong d_{xz}$

(C) $d_{xy} \cong d_{z^2} < d_{yz} \cong d_{xz} \cong d_{x^2-y^2}$ (D) $d_{x^2-y^2} \cong d_{xz} < d_{xy} \cong d_{yz} \cong d_{z^2}$

(5) Which of the following ions in its aqueous solution possesses the value of magnetic moment as 3.87 ?

(A) Cu^{2+} (B) Cr^{3+} (C) Co^{3+} (D) Fe^{3+}

(6) Which of the following is the alloy of iron ?

(A) Stainless steel (B) Brass (C) Bronze (D) Nichrome

(7) Which of the following compounds of transition elements is used in dry cell ?

(A) V_2O_5 (B) $KMnO_4$ (C) $K_2Cr_2O_7$ (D) MnO_2

(8) Which of the following elements is radioactive ?

(A) Pr (B) Pm (c) Gd (D) Tm

(9) What is the general electronic configuration of actinide series ?

(A) $[Xe]\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$ (B) $[Xe]\ 4f^{0-14}\ 5d^{0-10}\ 6s^2$

(C) $[Rn]\ 5f^{0-14}\ 5d^{0-2}\ 6s^2$ (D) $[Rn]\ 5f^{0-14}\ 6d^{0-2}\ 7s^2$

(10) Which of the following statements is incorrect ?

(A) Atoms of all the transition elements are paramagnetic.

(B) All the transition elements are metal elements.

(C) All the elements of d-block are transition elements.

(D) The position of d-block is between s and p-block element in the periodic table.

2. Answer the following questions in brief :

(1) Innertransition elements are the members of which period ?

(2) Elements of which block are called innertransition elements ?

(3) Which of the elements of the first transition series (Sc to Zn) do not act as transition element ?

(4) Which are the elements of first transition series elements having d^5 and d^{10} electronic configurations ?

(5) Aqueous solutions of which ions of first transition elements are blue coloured ?

(6) Write unit of magnetic moment.

(7) Which non-metal elements form interstitial compounds with elements of first transition series ?

(8) Which centres are responsible for catalytic function of catalyst ?

(9) Which alloy is filled in tooth cavity ?

(10) Which alloy is used for preparation of electric resistant wire ?

(11) Cupronickel is the alloy of which metals ?

(12) Which compound of transition elements acts as strong oxidizing agent in acidic and basic media ?

(13) By which common symbol, the elements of lanthanide series are shown ?

(14) Write general electronic configuration of lanthanide series elements.

(15) Which compound of f-block elements is useful in pigment ?

(16) Give definitions :

(i) Transition elements (ii) d-d transition (iii) Interstitial compounds (iv) Alloy (v) Lanthanide series (vi) Actinide series

3. Write answers of following questions :

(1) Write electronic configuration of Cr and Cu.

(2) Write formula to determine magnetic moment and give identification of symbols in it.

(3) Write two properties and two uses of $KMnO_4$.

(4) Write two properties and two uses of $K_2Cr_2O_7$.

(5) Write four applications of f-block elements.

(6) Write three laws presented by scientists Hume and Rothery for preparation of alloys.

(7) Explain giving reason :

(i) The values of second ionization enthalpy of Cr and Cu are found to be more than their neighbouring elements.

(ii) The atomic radius of Zn in first transition series increases instead of decreasing.

(iii) The atomic radii of elements Cr to Cu in first transition series are almost same.

(iv) In electronic configuration of Pd, Ag and Cd, d^{10} electrons are present even then Pd and Ag are considered transition elements, while Cd is not considered transition element.

(8) Calculate magnetic moments : Sc^{3+}, Ti^{4+}, V^{4+}, Cr^{3+}, Cr^{6+}, Mn^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

4. Answer the following questions in detail :

(1) Mention the general properties of transition elements.

(2) Discuss catalytic and magnetic properties of transition elements.

(3) Describe the characteristic capacity of transition metal ions to form complex compounds.

(4) Mention the preparation of potassium dichromate and potassium permanganate.

(5) Describe applications of d-block elements.

(6) Compare actinide elements with lanthanide elements.

(7) Write short notes :

(i) Interstitial compounds

(ii) Alloys

(iii) Chemical reactivity of lanthanide elements

(iv) Lanthanide contraction

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Unit

4

Complex Salts or Co-ordination Compounds

4.1 Introduction

The salt that is obtained according to the laws of chemical combination by combination of two or more salts (compounds) having independent existence and maintains the properties of the original salts is called double salt, e.g., if saturated aqueous solution of K_2SO_4 and $Al_2(SO_4)_3$ are mixed and crystallized, then crystals of alum- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ are obtained, which is called double salt. On qualitative analysis of solution of this alum, yellow precipitate with picric acid are obtained. This indicates presence of K^+, with NaOH gum-like gelatinous precipitates are obtained which indicates presence of Al^{3+} and with $BaCl_2$ gives white precipitates which indicates presence of SO_4^{2-} and thus K_2SO_4 and $Al_2(SO_4)_3$ maintain their properties. Hence it is a double salt In addition, $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ ferrous ammonium sulphate and carnalite are also double salts whose equations are shown below :

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Potassium alum}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$$

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow \underset{\text{Ferrous ammonium sulphate}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

$$KCl + MgCl_2 + 6H_2O \rightarrow \underset{\text{Carnalite}}{KCl \cdot MgCl_2 \cdot 6H_2O}$$

Similarly, by combination of two or more compounds of independent existence, according to the laws of chemical combination, compounds obtained with new properties are called complex salts or co-ordination compounds, viz. when KCN is added to ferrous cyanide $Fe(CN)_2$, and ferric cyanide $Fe(CN)_3$ are formed and then both of them become soluble. The crystals having formula

$Fe(CN)_2 \cdot 4KCN$ and $Fe(CN)_3 \cdot 3KCN$ are obtanined. They are known as potassium ferrocyanide $K_4[Fe(CN)_6]$ and potassium ferricyanide $K_3[Fe(CN)_6]$ respectively. In these two, the qualitative analysis of Fe^{2+}, Fe^{3+} or CN^- ions cannot be carried out but new ions $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ are obtained. In electrolysis; they move towards anode. Equations for preparing some complex salts are given below :

$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

$$Fe(CN)_3 + 3KCN \rightarrow K_3[Fe(CN)_6]$$

$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$$

$$CoCl_3 + 6NH_3 \rightarrow [Co(NH_3)_6]Cl_3$$

$$PtCl_4 + 2KCl \rightarrow K_2[PtCl_6]$$

From the equation of $CuSO_4$ and NH_3 as shown above, it appears that the valency of Cu^{2+} and SO_4^{2-} ions is satisfied even then $CuSO_4$ combines with four molecules of ammonia and gives complex salt.

The elements in the d-block of modern periodic table, are called transition elements. Among these transition elements, Scandium to Zinc (Z = 21 to 30), Yttrium to Cadmium (Z = 39 to 48) and Lanthanum to Mercury (Z = 57 to 80). That is the elements of fourth, fifth and sixth periods are very important in modern inorganic chemistry. Some of the properties of these elements are same. There is change in their valency and the aqueous solution of their salts are coloured. In the electronic configuration of these transition elements, electrons are arranged successively in d-orbitals. **When (n–1)d, ns and np or ns, np and nd orbitals of the atoms or ions of transition elements are vacant, these transition elements accept electron pairs from negative ions or neutral molecules, which are called complex (co-ordination) compounds.** The bond that is formed between metal ions of metallic elements in this type of compound and the negative ions or neutral molecules is called co-ordinate covalent bond. In these compounds, around the metal ion in the centre of the molecules are arranged negative ions or neutral molecules by co-ordinate covalent bond. Mostly the transition elements have more tendency to form complex compounds.

4.2 Werner's Theory

The question that why the other compounds combine with stable compounds after satisfaction of valency; had become the subject of discussion in the beginning of the nineteenth century. In 1905, Swiss scientist Alfred Werner prepared many new compounds by mixtures of cobalt chloride and ammonia, studied them thoroughly and gave a new theory, which is known as Werner's co-ordination theory. By the Werner's theory many clarifications were made in this field. **Werner obtained different compounds of $CoCl_3$ and NH_3 viz. $[Co(NH_3)_6]Cl_3$ (yellow), $[Co(NH_3)_5Cl]Cl_2$ (purple, $[Co(NH_3)_4Cl_2]Cl$ (violet / green) and $[Co(NH_3)_3Cl_3]$, (bluish green).** Werner received nobel prize for this work in 1913.

The theory given by Werner for the formulas and structures of complex salt is "Certain metals have secondary valency in addition to primary valency. With this it combines strongly with the metal ions, neutral molecules or negative ions in its first attraction sphere [ ]."

According to Werner, metal ion possesses two types of valency. Primary valency or ionizing valency and Secondary valency or non-ionisable valency.

(i) The primary valency is similar to positive electric charge of positive ion of metal or oxidation number of metal. It forms ionic bond. The other ion combined by this valency becomes free by ionization of compound.

(ii) Secondary valency is non-ionized. The negative ions or neutral molecules contained with secondary valency are not ionized.

(iii) Primary valency is satisfied by only negative ions, while secondary valency is satisfied by negative ions or neutral molecules (ligand).

(iv) The secondary valency of metal ion or metal elements form co-ordinate covalent bond, so the secondary valency is called co-ordination number of metal.

(v) The co-ordination number of metal ion is definite which is independent of primary valency.

(vi) Secondary valency being directional, different types of geometrical structures are obtained.

Note : (1) In some complex compounds, the positively charged ligand like ^{+}NO, $^{+}NO_2$ are also seen.

(2) Now it is proved that the some metal ions of transition elements possess more than one co-ordination number.

(3) To understand these geometrical structures, it is important to know the magnetic properties of complex compounds.

The bond between metal ion combined through secondary valency, and ligand is called co-ordinate covalent bond. This is indicated by → which indicates the co-ordination site. The electron pair present between metal ion and ligand are given by negative ion or neutral molecule.

The complex ion in complex compounds is shown by [ ] bracket (first attraction sphere) whereas outside the bracket, on the left side, the positive ion combined by ionic bond is shown viz. In $K_3[Fe(CN)_6]$ complex compound $[Fe(CN)_6]^{3-}$ complex negative ion is combined by ionic bond with positive ion K^+. Similarly in $[Cr(NH_3)_6]Cl_3$ complex compound $[Cr(NH_3)_6]^{3+}$ complex positive ion is combined with negative ion Cl^- by ionic bond.

4.3 Clasification of Ligands

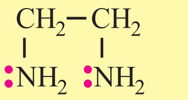
Generally the ligand has a negative electric change or is a neutral molecule. The classification of ligands is made on the basis of the number of electron pair donating atoms.

(I) Unidentate ligand : If only one atom of ligand of negative ion or neutral molecule donates one atom to metal ion by giving one electron pair and form one co-ordinate covalent bond, then it is called unidentate ligand. Neutral molecules like H_2O, NH_3, CO and negative ions like Cl^-, CN^-, F^- which combine with metal ion by giving one electron pair; viz. In $[Cr(NH_3)_6]Cl_3$ complex compound, nitrogen atom of each ammonia combine by giving one electron pair to chromium metal ion, it is called unidentate ligand. In $[Cr(H_2O)_6]Cl_3$ complex compounds each molecule of water co-ordinates with chromium metal ion by giving one electron pair, so it is unidentate ligand. In these unidentate ligands, nitrogen atom in ammonia molecule and oxygen atom in water molecule donate one electron pair to metal ion. Hence, the **atom present in negative ion or neutral molecule gives electron pair to metal-ion which is called the co-ordinate site of ligand** and it is shown as $M \leftarrow L$, where M is metal ion and L is ligand.

(II) Didentate ligand : The ligand which can donate two electron pairs and forms two co-ordinate covalent bonds, is called didentate ligand. In this type of ligand two atoms combine with metal ion by giving two electron pairs and form two co-ordinate covalent bonds. Thus, only one ligand satisfies two secondary valencies of metal ion viz. In ethane 1-2 diamine (ethylene diamine–en), its one molecule forms two co-ordinate covalent bonds by giving two electron pairs on two nitrogen atoms, to metal ion.

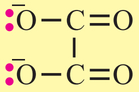
In oxalate $(OX)^{2-}$ negative ion, two electron pairs on two oxygen atoms are given to metal-ion and two co-ordinate covalent bonds are formed.

e.g.,



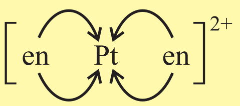
Ethane 1,2-diamine

$C_2O_4^{2-}$ OR $(OX)^{2-}$ OR



Oxalate

$[Pt(en)_2]^{2+}$



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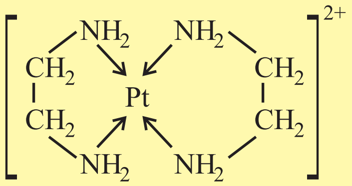
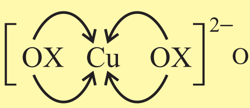


$[Cu(OX)_2]^{2-}$



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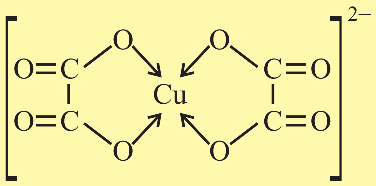
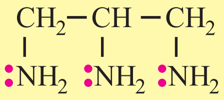


(III) Tridentate ligand : The ligand in which there are three co-ordination sites is called tridentate ligand. In this type of ligand, three atoms form three co-ordinate covalent bonds by giving three electron pairs. Thus only one ligand satisfies three secondary valencies of metal ion viz. Propane 1-2-3 triamine (Propylene triamine-ptn) one neutral molecule form three co-ordinate covalent bonds by giving three electron pairs on its three nitrogen atoms. Similary, PO_4^{3-} is a negative ion tridentale ligand.

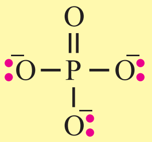
e.g.



Propane 1, 2, 3-triamine

(propylene triamine (ptn))

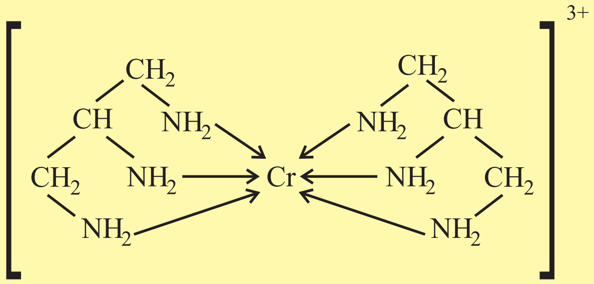
PO_4^{3-} OR

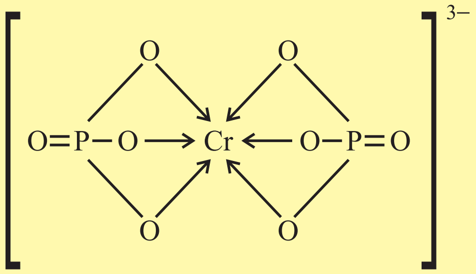


Phosphate

$[Cr\ (ptn)_2]^{3+}$

$[Cr\ (PO_4)_2]^{3-}$

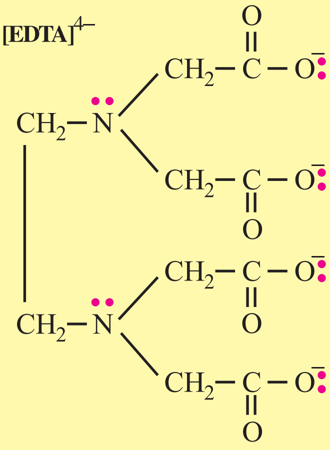




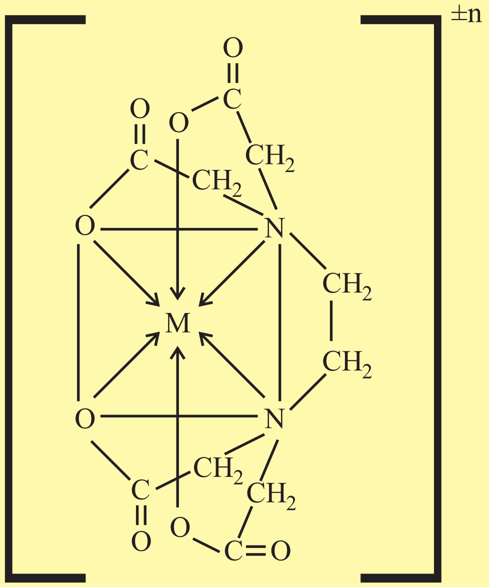
(IV) Hexadentate ligand : The ligand in which there are six co-ordination sites is called hexadentate ligand. Six atoms of this type of ligand give six electron pairs to metal ion and form six co-ordinate covalent bonds. Thus, only one ligand satisfies six secondary valencies of metal ion viz. In ethylene diamine tetraacetate $(EDTA)^{4-}$, four oxygen atoms and two nitrogen atoms give four electron pairs and two electron pairs respectively to metal ion and form six co-ordinate covalent bonds.

e.g. $[M\ EDTA]^{\pm n}$

$[EDTA]^{4-}$



$[M\text{-}EDTA]^{\pm n}$

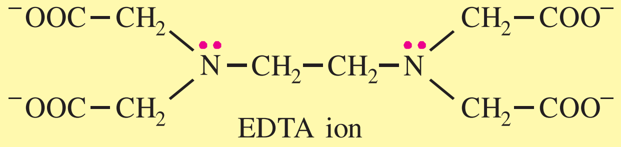


Generally, the ligand in which two or more co-ordination sites are there or the ligand in which two or more atoms donate electron pairs to metal ion and form co-ordinate covalent bond, is called multidentate ligand.

Some ligands and their types are shown in table 4.1

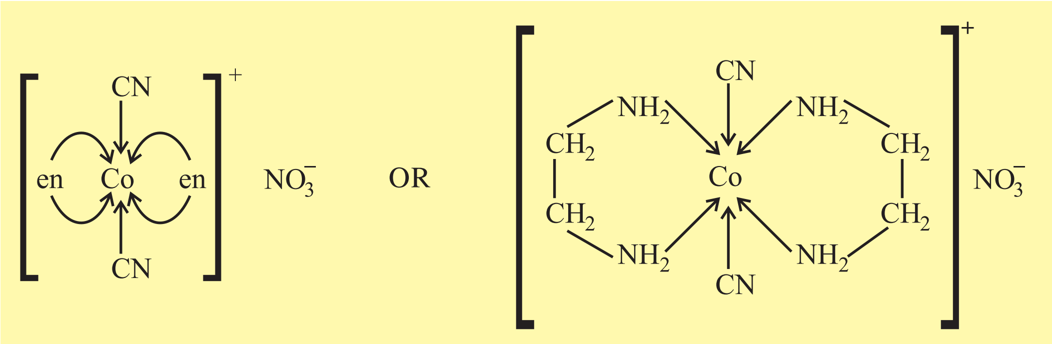
Table 4.1 Some ligands and their types

Type	Ligand	Electric charge
Unidentate Neutral ligand	$H_2\ddot{O}:$, $:NH_3$, $:CO$, $:NO$, $CH_3\ddot{N}H_2$, $C_5H_5\ddot{N}$ (py)	0
Unidentate Negative ion ligand	^-OH, F^-, Cl^-, Br^-, I^-, ^-CN, $^-NH_2$, NO_3^-, NO_2^-, $CH_3COO^-(AcO^-)$, O^{2-}, S^{2-}, N^{3-}	– 1
Unidentate Positive ion ligand	^+NO, $^+NO_2$,	+ 1
Didentate Neutral ligand	$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (en), $\underset{:NH_2}{\underset{\vert}{CH_2}}-CH_2-\underset{:NH_2}{\underset{\vert}{CH_2}}$ (pn)	0
Didentate Negative ion ligand	CO_3^{2-}, SO_4^{2-}, $\begin{array}{l}COO^-\\ \vert\\ COO^-\end{array}$ $(OX)^{2-}$	– 2
Tridentate Neutral ligand	$\underset{:NH_2}{\underset{\vert}{CH_2}}-\underset{:NH_2}{\underset{\vert}{CH}}-\underset{:NH_2}{\underset{\vert}{CH_2}}$ (ptn)	0

Tridantate Negative ion ligand	PO_4^{3-}, AsO_4^{3-}	– 3
Hexadentate Negative ion ligand	 EDTA ion	– 4

When multidentate ligands like en, OX^{2-}, pn, ptn, $(EDTA)^{4-}$ form co-ordinate covalent bond with metal ion, it results into cyclic structure involving central metal ion. **Thus, the complex compound formed by ligand and metal ion having cyclic structure is called chelate.** The stability of such chelate compounds is more than the stability of simple complex compounds (formed by monodentate ligand).

e.g. $[Co(CN)_2(en)_2]^+ NO_3^-$



4.4 Requirements for Formation of Complex Compounds

Some basic requirements are necessary for formation of complex compound. The capacity of transition element metal ions of formation of complex compounds is more than that of other elements.

Basic requirements :

(i) The ligand must have electron pair which can be easily donated.

(ii) There must be vacant orbitals in the metal ion to receive electron pairs.

(iii) The metal ions should have the symmetry of vacant orbitals same as the symmetry of orbitals of ligand having electron pairs. Hence, co-ordinate covalent bond can be formed by overlapping of orbitals having electron pair in ligand.

These basic requirements are satisfied by metal ions and so complex salts are easily formed. Even then, it is not necessary that each transition element forms complex compounds with equal ease. There is change in capacity of formation of complex compounds according to different oxidation states of metal ions. In addition, there is difference in the stability of the compounds that are formed.

4.5 Stability of Complex Compounds and Strength of Ligand

As the strength of different ligands to form co-ordinate covalent bond varies, stronger ligand possesses more attraction with metal ion. As a result, complexes having stronger ligands possess more stability and the complexes having weak ligand possess less stability. Hence, it can be said that the strength of the complexes is determined on the basis of strength of ligand. The basis of strength of ligand can be determined by same metal ion combined with different ligands. The order of strength of some complex compounds is as follows : **$Cl^- < F^- < OH^- < H_2O < NH_3 < CN^-$**

$[NiCl_4]^{2-} < [NiF_4]^{2-} < [Ni(OH)_4]^{2-} < [Ni(H_2O)_4]^{2-} < [Ni(NH_3)_4]^{2-} < [Ni(CN)_4]^{2-}$

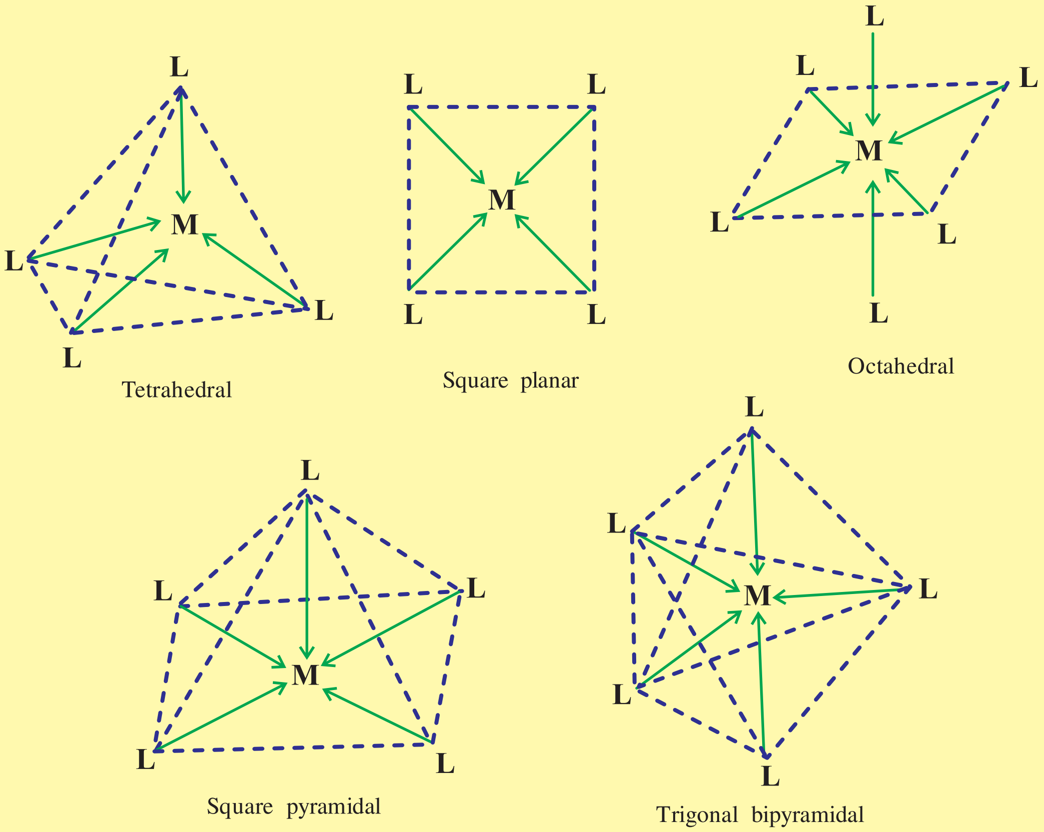
$[CuCl_4]^{2-} < [CuF_4]^{2-} < [Cu(OH)_4]^{2-} < [Cu(H_2O]^{2+} < [Cu(NH_3)_4]^{2+} < [Cu(CN)_4]^{2-}$

Hence, change in the capacity is seen in the formation of complex ions of metal ions of transition elements according to different conditions.

It is not necessary that any metal ion form only one type of complex salt with ligand. Sometimes different types of ligands form complex compounds with metal ion. This type of complex compounds are called mixed ligand complex compounds. viz. In the complex $[Cr(NH_3)_4(CN)_2]NO_3$, four ammonia molecules and two cyanide ions, total six unidentate ligands are combined. If ligand is of only one type, the complex salts are called simple complex compounds.

As in mixed ligand complex compounds two or more types of ligands combine and form complex compound, similary if only one metal ion is present in any complex compound, then it is called unicentred complex compound, e.g. $K[MnO_4]$. **If more than one metal ions are present in the complex compound then it is called polycentred complex compound.** e.g. $K_2[Cr_2O_7]$.

In unicentred or polycentred complex compounds, the three dimensional arrangement of ligand combined to metal ion are directional, so different geometrical structures formed accordingly are called co-ordination polyhedral. Mostly, the shape of this geometrical structure is tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal.



Tetrahedral Square planar Octahedral

Square pyramidal Trigonal bipyramidal

Fig. 4.1

4.6 Geometry of Complex Ions

The co-ordination number of metal ion and the geometrical structures of ions can be known from the studies of magnetic properties and crystal field theory. It is not necessary that metal ion should possess same co-ordination number and one definite type of geometrical structure containing complex ions. Sometimes, it may happen that the metal ion possesses more than one co-ordination number and even if the co-ordination number remains the same, it can form complex ions having different types of geometrical structures. In most of the metal complex ions, the co-ordination number 4 and 6 are very common and the complex ions showing these co-ordination numbers are found comparatively in larger number.

Co-ordination number 4 : The metal ions possessing co-ordination number 4 form complexes having two types of geometrical structures :

(i) Tetrahedral structure containing complex ions and (ii) square planar structure containing complex ions.

(i) Tetrahedral complex ions : Metal ions form tetrahedral complex ions and they are stable in special conditions. Most of the tetrahedral complex ions are obtained in negative ion form viz. MnO_4^- . While, tetrahedral complex like $[Ni(CO)_4]$ is obtained in form of neutral molecule.

(ii) Square planar complex ions : Metal ions of only some of the transition elements form square planar complexes. Square planar complexes are formed by combination of Ni^{2+} metal ion with negative ion and / or neutral molecule ligand viz. $K_2[Ni(CN)_4]$ and $[Ni(NH_3)_2Cl_2]$.

In table 4.2 some examples of tetrahedral and square planar complexes possessing co-ordination number 4 of some transition elements in the fourth period are shown.

Table 4.2 Some complexes of transition elements possessing co-ordination number-4

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound	Geometrical structure
Mn	+7	$3d^0$	$K[MnO_4]$	Tetrahedral
Co	+2	$3d^7$	$K_2[CoCl_4]$	Tetrahedral
Ni	0	$3d^{10}$	$K_4[Ni(CN)_4]$	Tetrahedral
	+2	$3d^8$	$K_2[NiCl_4]$	Tetrahedral
	+2	$3d^8$	$K_2[Ni(CN)_4]$	Square planar
	+2	$3d^8$	$[Ni(NH_3)_2Cl_2]$	Square planar

Co-ordination number 6 : The complex compounds of metal ions possessing co-ordination number 6 are easily available. The geometrical structures of these complexes are octahedral due to which different ligands deformations are also found viz. $[CrCl_2(en)_2]NO_3$ and $[Co(NH_3)_4CO_3]Cl$.

In table 4.3, some examples of octahedral complexes possessing co-ordination number 6 of elements of some transition elements of fourth period are given.

Table 4.3 Some complexes possessing co-ordination number 6 of transition elements

Transition Element	Oxidation state	Electrons of 3d-orbital	Complex compound (Octahedral structure)
Cr	0	$3d^6$	$[Cr(CO)_6]$
	+1	$3d^5$	$K_4[Cr(CN)_5(NO)]$
	+3	$3d^3$	$K[Cr(NH_3)_2(CO_3)_2]$
	+4	$3d^2$	$K_2[CrF_6]$
Mn	+2	$3d^5$	$[Mn(H_2O)_6]Cl_2$
	+3	$3d^4$	$[Mn(en)_3]Cl_3$
Fe	+2	$3d^6$	$K_4[Fe(CN)_6]$
	+3	$3d^5$	$Na_3[Fe(OX)_3]$
Co	+2	$3d^7$	$Na_4[Co(NO_2)_6]$
	+3	$3d^6$	$[Co(NH_3)_6]Cl_3$
	+4	$3d^5$	$K_2[CoF_6]$
Ni	+2	$3d^8$	$[Ni(H_2O)_6]Cl_2$
	+3	$3d^7$	$K_3[Ni(CN)_6]$
	+4	$3d^6$	$K_2[NiF_6]$

4.7 Hybridization of Orbitals of Metal Ions of Complex Compounds and Magnetic Properties

Most of the metal ions have geometrical structures- tetrahedral, square planar or octahedral. To understand this geometrical structures, hybridization of metal-ion orbitals and magnetic property are very useful.

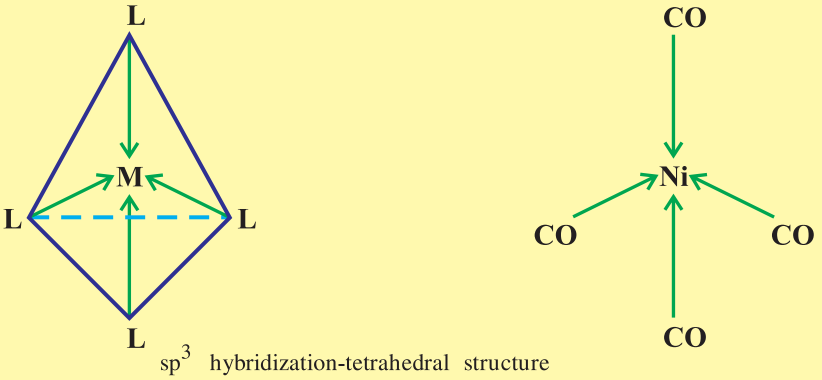
sp^3 hybridization : When one 4s-orbital and three $4p_x$, $4p_y$, $4p_z$ orbitals overlap with one another and get hybridised, then new four hybrid orbitals are produced. These four orbitals are called sp^3 hybrid orhitals. The energy value of these four hybrid orbitals are same and are extended towards the four corners from the centre of the tetrahedral. Also, the angle between any two sp^3 hybrid orbitals is $109^0 28'$. Hence, if the metal ion orbitals in complex ion hybridization of sp^3 type, then the geometrical structure of complex compounds is tetrahedral.

dsp^2 hybridization : When one 3d-orbital, one 4s-orbital and two $4p_x$, $4p_y$ orbitals of metal ion overlap with one another and get hybridized, new four hybrid orbitals are produced. These four hybrid orbitals are called dsp^2 hybrid orbitals. The value of energy of these four hybrid orbitals is same and are extended towards four corners from the centre of the plane square. Also, the angle between any two nearby dsp^2 orbital is 90^0. Hence, if the hybridization of metal ion orbitals in compound, is of dsp^2 type then, the geometrical structure of metal in the compound becomes of dsp^2 type; then the geometrical structure of complex compounds is square planar.

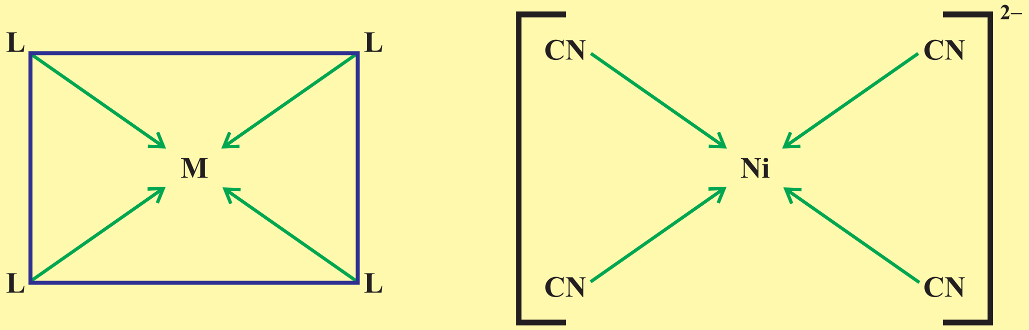
d^2sp^3 hybridization : When two 3d-orbitals, one 4s-orbital and three $4p_x$, $4p_y$, $4p_z$ orbitals overlap with one another and get hybridized, then new six hybrid orbitals are produced. These hybrid orbitals are called d^2sp^3 hybrid orbitals. The value of energy of these six hybrid orbitals is same and it is extended to six corners of octahedral from the centre of that octagon. Also, all these hybrid orbitals are on X-axis, Y-axis and Z-axis to one another. So the angle between any two nearby d^2sp^3 orbitals is 90^0. Hence, the complex compounds in which the hybridization of metal ion in complex compound is of d^2sp^3 type, the geometrical structure of this complex compound is octahedral.

sp^3d^2 hybridization : Sometimes, sp^3d^2 hybridisation can occur to produce octahedral structure when 3d-orbitals of metal ion are not available, then one 4s-orbital, three $4p_x$, $4p_y$, and $4p_z$ orbitals and two 4d-orbitals overlap with one another and sp^3d^2 hybridization occurs. Here also, in sp^3d^2 hybridization the geometrical structure is octahedral.

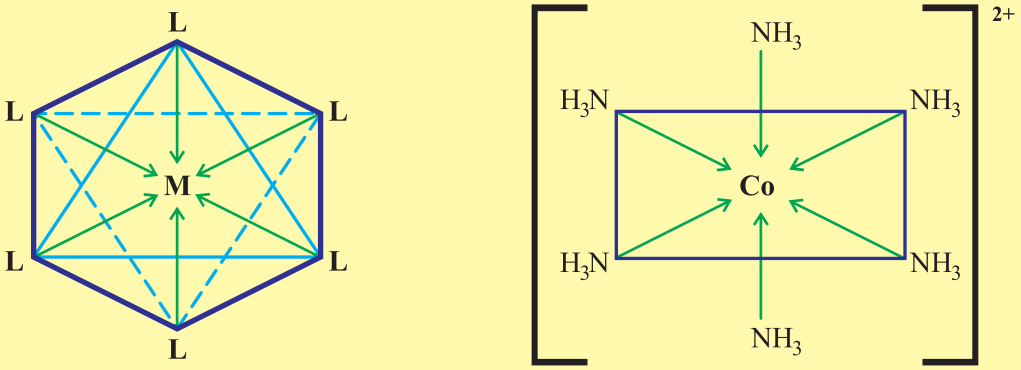
Hence, it can be said that in octahedral structure d^2sp^3 or sp^3d^2 hybridization occurs. To determine which type of hybridization is possessed by study of magnetic properties becomes very essential. In fig. 4.2 the geometrical structures of complex molecules or ions on the basis of sp^3, dsp^2, d^2sp^3 or sp^3d^2 hybridization are shown.



sp^3 hybridization-tetrahedral structure



dsp^2 hybridization-square planar structure



d^2sp^3 Or sp^3d^2 hybridization-octahedral structure

Fig. 4.2 Geometrical structures of complex ions

Magnetic properties : If the electrons of 3d-orbital of the metal ion are paired in transition element in any complex then the complex is called diamagnetic. If there are unpaired electrons then the complex is called paramagnetic. The theoretical value of magnetic moment can be found out by the equation $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons. The unit of this value is BM (Bohr magneton).

The magnetic moment of complex compounds of metal ions of transition elements is dependent on geometrical structure, type of ligand etc. In the detailed study of complex compounds, the calculation of magnetic moment is very helpful. In table 4.1, the theoretical and experimental values of magnetic moment of Sc^{2+} to Zn^{2+} (d^1 to d^{10}) ions are given.

Table 4.4 Unpaired electrons and magnetic moment of M^{2+} ions of transition elements

Ion	$3d^n$	Unpaired Electrons	Magnetic moment (μ) BM	
			Theoretical value	Experimental value
Sc^{2+}	d^1	1	1.73	1.73 – 1.74
Ti^{2+}	d^2	2	2.83	2.76
V^{2+}	d^3	3	3.87	3.86
Cr^{2+}	d^4	4	4.90	4.80
Mn^{2+}	d^5	5	5.92	5.96
Fe^{2+}	d^6	4	4.90	5.00 – 5.50
Co^{2+}	d^7	3	3.87	4.40 – 5.20
Ni^{2+}	d^8	2	2.83	2.90 – 3.40
Cu^{2+}	d^9	1	1.73	1.80 – 2.20
Zn^{2+}	d^{10}	0	0	0

4.8 IUPAC Nomenclature of Complex Compounds

There are different types of ligand for variety of complex compounds with various metal elements. Also many complex compounds possessing mixed ligands are prepared. In the earlier times, the names of the complex compounds were given on the basis of metal ion and their colours. Werner had named the complexes obtained from cobalt chloride and ammonia on the basis of their colours viz. greenio cobaltic ammonium chloride, violetio cobaltic ammonium chloride, purpleo cobaltic ammonium chloride etc. As many complexes were being formed, the accurate names of complex compounds could not be given. Hence to have accuracy in the names of the complex compounds, IUPAC method was used. The IUPAC nomenclature of monocentric complex compounds is done according to the definite rules as shown below :

(i) In showing name of ionic complex compound, the positive ion is written first and then the name of negative ion, is mentioned.

(ii) In complex compound co-ordination sphere [ ] in naming is done according to the rules.

  (a) In nomenclature in co-ordination sphere the name of ligand according to English alphabates is first shown and then the name of the metal is written.

(b) For the ligands having negative electric charge, the suffix 'O' is joined with the name of the ligand viz OH^- hydroxo, CN^- cyano, NH_2^- amido, NO_2^- nitro, ONO^- nitrito, NO_3^- nitratato, SCN^- thiocyanato, CNO^- cyanato, CO_3^{2-} carbonato, O^{2-} oxo, OX^{2-} oxalato, PO_4^{3-} phosphato, AsO_4^{3-} arsenato etc. As per IUPAC rules, 2004, Cl^- is written as chlorido instead of chloro and Br^- as bromido instead of bromo.

(c) The neutral ligand is shown according to its original name viz. $CH_3 \cdot NH_2$ methyl amine, $H_2N–CH_2–CH_2–NH_2$ ethane 1-2 diamine, $NH_2–CH_2–CH(NH_2)–CH_2–NH_2$ propane-1,2,3-triamine $H_2N–CH_2–CH_2–CH_2–NH_2$ propane 1,2-diamine but as exception H_2O aqua, NH_3 ammine, CO carbonyl, NO nitrosyl etc. are written.

(d) If the number of ligand of only one type is more than 1, then according to the number of ligands 2, 3, 4, 5, 6, the words di, tri, tetra, penta, hexa etc are used as prefix respectively. If organic ligand is there, and the prefix is a number, then ligand is placed in bracket and for numbers 2, 3, 4 etc. corresponding bis, tris, tetrakis prefix are added.

(e) If there is monocentred complex ion, in which only one metal ion, then there is definite order of showing its name.

(i) If the complex is negative ion, then write names of ligand successively. The suffix 'ate' is joined with metal ion and then its oxidation state is shown in ( ) bracket in Roman numbers viz. ferrate (II), ferrate (III), chromate (III), manganate (VII), cobaltate (III), nickelate (II), molybdate (VI).

(ii) If the complex is positive ion or neutral molecule, then first writing the name of ligand successively, the name of metal is added at the end and its oxidation state is shown in ( ) bracket, in Roman numbers. The whole part of complex positive ion, negative ion and neutral molecule is placed in the square bracket [ ].

The formulae and IUPAC names of some complex compounds on the basis of these rules are given below :

Formula	IUPAC
$K[MnO_4]$	Potassium tetraoxomanganate(VII)
$Na_2[CoCl_4]$	Sodium tetrachloridocobaltate(II)
$[Ni(CO)_4]$	Tetracarbonylnickel(0)
$K_2[NiCl_4]$	Potassium tetrachloridenickelate(II)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II)ion
$[Cu(NH_3)_4]Cl_2$	Tetraamminecopper(II)chloride
$[Cr(CO)_6]$	Hexacarbonylchromium(0)

$[Ni(H_2O)_2(NH_3)_4]SO_4$	Tetraamminediaquanickel(II)sulphate
$[Cr(OX)_3]^{3-}$	Trioxalatochromate(III)ion.
$[Co(en)_2(CN)_2]Cl$	Dicyanobis(ethane-1,2-diamine)cobalt(III)chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$(NH_4)_2[MoO_4]$	Ammonium tetraoxomolybdate(VI)
$K_2[CrF_6]$	Potassium hexafluoridoochromate(IV)
$Na_2[Fe(NO)(CN)_5]$ (Sodium intropusside)	Sodium pentacyanonitrosoniumferrate(II)
$Na_4[Co(NO_2)_6]$	Sodium hexanitrocobaltate(II)
$NH_4[Co(NH_3)_2(OX)_2]$	Ammonium diamminedioxalatocobaltate(III)
$[Pt(Pn)_2CO_3]SO_4$	Carbonatobis(propane-1,3-diammine)platinum(II)sulphate
$[Ag(NH_3)_2][Ag(CN)_2]$	Diammineargentinun(I) dicyanoargentate(I)
$[Cr(en)_3][Cr(OX)_3]$	Tris(ethane-1,2-diamine)chromium(III)trioxalatochromate(III)
$[Pt(NH_3)_2ClNO_2]$	Diamminechloridonitroplatinum(II)
$[Co(NH_3)_4CO_3]Cl$	Tetramminecarbonatocobalt(III)chloride.
$[Cr(NH_3)_4(ONO)Cl]NO_3$	Tetraamminechloridonitritochromium(III)nitrate
$Na_2[Ni(EDTA)]$	Sodium ethylenediamminetetraacetatonickelate(II)
$[Pt(Py)_4][PtBr_4]$	Tetrapyridineplatinum(II)tetrabromidoplatinate(II)
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodi(methanamine)copper(II)
$[Cr(NH_3)_6][Cr(SCN)_6]$	Hexaamminechromium(III)hexathiocyanatochromate(III)

Formula from the IUPAC name of the complex

(a) Tetrammineaquachloridocobalt(III)chloride

$[Co(NH_3)_4(H_2O)Cl]Cl_2$

(b) Potassium tetrahydroxozincate(II)

$K_2[Zn(OH)_4]$

(c) Sodium trioxalatoaluminate(III)

$Na_3[Al(C_2O_4)_3]$

(d) Dichloridobis(ethane-1-2-diamine)cobalt(III)ion.

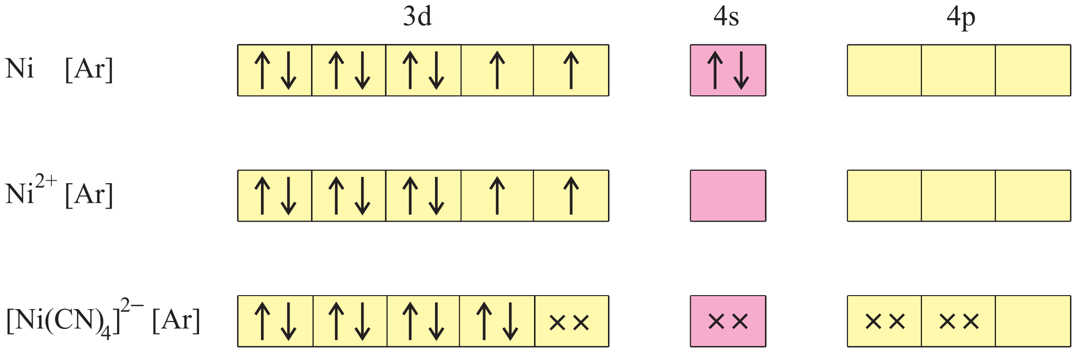
$[Co(en)_2Cl_2]^+$

(e) Pentacarbonyliron(0)

$[Fe(CO)_5]$

4.9 Geometrical Structures and The Magnetic Properties of Complex Compounds

$[Ni(CN)_4]^{2-}$ complex ion : In tetracyano nickelate (II) four CN^- strong ligands are combined with Ni^{2+} metal ion. In this compound, four ligands are joined and so possesses square planar or tetrahedral structure. Here the electronic configuration of Ni metal and Ni^{2+} ion are $[Ar]3d^84s^2$ and $[Ar]3d^8$ respectively. The arrangement of eight electrons in 3d-orbitals is shown in the following figure. The orbitals are shown by square blocks and the electrons by vertical arrow sign ↑ or ↓.



Unpaired electrons n = 0

dsp^2 hybridization.

Hence $\mu = 0$ BM

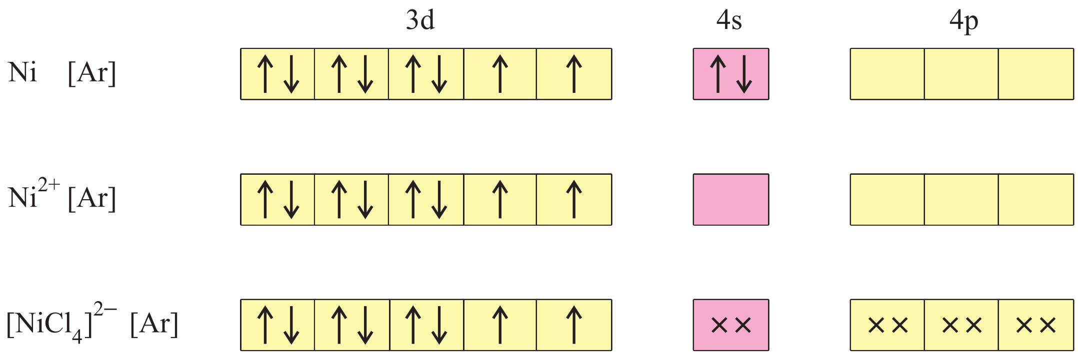
In one square block, the vertical arrows in opposite directions show electron pairs in which the rotation of both the electrons is in opposite directions. Here Ni^{2+} metal ion combines with four CN^- strong ligand and forms complex ion. Each CN^- strong ligand gives one electron pair to Ni^{2+} metal ion Hence Ni^{2+} metal ion receives four electron pairs from four ligands.

If the structure of $[Ni(CN)_4]^{2-}$ is square planar, then dsp^2 type hybridization occurs in Ni^{2+} metal ion. For this, one 3d-orbital, one 4s-orbital and two 4p-orbitals take part in hybridization of dsp^2, orbitals having equal energy are produced. For this, the arrangement of eight electrons in 3d-orbitals of Ni^{2+} metal ion, the charge is necessary because of the strong ligand like CN^-. In this two unpaired electrons in 3d-orbital, one unpaired electron of 3d-orbital enters into the other 3d-orbital having unpaired electron and forms a pair. As a result one 3d-orbital becomes vacant.

[Note : Because of strong ligands like CN^-, NH_3 and CO, the unpaired electrons get paired in rearrangement of electrons.]

This vacant one 3d-orbital, one 4s-orbital and two 4p-orbitals overlap and form dsp^2 four hybrid orbitals and arrange at 90^0 angle in square planar form. In the four dsp^2 orbitals produced, this four electrons pairs coming from four strong ligand CN^-, get arranged, which are shown by $\boxed{\times\times}$ sign. **Here $[Ni(CN)_4]^{2-}$ complex possesses dsp^2 hybridization and its all 3d-orbitals have paired electrons and so it becomes diamagnetic and its geometric structure is square planar.**

$[NiCl_4]^{2-}$ complex ion : In tetrachlorido nickelate (II) complex ion, Ni^{2+} metal ion is combined with four weak Cl^- ligands. As CN^- strong ligand comes nearer to the metal ion because it possesses more attraction, while weak Cl^- ligand does not come near to metal ion because it possesses less attraction. Hence, the 3d-orbital of Ni^{2+} ion is not capable of forming co-ordinate covalent bond with four Cl^- weak ligand. Hence, the rearrangement of electrons in 3d-orbitals if Ni^{2+} metal ion is not required. Here, one 4s, and three 4p-orbitals take part in hybridization and form sp^3 hybrid orbitals having same energy, which is arranged at the angle of $109^028'$ tetrahedrally in which the four electron pairs coming from four weak Cl^- ligand are arranged.

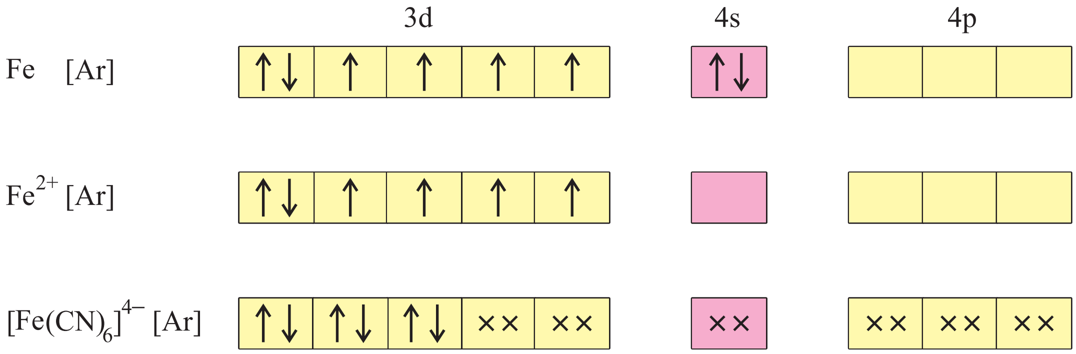


Unpaired electrons $n = 2$ sp^3 hybridization

Hence, $\mu = 2.83$ BM

Because of this $[Ni(Cl)_4]^{2-}$ complex ion has sp^3 type of hybridization and its geometrical structure becomes tetrahedral. As there are two unpaired electrons in two 3d-orbitals, the theoretical value of its magnetic moment becomes 2.83 BM and the value of experimental magnetic moment is 2.90 BM. So it becomes paramagnetic.

$[Fe(CN)_6]^{4-}$ complex ion (Ferrocyanide ion) : In hexacyano ferrate (II) complex ion Fe^{2+} metal ion has combined with six CN^- strong ligand and so it possesses octahedral structure. Here, the electronic configuration of Fe metal and Fe^{2+} ion are [Ar] $3d^6 4s^2$ and [Ar]$3d^6$ respectively. The arrangement of six electrons in 3d-orbitals is shown below :



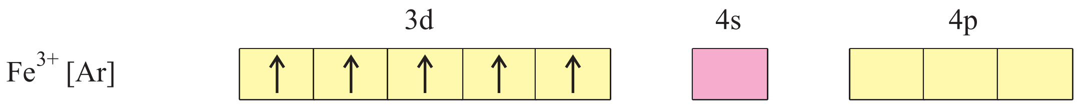
Number of unpaired electrons $n = 0$ d^2sp^3 hybridization

Hence, $\mu = 0$ BM

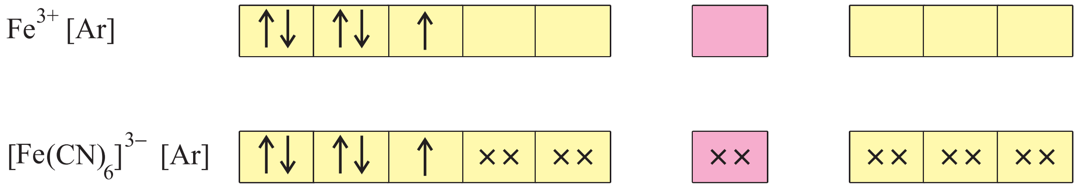
In Fe^{2+} ion d^2sp^3 type hybridization occurs. Octahedral structure is obtained in this hybridization. In d^2sp^3 hybridization, the inner 3d-orbital takes part.

For d^2sp^3 hybridisation there must be two 3d-orbitals vacant in Fe^{2+} metal ion. For this, the rearrangement of six electrons in 3d-orbitals is necessary i.e. as the CN^- ion is a strong ligand, total six electrons form three electron pairs and get arranged in 3d-orbitals. As a result the vacated two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and form d^2sp^3 hybridization; six d^2sp^3 hybrid orbitals having same energy, produced in the above are arranged octahedrally. In d^2sp^3 hybrid orbitals six electron pairs coming from six CN^- strong ligand are arranged. **Here, $[Fe(CN)_6]^{4-}$ complex ion possesses d^2sp^3 type hybrid orbitals and its geometrical structure is octahedral. In the 3d-orbitals of this complex only paired electrons are there and so it becomes diamagnetic.**

$[Fe(CN)_6]^{3-}$ Hexacyanoferrate (III) ion (Ferricyanide ion) : In hexacyanoferrate (III) complex ion, the oxidation state of Fe is +3 and its coordination number is 6. The electronic configuration of Fe^{3+} metal ion in this complex compound is [Ar] $3d^5$. As CN^- is a strong ligand, rearrangement of electrons in 3d-orbitals is necessary. On rearrangement of five electrons in 3d-orbitals, two orbitals become paired and one electron remains unpaired in 3d-orbital. Hence, two 3d-orbitals, one 4s-orbitals and three 4p orbitals overlap and form d^2sp^3 type hybridization. Six electron pairs coming from strong ligand CN^- are arranged in six d^2sp^3 hybrid orbitals having same energy. Here, $[Fe(CN)_6]^{3-}$ complex ion possesses d^2sp^3 hybridization.



On rearrangement of electrons because of strong ligand like CN^-

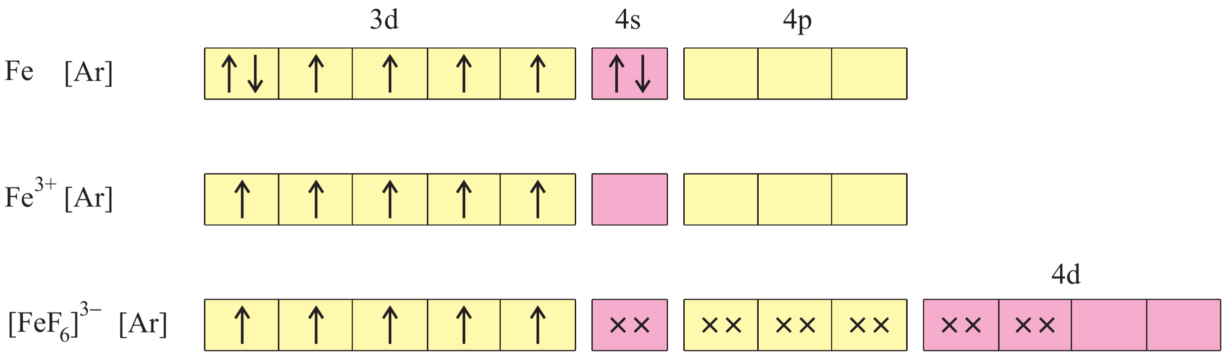


Unpaired electron n = 1 d^2sp^3 hybridization

Hence μ = 1.73 BM

$[Fe(CN)_6]^{3-}$ complex ion possesses d^2sp^3 hybridization whose geometrical structure is octahedral. As there is one unpaired electron in its 3d-orbit it becomes paramagnetic and the theoretical value of magnetic moment becomes 1.73 B.M. and the experimental value is about 1.8 BM.

$[FeF_6]^{3-}$ complex ion : In hexafluorido ferrate (III) ion, six weak F^- ligands combine with Fe^{3+} metal ion. As six F^- weak ligands are combined with Fe^{3+} metal ion, this complex compound possesses sp^3d^2 hybridisation and octahedral structure. In this complex ion in 3d-orbitals, five unpaired electrons are there and so it becomes paramagnetic. Its theoretical value of magnetic moment is 5.92 B.M.



Unpaired electrons n = 5 sp^3d^2 hybridization

Hence μ = 5.92 BM

If ligand had been strong, the electrons present in 3d-orbitals would have rearranged but as F^- is a weak ligand, the rearrangement of five electrons in 3d-orbital does not take place. So one 4s-orbital, three 4p-orbitals and two 4d-orbitals, aggregating six orbitals overlap and sp^3d^2 hybridization occurs. In this six sp^3d^2 hybrid orbitals having same energy, six electron pairs coming from six weak F^- ligand are arranged. **Here, $[FeF_6]^{3-}$ complex ion possesses sp^3d^2 hybridization. So, its geometrical structure is octahedral and complex is paramagnetic.** Generally, the basis of d^2sp^3 hybridisation or sp^3d^2 hybridisation is dependent on the strength of ligand.

$[Co(NH_3)_6]^{3+}$ complex ion : In hexaamminecobalt (III) complex ion the oxidation state of cobalt is +3. The electronic configuration of Co metal and Co^{3+} metal ion are $[Ar]3d^74s^2$ and $[Ar]3d^6$ respectively. Here, in Co^{3+} metal ion, the six electrons- one in 3d-orbital are paired and in four other 3d-orbitals unpaired electrons are present. When the strong ligand NH_3 gives six electron pairs to Co^{3+} metal ion, it forms six co-ordinate covalent bonds, the hybridization of Co^{3+} ion, is of d^2sp^3 and six electron pairs of six NH_3 strong ligand are arranged in six hybrid orbitals. Here, to have d^2sp^3 hybridization, two 3d-orbitals must be vacated. NH_3 being a strong ligand, there is rearrangement of six electrons in 3d-orbitals and become paired and two 3d-orbitals remain vacant. Two 3d-orbitals, one 4s-orbital and three 4p-orbitals overlap and d^2sp^3 hybridization occurs so that six hybrid orbitals having same energy get arranged octahedrally.

	3d					4s	4p		
Co [Ar]	↑↓	↑↓	↑	↑	↑	↑↓			
Co^{3+} [Ar]	↑↓	↑	↑	↑	↑				
$[Co(NH_3)_6]^{3+}$ [Ar]	↑↓	↑↓	↑↓	××	××	××	××	××	××

Unpaired electrons n = 0

d^2sp^3 hybridization

Hence diamagnetic $\mu = 0$ BM

Here, $[Co(NH_3)_6]^{3+}$ complex possesses d^2sp^3 hybridization and the complex becomes octahedral. As there is no unpaired electron in 3d-orbitals, the complex becomes diamagnetic.

$[MnO_4]^-$ complex ion : In tetraoxomanganate (VII) complex, four O^{2-} weak ligands are combined with Mn^{7+} metal ion, so it possesses tetrahedral structure. The electronic configuration of Mn metal and Mn^{7+} metal ion are $[Ar]3d^54s^2$ and $[Ar]3d^0$ respectively. Here 3d and 4s-orbitals are vacant. In Mn^{7+} metal ion, one 4s and three 3d-orbitals overlap and d^3s type hybridization occurs. In d^3s hybridisation, four hybrid orbitals having same energy are arranged on the four corners of tetrahedral. Four electron pairs of oxygen ions from co-ordination covalent bonds in hybrid orbitals.

	3d					4s	4p		
Mn [Ar]	↑	↑	↑	↑	↑	↑↓			
Mn^{7+} [Ar]									
MnO_4^- [Ar]			××	××	××	××			

d^3s hybridization.

In $[MnO_4]^-$ complex ion there is d^3s hybridization. The co-ordinate bonds formed by O^{2-} weak ligand electrons undergo d-d transition in d-orbital, so that eventhough there is no unpaired electron in Mn^{7+} of MnO_4^-, it gives coloured ion.

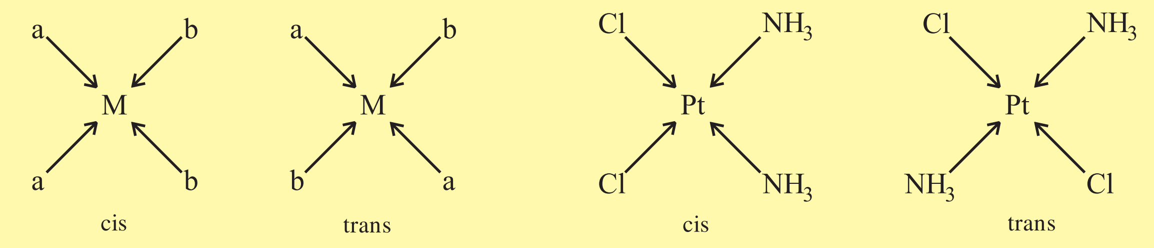
4.10 Isomerism in Complex Compounds

The complex compounds whose molecular formulae are same but the structural formulae are different, are called isomers of each other. Complex compounds possess geometrical isomerism, optical isomerism and structural isomerism.

Geometrical isomerism : Geometrical isomerism is generally observed in square planar and octahedral complex ions. If the two same ligands combined to metal ion are in nearby position to each other, then that isomer is called cis isomer and if they are in opposite positions then the isomer is called trans isomer.

In the square planar structure if there are M metal ion and two different types of two ligands a and b combine then two geometrical isomerism cis and trans are produced

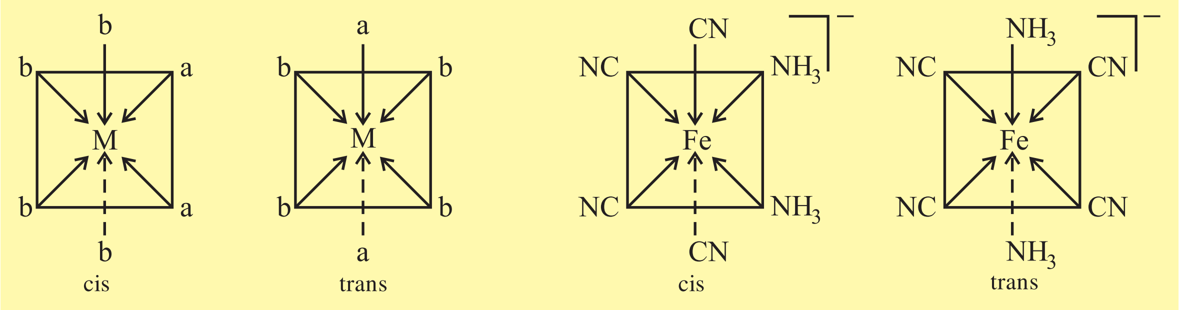
e.g. $[Pt(NH_3)_2Cl_2]$



cis trans cis trans

In octahedral structure, if M is metal ion and two ligands of type a and four ligands of type b are there, then two types of geometrical isomerism cis and trans are produced

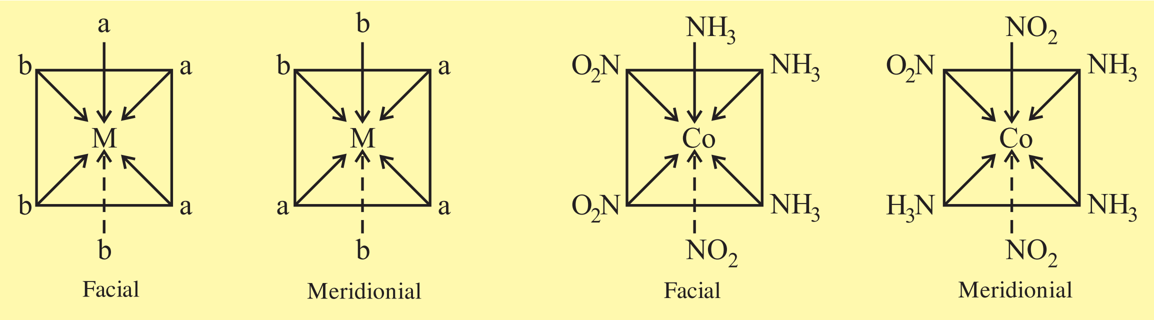
e.g. $[Fe(NH_3)_2(CN)_4]^-$



cis trans cis trans

In octahedral structure, if M is metal ion and three ligands of two types a and b are present then two types geometrical isomerism-facial and meridional- are produced

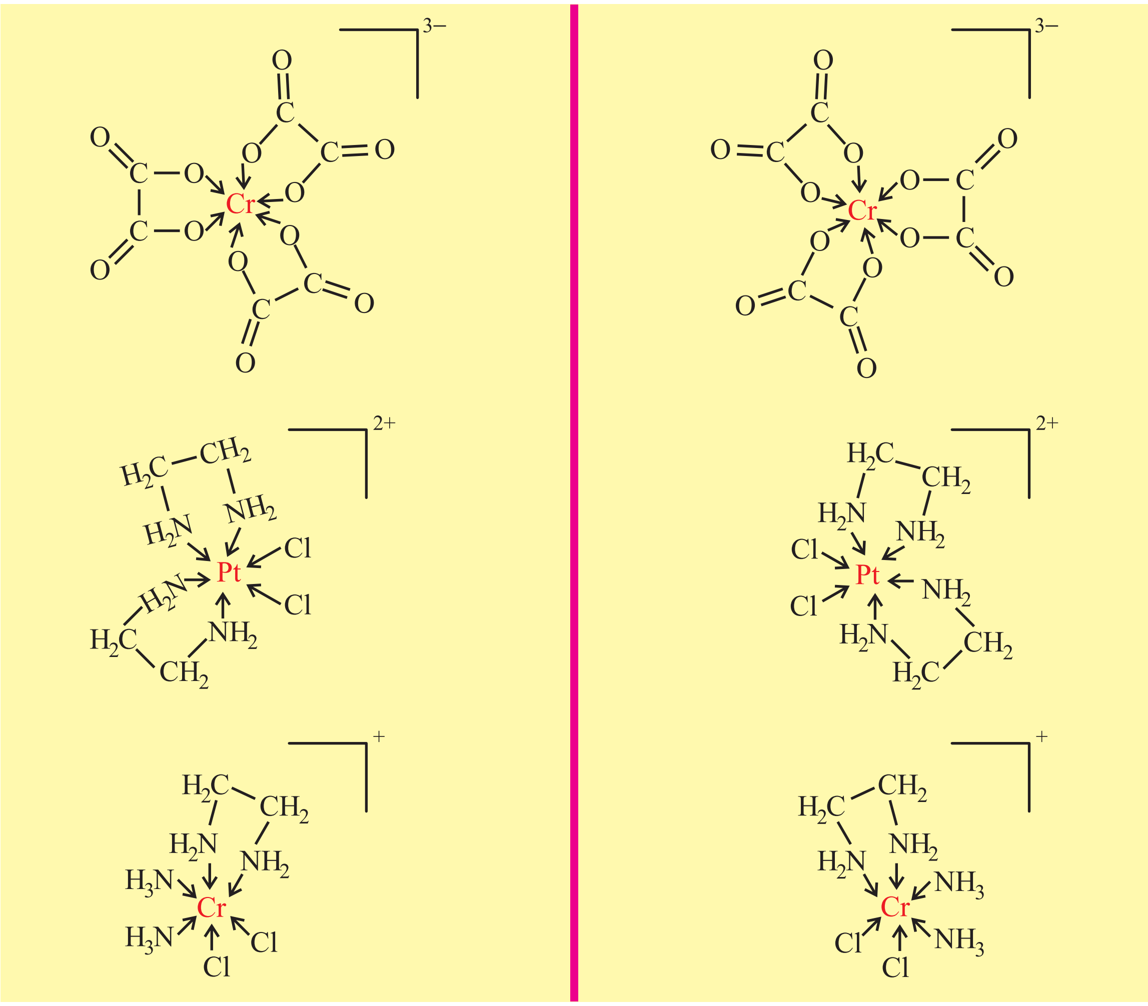
e.g. $[Co(NH_3)_3(NO_2)_3]$



Facial Meridionial Facial Meridionial

Optical isomerism : Optical isomerism is generally observed in octahedral complex-chelate ions. There are certain complex compounds in which molecular formula and structural formulas are same, but the two isomers produced, because of directional arrangement of ligands in it. They are mirror images to each other and the superimposition of two isomers on each other is not possible. This type of complex ions possess property of chirality and they are called optical isomers. **The main difference between these two isomers is that both the isomers rotate the plane polarized light to left or right in directions opposite to each other.** If it rotates angle of rotation on left side, then that isomer is called *l* (levo) or (–) and one which rotates angle of rotation on right side, than that isomer is called *d* (dextro) or (+). The equal proportion mixture of dextro and levo isomers is called racemic, *dl* or (±) mixture.

e.g. $[Cr(C_2O_4)_3]^{3-}$, cis $[PtCl_2(en)_2]^{2+}$, $[CrCl_2(NH_3)_2(en)]^{+}$

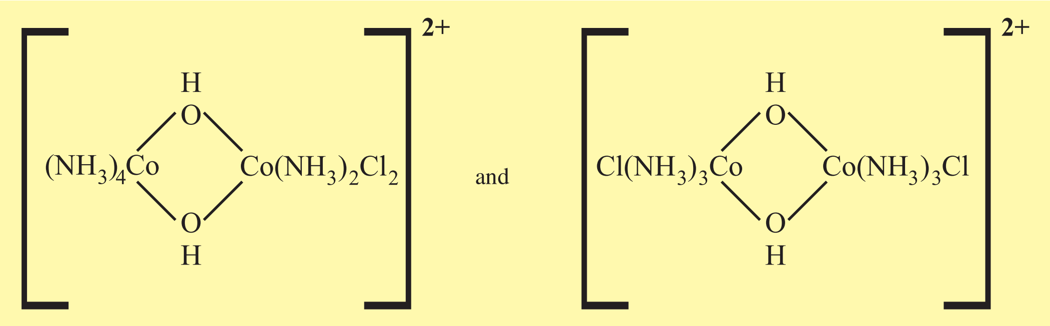


Structural isomerism : Various types of isomerism as compared to organic chemistry are observed because of different geometrical arrangements and different types of bonds in structural isomerism co-ordination. (i) Linkage isomerism (ii) Co-ordination isomerism (iii) Ionic isomerism (iv) Hydration isomerism.

(i) Linkage isomerism : NO_2^- ion combines with metal ion with nitrogen atom through co-ordination and acts as nitro ($-NO_2$) ligand or through any one of the oxygen by co-ordination and act as nitrito (ONO^-) ligand. Thus one ligand forms isomers by bonding of different atoms. Some of the examples are given below :

$[Co(NO_2)(NH_3)_5]^{2+}$ pentaamminenitrocobalt (III) ion and $[Co(O \cdot NO)(NH_3)_5]^{2+}$ pentaammine nitrito cobalt (III) ion and $[Co(NO_2)(NH_3)_5]Cl_2$ is yellow brown coloured and $[Co(O \cdot NO)(NH_3)_5]Cl_2$ is of red colour. Similarly CNS^- ion can be co-ordinated through nitrogen or sulphur and gives different isomers like. $[Mn(CO)_5SCN]^+$ and $[Mn(CO)_5NCS]^+$.

(ii) Co-ordination isomerism : When in co-ordination compounds, both positive ion and negative ion are complex ions then there is exchange between the two in the co-ordination sphere and isomers are formed e.g. $[Co(NH_3)_6]^{3+}$ $[Cr(CN)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ $[Co(CN)_6]^{3-}$; $[Cu(NH_3)_4]^{2+}$ $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$. This type of isomerism is observed when metal ion is in different oxidation states. e.g. $[Pt^{(II)}(NH_3)_4]$ $[Pt^{(IV)}Cl_6]$ and $[Pt^{(IV)}(NH_3)_4Cl_2]$ $[Pt^{(II)}Cl_4]$ **specific type of co-ordination isomerism is called position isomerism which is observed in cyclic complex compounds.**



(iii) Ionisation isomerism : The compounds whose propotion by weight and the component are same but they give different ions in solution, then that type of isomerism is called ionization isomerism. e.g.

$[Co(NH_3)_5NO_3]Cl$ and $[Co(NH_3)_5Cl]NO_3$

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

$[Cr(NH_3)_4Cl_2]NO_2$ and $[Cr(NH_3)_4Cl \cdot NO_2]Cl$

(iv) Hydration isomerism : This type of isomerism is a special type of ionization isomerism. Three isomeric forms of $CrCl_3 \cdot 6H_2O$ are known.

(a) $[Cr(H_2O)_6]Cl_3$ (violet). If it is kept over H_2SO_4, it does not lose water and $3Cl^-$ and $3Ag^+$ ions take part in precipitation.

(b) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (gray green). If it is placed over H_2SO_4, then it loses one molecule of water and $2Cl^-$ ions take part in precipitation with $2Ag^+$ ions.

(c) If $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green) is placed over H_2SO_4 it loses 2 molecules of water and Cl^- ion takes part in precipitation with Ag^+ ion. Here, both ionization and hydration isomerisms are found. In such isomers, difference in their physical and chemical as well as colour is found.

Limitations of valence bond theory : When co-ordination compounds are formed, the valence bond theory is mostly applied for magnetic nature and structural formation. It has following limitations :

(i) It consists of some assumptions.

(ii) It cannot interpret quantitatively the magnetic information.

(iii) It is not able to explain the colours of co-ordination compounds.

(iv) It cannot interpret quantitatively thermodynamics and kinetic stabilities of co-ordination compounds.

(v) It does not make exact prediction regarding the tetrahedral and square planar structures of four co-ordination number complexes.

(vi) It cannot distinguish the weak and strong ligands.

4.11 Crystal Field Theory

Crystal Field Theory (CFT) is known as electrostatic model in which it is believed that there is ionic bond between metal and ligand. According to this theory, negatively charged ligand or polar neutral molecule forms ionic bond with metal ion. All the five types of d-orbitals are degenerate (same energy) in free gaseous form of metal atom or ion (Fig. 4.2). In addition to this, if there is spherical negatively charged field having spherical symmetry around the metal atom or ion, even then d-orbitals remain degenerate but when ligands are arranged around the metal atom or ion then the d-orbitals do not remain degenerate but gets split (fig. 4.3). The splitting of orbitals depends on the nature of crystal field.

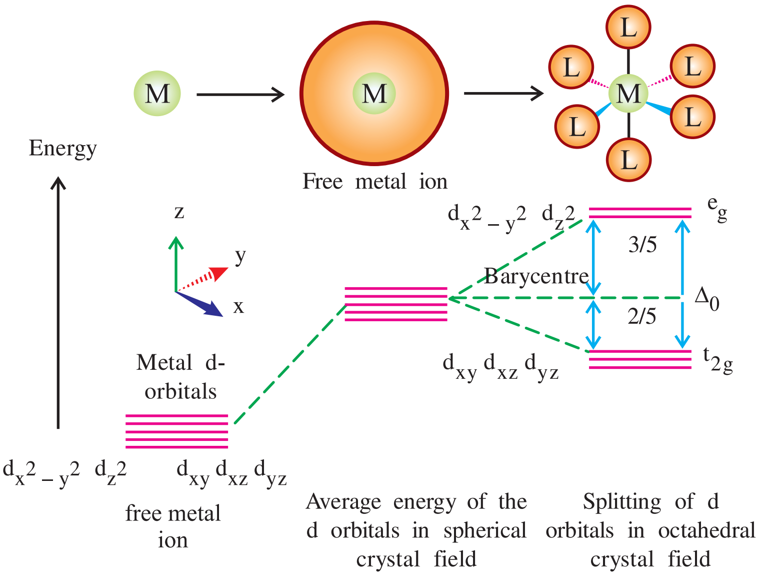


Fig. 4.3 d-orbital splitting in an octahedral crystal field

(A) Crystal field splitting in octahedral complexes : In octahedral complex, there are six ligands around the metal atom or ion. Here there is repulsion between electrons of d-orbital and electrons of ligand (or between negative ions); $d_{x^2-y^2}$ and d_{z^2} orbitals arranged on this axis experience more repulsion with ligand and will be raised in energy, while there is less repulsion between d_{xy}, d_{yz}, d_{xz} orbitals arranged between the axes, with ligand. Hence, their average energy of spherical crystal field decreases. As the degeneracy of these orbits is removed, it results into three orbitals having lower energy t_{2g} and higher energy possessing e_g orbitals. This type of phenomenon is called crystal field splitting. The splitting of energy of orbitals observed in octahedral complex is shown by Δ_0. Thus, in e_g orbitals there will be increase by $\frac{3}{5}\Delta_0$ and there will be $\frac{2}{5}\Delta_0$ decrese in energy of three t_{2g} orbitals.

The splitting of crystal field (Δ_0) depends on electric charge of metal ion and ligand. Some ligands produce strong field, so that the splitting of orbitals is more in proportion. While certain ligands produce weak field so that the splitting of orbitals is less in proportion. Generally, the series of ligands on the basis of increase in strength of fields by ligands, can be shown as below :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < NO_2^- < CN^- < CO$

The above series is called spectrochemical series. If in the metal ion, there are 1, 2 or 3 electrons in d-orbitals, then their arrangement will be in t_{2g} orbitals having low energy, according to Hund's rule. But if there are 4 electrons(d^4) in the d-orbitals then there are two possibilities as follows :

(i) The fourth electron will be arranged by pairing with any one electron present in t_{2g} orbitals.

(ii) The fourth electron will be arranged in e_g orbital neglecting giving energy for pairing.

Which of the above two possibilities can be possible depends on the splitting of crystal field (Δ_0) and on reactive magnitude energy of pairing; p.

(a) If $\Delta_0 < p$ then the fourth electron will be arranged in e_g orbital so that electronic structure will be $t_{2g}{}^3\ e_g{}^1$. For the ligands producing weak field, $\Delta_0 < p$ and form complexes having higher spins.

(b) If $\Delta_0 > p$ then the fourth electron will be arranged in t_{2g} orbital so that the electronic structure will be $t_{2g}{}^4\ e_g{}^0$ for ligands producing strong field $\Delta_0 > p$ and for complexes having low spins.

Experimental findings suggest that for complexes having d^4 to d^7 electronic configuration the ligands having stronger field give more stability than complexes having weak field.

(B) Crystal Field Splitting in Tetrahedral Complexes : In the formation of tetrahedral structure, the splitting of d-orbitals is in opposite nature to octahedral complexes. Like octahedral, if tetrahedral complex possesses equal distance between, metal, ligand, metal-ligand, then $\Delta_t = \frac{4}{9}\Delta_0$. Hence if the value of Δ_t is not sufficiently high, pairing of electrons does not occur. Hence low spin is observed in less proportions. The splitting of d-orbitals in tetrahedral structure is shown in the fig. 4.4.

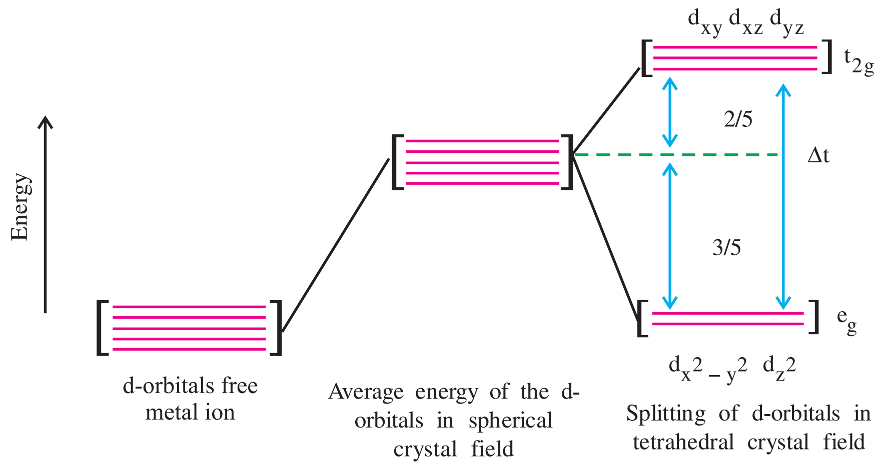


Fig. 4.4 d-orbital splitting in a tetrahedral crystal field

Colour in co-ordination compounds : We have studied earlier that the transition metal complexes exhibit wide variety of colours, which is one of their important properties. **This means that when white light passes through the sample, then it forms definite visible spectrum.** Others are removed from the white light. Hence, for a long time white light is not obtained. The absorption of colour is one complementary matter. The complementary colour is dependent on the wavelength If complex absorbs green colour, then it will be seen red.

In the table 4.5 absorption of different wavelengths and observed colours are shown.

Table 4.5 Absorbed wavelength of light and observed colour of complex compounds

Co-ordination compounds	Absorbed light wavelength nm	Absorbed colour of light	Colour observed of co-ordination compounds
$[CoCl(NH_3)_3]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_3(H_2O)]^{3+}$	500	Bluish green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellowish orange 🟧
$[Co(CN)_6]^{3+}$	310	Ultraviolet 🟪	Light yellow 🟨
$[Cu(H_2O)]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Bluish green 🟩	Light violet 🟪

The colours of co-ordination compounds can be explained on the basis of crystal field theory. e.g. $[Ti(H_2O)_6]^{3+}$, which has violet colour. This is octahedral complex in which one electron of d-orbital from metal ion complex is in stable state at t_{2g} one electron. (One electron Ti^{3+} is of $3d^1$ system) e_g state is vacant. If photon energy is by absorption of photon with yellow-green light, then the electron goes from t_{2g} layer to e_g layer $(t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1)$. Because of this, violet colour is shown. (As shown in fig. 4.5).

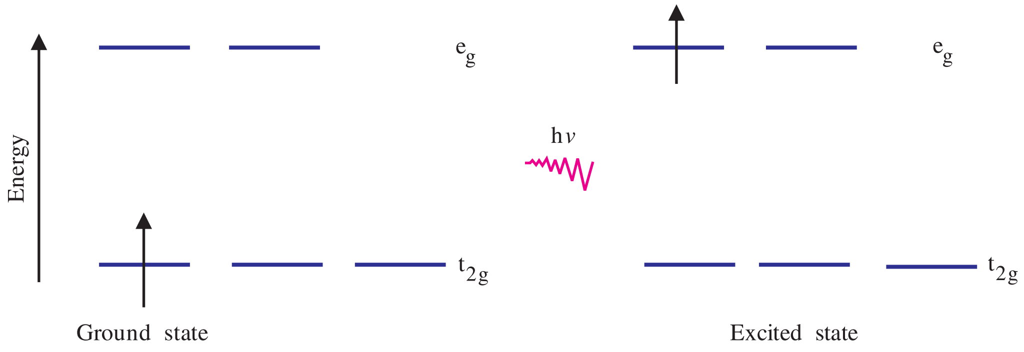


Fig. 4.5 Transition of an electron in $[Ti(H_2O)_6]^{3+}$

Here, one point is to be noted that in the absence of ligand, there is no splitting in crystal field. So the substance is colourless viz. $[Ti(H_2O)_6]Cl_3$; when heated water is removed and so it is changed to colourless substance. Similarly anhydrous $CuSO_4$ is white while $CuSO_4 \cdot 5H_2O$ is of blue colour.

The effect of ligand in complex can be explained by the example of $[Ni(H_2O)_6]^{2+}$. This complex is formed by dissolving $NiCl_2$ in water. Now, if didentate ligand ethane 1,2 diamine (en) is slowly added so that the molar ratio of en and Ni (en:Ni); is 1:1, 2:1, 3:1, the corresponding change in colour of complex is as follows :

$$\underset{\text{green}}{[Ni(H_2O)_6]^{2+}(aq)} + en(aq) = \underset{\text{light blue}}{[Ni(H_2O)_4(en)]^{2+}(aq)} + H_2O$$

$$[Ni(H_2O)_4(en)]^{2+}(aq) + en(aq) = \underset{\text{blue / light violet}}{[Ni(H_2O)_2(en)_2]^{2+}(aq)} + 2H_2O$$

$$[Ni(H_2O)_2(en)_2]^{2+}(aq) + en(aq) = \underset{\text{violet}}{[Ni(en)_3]^{2+}(aq)} + 2H_2O$$

This series of colours is shown in fig. 4.6

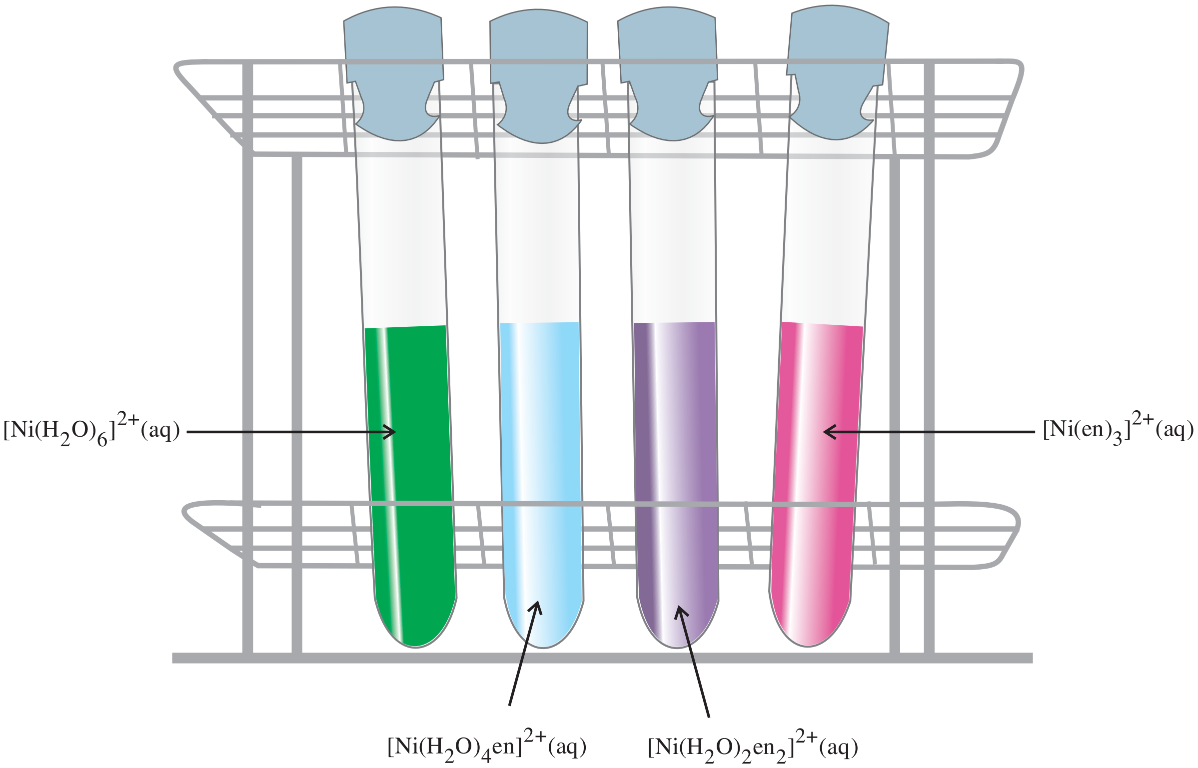


Fig. 4.6 Aqueous solutions of complex of nickel(II) with an increasing number of moles of ethane-1,2-diamine ligand

The magnetic properties, colour and the formation of structures of complex compounds can be successfully explained by crystal field model. The effect of many diversities is observed in charge of ligand and the ionic ligands. The position of anionic ligand is observed at the lower end in the spectrochemical series. Also there is no covalent bond character in bonding of central atom and that ligand. Thus, the limitation of CFT led to the development of field of study of molecular orbital theory.

The importance and uses (applications) of complex compounds : Co-ordination compounds. have wide range of applications and hence are very useful in mineral nutrition of plants and animals. It plays an important role in analytical chemistry. It possesses great utility in metallurgy, biological system and industries and drugs. They can be described as follows :

- Co-ordination compounds are useful in quantitative and qualitative methods in chemical analysis. We are familiar with the colour produced by their reaction on the basis of number of ligands with metal ions, (especially chelating ligands). Because of the results of the co-ordination compounds, the information about their proportion can be inferred and analysis can be carried out by classical and different instrumental methods. e.g. EDTA, DMG (Dimethyl glyoxime), α-nitroso-β-naphthol, cupferron, etc.

- By titration of hard water with Na_2EDTA the hardness of water can be determined. Ca^{2+} and Mg^{2+} ions give stable complexes with EDTA. The measurement of the order of stability of calcium and magnesium complexes with these ions can be carried out.

- In some important metal reactions such as silver or gold form important complexes. e.g. Gold is combined with cyanide in presence of oxygen and water, combine and solution of $[Au(CN)_2]^-$ is prepared from this solution. Gold can be obtained in metal form by addition of zinc.

- From co-ordination compounds, like successive decomposition reacts, the metals are formed by purification of metals. e.g. $[Ni(CO)_4]$ obtained from impure nickel. Then pure nickel is obtained from it by decomposition.

- Co-ordination compounds are very important in biological systems. The dye matter chlorophyll formed by magnesium is responsible for photosynthesis. Iron containing co-ordination compound haemoglobin dye-matter conducts O_2 and so red colour of blood is observed. Cobalt contains co-ordination conpound vitamin B_{12} or cyanocobalamine which is antimatter of petnicious anemia. The other compounds which are substances having biological importance are in enzyme formed by formation of compound with metal viz. carboxypeptidase and carbonic anhydrade (catalysts of biological system-Enzymes).

- Co-ordination compounds are useful as catalysts in many industrial reactions e.g. Rhodium complex $[(Ph_3P)_3RhCl]$ which is useful as Wilkinson catalyst in dehydrogenation of alkanes.

- By electroplating with silver and gold soft, attractive replicas are prepared through handicraft. Replicas can be made from complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ solutions also can be prepared from simple metal ion solutions.

- Film is stabilized by washing with solution of hypo (sodium thiosulphate) in white and black photography which is soluble in non-decomposable AgBr whose formation takes place from complex ion $[Ag(S_2O_3)_2]^{3-}$.

- In medicinal chemistry, chelate therapy is the important emerging method. For diagnosis of problem like presence of poisonous property of metals in plants and animals is a useful example. To remove the excess proportion of copper and iron, chelating ligands D-Penicilamine and desferrioxime are used for formation of co-ordinate compounds. EDTA is used for diagnostic test for poisoning of lead. From some co-ordinate compounds, the compound like platinum is useful in inhibiting the growth of tumours. e.g. cisplatin and related compound.

SUMMARY

- The salt that is obtained when two or more salts having independent existence combine according to the laws of combination and which maintain the properties of original salts is called double salt e.g. Alum is a double salt.

- Similarly, the compound that is obtained when two or more salts having independent existence combine according to laws of chemical combination and compound having new properties, formed is called complex compound. e.g. $K_3[Fe(CN)_6]$ is a complex salt.

- Most of the complex compounds are formed by elements of d-block (transition elements). In the electronic configuration of these elements, there is successive arrangement of electrons in d-orbitals. when the atom or ion of transition elements has vacant (n–1)d, ns and np or ns, np and nd orbitals, these transition elements accept negative ions or neutral molecules and they form the compounds which are called complex compounds. In this type of compounds, the bond that is formed between metal ions of elements and the negative ion or neutral molecules is called co-ordinate covalent bond. Around the centre of the metal ions of the molecules of these compounds, the negative ions or neutral molecules are combined with co-ordinate covalent bond.

- Alfred Werner, first of all gave the theory for complex compounds which is known as Werner's co-ordination theory. Some metals have the secondary valency in addition to their primary valence. By this the ions of that metal combine strongly with the negative ion or neutral molecules in first attraction sphere [ ].

- According to Werner's theory, the metal ion possesses two types of valencies : Primary valency and secondary valency.

- The primary valency of the metal is equal to its oxidation number or equal to the positive electric charge of the positive ion, which forms ionic bond, so that it gets ionized. The negative ion combines with primary valency.

- The secondary valency depends on the vacant orbitals in metal ion. The secondary valency is satisfied by negative ions or neutral molecules. It does not get ionized. The secondary valency mentions its co-ordination number. The secondary valency is fixed for the metal ion but now, it has been proved that the transition metal ions possess more than one co-ordination number. As the secondary valence being directional determines the geometrical shape of complex compound. From the magnetic properties also the shape of complex can be determined. e.g. In $[Cr(NH_3)_6]Cl_3$, Cr is metal ion and six molecules of neutral molecule ammonia (NH_3) are combined with it by secondary valency which do not get ionized. Hence, the co-ordination number is six. Three Cl^- are combined by primary valency which gets ionized. Hence the primary valency of Cr is three.

- Ligand is an ion having negative electric charge or neutral molecule. The classification of ligand is made on the basis of the number of electron pair donating atoms.

- If the negative ion or neutral molecule in the ligand forms one co-ordinate covalent bond by giving one electron pair to metal ion, then it is called unidentate ligand. Neutral molecules like H_2O, NH_3, CO, NO and negative ions like Cl^-, Br^-, CN^- act as unidentate ligands.

- The ligand which donates two electron pairs to metal ion, and form two co-ordinate covalent bonds is called didentate ligand. e.g. ethane 1,2-diamine (en), neutral and SO_4^{2-}, CO_3^{2-} negative ions act as didentate ligands.

- The ligand in which three co-ordinate sites are indicated then it is called tridentate. In this type of ligand the atoms donate three pairs of electrons to metal ion and form three co-ordinate covalent bonds. e.g. Propane-1, 2, 3-triamine (ptn) neutral and PO_4^{3-}, AsO_4^{3-} act as negative tridentate ligand.

- Six atoms in EDTA, (ethylene diaminetetracetate) ion, the six atoms donate six electron pairs and form six co-ordinate covalent bonds, which act as hexadentate ligand.

- Generally, the ligand in which two or more than two co-ordination sites are indicated, or the ligand in which two or more than two atoms form co-ordinate covalent bonds by donating electron pairs to metal ion is called polydenate ligand, which combines with metal ion and form complex compounds. They are called chelate compounds which are cyclic and possess higher stablity.

- The basic requirements for formation of complex compounds are ligand which can easily donate electron pairs, there must be vacant d-orbitals in the metal ion to accept electron pairs and the metal ion should have the symmetry same as that of the ligand.

  The ion satisfying these basic requirements can easily form complex compounds.

- The strength of formation of co-ordinate covalent bonds of different ligands being different, the stronger ligand possesses more attraction towards metal ion and form strong coordinate covalent bond. As a result, the stability of complex having strong ligand is more and the weak ligand containing complex compounds have less stability e.g. The strength of $[Ni(CN)_4]^{2-}$ is more than that of $[NiCl_4]^{2-}$.

- A complex compound, in which different types of ligands combine with metal ion and form complex compound, is called mixed ligand complex. If in any of the complex compounds only one metal ion is present, then it is called unicentred complex compound. If in any complex compound, more than one metal ions are present then it is called polycentred complex compound. In such unicentred or polycentred complex compounds, the three dimensional arrangement of ligand, the different geometrical structures are produced in co-ordination compounds, it is called polyhedra. Mostly the geometrical structures are of shapes-tetrahedral square planar, octahedral square pyramidal, trigonal bipyramidal. To understand these geometrical structures, the hybridization of orbitals of metal ion and magnetic properties are very useful. sp^3 hybridisation, dsp^2 hybridisation, d^3s hybridization in metal ions of co-ordination number four is seen. In sp^3d^2 hybridization and d^2sp^3 hybridization, the metal ions of transition elements is seen in metal ions having co-ordination number six. The metal ions of transition elements, magnetic moments of complex compounds of ions, their geometrical structures, types of ligands etc. are described.

- The nomenclature of complex compounds keeping in mind the rules of IUPAC is carried out. In complex compounds the rules are applicable.

- In nomenclature in co-ordination sphere, the name of the ligand according to English alphabets are first mentioned. Then the name of metal is written. The suffix "O" is attached after the name of negatively charged ligand. The name of the neutral ligand is mentioned as its original name. If the number of same ligand is more than the one the prefixes di, tri, tetra…etc. are applied. In the prefix of organic ligand, the prefix is a number then the ligand is placed in bracket and the prefix bis, tris, are attached. If the complex is negative ion then the name of ligand is written first and, in the end the suffix 'ate' is applied to the metal ion. Its oxidation state is shown in Roman number in bracket. If the complex is positive ion or neutral molecule, then successively writing the name of ligand, the name of metal is added at the end and oxidation state is shown in the Roman number.

- The geometry of complex compounds and magnetic properties of the complex depends on the hybridization in it. In complexes having co-ordination number 6 if strong ligand is attached with metal ion in complex, the oxidation state is shown in Roman numbers.

- In complex compounds, the geometrical structures are dependent on hybridization in it. In complex having co-ordination number 4, if the strong ligand is combined with metal ion then dsp^2 hybridization takes place in the complex and the structure is square planar. The example of this are $[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$ etc. If the co-ordination number is 4 in the complex, and the weak ligand combines with the metal ion then sp^3 hybridization takes place e.g. $[NiF_4]^{2-}$, $[Ni(H_2O)_4]^{2+}$, etc. If the co-ordination number in complex ion is six, and the strong ligand is combined with metal ion, then d^2sp^3 hybridization and if weak ligand is combined with metal ion, then sp^3d^2 hybridization takes place, e.g. In $[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ d^2sp^3 hybridization is there, while in $[FeF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ sp^3d^2 hybridization is there. In MnO_4^- and CrO_4^{2-} there is d^3s hybridization, there are no unpaired electrons in d-orbital due to Mn^{7+} and Cr^{6+} oxidation states; but d-d transition takes place by electrons of ligand, and so it becomes coloured.

- Three types of isomerism are observed in complex compounds-geometrical isomerism, optical isomerism and structural isomerism.

- In geometrical isomerism, complex compounds having co-ordination number four- ML_2A_2 type, cis and trans isomerism is observed. In complex compounds having co-ordination number six - ML_4A_2 type, cis and trans while in ML_3A_3 facial and meridional isomerism are observed. In optical isomerism, leavo and dextro isomers are observed.

- In structural isomerism, ionic isomerism, hydration isomerism, co-ordination number isomerism and linkage isomerism are observed.

- In formation of co-ordination compounds the magnetic nature and structural formation with the help of valence bond theory; it has limitations. It cannot interpret the quantitatively the magnetic information and can not explain about the colour in co-ordination compounds. It can not give meaning of thermodynamical stability of co-ordination compounds, also it is not able to detect the difference between weak and strong ligand. To overcome these limitations the crystal field theory (CFT) was presented.

- Crystal field theory is known as electrostatic model in which it is believed that there is ionic bond between metal ion and ligand. According to this theory negatively charged ligand or neutral molecule forms ionic bond. In free metal atom in gaseous state, all the five types of d-orbitals are of equal energy (degenerate) but when ligands are arranged around the metal atom or ion in the complex, the d-orbitals do not remain of equal energy but get splitted. The splitting of orbitals depends on the nature of the crystal field.

- The crystal field splitting (Δ_0) depends on the field produced by electric charge of metal ion and the ligand. Some ligands produce strong field and so splitting is in more proportion. Some ligands produce weak field, so that the splitting is in less proportion. The series of ligands on the basis of the strength of the field produced by ligand can be shown as below :

  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$: Spectrochemical series.

- Metal complexes have large magnitude of colours. When the white light passes through the sample, then it forms a specific visible spectrum and the remaining colours of white light are removed. The absorption of colour by complex compounds is dependent on wavelength. If green colour is absorbed then it appears of red colour.

- The colour of co-ordination compounds can be explained on the basis of crystal field theory e.g. $[Ti(H_2O)_6]^{3+}$ violet colour, $[Ni(H_2O)_6]^{2+}$ green colour, and $[Ni(en)_3]^{2+}$ violet colour,

- Co-ordination compounds have great importance. They have immense utility value in nutrition of minerals in plants and animals, analytical chemistry, metallurgy, biological systems and industries. They are also used in various drugs.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) What type of bond is L → M in complex compounds ?

(A) Ionic (B) Metallic

(C) Co-ordinate covalent (D) Covalent

(2) Who gave metal co-ordination theory ?

(A) Albert Werner (B) Schrodinger

(C) August Hofmann (D) Alfred Werner.

(3) What is the nature of ligand in complex compounds ?

(A) Bronsted-Lowry base (B) Lewis base

(C) Lewis acid (D) Arrhenius acid.

(4) Which of the following cannot act as ligand ?

(A) H_2O (B) NO_3^- (C) CO_2 (D) CO

(5) Which of the following compounds is a double salt ?

(A) Potassium permanganate (B) Ferrous ammonium sulphate

(C) Ammonium chromate (D) All the given.

(6) What is the primary valency of metal ion in the complex $[Co(en)_2Cl_2]NO_3$?

(A) 4 (B) 6 (C) 2 (D) 3

(7) What is the electrical charge of pentacarbonyl iron (0) complex ?

(A) one (B) two (C) three (D) zero

(8) What is the secondary valency of metal ion in $[Cr(NH_3)_4OX]NO_3$?

(A) 2 (B) 4 (C) 6 (D) 8

(9) What is the valency of Fe which does not ionize in $K_3[Fe(OX)_3]$?

(A) Three (B) Four (C) Six (D) One

(10) How many ions are obtained by ionization of $(NH_4)_2[MoO_4]$ complex compound in aqueous solution ?

(A) 2 (B) 4 (C) 0 (D) 3

(11) How many ions will be obtained by ionization of ferric hexacyanoferrate(III) complex compound ?

(A) 7 (B) 4 (C) 2 (D) 3

(12) What is the geometrical shape of $K_4[Ni(CN)_4]$?

(A) Octahedral (B) Square planar

(C) Tetrahedral (D) Trigonal pyramidal

(13) Which of the following is not the chelating ligand ?

(A) en (B) ptn (C) OX^{2-} (D) CO

(14) O^{2-} is the example of what type of ligand ?

(A) Didentate (B) Tridentate (C) Unidentate (D) Hexadentate.

(15) How many co-ordination sites are in edta ligand ?

(A) six (B) four (C) three (D) two

(16) What will be the hybridization in $[Ni(CN)_4]^{2-}$ complex ion ?

(A) sp^3 (B) dsp^2 (C) sp^3d^2 (D) d^2sp^3

(17) Which of the following compounds possesses paramagnetic property ?

(A) $[Ni(NH_3)_4]^{2+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Co(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{3-}$

(18) By which of the following, poisoning of lead in the body can be removed ?

(A) ptn (B) EDTA (C) pn (D) OX^{2-}

(19) Which complex is used to stop the growth of tumour in body ?

(A) Chlorophyll (B) Cisplatin (C) Haemoglobin (D) Ferrocene.

(20) What is the colour of $[Ni(H_2O)_6]^{2+}$ complex compound ?

(A) Violet (B) Green (C) Blue (D) Pink

(21) Mention the electric charge on edta.

(A) 6- (B) 2- (C) 3- (D) 4-

(22) Which of the following complex ion does not possess tetrahedral shape ?

(A) $[MnO_4]^-$ (B) $[Ni(CO)_4]$ (C) $[Ni(CN)_4]^{2-}$ (D) $[Cu(NH_3)_4]^{2+}$

(23) What is theoretical magnetic moment of complex compound $K_2[NiF_4]$?

(A) 1.73 BM (B) 2.83 BM (C) 3.87 BM (D) Zero.

(24) Which of the following ligands acts as strongest ligand ?

(A) Cl^- (B) NH_3 (C) CO (D) CN^-

(25) The number of Cl^- combined by secondary valency in $[Fe(NH_3)_4Cl_2]Cl$ is ....

(A) 1 (B) 2 (C) 3 (D) 0

(26) Which of the following complex ions is most stable ?

(A) $[FeCl_6]^{3-}$ (B) $[Fe(H_2O)_6]^{3+}$ (C) $[Fe(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{4-}$

(27) Which of the following complex ions does not possess optical isomerism ?

(A) $[Co(en)(NH_3)_4]^{2+}$ (B) $[Co(H_2O)_4(en)]^{3+}$

(C) $[Co(en)_2(NH_3)_2]^{2+}$ (D) $[Co(NH_3)_3CI_3]^+$

(28) Aqueous solution of which complex will be possessing high conductance ?

(A) Hexamminecobalt(III)chloride

(B) Tetramminedichloridocobalt(III)chloride

(C) Pentamminechloridocobalt(III)chloride

(D) Triamminetrichloridocobalt(III)

(29) Which of the following is the correct order of spectrochemical series ?

(A) $Cl^- < F^- < C_2O_4^{2-} < NO_2^- < CN^-$ (B) $F^- < Cl^- < NO_2^- < CN^- < C_2O_4^{2-}$

(C) $CN^- < C_2O_4^{2-} < Cl^- < NO_2^- < F^-$ (D) $C_2O_4^{2-} < F^- < Cl^- < NO_2^- < CN^-$

(30) Which transition of electrons will be observed in the following when Ti^{3+} ion having complex absorbs visible light ?

(A) $t_{2g}^0e_g^1 \rightarrow t_{2g}^1e_g^0$ (B) $t_{2g}^2e_g^0 \rightarrow t_{2g}^1e_g^1$ (C) $t_{2g}^1e_g^1 \rightarrow t_{2g}^0e_g^2$ (D) $t_{2g}^1e_g^0 \rightarrow t_{2g}^0e_g^1$

(31) The co-ordination number, oxidation number, number of electrons in d-orbital and number of unpaired electrons is respectively in complex $[Co(NH_3)_4CO_3]ClO_4$

(A) 6, 3, 6, 0 (B) 7, 2, 7, 1 (C) 5, 2, 6, 4 (D) 6, 2, 7, 3

2. Answer the following questions in brief :

(1) What is meant by double salt ?

(2) What is meant by complex salt ?

(3) How many types of valencies, the metal ion possesses in complex compound ? and which ?

(4) Write the valencies of metal ion in $[Fe(CN)_6]^{4-}$ complex compound.

(5) What type of ligands are PO_4^{3-} and O^{2-} ?

(6) What type of bonds are present of the metal ion in complex compound ?

(7) What is meant by co-ordination site ?

(8) What is called ligand ?

(9) Why are the geometrical shapes produced in complexes ?

(10) What is meant by co-ordination covalent bond ?

(11) What is meant by secondary valency ? By which type of ions is it satisfied ?

(12) What is meant by polydentate ligand ? Give any one example.

(13) What is meant by chelate complex ? Give any one example.

(14) Draw the structure of $[M\text{-}EDTA]^{\pm n}$

(15) What is meant by mixed ligand complex ? Give an example.

(16) What is meant by unicentred and polycentred complex compounds ? Give an example.

(17) Give two examples of complex ions having co-ordination number 4 for different magnetic moments.

(18) Explain chelate therapy.

(19) In refining of which metal, the use of complex compounds is made ?

(20) Describe the use of edta.

(21) Mention limitations of crystal field theory.

(22) What type of isomerism is observed in $[Cr(NH_3)_4Cl_2]NO_2$?

(23) Mention how many types of isomerism are there in $[Pt(en)_2Cl_2]^{2+}$ complex ion and mention them.

(24) Give two examples of complex ions having sp^3d^2 hybridisation.

(25) Describe Werner's co-ordination theory.

3. Answer the following questions :

(1) Explain the difference between double salt and complex salt.

(2) What is called tridentate ligand ? Explain giving example.

(3) Explain giving example, hexadentate ligand.

(4) Mention the basic requirements for the formation of complex compounds.

(5) Explain stability of complex compounds.

(6) Explain sp^3d^2 and dsp^2 hybridisation.

(7) Explain the hybridization and geometrical structure of MnO_4^- complex ion.

(8) Explain geometrical isomerism.

(9) Explain optical isomerism.

(10) Write limitations of valence bond theory.

(11) Explain crystal field theory.

(12) Explain the application of complexes in biological systems and photography.

4. Answer the following questions in detail :

(1) Write the points of Werner's co-ordination theory.

(2) What is meant by ligand ? Explain its classification.

(3) Explain the hybridization of orbitals of metal ions in complex compounds and the magnetic properties.

(4) Explain the geometrical structures and magnetic properties of the following complex compounds with the help of hybridization. $[Ni(CN)_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[FeF_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[NiCl_4]^{2-}$

(5) Explain in detail the structural isomerism with examples.

(6) Explain crystal field splitting in octahedral complexes and write the limitations of crystal field theory.

(7) Explain in detail, "Colour in co-ordination compounds."

(8) Describe the importance and applications of co-ordination compounds.

(9) Write the IUPAC names of the complex compounds shown below :

$K_3[Fe(CN)_5NO]$

$K_3[Fe(CN)_4Cl_2]$

$Na_3[Fe(OX)_3]$

$K_2[CoF_4]$

$(NH_4)[Co(CO_3)Cl_2]$

$Na[Cr(en)(OX)_2]$

$K_3[Co(CN)_6]$

$Na_2[CoCl_6]$

$Na_2[PtCl_6]$

$[Cr(NH_3)_6][Cr(NO_2)_6]$

$K_4[Cr(CN)_5NO]$

$[Pt(en)_2(CO)_2]Cl_4$

$[Au(CN)_4C_2O_4]^{3-}$

$(NH_4)_2[MoO_4]$

$NH_4[Co(H_2O)_2(NO_3)_4]$

$[Fe(H_2O)_6]Cl_2$

$[Cr(en)_2(pn)_2]Cl_3$

$[Co(H_2O)_4Cl_2]_2SO_4$

$Fe_3[Fe(CN)_6]_2$

$K_2[Fe(CN)_4(H_2O)CNO]$

$[Pt^{II}(NH_3)_4][Pt(OX)_3]$

$[Ni(NH_3)_2Cl_2]$

$[Cr(NH_3)_4CO_3]_3PO_4$

$[Ag(NH_3)_2][AgOX]$

$[MnO_4]^-$

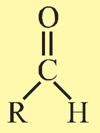
Unit

5

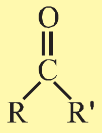
Aldehydes, Ketones and Carboxylic Acids

5.1 Introduction

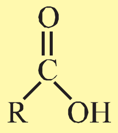
Organic compounds containing double bond ($>C=O$) between carbon and oxygen are called carbonyl compounds. In **aldehydes** the carbonyl group is attached to one hydrogen atom and one alkyl or aryl group, while in **ketones** it is attached to one alkyl and one aryl group or to two alkyl or two aryl groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as **carboxylic acids.** In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group, the compounds are known as **esters,** but if it is substituted by acyl group, the compounds are known as **acid anhydrides.** If the carbonyl group is attached to chloro and to amino group, the compounds are known as **acid chlorides** and **amides** respectively. The general formula of these compounds are as below :



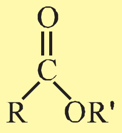
Aldehyde



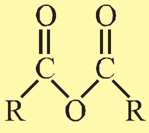
Ketone



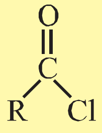
Carboxylic acid



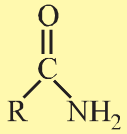
Ester



Anhydride



Acid chloride



Amide

Aldehydes and ketones have same general molecular formula $C_nH_{2n}O$, but have different functional groups, therefore, they **are called functional group isomers.** For example compounds having molecular formula C_3H_6O will be CH_3CH_2CHO which is aldehyde (functional group is aldehyde) and CH_3COCH_3 which is ketone (functional group is ketone).

5.2 Structure and Nomenclature of Carbonyl Group

Structure of Carbonyl Group : The $>C=O$ bond of carbonyl group in aldehyde and ketone is made up of one σ-bond and one π-bond. In the formation of carbonyl group compounds, the carbonyl carbon atom is sp^2 hybridised and forms three sp^2 hybrid orbitals. One of the sp^2 hybridised orbitals of carbon overlaps with p-orbital of oxygen atom forming a σ-bond between carbon and oxygen atom. The remaining two hybridised sp^2 orbitals of carbon atom, form additional two σ-bonds, either by overlapping with 1s-orbital of two hydrogen atoms as in formaldehyde or with 1s-orbital of one hydrogen atom and one sp^3 hybrid orbital of an alkyl group carbon in aldehydes other than formaldehyde or with two sp^3 hybrid orbitals of two alkyl groups carbon in ketones. All the three σ-bonds lie in the same plane and are inclined to one another at an angle 120^0 as shown in figure 5.1. The half-filled $2p_z$-orbital of carbon atom overlaps sideway with $2p_z$-orbital of oxygen atom to form a π-bond, and the electron cloud of the π-bond lies both above and below the C–O σ-bond. Thus, the carbonyl carbon and oxygen atoms and two atoms which are directly bonded to the carbonyl carbon lie in the plane as shown in figure. 5.1. This has been also confirmed by **electron diffraction** and **spectroscopic studies.**

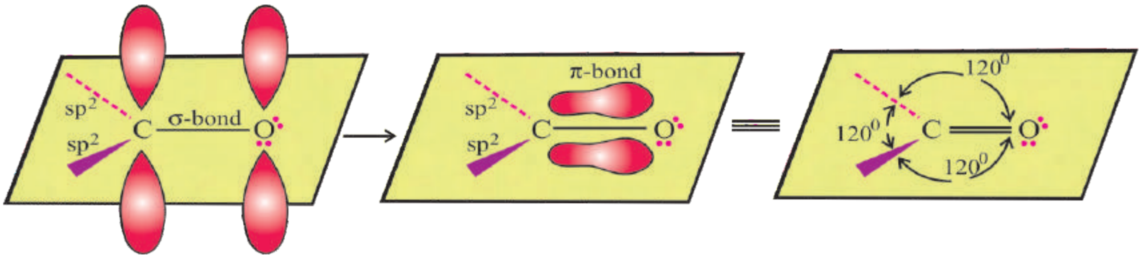


Fig 5.1 Orbital diagram for the formation of carbonyl group

Nature of carbonyl group : In carbonyl group the carbon-oxygen double bond is polarized due to higher electronegativity of oxygen atom relative to that of carbon atom. As a result the oxygen atom tends to attract the electron cloud of the π-bond towards itself as shown in figure 5.2. As a result the carbonyl carbon becomes an electrophile (Lewis acid) and oxygen becomes a nucleophile (Lewis base).

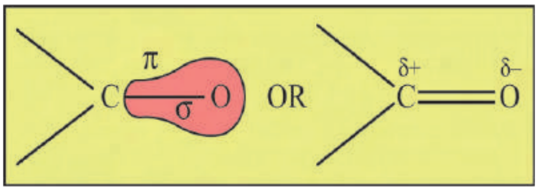
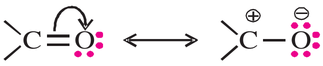


Fig 5.2 Electron cloud gets attracted more towards oxygen atom

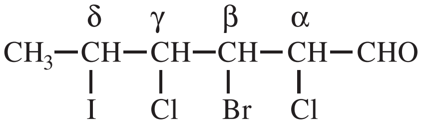
Thus the carbonyl group is **polar in nature.** Hence, such compounds have dipole moments. For example, aldehydes and ketones have 2.3-2.8 D dipole moments. The high polarity of the carbonyl group is explained on the basis of resonance structures shown below :



$$>C=\ddot{O}: \longleftrightarrow >\overset{\oplus}{C}-\overset{\ominus}{\ddot{O}}:$$

Nomenclature of carbonyl compounds :

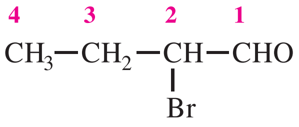
Aldehydes and ketones-IUPAC and Common names : The common names of aldehydes are obtained by replacing the terminal **"-ic acid"** by **"aldehyde"** from the common name of the corresponding carboxylic acid. For example, formic acid, acetic acid, benzoic acid; their corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively. In substituted aldehydes the positions of the substituents are indicated by Greek alphabets α, β, γ, δ etc. with the carbon atom next to the –CHO group being designated as α.

For example, 

$CH_3-\underset{I}{\overset{\delta}{CH}}-\underset{Cl}{\overset{\gamma}{CH}}-\underset{Br}{\overset{\beta}{CH}}-\underset{Cl}{\overset{\alpha}{CH}}-CHO$

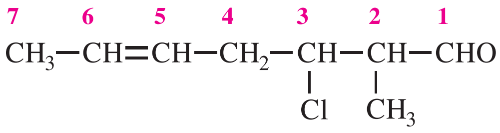
β-Bromo, α-γ dichloro, δ-iodo caproaldehyde

The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet **'e' from its name by - 'al'.** e.g., methane, a hydrocarbon-its corresponding aldehyde, HCHO and its IUPAC name is methanal. In substituted aldehydes the carbon chain containing aldehyde group, the position of the subsituents are indicated by numbers. The numbering of the substituted aldehyde carbon chain is done in such a way so that the aldehyde group at end of the chain gets number 1. For example,



$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{Br}{\overset{2}{CH}}-\overset{1}{CHO}$

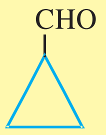
2-Bromobutanal



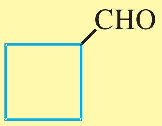
$\overset{7}{CH_3}-\overset{6}{CH}=\overset{5}{CH}-\overset{4}{CH_2}-\underset{Cl}{\overset{3}{CH}}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CHO}$

3-Chloro-2-methylhept-5-enal

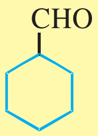
The IUPAC names of aliphatic cyclic aldehydes are given by adding **suffix carbaldehyde** after the full name of the cycloalkane. For example,



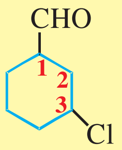
Cyclopropane
carbaldehyde



Cyclobutane
carbaldehyde

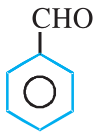


Cyclohexane
carbaldehyde

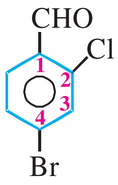


3-Chlorocyclo
hexanecarbaldehyde

The IUPAC names of aromatic aldehyde compounds - like aldehyde group on benzene ring are given by benzenecarbaldehyde (or benzaldehyde) and the position of the substituents are indicated by numbering, starting from the carbon having –CHO group. For example,



Benzenecarbaldehyde OR
benzaldehyde



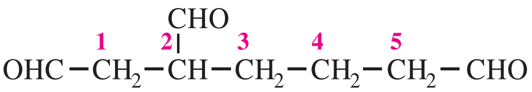
4-Bromo-2-chlorobenzene carbaldehyde
OR 4-bromo-2-chlorobenzaldehyde

When two aldehyde groups are linked to carbon chain then only such aliphatic compounds are named which includes the functional group in calculation of carbon numbers and suffix ‘dial’ is added. For example,

$OCH-CH_2-CH_2-CHO$ Butanedial

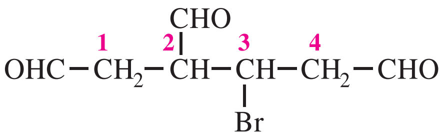
$OCH-CH_2-CH_2-CH_2-CH_2-CHO$ Haxanedial

When more than two aldehyde groups are linked to carbon chain then such compounds are named as a derivative of the hydrocarbon which does **not include the carbon atoms of the functional groups.** For example,



$$OHC-\overset{1}{CH_2}-\overset{\overset{CHO}{2|}}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-CHO$$

Pentane-1,2,5-tricarbaldehyde

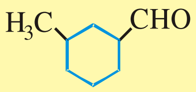
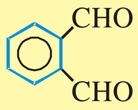
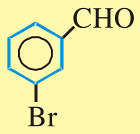


$$OHC-\overset{1}{CH_2}-\overset{\overset{CHO}{2|}}{CH}-\overset{3}{\underset{\underset{Br}{|}}{CH}}-\overset{4}{CH_2}-CHO$$

3-Bromobutane-1,2,4-tricarbaldehyde

The common and IUPAC names of the aldehydes are given in table 5.1

Table 5.1 Common and IUPAC names of some aldehydes

Structure	**Common name**	**IUPAC name**
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanal	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
CH_2=CHCHO	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde

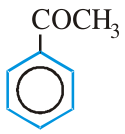
The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl groups (in the alphabetical order) attached to the ketone group as two separate words and adding the suffix ketone. If both the attaching groups are same the **prefix di is used.** For example,

CH_3COCH_3

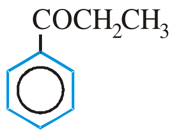
Dimethylketone

$CH_3COCH_2CH_3$

Ethylmethylketone



Methylphenylketone



Ethylphenylketone

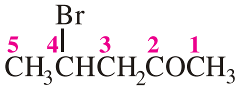
The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet **'e' by the suffix 'one'.** For substituted ketones the positions of the substituents are indicated by numbering the chain in such a way that the keto group gets the lowest number. For example,

CH_3COCH_3

Propan-2-one

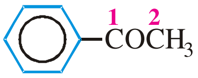
OR

Propanone

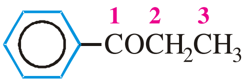


$\overset{5}{C}H_3\overset{\overset{Br}{|}}{\overset{4}{C}}H\overset{3}{C}H_2\overset{2}{C}O\overset{1}{C}H_3$

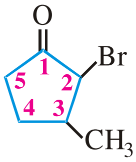
4-Bromopentan-2-one



1-Phenylethan-1-one



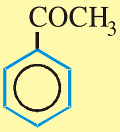
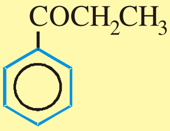
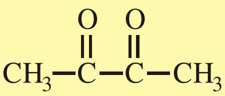
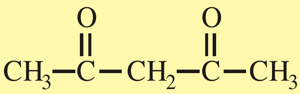
1-Phenylpropan-1-one



2-Bromo-3-methylcyclopentanone

The common and IUPAC names of the ketones are given in table 5.2

Table 5.2 Common and IUPAC names of some ketones

Structure	Common name	IUPAC name
$CH_3COCH_2CH_2CH_3$	Methyl n-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one
	Methylphenylketone OR Acetophenone	1-Phenylethan-1-one
	Ethyl phenyl ketone	1-Phenylpropan-1-one
 $CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-CH_3$	Biacetyl	Butane-2,3-dione
 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	Acetyl acetone	Pentane-2,4-dione

5.3 Physical Properties of Aldehydes and Ketones

Aldehydes and ketones possess polar carbonyl group and hence exhibit weak intermolecular association due to **dipole-dipole** interactions between the opposite ends of the $>C=O$ dipoles.

Intermolecular dipole-dipole attraction

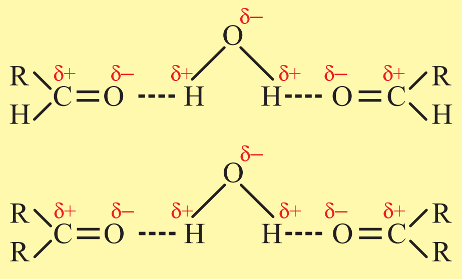
So, the boiling points of aldehydes and ketones are a little higher than non-polar compounds like hydrocarbons and weakly polar compounds like ethers of comparable molecular mass. The boiling points of aldehydes and ketones are lower than those of alcohols and carboxylic acids of comparable molecular mass because in carboxylic acid and alcohol molecules there exists an intermolecular hydrogen bonding which is stronger than dipole-dipole interaction. Among the isomeric aldehydes and ketones, the ketones have slightly higher boiling points. This happens due to the presence of two electron-donating alkyl groups around the carbonyl group which makes them more polar, so the order of boiling points is **carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde > ether > hydrocarbon.**

The boiling points of comparable molecular mass of the following compounds are given in table 5.3.

Table 5.3 Boiling points of some organic compounds

Compound	Boiling point (K)	Molecular mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Propanone	329	58
Propan-1-ol	370	60
Ethanoic acid	391	60

The lower members of aldehydes and ketones upto three carbon atoms such as methanal, ethanal, propanal and propanone are soluble in water due to hydrogen bond formation between the polar carbonyl group and the water molecules.



Hydrogen bonding of aldehyde and ketone with water molecules

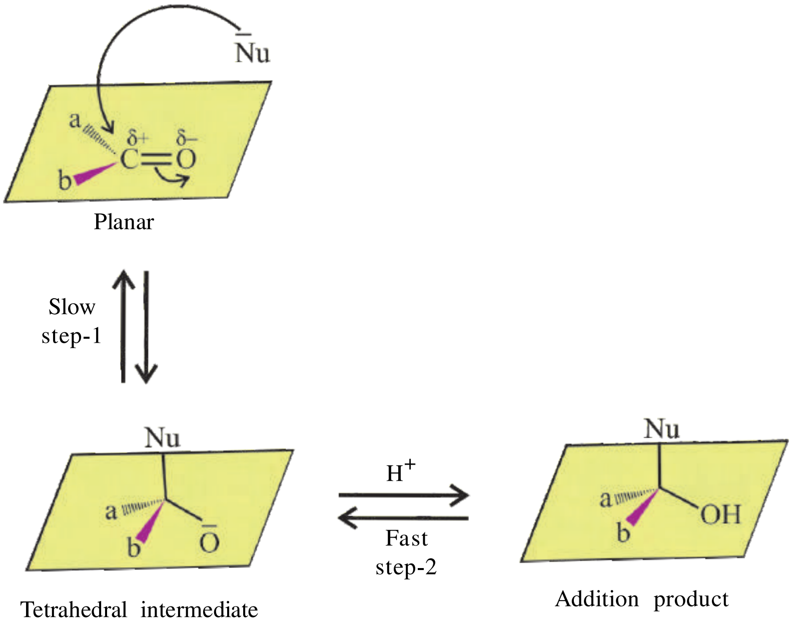
But the solubility of aldehydes and ketones in water decreases rapidly with the increase in length of alkyl chains. Similarly the solubility of aromatic aldehydes and ketones is much lower than their corresponding aliphatic aldehydes and ketones due to the presence of larger hydrocarbon parts (like benzene ring etc.). However all aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohol, chloroform etc. The lower aldehydes have strong pungent odours, but as the size of the aldehyde molecules increases the odour becomes less pungent and more fragrant. However, the ketones are generally in liquid forms having pleasant smell. A number of naturally occurring aldehydes and ketones are used in the preparation and blending of perfumes and as flavouring agents.

5.4 Chemical Reactions of Aldehydes and Ketones

Aldehydes and ketones have the same functional group i.e. polarized carbonyl group. So they undergo similar chemical reactions. However, the presence of a hydrogen atom on the carbonyl group of aldehydes makes them much **more reactive than ketones.** This hydrogen atom is responsible for many reactions of aldehydes and thus they differ from ketones. Some chemical reactions of aldehydes and ketones are as follows :

(i) Nucleophilic addition reactions : Aldehydes and ketones have the carbonyl group containing double bond and so they can undergo addition reactions. Alkenes have $>C=C<$ and they undergo electrophilic addition reactions, while the aldehydes and ketones undergo nucleophilic addition reactions because the **carbonyl group is polar and the carbon atom is slightly positively charged which is readily attracted by the nucleophile.**

The mechanism of nucleophilic addition reactions : The structure of carbonyl group is planar and it is polar, so the nucleophile is attracted to the positively charged carbon atom of carbonyl group either from above or below the plane of sp^2 hybridised orbital of carbonyl group. So it results in formation of an anion (tetrahedral alkoxide) by the complete transfer of π-electrons of the carbon-oxygen double bond to the oxygen atom. During this process, the hybridisation of carbon atom changes from sp^2 to sp^3 and hence, the oxygen atom gets pushed out of the plane of the carbonyl group and **form new carbon nucleophile (Nu) bond which is slow step so, it is the rate determining step and it is also reversible.** In the second step the proton (which is obtained from weak acidic medium) gets attracted by oxygen of carbonyl group (tetrahedral alkoxide) and the electrically neutral product is formed. **The second step is also reversible.**



Relative reactivities of aldehydes and ketones : Aldehydes are generally more reactive than corresponding ketones in nucleophilic addition reaction, due to the following reasons.

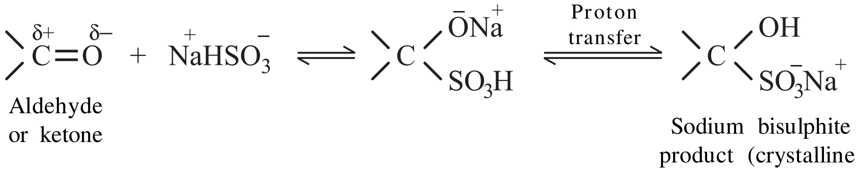
(i) Steric effects : As the number and size of the alkyl group attached to the carbonyl group increases, the attachment of nucleophile on the carbonyl group carbon becomes more and more difficult, due to **steric hinderance** (crowding) i.e. **as the crowding increases, the reactivity of carbonyl group compound decreases,** so the reactivity of formaldehyde is more as there is no alkyl group, while the other aldehydes having one alkyl group the reactivity is less compared to formaldehyde while ketones having two alkyl groups, the reactivity is less than the corresponding aldehydes.

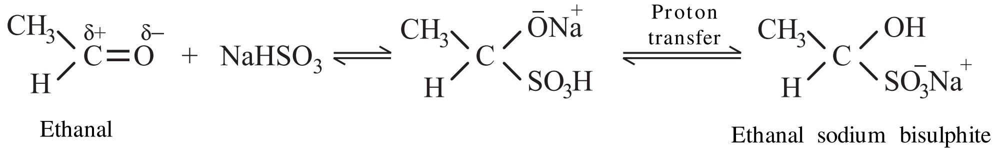
(ii) Inductive effect : The attachment of nucleophile on the carbonyl group depends upon the magnitude of the positive charge on the carbonyl carbon. The alkyl group **electron donating and hence has inductive effect (+I effect).** So more the number of alkyl groups on carbonyl carbon, **the magnitude of the positive charge on carbonyl carbon decreases,** which lowers the reactivity towards nucleophilic addition reactions. Therefore formaldehyde is **more reactive** compared to other aldehydes and ketones which are less reactive than aldehydes.

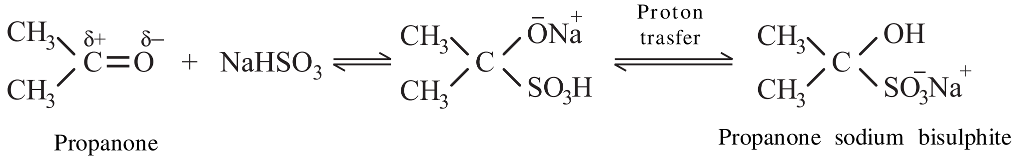
The aromatic aldehydes and ketones are **less reactive** than aliphatic aldehydes and ketones because the electron-donating resonance effect of benzene ring which **increases the electron density on carbonyl carbon,** hence it gets repelled by the nucleophiles. The aromatic aldehyde (like benzaldehyde) is more reactive than alkyl aryl ketone (like acetophenone) while diaryl ketones (like benzophenone) is less reactive than alkyl aryl ketone.

Nucleophilic addition reactions :

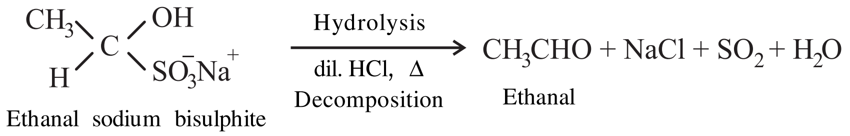
(i) Addition of sodium hydrogen sulphite ($NaHSO_3$) : Due to less steric hindrance most of the aldehydes and aliphatic methyl ketones, react with sodium hydrogen sulphite and form additive compounds, while the acetophenone does not react.

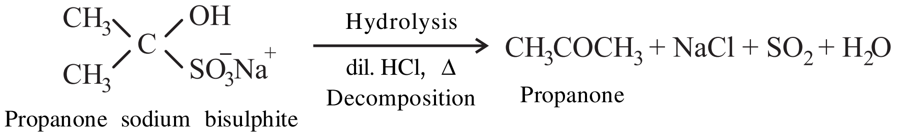






The proton transfer equilibrium lies more towards the **right side for most of the aldehydes and to the left side for most of the ketones.** The bisulphite product obtained, are usually crystalline solids. If they are heated with dilute mineral acids or aqueous alkalies they decompose, due to hydrolysis and regenerate the original aldehyde or ketone.

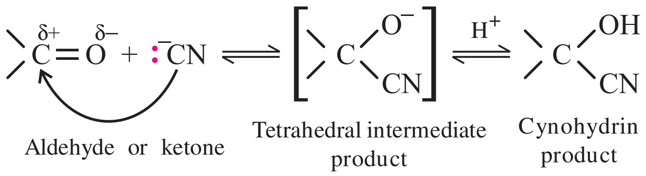


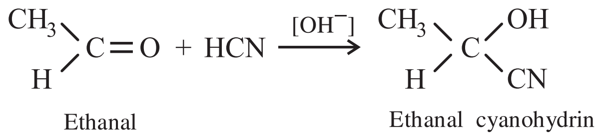


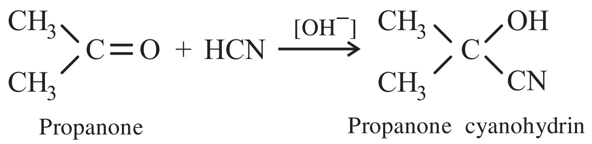
Therefore, this reaction is useful for separation and purification of aldehydes and ketones from non-carbonyl compounds.

(ii) Addition of Hydrogen cyanide (HCN) : The aldehydes and ketones react with hydrogen cyanide and give product cyanohydrins. The reaction is extremely slow and so it is carried out in **presence of base which acts as a catalyst.** The reaction occurs very slowly with pure HCN but in presence of base (as a catalyst) the $:^{-}CN$ is generated which is a stronger nucleophile and gets added readily to carbonyl compounds and the product cyanohydrin is obtained. For example,

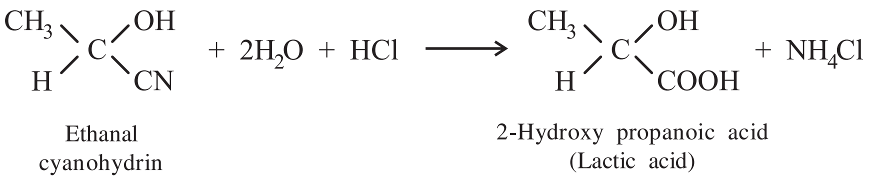
$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$





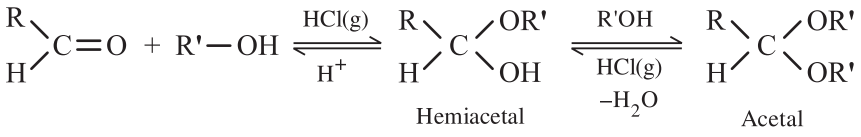


Cyanohydrins are important synthetic substances because they can be readily hydrolysed to give 2-hydroxy acids.

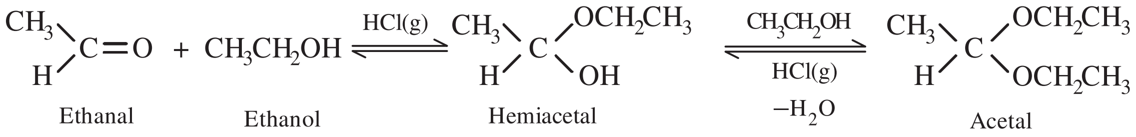


(iii) Addition of Grignard reagent : Aldehydes and ketones react with Grignard reagent to form nucleophilic addition compounds. This intermediate product upon hydrolysis with water or dilute mineral acid gives 1^0, 2^0 or 3^0 alcohols. This you have studied in unit 7 of Semester III.

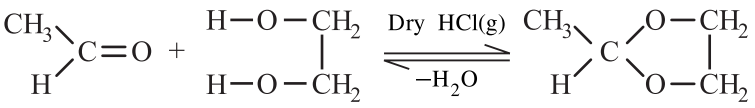
(iv) Addition of alcohols : Aldehyde reacts with one equivalent of monohydric alcohol in presence of dry hydrogen chloride to yield alkoxy alcohol intermediate known **as hemi acetal** (hemi means half). Being unstable it immediately reacts with one more molecule of alcohol to form stable gem-di alkoxy compound **known as acetal.**



Dry hydrogen chloride protonates the oxygen of aldehyde (carbonyl compound) hence the density of positive charge on carbonyl carbon increases i.e. the electropositivity of carbonyl carbon increases, which **facilitates the nucleophilic attachment.** Dry HCl gas absorbs the water molecules which is produced during acetal formation and shifts the equilibrium in the forward direction. For example,

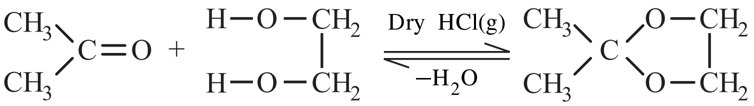


Instead of two molecules of monohydric alcohol in presence of dry hydrogen chloride or paratoluene sulphonic acid (PTS), one molecule of dihydric alcohol such as ethane-1, 2-diol (ethylene glycol) is used, then cyclic acetal (ethylene glycol-acetal) is formed.



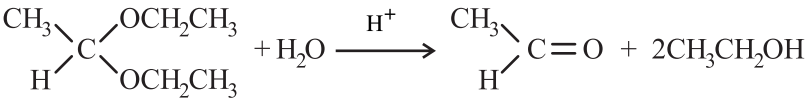
Ethanal   Ethane-1-2-diol   Cyclic acetal

Ketones do not react with monohydric alcohols but react with dihydric alcohols in presence of dry hydrogen chloride or PTS and give **cyclic ketals.** For example,

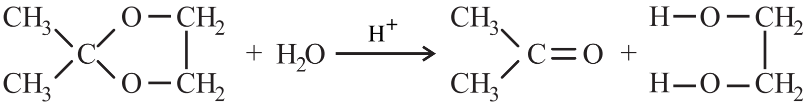


Propanone   Ethylene glycol   Cyclic ketal (Ethylene glycol ketal)

In the formation of acetals and ketals the reactions are reversible; so they are decomposed by dilute acid and the aldehydes and ketones are regenerated. For example,



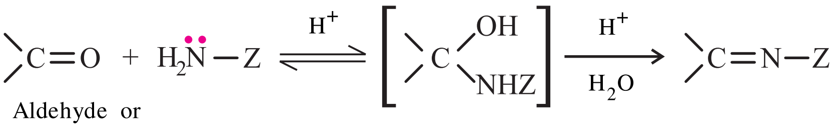
Acetal   Ethanal   Ethanol



Ketal   Propanone   Ethylene glycol

Nucleophilic addition reactions followed by elimination of a molecule of water :

(v) Addition of ammonia and its derivatives : Aldehydes and ketones react with ammonia ($\ddot{N}H_3$) and its derivatives ($H_2\ddot{N}-Z$). The reaction is catalysed by acid, hence the carbonyl groups gets protonated, so the positive charge on carbonyl carbon is increased and as a result the weak nucleophile like ammonia and its derivatives readily attach to the carbonyl group. For example,

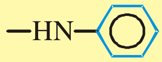
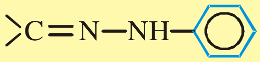
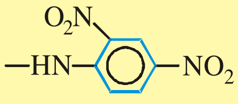
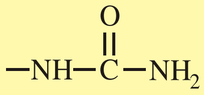
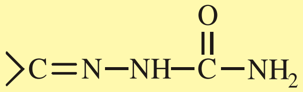


Aldehyde or ketone   Intermediate   Product

The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$. The $\ddot{N}H_3$ and its N–substituted derivatives and product are given in table 5.4

Table 5.4 Some N-Substituted Derivatives of Aldehydes and Ketones

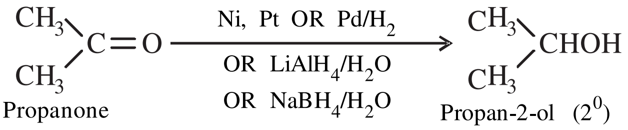
Z	Reagent's name	Carbonyl derivative	Product's name
–H	Ammonia	$>C=NH$	Imine
–R	Amine	$>C=NR$	Substituted imine (Schiff's base)
–OH	Hydroxylamine	$>C=N-OH$	Oxime

$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2,4-Dinitrophenyl hydrazine		2,4-Dinitrophenyl hydrazone
 $-NH-\overset{O}{\overset{\parallel}{C}}-NH_2$	Semicarbazide	 $>C=N-NH-\overset{O}{\overset{\parallel}{C}}-NH_2$	Semicarbazone

Reduction reactions of aldehydes and ketones :

(i) Reduction to alcohols : Aldehydes and ketones on **reduction give 1^0 and 2^0 alcohols** respectively. Reduction is carried out either catalytically with H_2 in presence of Ni, Pt or Pd or chemically by lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). $LiAlH_4$ is a much more powerful reducing agent than $NaBH_4$.

$$\underset{\text{Methanal}}{HCHO} \xrightarrow[\text{OR } LiAlH_4/H_2O \text{ OR } NaBH_4/H_2O]{\text{Ni, Pt OR Pd}/H_2} \underset{\text{Methanol } (1^0)}{CH_3OH}$$



(isopropyl alcohol)

(ii) Reduction to hydrocarbons : The carbonyl group of aldehydes or ketones is reduced to **methylene ($-CH_2-$) group** to form hydrocarbon by using different reducing agents.

(a) Wolff-Kishner reduction : Aldehyde or ketone is heated with hydrazine (NH_2NH_2) and KOH in high boiling solvent like ethylene glycol which results **into formation of hydrocarbon.** For example,

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[-H_2O]{NH_2NH_2} CH_3CH{=}NNH_2 \xrightarrow[\text{KOH 453-473 K}]{\text{Ethylene glycol}} \underset{\text{Ethane}}{CH_3CH_3} + N_2$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[\text{4[H] Ethylene-glycol 453-473 K}]{NH_2NH_2,\ \text{KOH}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + N_2$$

(b) Clemmensen reduction : Aldehyde or ketone is **reduced to hydrocarbon,** on treatment with zinc amalgam and concentrated hydrochloric acid. For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + 4[H] \xrightarrow[\text{Con. HCl}]{\text{Zn-Hg}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O$$

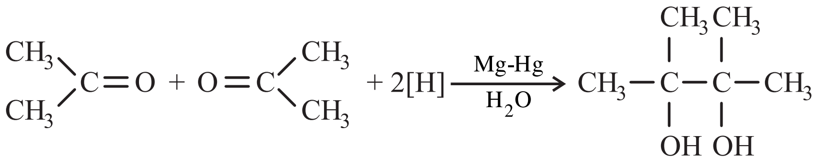
$$\underset{\text{Propanone}}{CH_3COCH_3} + 4[H] \xrightarrow[\text{Con. HCl}]{\text{Zn-Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

(c) Reduction with HI and Red P : Aldehyde or ketone when heated with hydroiodic acid and red phosphorus **is reduced to hydrocarbon.** For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + 4HI \xrightarrow[423\ K]{\text{Red P}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O + 2I_2$$

$$\underset{\text{Propanone}}{CH_3COCH_3} + 4HI \xrightarrow[423\ K]{\text{Red P}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$$

(iii) Reduction to pinacols (Bimolecular reduction) : Ketones on reduction with magnesium amalgam and water form **pinacol.** For example,



Propanone Propanone

2, 3-Dimethyl-butane-2,3-diol (Pinacol)

Oxidation of aldehydes and ketones : Aldehydes are easily oxidized to carboxylic acids containing the same number of carbon atoms, because of the presence of hydrogen atom on carbonyl group which is converted to –OH group, without involving the cleavage of any other bond. So they easily **get oxidized by both strong and weak oxidizing agent.** While ketones can be oxidized by powerful oxidizing agent only, because during oxidation carbon-carbon bond cleavage results into mixture of carboxylic acids, each containing less number of carbon atoms than the original ketone. The mild oxidizing agents given below are used to distinguish aldehydes from ketones.

Oxidation of aldehydes :

(i) Tollens' test : Aldehyde and freshly prepared ammoniacal silver nitrate solution (Tollens' reagent) when gently warmed, the aldehyde is oxidized to carboxylate ion, Tollens' reagent is reduced to metallic silver which gets deposited on the inner wall of test-tube giving shining surface like mirror. Hence this test is also **known as silver mirror test.** Aromatic and aliphatic aldehydes are both oxidized by Tollens' reagent. **In laboratory the aldehydes can be detected by Tollens' test.**

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

(ii) Fehling's test : Fehling solution A ($CuSO_4$ solution) and Fehling solution B (alkaline solution of sodium potassium tartarate-Rochelle salt) are mixed in equal proportion and the mixture is heated with aldehyde, gives **red precipitate of cuprous oxide.** This test is **known as Fehling's test.** This test is only for aliphatic aldehydes because the **aromatic aldehydes are not reduced by the Fehling solution. In laboratory the aldehydes can be detected by Fehling's test.**

$$RCHO + 2Cu^{2+} + 5OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{Red ppts}}{Cu_2O} + 3H_2O$$

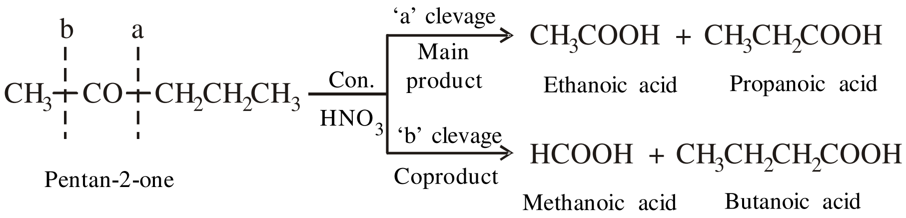
(iii) Benedict's test : This test is similar to Fehling's test but instead of tartarate ions the citrate ions were used. The reaction is same and this test is also not given by aromatic aldehydes.

Oxidation of ketones :

(i) By strong oxidizing agents : The ketones are oxidized by strong oxidizing agents like con. HNO_3, $KMnO_4 / H_2SO_4$, $K_2Cr_2O_7 / H_2SO_4$ etc. and give mixture of carboxylic acids. **Symmetrical ketones give mixture of two carboxylic acids.** For example,

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3[O] \xrightarrow[+ H_2SO_4]{K_2Cr_2O_7} \underset{\substack{\text{Ethanoic}\\\text{acid}}}{CH_3COOH} + \underset{\substack{\text{Methanoic}\\\text{acid}}}{HCOOH} \xrightarrow{[O], \Delta} \underset{\substack{\text{Ethanoic}\\\text{acid}}}{CH_3COOH} + CO_2 + H_2O$$

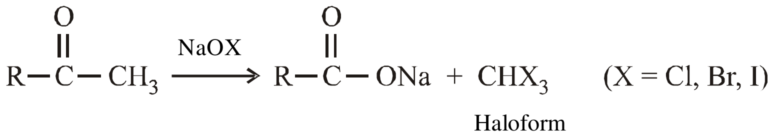
Unsymmetrical ketone gives mixture of four carboxylic acids. For example,



In case of unsymmetrical ketones, the keto group stays preferentially with the smaller alkyl group and is the main product and this is known as Popoff's rule.

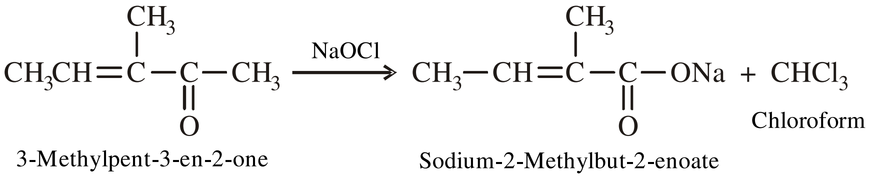
(ii) Oxidation with sodium hypohalide (NaOX or X_2 + NaOH) (Iodoform test) :

Aldehydes or ketones containing $CH_3CO–$ group, when treated with an excess of halogen in presence of alkali give haloform. For Example,



$$R-\overset{\overset{\large O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{\large O}{\|}}{C}-ONa + \underset{\text{Haloform}}{CHX_3} \qquad (X = Cl, Br, I)$$

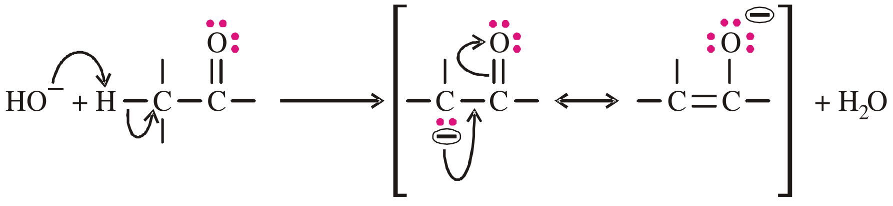
During halo formation reaction, if carbon-carbon double bond is present in the molecules, the double bond is not oxidized; hence, double bond remains unaffected. For example,



$$\underset{\text{3-Methylpent-3-en-2-one}}{CH_3CH=\overset{\overset{\large CH_3}{|}}{C}-\underset{\underset{\large O}{\|}}{C}-CH_3} \xrightarrow{NaOCl} \underset{\text{Sodium-2-Methylbut-2-enoate}}{CH_3-CH=\overset{\overset{\large CH_3}{|}}{C}-\underset{\underset{\large O}{\|}}{C}-ONa} + \underset{\text{Chloroform}}{CHCl_3}$$

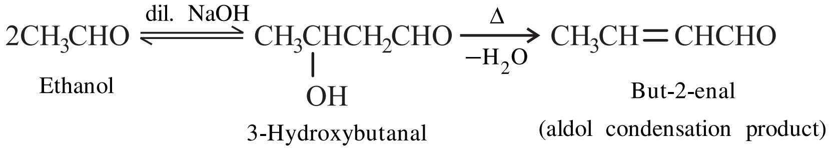
Reaction due to α–hydrogen of aldehydes and ketones :

The hydrogen atoms present on the carbon atom next to the carbonyl group of aldehydes and ketones are called α–hydrogen atoms, and the acidity of α–hydrogen atom is due to electron with-drawing, inductive effect of the carbonyl group and also due to resonance stabilization of the conjugate base (enolate ion).



Due to acidity of α–hydrogen of aldehydes and ketones, they undergo a number of reactions such as aldol condensation, cross aldol condensation etc.

(i) Aldol condensation : In this reaction, two same molecules of an aldehyde or ketone, having **atleast one α–hydrogen atom** undergo a reaction in presence of dilute alkali (dil. NaOH, Na_2CO_3, $Ba(OH)_2$ etc.) to form β–hydroxy aldehyde (Aldol) or β–hydroxy ketone (Ketol) respectively. This reaction is **known as aldol condensation reaction.** The name aldol is derived from the name of two functional groups aldehyde and alcohol present in the product. Same way ketol is derived from two functional groups of ketone and alcohol present in the product. The aldol and ketol readily lose water molecule to give α–β unsaturated carbonyl compounds which are aldol condensation product and the reaction is called aldol condensation. For example,

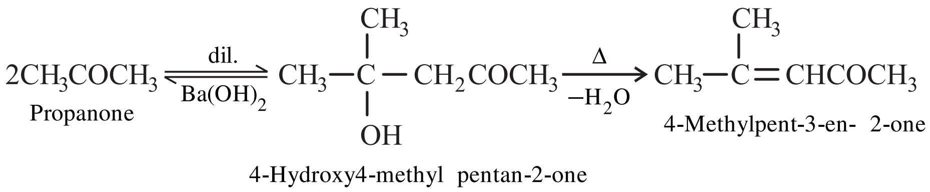


$$2CH_3CHO \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO \xrightarrow[-H_2O]{\Delta} CH_3CH{=}CHCHO$$

Ethanol

3-Hydroxybutanal

But-2-enal
(aldol condensation product)



$$2CH_3COCH_3 \underset{Ba(OH)_2}{\overset{\text{dil.}}{\rightleftharpoons}} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\displaystyle CH_3}{C}{=}CHCOCH_3$$

Propanone

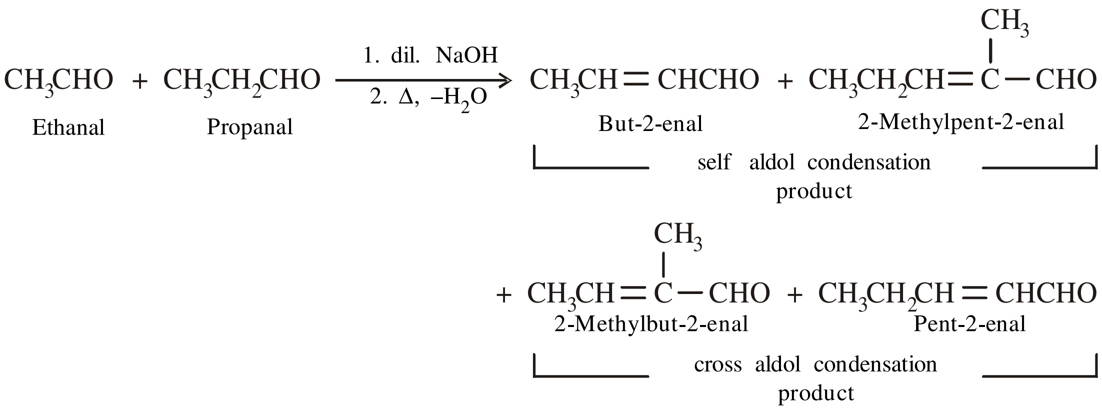
4-Hydroxy4-methyl pentan-2-one

4-Methylpent-3-en- 2-one

Formaldehyde, benzaldehyde and benzophenone do not undergo aldol condensation since they do not have an α–hydrogen atom.

(ii) Cross-aldol condensation : An aldol condensation between **two different aldehydes or two different ketones or between one aldehyde and one ketone is called cross aldol condensation** and gives mixture of four products which are difficult to separate. So cross aldol condensations are of little synthetic value. However, if one carbonyl compound does not possess α–hydrogen atom then cross aldol condensations are of great synthetic utility. e.g.,

(I)



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta,\ -H_2O]{1.\ \text{dil. NaOH}} \underbrace{CH_3CH{=}CHCHO + CH_3CH_2CH{=}\overset{\displaystyle CH_3}{C}-CHO}_{\text{self aldol condensation product}}$$

$$+ \underbrace{CH_3CH{=}\overset{\displaystyle CH_3}{C}-CHO + CH_3CH_2CH{=}CHCHO}_{\text{cross aldol condensation product}}$$

Ethanal Propanal

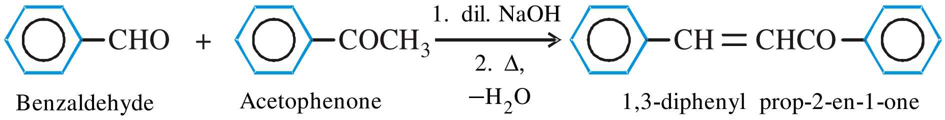
But-2-enal 2-Methylpent-2-enal

self aldol condensation product

2-Methylbut-2-enal Pent-2-enal

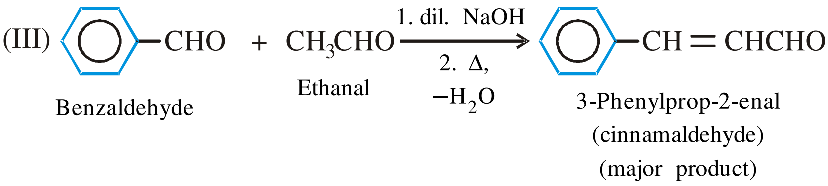
cross aldol condensation product

(II)



Benzaldehyde Acetophenone

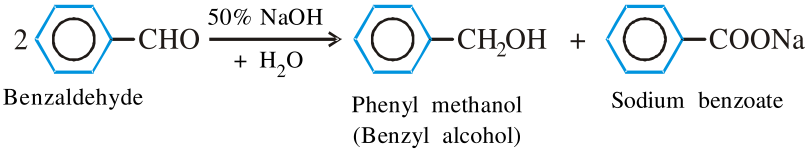
1,3-diphenyl prop-2-en-1-one
(major product)



(iii) Cannizzaro reaction : Aldehydes which do not have an α–hydrogen atom, when treated with concentrated alkali solution, undergo **disproportionation,** i.e., self-oxidation and reduction occur. One molecule of aldehyde is reduced to the corresponding alcohol, at the cost of the other molecule of aldehyde which is oxidized to the corresponding carboxylic acid salts. This reaction is called **Cannizzaro** reaction. For example,

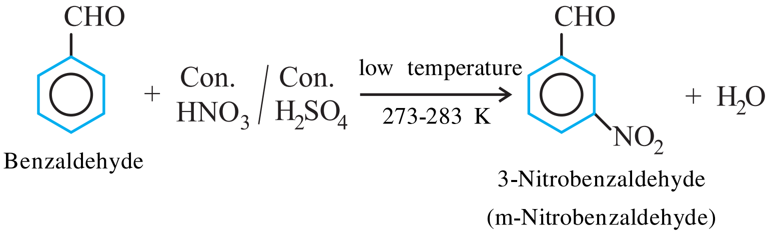
$$2HCHO \xrightarrow[\text{or con. KOH} \atop + H_2O]{50\ \%\ NaOH} CH_3OH + HCOONa\ (\text{or}\ \ HCOOK)$$

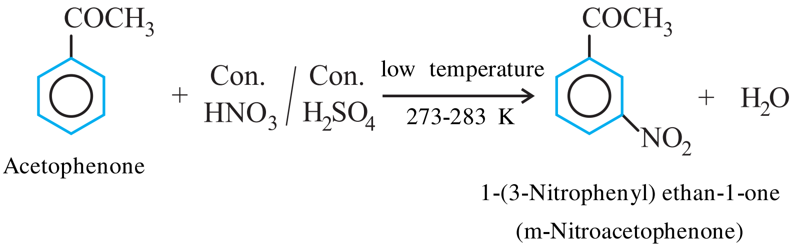
Methanal Methanol Sodium formate



Electrophilic substitution reactions of aromatic aldehydes and ketones :

Nitration : Aromatic aldehydes and ketones undergo the electrophilic substitution reactions of the benzene nucleus. Since the aldehyde and ketone functional groups are electron withdrawing groups and so act as deactivating group and hence act as meta-directing group. So substitution occurs at meta-position. For example,





Substitution reactions like halogenation, sulphonation also occur at m-position.

5.5 Uses of Aldehydes and Ketones

In chemical industry, aldehydes and ketones are used as solvents, starting materials and reagents, for the synthesis of other products. **Formaldehyde** is used in manufacturing of bakelite, resins and other polymers. A 40% solution of formaldehyde in water is called **formalin** which is used for the preservation of dead bodies of animals of biological or anatomical specimens. It is also used as a disinfectant and germicide. Formaldehyde is used in leather industry. Acetaldehyde is used for giving the shining like silver to mirror. Benzaldehyde is used as a flavouring agent in perfume industry and is also used in manufacturing of dye like malachite green. Acetone is used in manufacturing liquid nail polish and also as nail polish remover. Acetone and methylethyl ketone are common industrial solvents. Some aldehydes and ketones for example butyraldehyde, vanillin, acetophenone, camphor etc. are well-known for their odours and flavours.

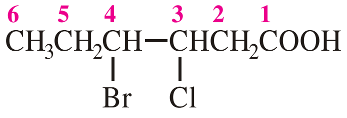
5.6 Corboxylic Acids

Organic compounds containing –COOH as the functional group are called carboxylic acids. The –COOH group is made up of a carbonyl group ($\rangle C=O$) and hydroxyl group (–OH). So 'Carb' from carbonyl and 'oxyl' from hydroxyl, hence –COOH is called carboxyl group. The –COOH attaches to aliphatic alkyl (or hydrogen atom) or aromatic group, and according to that it may be aliphatic or aromatic carboxylic acid. Aliphatic or aromatic carboxylic acids have one or more than one –COOH groups. A large number of carboxylic acids are found in nature. Higher numbers (C_{12} to C_{18}) of aliphatic acids occur in nature known **as fatty acids,** which occur in natural fats as triesters of glycerol. Carboxylic acid serves as starting material for preparing a number of other important compounds such as acid chloride, acid anhydride, ester, amide etc.

5.7 Common and IUPAC Nomenclature of Carboxylic Acids

The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (Plant or animal product) from which they were first isolated. For example, formic acid was first obtained by distillation of red ants (Latin : formica means red ant). The acetic acid (Latin: acetum means vinegar). The butyric acid (Latin : butyrum means butter) and caprylic, caproic and capric acids (Latin : caper means goat).

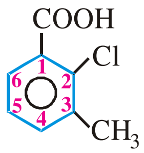
The IUPAC names of the saturated monocarboxylic acids are given by replacing the ending alphabet -'e' in the name of the corresponding hydrocarbon with the suffix **'-oic acid'.** For the naming of substituted and branched chain acids, select the –COOH group containing longest chain. The positions of the substituents are indicated by **numbering the carboxylic carbon as number one.** For Example,



$$\overset{6}{C}H_3\overset{5}{C}H_2\underset{\underset{Br}{|}}{\overset{4}{C}H}-\underset{\underset{Cl}{|}}{\overset{3}{C}H}\overset{2}{C}H_2\overset{1}{C}OOH$$

4-Bromo-3-chlorohexanoic acid

The IUPAC names of aromatic monocarboxylic acids are derived by benzene carboxylic acid or benzoic acid and the position of the substituents are indicated by **number with carbon atom carrying** –COOH group being numbered one. For example,

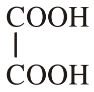


The IUPAC name is 2-Chloro-3-methyl benzene carboxylic acid

OR

2-Chloro-3-methylbenzoic acid

Aliphatic or aromatic carboxylic acid **having more than one –COOH** groups are named as di, tri, tetra... and polycarboxylic acids, according to two, three, four.... and many carboxyl groups present in respective molecules. In case of aliphatic dicarboxylic acids the position of –COOH groups are not indicated, but in case of aromatic dicarboxylic acid and other carboxylic acids, the position of the –COOH groups are indicated by the number and the numbers are indicated before the multiplicative prefix. **The ending -'e' of the hydrocarbon is retained in carboxylic acid having more than one** –COOH groups. For example,

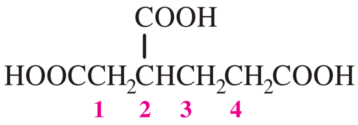


$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

Ethane dioic acid

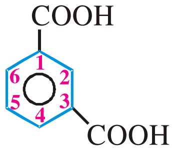
$HOOCCH_2CH_2CH_2COOH$

Pentane dioic acid



$$\overset{\displaystyle \mathrm{COOH}\atop |}{\underset{1\ \ 2\ \ 3\ \ 4}{\mathrm{HOOCCH_2CHCH_2CH_2COOH}}}$$

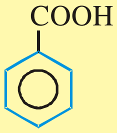
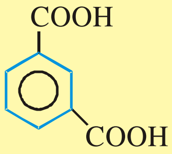
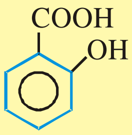
Butane-1,2,4-tricarboxylic acid



Benzene-1,3-dicarboxylic acid

Common and IUPAC names of some carboxylic acids are given in table 5.5.

Table 5.5 Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
HOOC–COOH	Oxalic acid	Ethanedioic acid
$HOOC–CH_2COOH$	Malonic acid	Propanedioic acid
$HOOC–(CH_2)_2–COOH$	Succinic acid	Butanedioic acid
$HOOC–(CH_2)_3–COOH$	Glutaric acid	Pentanedioic acid
$HOOC–(CH_2)_4–COOH$	Adipic acid	Hexanedioic acid
$HOOC–CH_2–CH(COOH)CH_2COOH$	–	Propane-1,2,3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid OR Benzoic acid
	Isophthalic acid	Benzene-1,3-dicarboxylic acid
	Salicylic acid	2-Hydroxybenzenecarboxylic acid OR 2-Hydroxybenzoic acid

5.8 Structure of Carboxylic Group

In carboxylic acid compounds the carbon atom of carboxyl group is attached to one oxygen atom by single bond and another by double bond, but **electron and neutron diffraction studies** have proved that –COOH has planar structure having angle of about 120^0, so the two oxygen atoms are sp^2

hybridised. The π electrons of double bond are delocalized between carbon and oxygen bond as shown in figure 5.6.

Here, σ and π bond between carbon and oxygen, carbon and both oxygen atoms are sp^2 hybridised R–C–O and O–C–O angle 120^0.

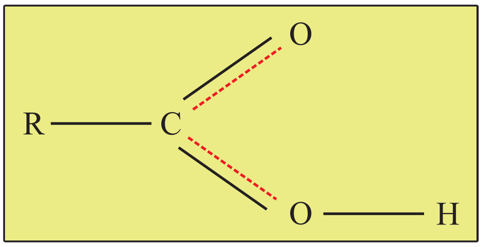


Fig 5.6

5.9 Methods of Preparation of Carboxylic Acids

Some important general methods of preparation of carboxylic acid are as follows :

(i) From primary alcohols and aldehydes : The primary alcohols are readily oxidized to the corresponding carboxylic acids with common oxidizing agents such as $KMnO_4$ in **neutral, acidic or alkaline medium** or by $K_2Cr_2O_7$ or CrO_3 (chromium trioxide) in acidic medium. Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic medium often give some amount of esters. Therefore the oxidation with $KMnO_4$ is preferred. Under these conditions the potassium salts of the carboxylic acid is first obtained, which on treatment with dil H_2SO_4 gives carboxylic acids. For example,

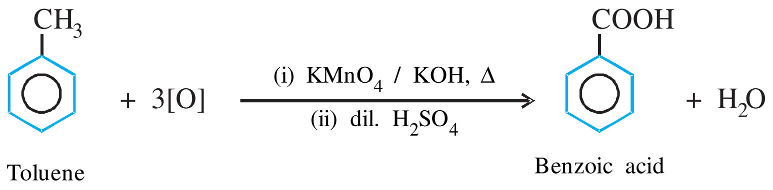
$$\underset{\text{Ethanol}}{3CH_3CH_2OH} + 4KMnO_4 \rightarrow \underset{\text{Potassium ethanoate}}{3CH_3COOK} + KOH + 4MnO_2 + 4H_2O$$

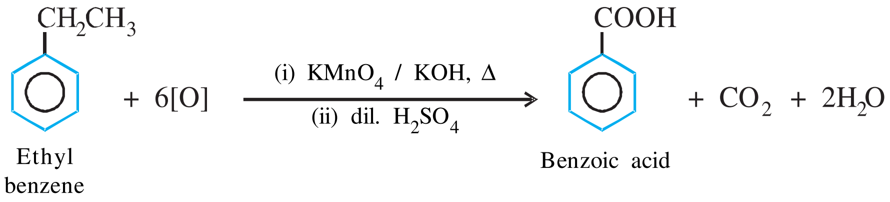
$$\underset{\text{Potassium ethanoate}}{2CH_3COOK} + H_2SO_4 \rightarrow \underset{\text{Ethanoic acid}}{2CH_3COOH} + K_2SO_4$$

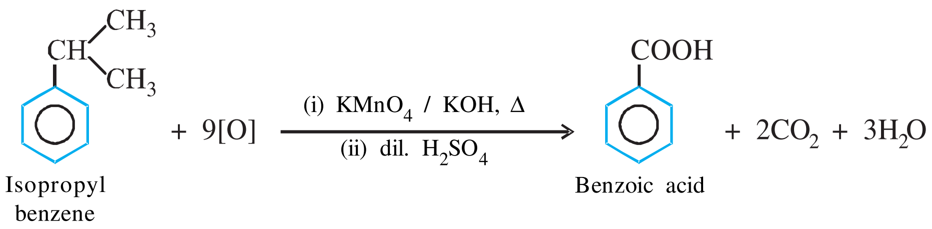
$$\underset{\text{Heptanol}}{CH_3(CH_2)_6OH} \xrightarrow{CrO_3\ /\ H_2SO_4} \underset{\text{Heptanoic acid}}{CH_3(CH_2)_5COOH}$$

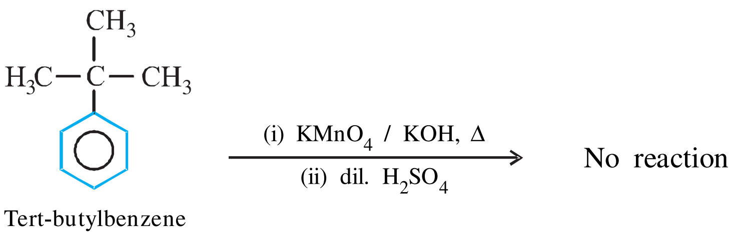
Aldehydes are easily oxidized to corresponding carboxylic acids with $KMnO_4$ in neutral, acidic or alkaline medium or by $K_2Cr_2O_7$ or CrO_3 in acidic medium and also even with mild oxidizing agent such as Tollens' reagent which is discussed in unit 5.4.

(ii) From alkylbenzene and alkenes : Aromatic carboxylic acids are prepared by the vigorous oxidation of alkylbenzene with acidic or alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$ (chromic acid) or dil. HNO_3. During these oxidation the entire side chain is oxidized to carboxylic acid group irrespective of the length of the side chain. **1^0 and 2^0 alkyl groups are oxidized in this manner but the 3^0 alkyl group is not oxidized and remains unaffected.** For example,

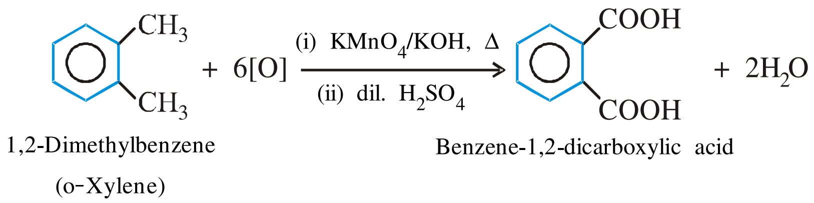


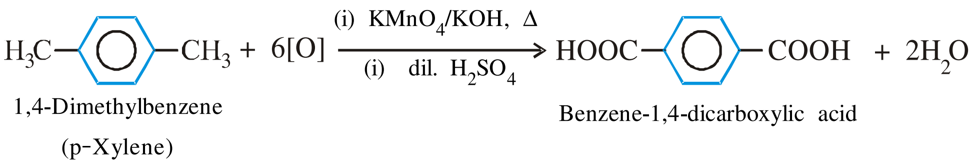






If there are two or more than two alkyl groups in benzene ring, each group is oxidized to –COOH group. For example,



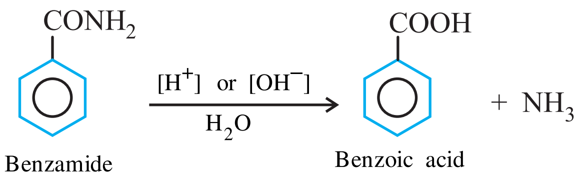


Substituted alkenes are also oxidized to carboxylic acid by acidic $K_2Cr_2O_7$ or alkaline $KMnO_4$. For example,

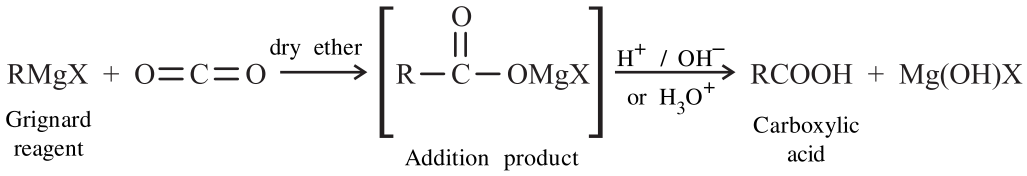
$$\underset{\text{But-2-ene}}{CH_3\text{–}CH\text{=}CH\text{–}CH_3} \xrightarrow[\text{(ii) dil. } H_2SO_4]{\text{(i) } KMnO_4 \text{ / KOH, } \Delta} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

(iii) From nitriles and amides : Nitriles are hydrolysed to amide and then to carboxylic acid on boiling with mineral acids or alkalies as a catalyst. For example,

$$\underset{\text{Ethane nitrile}}{CH_3CN} \xrightarrow[H_2O]{[H^+] \text{ or } [OH^-]} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\Delta]{[H^+] \text{ or } [OH^-]} \underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3$$

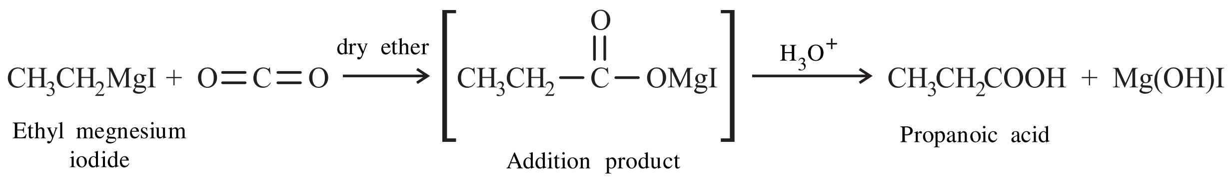


(iv) From Grignard reagent : Carboxylic acids can be prepared by bubbling CO_2 gas into the ethereal solution of a suitable Grignard reagent or by adding the solution of Grignard reagent to crushed dry ice (solid CO_2) suspended in ether. First the addition product is obtained, which on decomposition with mineral acid gives carboxylic acid. For example,



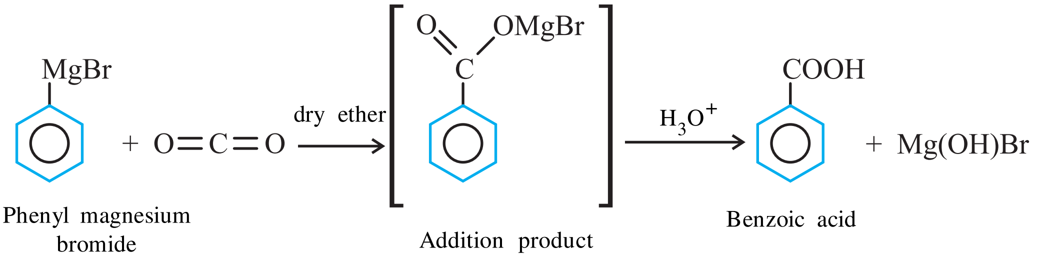
$$RMgX + O{=}C{=}O \xrightarrow{\text{dry ether}} \left[R-\overset{\overset{\large O}{||}}{C}-OMgX\right] \xrightarrow[\text{or } H_3O^+]{H^+ / OH^-} RCOOH + Mg(OH)X$$

Grignard reagent; Addition product; Carboxylic acid



$$CH_3CH_2MgI + O{=}C{=}O \xrightarrow{\text{dry ether}} \left[CH_3CH_2-\overset{\overset{\large O}{||}}{C}-OMgI\right] \xrightarrow{H_3O^+} CH_3CH_2COOH + Mg(OH)I$$

Ethyl megnesium iodide; Addition product; Propanoic acid



In both the methods-nitriles and Grignard reagent are useful for converting the alkyl halide to the carboxylic acid, having carbon atom or atoms more than that present in alkyl halide.

(v) From acid chloride and anhydrides : Acid chloride when hydrolysed by water gives carboxylic acid, and more readily hydrolysed with aqueous alkali to give carboxylate ions, which on acidification gives corresponding carboxylic acids. For example,

$$\underset{\text{Acid chloride}}{R-COCl} \xrightarrow[\text{Hydrolysis}]{H_2O} \underset{\text{Carboxylic acid}}{RCOOH} + HCl$$

$$\underset{\text{Acid chloride}}{R-COCl} \xrightarrow[\text{Hydolysis} \; -HCl]{OH^- / H_2O} \underset{\text{Carboxylate ion}}{RCOO^-} \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{RCOOH} + H_2O$$

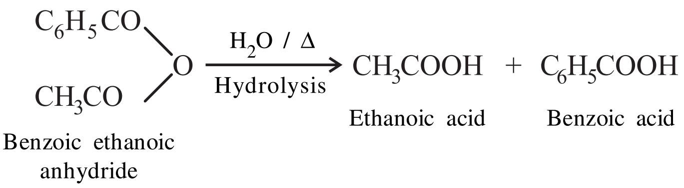
$$\underset{\text{Ethanoyl chloride (Acetyl chloride)}}{CH_3COCl} \xrightarrow[\text{Hydrolysis}]{H_2O} \underset{\text{Ethanoic acid}}{CH_3COOH} + HCl$$

$$\underset{\text{Ethanoyl chloride (Acetyl chloride)}}{CH_3COCl} \xrightarrow[\text{Hydrolysis} \; -HCl]{OH^- / H_2O} \underset{\text{Ethanoate ion}}{CH_3COO^-} \xrightarrow{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH + H_2O}$$

Anhydrides on hydrolysis with water gives carboxylic acids. For example,

$$\underset{\text{Ethanoic anhydride (Acetic anhydride)}}{(CH_3CO)_2O} \xrightarrow[\text{Hydrolysis}]{H_2O / \Delta} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow[\text{Hydrolysis}]{H_2O\,/\,\Delta} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$



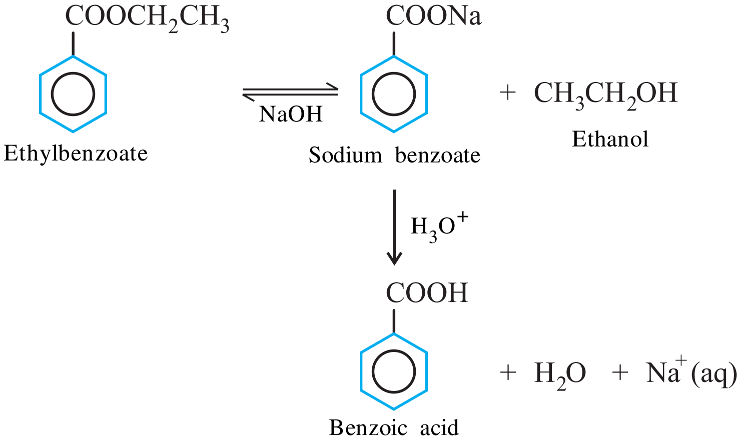
(vi) From ester : Hydrolysis of esters in presence of mineral acids give carboxylic acids directly while hydrolysis in presence of alkali gives carboxylates, which on acidification give corresponding carboxylic acid. For example,

$$\underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3} \overset{H_3O^+}{\rightleftharpoons} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3} \overset{NaOH}{\rightleftharpoons} \underset{\text{Sodium ethanoate}}{CH_3COONa} + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

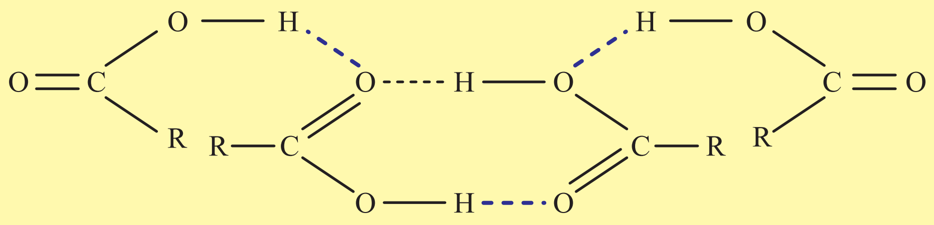
$$\Big\downarrow H_3O^+$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + Na^+(aq) + H_2O$$

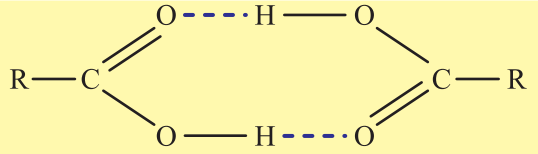


5.10 Physical Properties of Carboxylic Acids

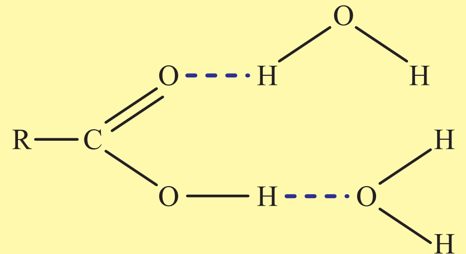
The first three aliphatic acids (C_1 to C_3) are colourless liquids with pungent smell. The next three (C_4 to C_6) are colourless oily liquids with unpleasant smell and remaining three (C_7 to C_9) are colourless liquids with unpleasant smell at room temperature, while carboxylic acids with ten or more carbon atoms are colourless, waxy solids with no distinct smell due to low volatality. Aromatic carboxylic acids are solid with no distinct smell. C_1 to C_4 aliphatic carboxylic acids are fairly soluble in water, while C_5 and C_6 are slightly soluble and remaining are insoluble in water. The aromatic acids are almost insoluble in cold water, but soluble in hot water. The solubility of lower members of aliphatic carboxylic acids is due to hydrogen bond formation. The hydrogen bonding of carboxylic acid is stronger than that of alcohol, so the melting points and boiling points of carboxylic acids are more than those of alcohols of comparable molecular mass. In liquid state, the carboxylic acid molecules are associated with other carboxylic acid by formation of strong hydrogen bonding. The hydrogen bonding is so strong that they are not broken even in vapour phase. **In vapour phase or in aprotic solvents most of the carboxylic acids exist as cyclic dimers.**



Association of carboxylic acid molecules in liquid state



Dimer form in aprotic solvent or vapour phase



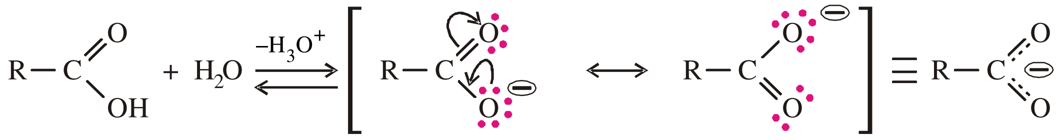
Hydrogen bonding in aqueous solution

Carboxylic acids in aqueous solution form intermolecular hydrogen bond with water molecules, so the carboxylic acids with lower molecular masses are soluble in water.

5.11 Chemical Reactions of Carboxylic Acids

Acidic nature of carboxylic acid : Alcohols, phenols and carboxylic acids contain an –OH group, but the carboxylic acids are much stronger acid than alcohols and phenols. Comparison of acidic character of alcohols, phenols and carboxylic acids are based on the stability of resonance structure of their negative ions.

(a)



Carboxylic acid

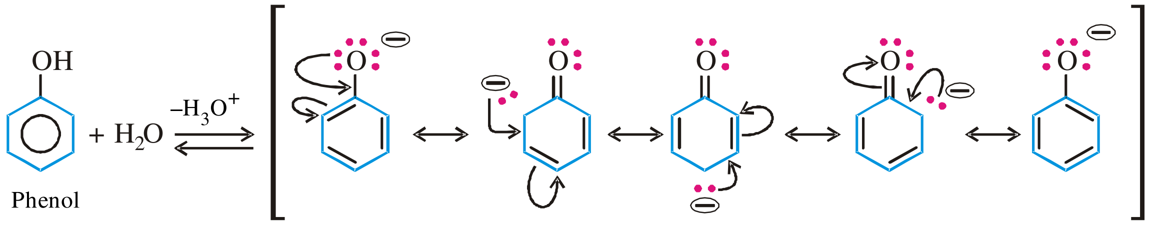
Carboxylate ion stabilized by resonance.

(b) $R-OH + H_2O \rightleftharpoons RO^- + H_3O^+$

Alcohol

Not stabilized

(c)



As shown in reaction (a) carboxylate anions are stabilized by their resonance structures, so tendency to release proton is more, while the alkoxide ions as shown in reaction (b) are not stabilised by resonance, hence, alcohols have less tendency to release a proton, so the alcohols are much weaker acids than carboxylic acids, though both contain an –OH group. In case of phenoxide ion as shown in reaction (c) having resonating structure I to III, but the structures carry a negative charge on the less electronegative carbon atom. Therefore their contribution towards the resonance stabilization of phenoxide ion is very small, while in carboxylate ion the negative charge on the more electronegative oxygen atom, **so carboxylic acids are stronger acids than alcohols and phenols. but are weaker acids than the mineral acids** (HCl, HNO_3, H_2SO_4) and sulphonic acids. In aqueous solutions, the carboxylic acid ionizes and exist in dynamic equilibrium between carboxylate ion and hydronium ion.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

So the equilibrium constant can be expressed as $K_{eq} = \dfrac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$ (5.1)

Since water is taken in large excess hence $[H_2O]$ remains constant, so the equation (5.1) can be written as

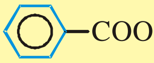
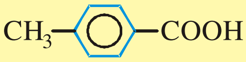
$$K_{eq} \times [H_2O] = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} = K_a \qquad (5.2)$$

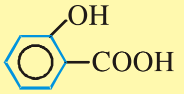
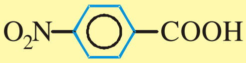
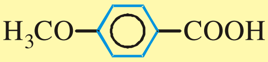
The equilibrium constant K_a is called the dissociation constant of the acid, and it varies with the temperature for a given acid. From equation (5.2) it is clear that at constant temperature, K_a is directly proportional to the $[H_3O^+]$. Therefore the value K_a is a measure of the acid strength of an acid, so higher the value of **K_a, greater is the tendency of the acid to ionize and hence stronger is the acid.** For convenience, the strength of an acid is generally indicated by its pK_a value, rather than its K_a value

$$pK_a = -\log K_a$$

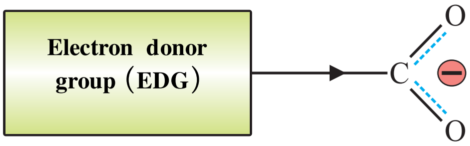
So, if carboxylic acid having smaller numerical value of pK_a, then it is very strong i.e. **better is a proton** donor. Strong acids have **pK_a values < 1,** the acids with pK_a values between **1 and 5** are considered to be moderately strong acids, weak acids have pK_a values between **5 and 15** and extremely weak acids have **pK_a values > 15.** K_a and pK_a values of some acids at 298 K temperature are given in table 5.6.

Table 5.6 K_a and pK_a values of some acids at 298 K (For information only)

Acid	K_a	pK_a	Acid	K_a	pK_a
HCOOH	17.7×10^{-5}	3.75	ICH_2COOH	67×10^{-5}	3.17
CH_3COOH	1.75×10^{-5}	4.76	$CH_2=CHCOOH$	5.5×10^{-5}	4.3
CH_3CH_2COOH	1.3×10^{-5}	4.88		6.3×10^{-5}	4.2
$ClCH_2COOH$	136×10^{-5}	2.87		4.2×10^{-5}	4.38

$Cl_2CHCOOH$	5530×10^{-5}	1.26		105×10^{-5}	2.98
Cl_3CCOOH	23200×10^{-5}	0.64		36×10^{-5}	3.44
FCH_2COOH	260×10^{-5}	2.59		3×10^{-5}	4.48
$BrCH_2COOH$	125×10^{-5}	2.90			

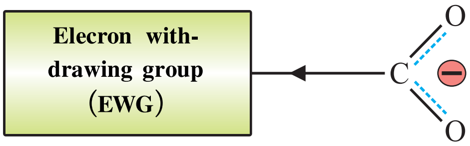
The acid strength of carboxylic acid depends on the effect of various substituents. For example,



(i) Effect of electron donating groups (EDG) :

The alkyl group has electron donating inductive effect (+I effect), hence it will increase the electron density in the –OH bond, so **release of** H^+ ions will be more difficult, hence, the formic acid is stronger acid than acetic acid. Further the +I effect of the alkyl groups increases in the order

$CH_3– < CH_3CH_2– < (CH_3)_2CH– < (CH_3)_3C–$ Hence the relative strength of carboxylic acid will be as **$CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C–COOH$**



(ii) Effect of electron withdrawing group (EWG) :

Electron withdrawing group having –I effect, and it decreases in the order –F > –Cl > –Br > –I > –Ph. So the strength of the carboxylic acids will be as.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > C_6H_5CH_2COOH$

Further, greater the number of electron withdrawing goups (substituents), stronger will be the acid (strength).

$Cl_3\ C\ COOH > Cl_2\ CH\ COOH > Cl\ CH_2\ COOH$

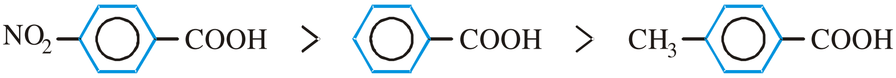
The inductive effect decreases rapidly with distance, so acidic strength order is

$$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCOOH > CH_3\overset{\overset{Cl}{|}}{C}HCH_2COOH > \overset{\overset{Cl}{|}}{C}H_2CH_2CH_2COOH$$

(iii) The phenyl or vinyl group directly attached to carboxyl group have weaker electron donating effect than alkyl group. So unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids, but formic acid does not contain any alkyl group, therefore it is stronger acid than unsubstituted aromatic acid, so the order of acidic strength is

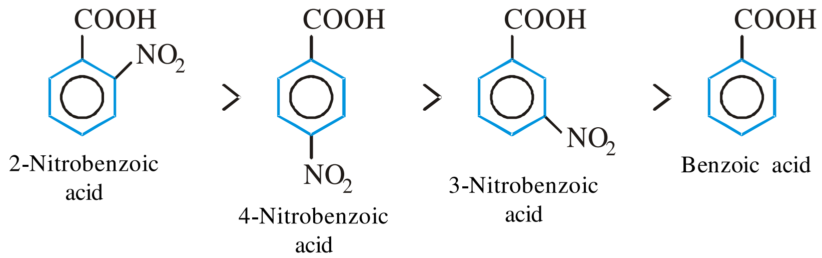
Formic acid > Benzoic acid > Acetic acid.

For substituted aromatic carboxylic acid the presence of electron withdrawing group on the phenyl or aromatic carboxylic acid increases their acidic strength, while electron donating group, decreases their acidic strength. For example,



4–Nitrobenzoic acid   Benzoic acid   4–Methylbenzoic acid.

Electron withdrawing or electron donating group effect is more pronounced at 1,2 position (ortho position) than 1,4 position (para position) than 1,3 position (meta position). For example the acid strength is



2-Nitrobenzoic acid > 4-Nitrobenzoic acid > 3-Nitrobenzoic acid > Benzoic acid

(1) Reactions involving cleavage of O–H bond : The reactions showing the acidic character of the carboxylic acids i.e. cleavage of O–H bond are given below :

(i) Reaction with metal : Carboxylic acids like alcohols react with electropositive metals such as Na, K, Ca, Mg, Zn etc. to form their respective salts and liberate H_2 gas. For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + Na \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \frac{1}{2} H_2$$

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

(ii) Reaction with alkalies : Similar to phenols the carboxylic acids neutralize alkalies and form salts. For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_4OH \rightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} + H_2O$$

(iii) Reaction with carbonates and hydrogen carbonates : However unlike phenols the carboxylic acids react with weaker bases such as carbonates and hydrogen carbonates to evolve CO_2 gas. For example,

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Na_2CO_3 \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + CO_2 + H_2O$$

This reaction is used to detect the presence of –COOH group in organic compounds. As most of the phenols do not produce CO_2 gas with $NaHCO_3$. Hence this reaction is **also useful to distinguish phenols from carboxylic acids.**

(2) Reaction involving cleavage of C–OH bond : The hydroxyl group of a carboxylic acid like the hydroxyl group in alcohols, can be replaced (substituted) by group like –Cl, –OR', $–NH_2$ and –OCOR' to form acid chloride, esters, amides, and anhydrides, respectively. These derivatives are known as functional group derivatives of carboxylic acids.

(i) Formation of acid chlorides : Carboxylic acid reacts with $SOCl_2$ (thionyl chloride) or PCl_5 or PCl_3 to form acid chloride. For example,

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2(g) + HCl(g)$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

For the production of acid chloride, the reaction with $SOCl_2$ is preferred, because in this reaction the other two products SO_2 and HCl both are in gaseous state, so it is very easy to remove them from acid chloride, **hence purification of acid chloride becomes very easy.**

(ii) Formation of esters : When carboxylic acids are heated with alcohols or phenols in presence of con. H_2SO_4 or HCl, esters are formed. The reactions are known as esterifications **(Fischer-Speier esterification).** This reaction is reversible and hence the rate of reaction can be increased by taking excess amount of carboxylic acid or alcohol or by removing water from the reaction mixture.

$$CH_3COOH + CH_3CH_2OH \underset{\Delta}{\overset{\text{con. } H_2SO_4}{\rightleftharpoons}} CH_3COOCH_2CH_3 + H_2O$$

Acetic acid — Ethanol — Ethyl ethanoate (Ethyl acetate)

$$C_6H_5COOH + CH_3OH \underset{\Delta}{\overset{\text{con. } H_2SO_4}{\rightleftharpoons}} C_6H_5COOCH_3 + H_2O$$

Benzoic acid — Methanol — Methyl benzoate

(iii) Formation of anhydrides : Two molecules of carboxylic acids combine in presence of strong dehydrating agent such as P_2O_5 or mineral acid, such as con. H_2SO_4, on heating gives acid anhydrides. For example,

$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

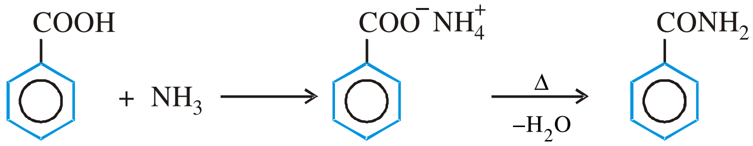
Acetic acid — Ethanoic anhydride (Acetic anhydride)

By treating acid chlorides with sodium salts of carboxylic acids, the acid anhydrides are obtained.

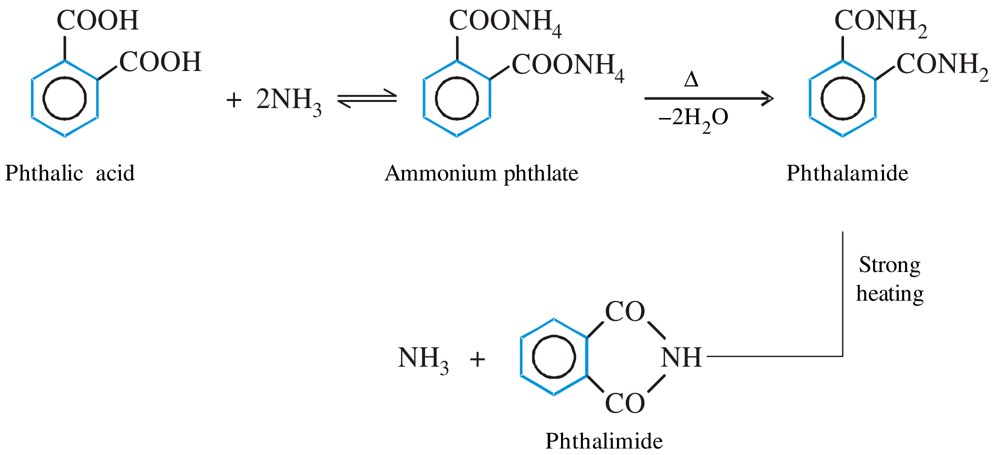
$$CH_3COCl + CH_3COONa \rightarrow (CH_3CO)_2O + NaCl$$

Ethanoyl chloride (Acetyl chloride) — Sodium acetate — Ethanoic anhydride (Acetic anhydride)

(iv) Formation of Amides : Carboxylic acids react with NH_3 to give ammonium salts, which on further heating at high temperature, lose a molecule of water to form amide. For example,



Benzoic acid — Ammonium benzoate — Benzamide



$$CH_3COOH + NH_3 \rightarrow CH_3COONH_4 \xrightarrow[\text{Higher temperature}]{\Delta} CH_3CONH_2 + H_2O$$

Acetic acid Ammonium acetate Acetamide

(3) Reactions involving –COOH group as a whole :

(i) Reduction : The reduction of carboxylic acids with Lithium Aluminium hydride ($LiAlH_4$) or better with diborane (B_2H_6) gives **primary alcohol.** Using this reaction the –CO– group can be reduced to $–CH_2–$ group. For example,

$$CH_3COOH \xrightarrow[H_2O]{\text{(i) } LiAlH_4 \text{ or } B_2H_6} CH_3CH_2OH$$

Ethanoic acid Ethanol (1^0 alcohol)

Diborane does not easily reduce functional groups like ester, nitro, halo etc., and sodium borohydride does not reduce the carboxyl group.

Carboxylic acid on reduction with hydroiodic acid and red phosphorus at 473 K give alkanes. In this reaction the –COOH group is reduced to $–CH_3$ group.

$$CH_3COOH + 6HI \xrightarrow[473\text{ K}]{\text{Red P}} CH_3–CH_3 + 2H_2O + 3I_2$$

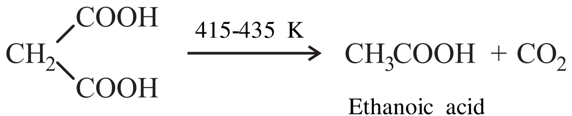
Ethanoic acid Ethane

(ii) Decarboxylation : Carboxylic acids and their salts lose carbon dioxide to form hydrocarbon and reaction is known **as decarboxylation reaction.** The sodium salts of carboxylic acid are heated with sodalime (NaOH and CaO mixture in the proportion ratio of 3:1) give alkane. e.g.,

$$CH_3COONa + NaOH \xrightarrow{CaO / \Delta} CH_4 + Na_2CO_3$$

Sodium acetate Methane

If two carboxylic groups are attached to the same carbon atom called gem-dicarboxylic acid undergo decarboxylation simply on heating at 415-435 K temperature. For example,



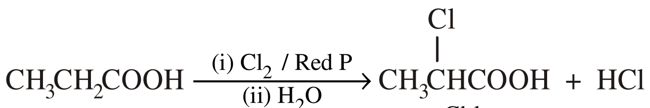
$$CH_2(COOH)_2 \xrightarrow{415\text{-}435\text{ K}} CH_3COOH + CO_2$$

Propanedioic acid Ethanoic acid

On electrolysis of aqueous solution of sodium or potassium salts of fatty acids at anode due to oxidation, CO_2 is liberated and alkane having double carbon is obtained. At cathode H_2 gas liberated and this process is called **Kolbe's electrolytic reduction or electrolytic decarboxylation.**

(4) Substitution reactions in the hydrocarbon part of carboxylic acids :

(i) Halogenation : Carboxylic acid having an α-hydrogen atoms are halogenated at the α-position on treatment with dichlorine or dibromine in the presence of small amount of red phosphorus to give α-halocarboxylic acid. This reaction is known as **Hell-Volhard-Zelinsky reaction.** For example,



$$CH_3CH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 \text{ / Red P}} CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCOOH + HCl$$

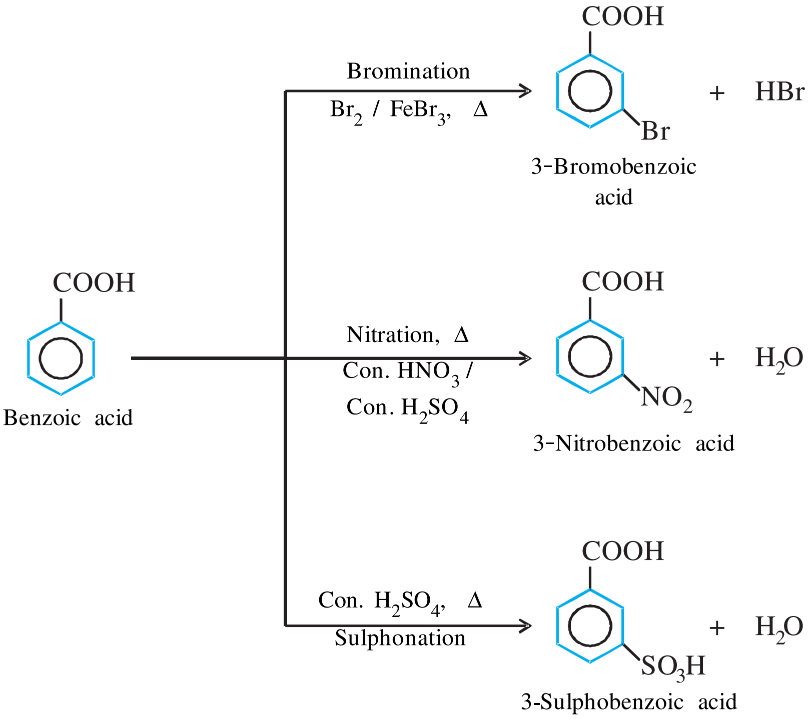
Propanoic acid → α-Chloro-propanoic acid

If more than one mole of Cl_2 or Br_2 are used then the 2nd and 3rd α-hydrogen atoms are successively substituted. For example,

$$CH_3COOH \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ /Red P}} ClCH_2COOH \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ Red P}} Cl_2CHCOOH \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ Red P}} Cl_3CCOOH$$

Ethanoic acid, Chloro ethanoic acid, Dichloro ethanoic acid, Trichloro ethanoic acid

(ii) Ring substitution : Aromatic carboxylic acids undergo the electrophilic substitution reactions like halogenation, nitration and sulphonation. Since the –COOH group acts as a deactivating and hence **m-directing group, so the reactions take place only under vigorous conditions.** The –COOH group deactivates the benzene ring and catalyst aluminium chloride (Lewis acid) gets bonded to the carbonyl group. So they do not undergo Friedel-Carfts reactions.

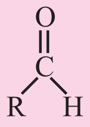


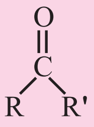
5.12 Uses of Carboxylic Acids

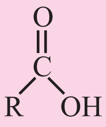
Methanoic acid is used in leather industry, rubber industry, in medicine, in dyeing and electroplating industry, Ethanoic acid is used as coagulant for latex, manufacturing of plastic, rayon and silk. It is also used as a solvent in laboratory and as vinegar in the manufacturing of pickles in food industry. Hexanedioic acid is used in manufacturing of nylon 6,6. Benzoic acid is used in medicine as urinary antiseptic and for making aniline blue in dye industry, and sodium benzoate as food preservatives. Higher fatty acids are used for manufacturing of soaps and detergents. Benzene-1,2-dicarboxylic acid is used in the manufacturing of resins and benzene-1,4-dicarboxylic acid is used in manufacturing of polyesters.

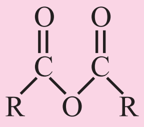
SUMMARY

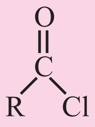
Organic compounds containing carbon-oxygen double bond ($>C=O$) are called carbonyl group or carboxyl group compounds. In aldehydes, the carbonyl group is attached to one hydrogen atom and one alkyl (or aryl or hydrogen atom) group, while in ketones it is attached to one alkyl and one aryl group or to two alkyl (or aryl) groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as carboxylic acids. In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group the compounds are known as esters, but if it is substituted by acyl group, the compounds are known as acid anhydrides. If the carbonyl group is attached to chlorine and to amino group the compounds are known as acid chlorides and amides respectively. The general formula of these compounds are expressed as

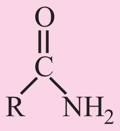

Aldehyde

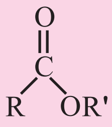

Ketone


Carboxylic acid

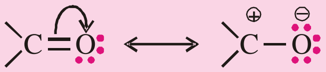

Anhydride


Acid chloride


Amide


Ester

- Aldehydes and ketones have same general molecular formula $C_nH_{2n}O$ but different functional groups like aldehydes and ketones. Therefore they are called functional groups isomers. e.g., C_3H_6O can be CH_3CH_2CHO and CH_3COCH_3 i.e. aldehyde and ketone respectively.
- Carbonyl carbon atom is sp^2 hybridised and form three σ bonds and one π bond. All the three σ-bonds lie in same plane having angle 120^0. The π-bond lies both above and below the C–O σ bond. Thus the carbonyl carbon and oxygen atoms are directly bonded to the carbonyl carbon which lie in one plane, and is confirmed by electron diffraction and spectroscopic studies.
- Due to higher electronegativity of oxygen atom relative to carbon atom the carbonyl group is polarized and carbonyl carbon becomes electrophile (Lewis acid) and oxygen becomes nucleophile (Lewis base). Carbonyl group is polar in nature and has dipole moments. Aldehydes and ketones have dipole moments 2.3-2.8 D. The resonance structures are as shown below :



- The common names of aldehydes are obtained by replacing the terminal -'ic acid' by 'aldehyde' from the common name of the corresponding carboxylic acid.
- Formic acid, acetic acid and benzoic acid the corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively.
- In the substituted aldehydes, the positions of the substituents are indicated by Greek alphabets α, β, γ, δ etc. with the carbon atom next to the –CHO group designated as α

- The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet 'e' from its name by -'al' like methanal, ethanal etc.
- The position of substituents are indicated by numbers. The numbering of the substituents are done in such a way that the aldehyde group at the end of the chain gets number 1.
- Names of aliphatic cyclic aldehydes are given by adding suffix carbaldehyde after the full name of the cycloalkane.
- Name of aromatic aldehydes are given as benzene carbaldehyde (or benzaldehyde) and the position is indicated by numbering starting from the carbon having –CHO group.
- More than two –CHO groups are named as derivatives of the hydrocarbon which do not include the carbon atoms of the functional group.
- The common and IUPAC names of aldehydes are given in table 5.1 in the unit.
- The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl group (in the alphabetical order) attached to the ketone group as two separate words and adding suffix ketone.
- If both attaching groups are same the prefix di is used.
- The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet-'e' by the suffix -'one'.
- For substituted ketone the positions of the substituents are indicated by numbering the chain in such a way that the ketone group gets the lowest number.
- The common and IUPAC names of the ketones are given in table 5.2.
- The polar carbonyl groups have dipole-dipole interaction between opposite ends of the $\rangle C=O$ group dipoles and hence due to weak intermolecular attraction the melting points and boiling points of aldehydes and ketones are higher than corresponding non-polar compounds.
- The order of boiling points is carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde>ether>hydrocarbon.
- Due to hydrogen bonding with water molecules the aldehydes and ketones upto three carbon are soluble in water.
- The aromatic aldehydes and ketones due to presence of larger hydrocarbon parts (like benzene ring etc.), are insoluble in water.
- All adehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohols, chloroform etc.

- Due to presence of hydrogen atom, the carbonyl group of aldehyde is much more reactive than ketone.
- Aldehydes and ketones undergo nucleophilic addition reaction because the carbonyl carbon atom is slightly positively charged.
- In nucleophilic addition reaction the first step is reversible and also slow, so it a rate determining step. The second step is reversible.
- Due to steric effect and inductive effect the aldehydes are more reactive than ketones.
- Most of the aldehydes and aliphatic methyl ketones, due to less steric hindrance are more reactive.
- Aldehydes and ketones react with $NaHSO_3$ and give bisulphite addition product which are usually crystalline solids. On hydrolysis they give original aldehydes and ketones, so this reaction is useful for separation and purification of aldehydes and ketones.
- Addition of HCN and Grignard reagent to the aldehyde and ketone which give α-hydroxy carboxylic acid and 1^0, 2^0, 3^0 alcohols respectively.
- Addition of alcohol to aldehyde give hemiacetal and further acetal, while ketone give the same product.
- Nucleophilic addition reaction of aldehydes and ketones with NH_3 and its derivatives ($H_2N–Z$) and reaction catalysed by acids.
- Aldehydes and ketones on reduction give 1^0 and 2^0 alcohols respectively.
- Aldehydes and ketones can be reduced to hydrocarbon by using different reactions like Wolff-Kishner reduction, Clemmensen reduction and reagents like red phosphorus and HI and reduction with magnesium amalgam and water give the product-hydrocarbon.
- Oxidation of aldehydes : Tollens' test, Fehling's test and Benedict's test give the product carboxylic acid. Fehling's test and Benedict's test are not given by aromatic aldehydes.
- Oxidation of ketones by strong oxidizing agents like con. HNO_3, $KMnO_4$ / H_2SO_4, $K_2Cr_2O_7$ / H_2SO_4 give mixture of carboxylic acids.
- Oxidation of aldehydes and ketones containing CH_3CO-group give iodoform test.
- Aldol condensation and cross aldol condensation are the reactions given by aldehydes and ketones having α-hydrogen atom or atoms using dilute alkali as catalyst.
- Cannizzaro reaction is given by aldehydes and ketones which do not have an α-hydrogen atom by using con. NaOH or 50 % NaOH.
- Electrophilic substitution reactions of aromatic aldehydes and ketones are nitration, sulphonation and halogenation.
- Aldehydes and ketones are used in different fields.

- The carboxylic acids contain –COOH group, contain carbonyl and hydroxyl group so by combining the 'carb' and 'oxyl', the –COOH is called carboxyl group.
- The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (plant or animal products) from which they were first isolated.
- The IUPAC names of monocarboxylic acids are given by replacing the ending alphabet 'e' in the name of corresponding hydrocarbon with suffix “-ioc acid.”
- For naming substituted and branched acids, the longest chain having carboxylic acid group is selected and number one is assigned to carboxylic carbon; then the successive number are assigned to carbon of the chain and the substitution is expressed.
- The IUPAC names of aromatic monocarboxylic acids are derived from benzene carboxylic acid (Benzoic acid) and the position of the substituents are indicated by number with carbon atom carrying –COOH group being number one.
- In aliphatic dicarboxylic acids, the position of –COOH group is not indicated, but in aromatic dicarboxylic acid and other (tri, tetra…poly) carboxylic acid, it is indicated by number before the multiplicative prefix and the ending -'e' of the hydrocarbon is retained.
- The common and IUPAC names of some carboxylic acids are given in table 5.5.
- The –COOH group is represented as a resonance hybrid of the three resonating structures.
- **Carboxylic acids are prepared from :**
  - → Primary alcohol and aldehyde
  - → Alkyl benzene and alkenes
  - → Nitriles and amides.
  - → Grignard reagents
  - → Acid (chloride) halide and anhydrides
  - → Esters
- Carboxylic acid in aqueous solution form intermolecular hydrogen bonding with water molecules.
- Carboxylic acids are cyclic dimer in vapour phase or in aprotic solvents.
- Carboxylic acids are stronger acids than phenol and alcohols.
- For convenience the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

  $pK_a = -\log K_a$
- The acidic strength of carboxylic acids depends on the effect of various substituents like

→ effect of electron-donating group

→ effect of electron withdrawing group

→ attachment of phenyl or vinyl group directly to carbonyl group.

- The reactions of carboxylic acid are

  → Reactions involving cleavage of O–H bond.

  → Reactions involving cleavage of C–OH bond

  → Reactions involving –COOH group

- Substitution reaction in hydrocarbon part of carboxylic acid are halogenation and ring substitution as bromination, nitration and sulphonation.

- Carboxylic acids are used in different fields.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which of the following compounds has highest boiling point ?

(A) propanoic acid (B) propanol (C) propanone (D) propanal

(2) Which of the following compounds has highest solubility in water ?

(A) pentanone (B) butanone (C) formaldehyde (D) propanone

(3) Which of the following compounds has highest reactivity in nucleophilic addition reaction ?

(A) propanone (B) methanal (C) ethanal (D) butanone

(4) Propanone + NH_2NH_2 + KOH $\xrightarrow[\Delta]{\text{Ethylene glycol}}$?

(A) propanal (B) propanol (C) propene (D) propane

(5) Ethanol + $KMnO_4 \rightarrow$?

(A) ethanal (B) ethanoic acid

(C) ethane (D) potassium ethanoate

(6) tert-butyl benzene $\xrightarrow[\text{(ii) dil. } H_2SO_4]{\text{(i) } KMnO_4 / KOH, \Delta}$?

(A) tert-butyl benzoic acid (B) benzoic acid

(C) tert-butanol (D) No reaction.

(7) But-2-ene $\xrightarrow[\text{(ii) dil } H_2SO_4]{\text{(i) } KMnO_4 / KOH, \Delta}$?

(A) butanoic acid (B) ethanoic acid (C) butanol (D) ethanol

(8) Ethane nitrile $\xrightarrow[\Delta]{[H^+] \text{ or } [OH^-]}$?

(A) ethanol (B) ethanal (C) ethanoic acid (D) ethene

(9) Ethylbenzoate + NaOH $\rightarrow$?

(A) benzoic acid (B) benzene

(C) benzaldehyde (D) potassium benzoate

(10) Which of the following acids has highest relative acid strength ?

(A) acetic acid (B) propanoic acid

(C) isopropanoic acid (D) benzoic acid.

(11) Acetyl chloride + sodium acetate $\xrightarrow[\Delta]{}$

(A) ethyl acetate (B) ethyl chloride

(C) acetic anhydride (D) ethanol

(12) Sodium acetate + Sodalime $\xrightarrow{\Delta}$?

(A) acetic acid (B) ethane (C) methane (D) ethanal

(13) Propanoic acid $\xrightarrow[H_2O]{Cl_2 \text{ / Red P}}$?

(A) propanal (B) propanol

(C) propane (D) α-chloro propanoic acid.

(14) Which substance is used in leather industry ?

(A) methanoic acid (B) ethanoic acid (C) benzoic acid (D) pentanoic acid.

(15) Which substance is used in medicine as urinary antiseptic ?

(A) benzoic acid (B) acetic acid (C) methanoic acid (D) formic acid

2. Write the answers of the following questions in brief :

(1) Draw general structural formula of anhydride.

(2) Draw resonance structure of carbonyl group.

(3) Indicate hydrogen bonding between aldehyde and the water molecules.

(4) Write equation for reduction of methanal with $LiAlH_4$.

(5) Write the equation for Wolff-Kishner reduction of ketone.

(6) Write uses of formaldehyde.

(7) Write uses of acetaldehyde.

(8) Write uses of acetone.

(9) Draw resonance structurs of carboxylate ion.

(10) Write equation for hydrolysis of ethyl acetate.

(11) Write the reaction of formation of pinacol.

(12) Draw structure of association of carboxylic acid in liquid state.

(13) Draw dimer form of carboxylic acid in vapour state or in aprotic solvent.

(14) Draw hydrogen bonding between carboxylic acid and water molecules.

(15) Draw resonance structure of phenoxide ions.

(16) Explain pK_a in short. What does it indicate ?

(17) Write equation for reaction of acetic acid with Na_2CO_3.

(18) Write equation for acetic acid with $SOCl_2$.

(19) Write equation for heating acetic acid with P_2O_5.

(20) Write equation of nitration of benzoic acid.

(21) Write uses of methanoic acid.

(22) Write uses of benzoic acid.

(23) Write uses of ethanoic acid.

(24) Write uses of fatty acids ?

(25) Write equation of halogenation of propanoic acid.

3. Write answers of the following questions :

(1) Explain nature of carbonyl group.

(2) Explain addition of $NaHSO_3$ to aldehyde and ketone.

(3) Explain addition of HCN to aldehyde and ketone.

(4) Explain acetal formation.

(5) Explain ketal formation.

(6) Explain reduction of aldehyde.

(7) Explain Wolff-Kishner reduction.

(8) Explain Clemensen reduction.

(9) Explain Tollens' test.

(10) Explain Fehling's test.

(11) Explain Benedict's test.

(12) Explain Cannizzaro reaction.

(13) Explain preparation of carboxylic acid from 1^0 alcohol.

(14) Explain acidic nature of carboxylic acid.

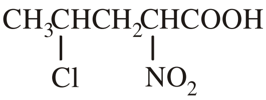
(15) Explain reduction of acetic acid.

(16) Explain decarboxylation

(17) Explain halogenation of acetic acid.

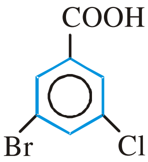
(18) Explain ring substitution in benzoic acid.

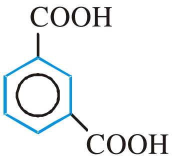
(19) Give IUPAC names :

(i)

$CH_3\underset{Cl}{\underset{|}{CH}}CH_2\underset{NO_2}{\underset{|}{CH}}COOH$

(ii) $CH_3CH_2CH_2CN$

(iii) $CH_3CH_2COOCH_2CH_3$

(iv)


(v)


(vi)

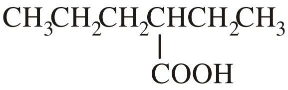
$CH_3\underset{Br}{\underset{|}{CH}}CH_2CH_2CHO$

(vii)

$CH_3CH_2\underset{Cl}{\underset{|}{CH}}COCH_2CH_3$

(viii) $CH_3COCH_2CH_2CH_3$

(ix) $HOOCCH_2CH_2CH_2COOH$

(x)

$CH_3CH_2CH_2\underset{COOH}{\underset{|}{CH}}CH_2CH_3$

(xi)

$CH_3CH_2-\overset{COOH}{\overset{|}{CH}}-CH_2CH_2COOH$

(xii)

$CH_3CH_2\underset{Cl}{\underset{|}{CH}}\underset{Br}{\underset{|}{CH}}\underset{I}{\underset{|}{CH}}COCH_3$

(xiii)

$CH_3\underset{COOH}{\underset{|}{CH}}\underset{COOH}{\underset{|}{CH}}CH_2CH_2COOH$

(xiv) $CH_3CH_2CH=CHCH_2COOH$

4. Write the answers of the following questions in detail :

(1) Explain the nucleophilic addition reactions of aldehydes and ketones.

(2) Explain the relative reactivity of aldehydes and ketones.

(3) Explain nucleophilic addition reactions followed by elimination of a molecule of water for aldehydes and ketones.

(4) Explain reduction of aldehydes.

(5) Explain oxidation of aldehydes.

(6) Explain oxidation of ketones.

(7) Explain aldol and cross aldol condensation.

(8) Explain electrophilic substitution reactions of aromatic aldehyde and ketones.

(9) Give the different methods of preparation of carboxylic acid.

(10) Explain the factors that affect the acidic strength of carboxylic acids.

(11) Explain reaction involving cleavage of C–OH bond in carboxylic acid.

(12) Explain reaction involving cleavage of O–H bond in carboxylic acid.

(13) Explain reaction involving of –COOH (as a whole) in carboxylic acid.

●

Unit

6

Organic Compounds Containing Nitrogen

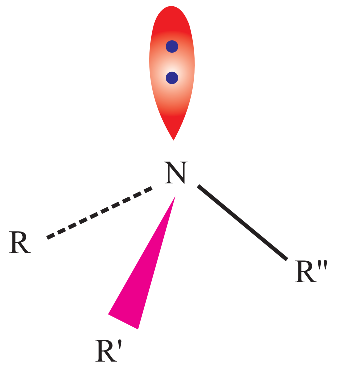
6.1 Introduction

In organic compounds the important functional groups containing nitrogen are amino, cyano or nitrile, isocyanide and nitro groups. If amino group is attached with carbon then an amino compound, is formed if cyano or nitrile group is attached then cyanide or nitrile compounds, the isocyanides group is attached then isocyanide compounds and if nitro group is attached then nitro compounds are made. In this unit, we shall study amine compounds, cyanide (nitrile) compounds, isocyanide compounds and nitro compounds.

6.2 Amines (Structure of Amine Compounds)

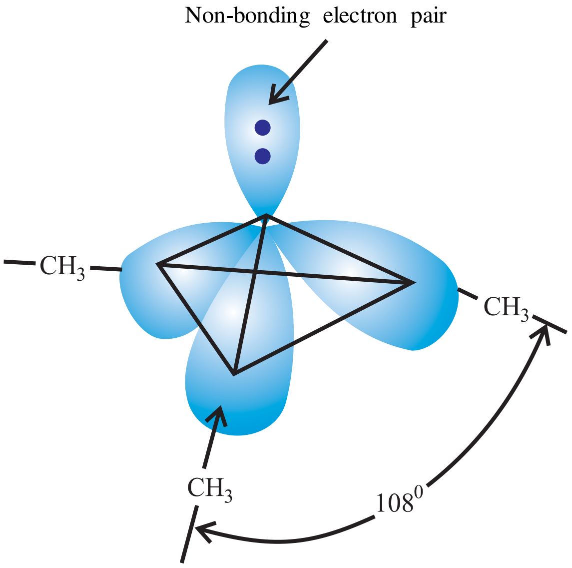
As the hydrogen present in water is replaced by hydrocarbon group, alcohol, phenol and ether are formed, similarly if hydrogen present in ammonia is replaced by hydrocarbon group then amine is formed. So, the structures of amine compounds are similar to structure of ammonia. **In the amine class of compounds, mainly carbon, hydrogen and nitrogen elements are present. One, two or all the three hydrogen atoms present in ammonia are displaced by alkyl or aryl groups.**

Like ammonia, in amine compounds, nitrogen atom is trivalent and possesses one nonbonding electron pair. Therefore the atomic orbital of nitrogen atom in amine compounds possess sp^3 hybridisation and the compounds possess pyramidal structure. Each sp^3 hybrid orbit of nitrogen gets overlapped with atomic orbital of carbon and forms amine compounds. The fourth orbital of nitrogen possesses nonbonding electron pair. Because of the presence of non-bonding electron pairs, C–N–R (where R is H or C) bond angle decreases slightly from $109^0\ 28'$. As shown in the fig 6.1 the bond angle in trimethyl amine is 108^0.



Electronic structure of amines

N–R, N–R' and N–R" σ–bond
N sp^3 hybridisation
any R–N–R angle ≈ 109.5^0



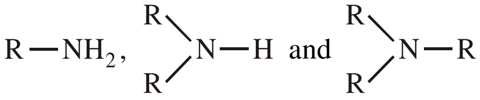
Pyramidal shape of tertiary amine

Fig. 6.1

6.3 Classification of Amine Compounds

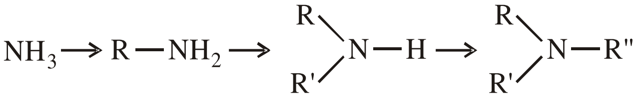
The classification of amine compounds is made on the basis of alkyl or aryl groups combined with nitrogen of amino group. If alkyl group is attached it is called alkyl amine and if aryl group is attached it is called aryl amine.

On replacement of hydrogen present in ammonia, if one alkyl or aryl group is attached with nitrogen, it is called primary (1^0) amine, if two groups are attached then secondary (2^0) and if three groups are joined, then tertiary (3^0) amine. The general formula of compounds in amino class is shown as :



$$R-NH_2,\quad R_2N-H \text{ and } R_2N-R$$

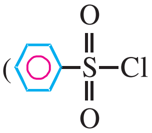
where R = alkyl or aryl group. If all the alkyl or aryl groups in amine compounds are same they are called simple amines and if different groups are there then, they are called mixed amines. Alkyl amines are called aliphatic amines and aryl amines are called aromatic amines.



$$NH_3 \rightarrow R-NH_2 \rightarrow RR'N-H \rightarrow RR'N-R''$$

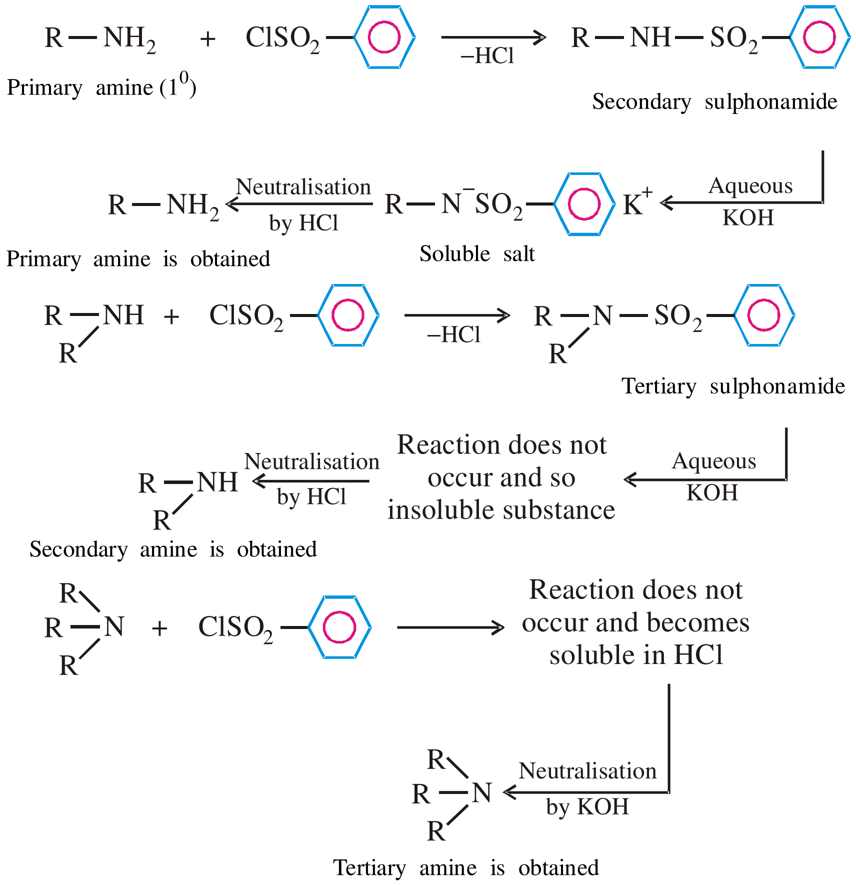
Primary (1^0) Secondary (2^0) Tertiary (3^0)

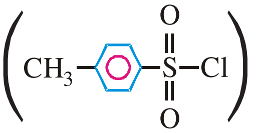
Separation of primary, secondary and tertiary amines : The separation of alkyl or aryl mixture of primary, secondary and tertiary amine can be carried out by the use of Hinsberg's reagent.

Benzene sulphonylchloride ( or $C_6H_5SO_2Cl$) is called Hinsberg's reagent.

In the mixture of primary, secondary and tertiary alkyl (aliphatic) and aryl (aromatic) amines, if benzene sulphonylchloride is added, then by the chemical reaction of primary, and secondary amine, secondary sulphonamide and tertiary sulphonamide are formed respectively; while tertiary amine does not react. To this mixture when dilute hydrochloric acid (HCl) is added the unreacted tertiary amine becomes soluble and the secondary sulphonamide and tertiary sulphonamide being insoluble in acid are obtained as residue by filtration. By neutralization of filtrate, tertiary amine is separated.

In the residue of secondary and tertiary sulphonamide, aqueous solution of potassium hydroxide (KOH) is added so that secondary sulphonamide becomes soluble. This reaction mixture is filtered and by neutralisation of the filtrate with acid, primary amine and secondary amine from residue gets separated by neutralisation.



Presently paratoluene sulphonylchloride () **is used of instead benzene sulphonylchloride.**

6.4 Nomenclature of Amine Compounds (IUPAC and Common)

For nomenclature of primary alkyl amine, after the alkyl group ‘amine’ word is placed viz. methylamine, ethylamine etc.

For common nomenclature of secondary alkyl amine, if two alkyl groups attached to nitrogen are the same then the prefix ‘di’ is placed before alkyl group followed by ‘amine’ viz dimethylamine, diethylamine etc. If the two alkyl groups attached to nitrogen are different then, the alkyl groups are arranged in the English alphabetical order and the word 'amine' is placed in the end. viz. ethylmethylamine, methylpropylamine etc.

For common nomenclature of tertiary amine if the three alkyl groups attached to nitrogen are same then the word tri is placed as the prefix before alkyl group and then the word 'amine' is placed in the end. Viz. trimethylamine, triethylamine etc. If two alkyl groups from the attached three alkyl groups are common, then the prefix di is placed before the two common alkyl groups and then the name of third alkyl group is attached and at the end the word 'amine' is placed viz. ethyldimethylamine, diethylmethylamine. If all the three alkyl groups attached to nitrogen are different then the alkyl groups are arranged in the English alphabetical order and then in the end word 'amine' is placed viz. ethylmethylpropylamine, butylethylmethylamine.

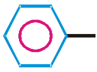
Amine compounds having more than one amine group according to the number of amino groups prefix di, tri, tetra etc. are attached. viz. $H_2N-CH_2-CH_2-NH_2$ is ethylenediamine, $H_2N-CH_2-CH(NH_2)-CH_2-NH_2$ is propylenetriamine.

IUPAC names :

(i) For IUPAC nomenclature of primary amine, the longest carbon chain of original hydrocarbon is determined and then 'e' is removed from the name of hydrocarbon and suffix amine is applied viz. methan + amine = Methanamine, ethan + amine = ethanamine, benzen + amine = benzenamine.

CH_3-NH_2 Methanamine

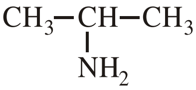
$CH_3-CH_2-NH_2$ Ethanamine


NH_2 or $C_6H_5 \cdot NH_2$ Benzenamine

It is necessary to note here that the common name of benzenamine is aniline. It is also accepted as IUPAC name.

(ii) If there are more than two carbon in primary alkylamine then in the longest carbon chain at original hydrocarbon, the position of amino group showing lowest number, suffix amine is shown earlier to it. viz. propan-1-amine, propan-2-amine.

$CH_3-CH_2-CH_2-NH_2$ Propan-1-amine

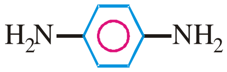

$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$ Propan-2-amine

(iii) For amine compounds having more than one carbon, in the number of amino group if it is two, three... etc. then di, tri, ... etc. are written as prefix before the 'amine' group, respectively **Here, the last letter 'e' is not removed** e.g.,

$H_2N-CH_2-CH_2-NH_2$ Ethane-1,2-diamine

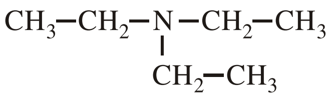
$H_2N-CH_2-CH(NH_2)-CH_2-NH_2$ Propane-1,2,3-triamine

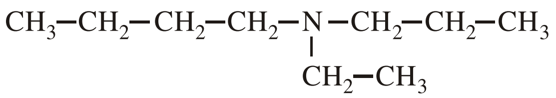
$H_2N–(CH_2)_6–NH_2$ Hexane-1,6-diamine

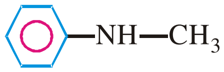

Benzene-1,4-diamine

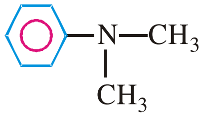
(iv) For the names of secondary and tertiary amines, the names are written according to rules (i), (ii) and (iii). Here symbol N is used to show the position of displacers of hydrogen in amine group e.g.

$CH_3–NH–CH_2–CH_3$ N-Methylethanamine


$$CH_3-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{N}}-CH_2-CH_3$$
N, N-Diethylethanamine

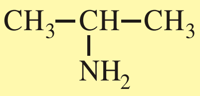

$$CH_3-CH_2-CH_2-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{N}}-CH_2-CH_2-CH_3$$
N-Ethyl-N-propylbutanamine

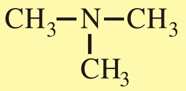
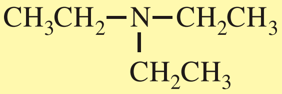
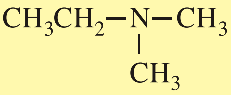
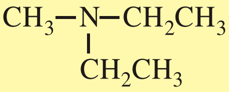
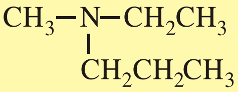
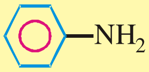
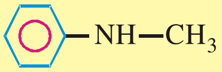
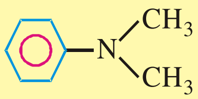

N-Methylbenzenamine


N, N-Dimethylbenzenamine

The structural formula, IUPAC name, common name, type and boiling points of certain amine compounds are given in table 6.1.

Table 6.1 Amine compounds

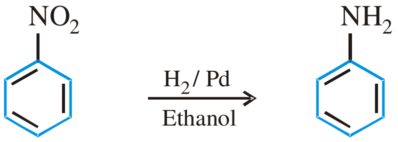
Sr.	Structural formula	Common name	IUPAC name	Type	Boiling point
1.	CH_3NH_2	Methylamine	Methanamine	1^0	280 K
2.	$CH_3CH_2NH_2$	Ethylamine	Ethanamine	1^0	290 K
3.	$CH_3CH_2CH_2NH_2$	Propylamine	Propan-1-amine	1^0	322 K
4.	 $CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-CH_3$	Isopropylamine	Propan-2-amine	1^0	306 K
5.	$CH_3–NH–CH_3$	Dimethylamine	N-Methylmethanamine	2^0	280 K
6.	$CH_3CH_2–NH–CH_2CH_3$	Diethylamine	N-Ethylethanamine	2^0	329.K
7.	$CH_3CH_2CH_2–NH–CH_2CH_2CH_3$	Dipropylamine	N-Propylpropan-1-amine	2^0	383 K

8.	$CH_3-NH-CH_2CH_3$	Ethylmethylamine	N-Methylethanamine	2^0	309 K
9.	$CH_3-NH-CH_2CH_2CH_3$	Methylpropylamine	N-Methylpropan-1-amine	2^0	335 K
10.	 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$	Trimethylamine	N, N-Dimethyl methanamine	3^0	276 K
11.	 $CH_3CH_2-\underset{\displaystyle CH_2CH_3}{\underset{\vert}{N}}-CH_2CH_3$	Triethylamine	N, N-Diethyl ethanamine	3^0	363 K
12.	 $CH_3CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_3$	Ethyldimethylamine	N, N-Dimethyl ethanamine	3^0	310 K
13.	 $CH_3-\underset{\displaystyle CH_2CH_3}{\underset{\vert}{N}}-CH_2CH_3$	Diethylmethylamine	N-Ethyl-N-methyl ethanamine	3^0	339 K
14.	 $CH_3-\underset{\displaystyle CH_2CH_2CH_3}{\underset{\vert}{N}}-CH_2CH_3$	Ethylmethylpropylamine	N-Ethyl-N-methyl propan-1-amine	3^0	367 K
15.		Aniline	Benzenamine or aniline	1^0	475 K
16.		N-Methylaniline	N-Methylbenzenamine	2^0	469 K
17.		N, N-Dimethylaniline	N, N-Dimethyl benzenamine	3^0	467 K

6.5 Preparation of Amine Compounds

The methods for preparation of amine compounds are as follows :

(i) Reduction of nitro compounds : Amine is produced by reduction reaction of nitro compounds by passing dihydrogen gas in presence of catalyst like nickel, palladium or platinum. Amine is also produced by their reduction in presence of metal in acidic medium. By reduction of nitroalkanes, alkanamines are formed. **In reduction of nitroalkane $LiAlH_4$ or $NaBH_4$ is also used.**



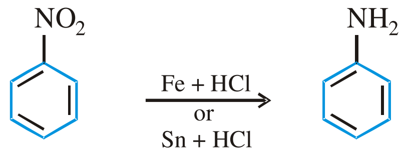
Nitrobenzene

Benzenamine or aniline

$$CH_3-CH_2-NO_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2-NH_2$$

Nitroethane

Ethanamine



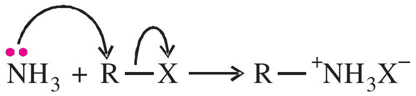
Nitrobenzene

Benzenamine or
Aniline

Presently, iron scrap and hydrochloric acid is used in larger proportions.

(ii) Ammonolysis of halides : As studied earlier in semester III, the carbon-halogen bond which is present in alkyl or aryl halide is easily broken by nucleophilic reagent. Hence by reaction of ethanolic ammonia on alkyl or aryl halide, the nucleophilic reagent (NH_2) substitutes the halogen and amine is formed. **The C–X bond is broken by molecule of ammonia so the reaction is called ammonolysis.**

The ammonolysis reaction of alkyl halide is carried out in air tight tube at 373 K temperature. Primary amine is first obtained, then it reacts with alkyl halide by chain reaction and secondary and tertiary amines are formed. In the end quarternary ammonium salt is formed.



$$\ddot{N}H_3 + R - X \longrightarrow R - \overset{+}{N}H_3X^-$$

By the reaction of ammonium salt with strong base free amine is obtained.

$$R - \overset{+}{N}H_3\overset{-}{X} + NaOH \rightarrow R - NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

$$\underset{\substack{(1^0)\\ \text{Primary}}}{R - NH_2} \xrightarrow{RX} \underset{\substack{(2^0)\\ \text{Secondary}}}{R_2NH} \xrightarrow{RX} \underset{\substack{(3^0)\\ \text{Tertiary}}}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quarternary}\\ \text{ammonium salt}}}{R_4\overset{+}{N} - \overset{-}{X}}$$

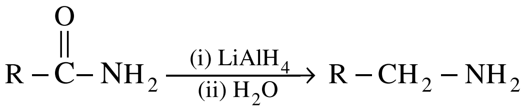
The disadvantage of ammonolysis is that the mixture of primary, secondary, tertiary and quarternary salt is obtained as product but by the use of ammonia in larger proportion primary amine can be obtained.

The order of reactivity of halide with amines is RI > RBr > RCl

(iii) Reduction of nitrile : By reaction of nitrile with lithium aluminium hydride ($LiAlH_4$) or by catalytic hydrogenation reaction, reduction takes place and primary amine is obtained. **This reaction is useful in increasing the number of carbons in the amine series i.e.** reaction of amine with one carbon can be started for preparation of amines.

$$R - C \equiv N \xrightarrow[Na(Hg) / C_2H_5OH]{H_2/Ni} R - CH_2 - NH_2$$

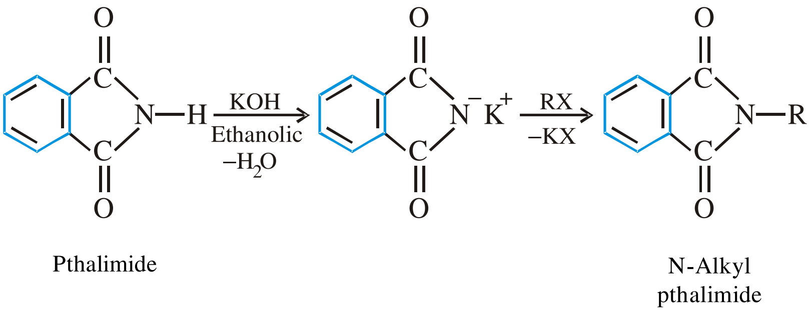
(iv) Reduction of amide : Amines are obtained by reduction of amide with lithium aluminium hydride.

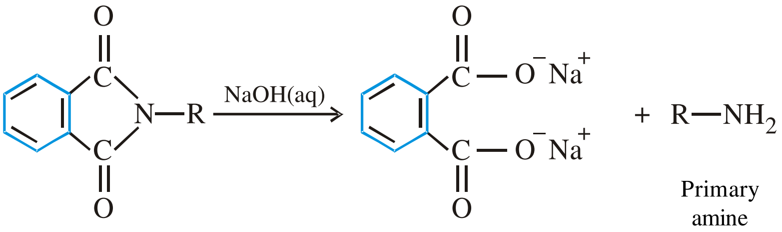


$$R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R - CH_2 - NH_2$$

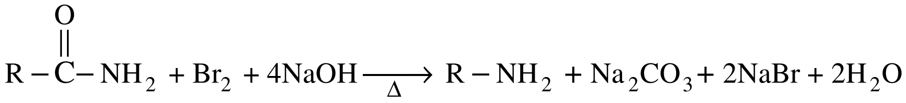
Amide　　　　Amine

(v) Gabriel pthalimide synthesis : Gabriel synthesis is used in the preparation of primary amines. By reaction of pthalimide with ethanolic potassium hydroxide, potassium salts of pthalimide are obtained which are when heated alkyl halide primary amines are obtained by alkaline aromatic hydrolysis. Primary aromatic amine can not be prepared by this method beacuse nucleophilic aryl halide, does not become favourable anion for phthalimide.





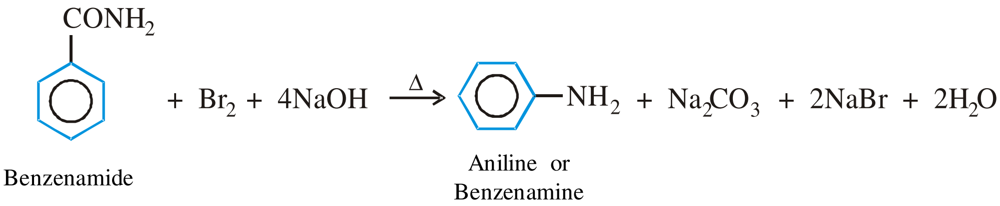
(vi) Hoffmann reaction : In Hoffmann reaction to prepare primary amine, the amide is heated with ethanolic solution of sodium hydroxide so that during the decomposition reaction, in place of carbonyl carbon in amide the nitrogen atom migrates to alkyl or aryl group. **Primary amine having one carbon less than amide is thus obtained.**



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

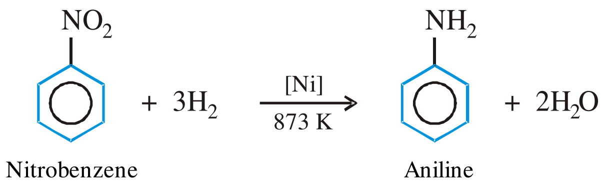
$$CH_3CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Ethanamide Methanamine

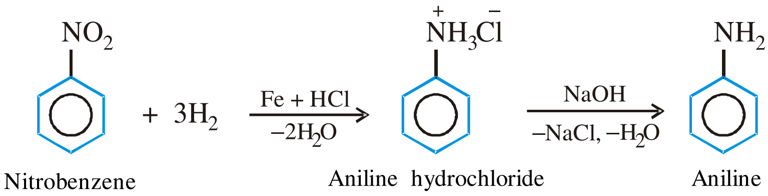


Industrial production of Aniline : As the use of aniline is widespread in chemical industry, its industrial production is carried out by reduction of nitrobenzene or by ammonolysis reaction with chlorobenzene.

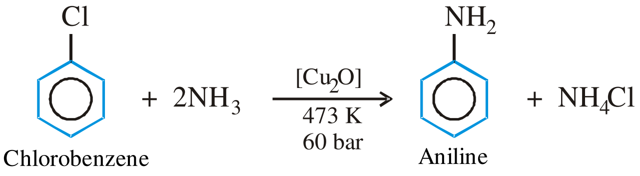
(a) The mixture of vapour of nitrobenzene and dihydrogen gas is heated at 873 K in presence of nickel catalyst, aniline is formed by reduction. Pure aniline is obtained by this method.



(b) By reduction of nitrobenzene with iron and hydrochloric acid, aniline hydrochloride is formed which is neutralised with sodium hydroxide and so aniline is separated.



When the mixture of chlorobenzene and two moles of ammonia are heated at 60 bar pressure and 473 K temperature in closed vessel in presence of Cu_2O catalyst, aniline is produced by ammonolysis reaction.



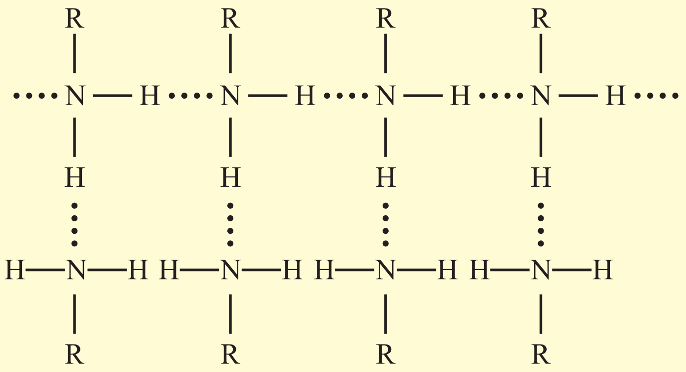
Pure aniline is almost colourless liquid having bad smell. It becomes dark red coloured when kept open in air for a long time because of oxidation. **The industrial use of aniline is in the manufacture of drugs, resin, varnish, as well as solvent and in vulcanisation of rubber.**

6.6 Physical Properties of Amines

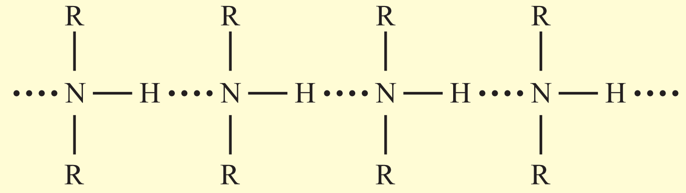
The boiling points of the primary amines having same number of carbon atoms containing alkane are higher; also the boiling points increases successively with the increase in number of carbon atoms in primary amine viz, in methanamine (boiling point 280 K), ethanamine (boiling point 290 K) propanamine (boiling point 322 K) increases successively with the increase in number of carbon atoms. In the isomeric alkyl amines having same molecular formula, the boiling point decreases from primary amine to tertiary amine, viz. (1^0) Propanamine (boiling point 322 K), (2^0) ethylmethyl amine (boiling point 309 K) and (3^0) trimethyl amine (boiling point 276 K) boiling points are decreasing.

As the electronegativity of nitrogen is less than that of oxygen, the $N^{-\delta}–H^{+\delta}$ bond in amines is less polar than the $O^{-\delta}–H^{+\delta}$ bond in alcohol. Hence, amine compounds are more polar than alkane but less polar than alcohol. Also, the intermolecular attraction in amine is less than that in alcohol. Hence, the boiling points of amine are higher than those of their corresponding alkanes and lower than those of their corresponding alcohols, viz ethanamine (boiling point 290 K) is more than ethane (boiling point 184 K) but lower than ethanol (boiling point 351 K).

There are intermolecular hydrogen bonds in primary and secondary amines while they are not there in tertiary amine. Hence, in isomeric primary alkyl amines having same molecular formula, it is highest, in secondary amine it is comparatively less and it is least in tertiary amine. viz. in (1^0) propanamine, (2^0) ethylmethylamine and (3^0) trimethylamine there is decrease in boiling point which is shown in fig 6.2.



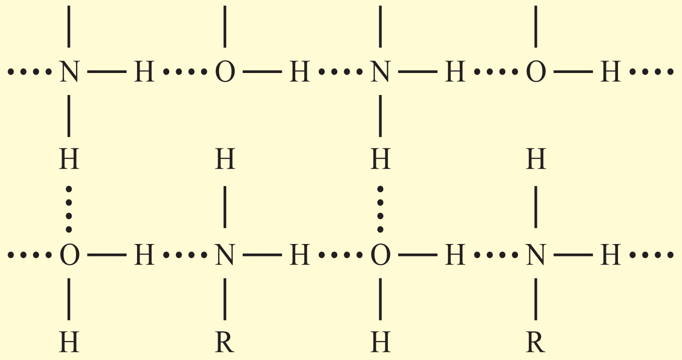
Intermolecular hydrogen bond between molecules of 1^0 amine



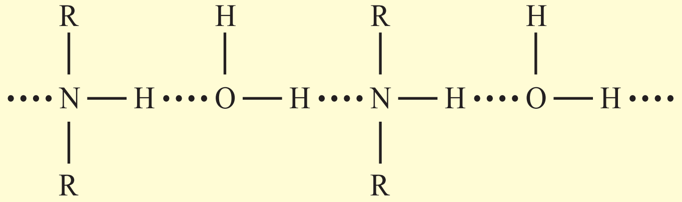
Intermolecular hydrogen bond between molecules of 2^0 amine

Fig. 6.2

In the aqueous solutions of primary and secondary amine compounds, water and amine molecules form hydrogen bond so the intermolecular attraction increases. In primary amines, there are two hydrogen atoms on the nitrogen and in secondary amine one hydrogen atom on nitrogen so the number of hydrogen bonds in primary amine becomes double. Hence, secondary amines corresponding to their primary amines having less molecular mass are less soluble in water as shown in the Fig 6.3.



Intermolecular hydrogen bond between molecules of 1^0 amine and water



Intermolecular hydrogen bond between molecules of 2^0 amine and water

Fig. 6.3

6.7 Chemical Reactions of Amine Compounds

(1) Basic characteristics of amine compounds : In amine compounds, the nitrogen atom has a non bonding electron pair, so amine compounds behave as Lewis base. **As amine compounds possess basic property, they react with acid and form salts.**

$$R-\overset{\bullet\bullet}{N}H_2 + HX \rightleftarrows R-\overset{+}{N}H_3\overset{-}{X} \text{ (Salt)}$$

These amine salts are soluble in water but insoluble in organic (non polar) solvents like ether. By reaction of amine salts with base like NaOH, the original amine compound is obtained back.

$$R-\overset{+}{N}H_3\overset{-}{X} + OH^- \rightarrow R-\overset{\bullet\bullet}{N}H_2 + H_2O + \overset{-}{X}$$

The strength of amines as base can be explained easily as follows according to K_b or pK_b values.

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + OH^-$$

$$K = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

$$K\,[H_2O] = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$\therefore\ K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]} \quad \text{or} \quad pK_b = -\log K_b$$

Higher value of K_b (or lower value of pK_b) shows more basicity of amine. In table 6.2 the values of pK_b of some amine compounds are shown. For ammonia the value of pK_b is 4.75. The values of pK_b of aliphatic amines are between 3 to 4.22 and so they are a stronger base than ammonia; while the values of pK_b of aromatic amines are higher than 4.22, and so they are weak base.

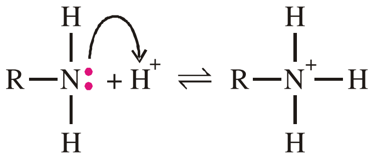
Table 6.2 pK_b values of aqueous solution of amines

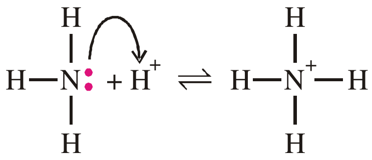
Sr.	Name of amine	pK_b
1.	Methanamine	3.38
2.	N-Methylmethanamine	3.27
3.	N, N-dimethylmethanamine	4.22
4.	Ethanamine	3.29
5.	N-Ethylethanamine	3.00
6.	N, N-Diethylethanamine	3.25
7.	Benzenamine	9.38
8.	Phenylmethanamine	4.70
9.	N-Methylaniline	9.70
10.	N, N-Dimethylaniline	8.92

Relation between basicity of amines and structure : The basicity of amines is related with their structures. The basicity of amine depends on the tendency to form positive ion easily by receiving proton from acid. If the corresponding positive ion of amine is more stable then, amine is more basic.

(a) Basicity of aliphatic amine (alkanamine) :

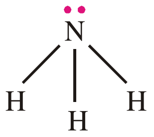
(i) Comparison of alkanamine with ammonia : The basicities of alkanamies and ammonia are compared by taking into consideration their reaction with proton (H^+).



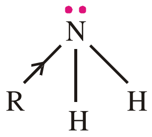


Because of the electron donating property of alkyl group, in alkanamine, alkyl group produces + I effect (You have studied + I effect in semester I). Hence, in alkalanine the non-bonding electron pair is easily available for sharing with proton. In addition, they attain stability because of + I effect of alkyl group, the **displaced ammonium ion formed from amine by, spreading of positive charge. Hence, alkanamines are stronger base than ammonia.**

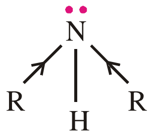
(ii) Comparison of primary, secondary and tertiary alkanamines : Going from tertiary amine to primary amine, the + I effect of alkyl group is decreasing because of the three groups attached with nitrogen atom in primary, secondary and tertiary amines having one, two and three alkyl groups are attached respectively.



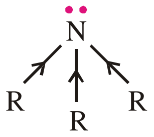
Ammonia



Primary Amine



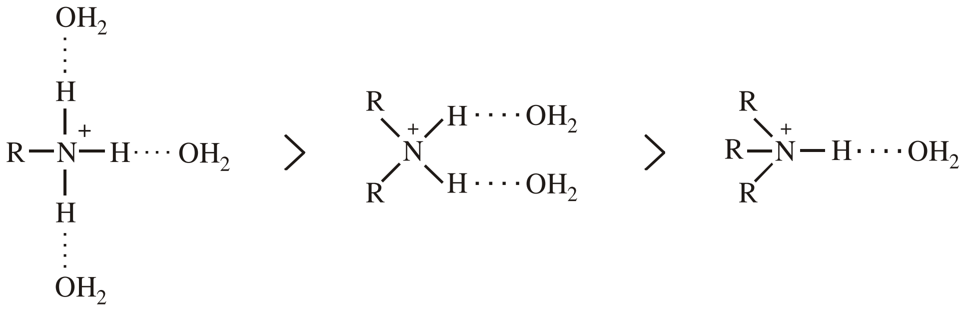
Secondary Amine



Tertiary Amine

Alkyl group is electron releasing group and so it sends the electrons of bond towards N. Thus the electron density of N-atom increases. As there are more number of alkyl group in tertiary amine, N atom will have more electron density in the compound. So such compounds can easily donate electron pair. **Hence, the order of basicity of ammonia, primary amine, secondary amine and tertiary amine gaseous phase is Tertiary amine > secondary amine > primary amine > ammonia.**

The strength of different types of alkanamines in aqueous medium are not observed in the above order, because in addition to + I effect of alkyl group due to the solvation (hydration) with molecule of water, the stability of displaced positive ion affect the stability. More the size of the positive ion less is the solvation. Hence the stability of positive ion is less. The order of stability of different positive ions in aqueous medium is as below :



So the order of basicity of alkanamines will be primary amine > secondary amine > tertiary amine.

Also, if the alkyl group is small (viz. $-CH_3$) then there is no steric hindrance for H–bond but for alkyl group bigger than $-CH_3$ (viz. $-C_2H_5$). If $-C_2H_5$ is present then the steric hindrance increases and so there is a difference in basic strength. Thus, +I effect, solvation effect and steric hindrance of alkyl group play an important role in determining the strength of alkanamine as base in aqueous medium.

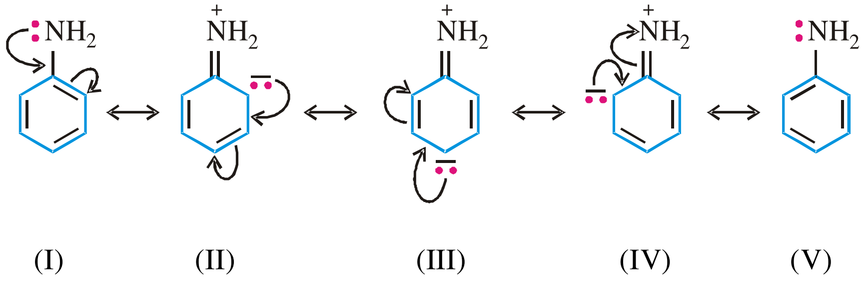
The order of strength as base in methyl displaced amines and ethyl displaced amines is respectively as follow :

$(C_2H_5)_2{-}NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ **and**

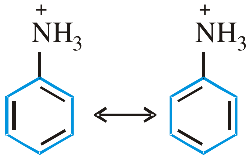
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(b) Basicity of aromatic amine (Aryl amine) :

(i) The basicity of aryl amine is less than that of ammonia because of the resonance of aniline as follows : the non-bonding electron pair on N delocalises on benzene ring. Hence, the non-bonding electron pair is not easily available for protonation on N.



Also, the anilinium ion that is obtained by protonation of aniline possesses two resonance structures.



So, the stability of aniline is more than anilinium ion. Hence, the tendency of aniline or aromatic amine to receive proton is less.

The resonance structures are not available in ammonia and aliphatic amine compounds, like aniline, so the electron pair on their N atom is localised. Hence, these compounds can easily donate electron pairs so that their basicity is more than that of aniline. As discussed in the earlier points, keeping in mind the order of basicity of aliphatic amine and ammonia the order of basicity of amine compounds can be written as follows :

Tertiary amine > secondary amine > primary amine > ammonia > aniline.

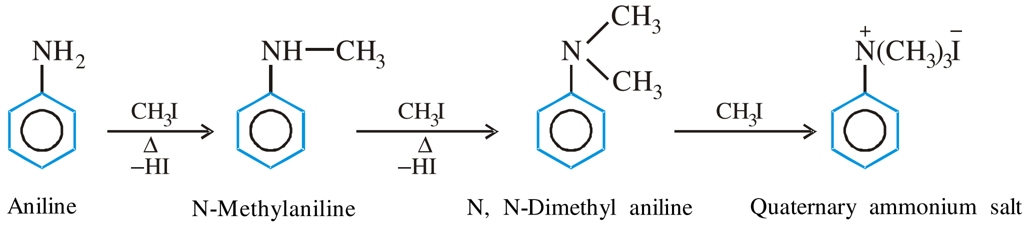
(ii) In the case of substituted aniline, it is found that because of the presence of electron donating groups like –OCH_3, –CH_3 the strength as base increases. While because of the presence of electron attracting groups like –NO_2, –SO_3H, –COOH its strength as a base decreases.

(2) Alkylation : By reaction of aliphatic and aromatic primary (1^0) amines with alkyl halide, secondary (2^0) amine is obtained. If it reacts with more amount of alkyl halide, then successively tertiary and then quarternary ammonium salt is obtained.

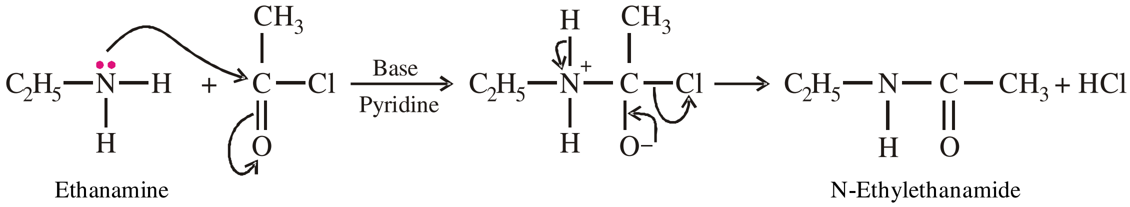
(a) On reacting ethanamine with ethyl iodide, N-ethylethanamide is obtained. By reacting this product with more amount of ethyl iodide, first N, N-diethylethanamine and then tetramethyl ammonium iodide salt is obtained

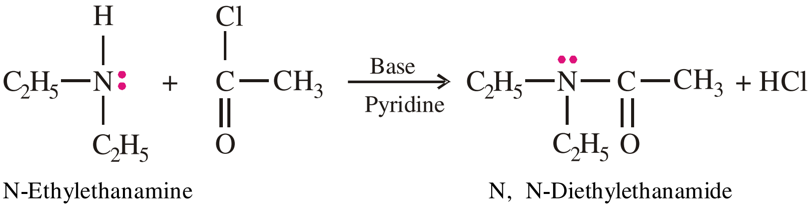
$$\underset{\text{Ethanamine}}{C_2H_5NH_2} + C_2H_5I \xrightarrow[-HI]{} \underset{\substack{\text{N-Ethyl}\\ \text{ethanamine}}}{(C_2H_5)_2NH} \xrightarrow[-HI]{+C_2H_5I} \underset{\substack{\text{N, N-Diethyl}\\ \text{ethanamine}}}{(C_2H_5)_3N} \xrightarrow{+C_2H_5I} \underset{\substack{\text{Quaternary ethyl}\\ \text{ammonium iodide (salt)}}}{(C_2H_5)_4\overset{+}{N}\overset{-}{I}}$$

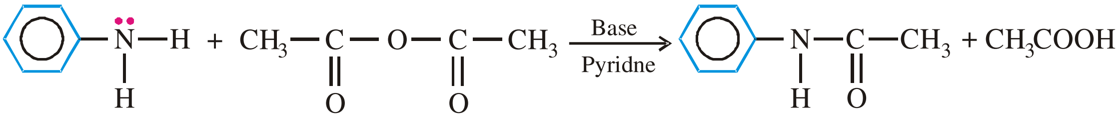
(b) Similarly, on heating aniline with methyl iodide N-Methylaniline is obtained. If methyl iodide is taken in excess proportion then tertiary amine and then quaternary ammonium salt is obtained.



(3) Acylation : When aliphatic and aromatic primary and secondary amines react with acid chloride or acid anhydride, nucleophilic subtitution reaction takes place and amide product is obtained. This reaction is known as acylation. This reaction is carried out in pyridine which is a stronger base than amine.

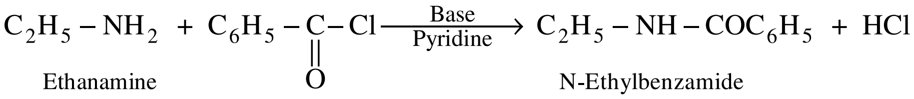






N-Phenylethanamine
(Acetanilide)

Primary and secondary amine react with benzoyl chloride. This reaction is called benzoylation.



$$C_2H_5-NH_2 + C_6H_5-\underset{\substack{\|\\O}}{C}-Cl \xrightarrow[\text{Pyridine}]{\text{Base}} C_2H_5-NH-COC_6H_5 + HCl$$

Ethanamine N-Ethylbenzamide

$$C_6H_5-NH_2 + C_6H_5COCl \xrightarrow[\text{Pyridine}]{\text{Base}} C_6H_5-NH-CO-C_6H_5 + HCl$$

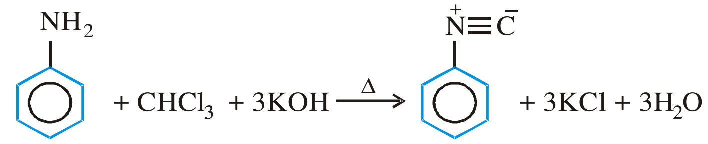
Aniline N-Phenylbenzamide

(4) Carbylamine reaction : On heating aliphatic or aromatic primary amine with chloroform ($(CHCl_3)$) and alcoholic potassium hydroxide (KOH) foul smell possessing poisonous isocyanide (carbylamine) is formed. This reaction is called carbylamine test or isocyanide identification. Secondary and tertiary amines do not give this test. **This test is used in laboratory for the identification of primary amine.**

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

$$CH_3-CH_2-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-CH_2-NC + 3KCl + 3H_2O$$

Ethanamine Ethyl isocyanide



Aniline or
Benzenamine

Phenyl isocyanide

(5) Reaction with nitrous acid : All the three types (1^0, 2^0 and 3^0) amine compounds react with nitrous acid (HNO_2) in different ways. Here, nitrous acid is prepared by the reaction of sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl)

(a) Primary alkyl amine reacts with nitrous acid (HNO_2) and gives alkyldiazonium salt which is unstable and so this salt releases nitrogen and changes to alcohol.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N_2}\bullet\overset{-}{Cl}] \xrightarrow{H_2O} R-OH + N_2 + HCl$$

Alkanamine Unstable Alcohol

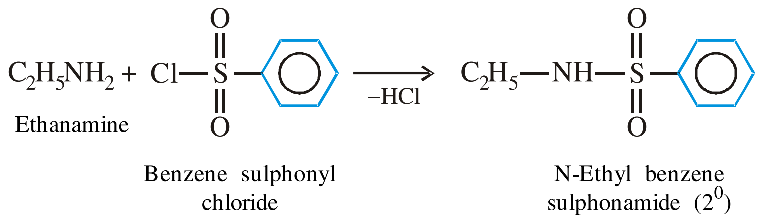
$$CH_3–CH_2–NH_2 + HNO_2 \xrightarrow[+ HCl]{NaNO_2} [CH_3–CH_2–\overset{+}{N_2}\,\overset{-}{Cl}] \xrightarrow{H_2O} CH_3–CH_2–OH + N_2 + HCl$$

Ethanamine Unstable Ethanol

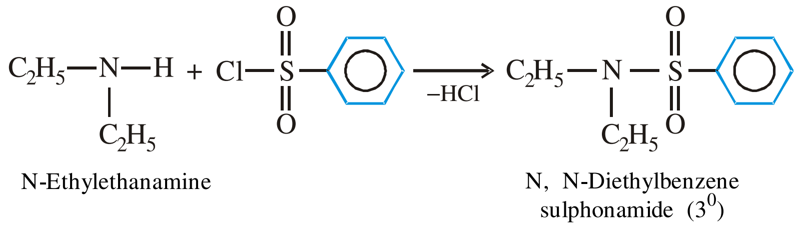
(b) Aromatic primary amine reacts with nitrous acid (HNO_2) at low temperature (273-278 K) and forms diazonium salt. The use of this salt in synthesis of aromatic compounds is very important which we shall study later on in this unit.

$$\underset{\text{Benzenamine}}{C_6H_5NH_2} \xrightarrow[\text{[HNO}_2\text{]} \quad 273\text{-}278\text{ K}]{NaNO_2 + HCl} C_6H_5 - \overset{+}{N}_2 \overset{-}{Cl} + NaCl + 2H_2O$$

(6) Reaction with Hinsberg reagent : Primary amine and secondary amine react with benzene sulphonyl chloride (Hinsberg reagent) and give sulphonamide product while in tertiary amine, because hydrogen is not attached with N, it does not undergo this reaction.



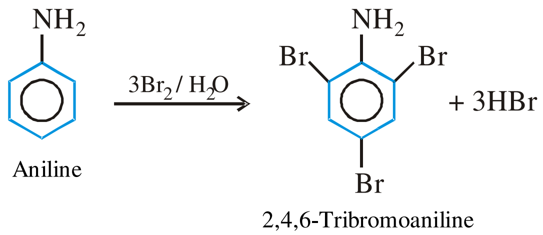
In this compound, acidic hydrogen is combined with nitrogen, so it is soluble in alkali.



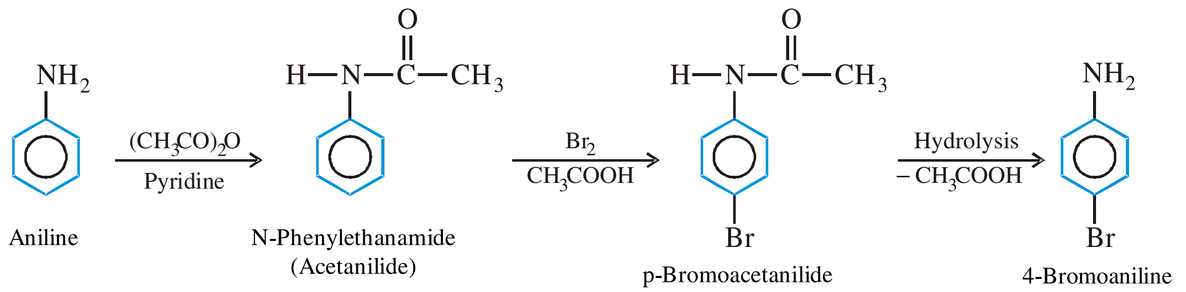
In this compound, acidic hydrogen is not joined with N, and so it is insoluble in alkali.

(7) Electrophilic substitution reaction : Aromatic amines give electrophilic substitution reactions. **In case of $-NH_2$ group electron density is very high on o- and p- position so ortho and para substituted products are obtained.**

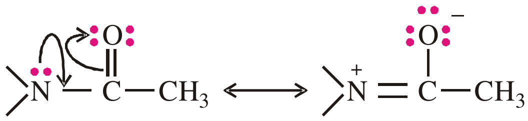
(a) Bromination : At room temperature aniline reacts with bromine water and gives white precipitates of 2,4,6-tribromoaniline.



If only monosubstituted aniline derivative is desired then first, acetylation of $-NH_2$ group with acetic anhydride, (electrophilic substitution) is carried out. At the end of this reaction the amide product is hydrolysed so that monosubstituted aromatic amine is obtained.

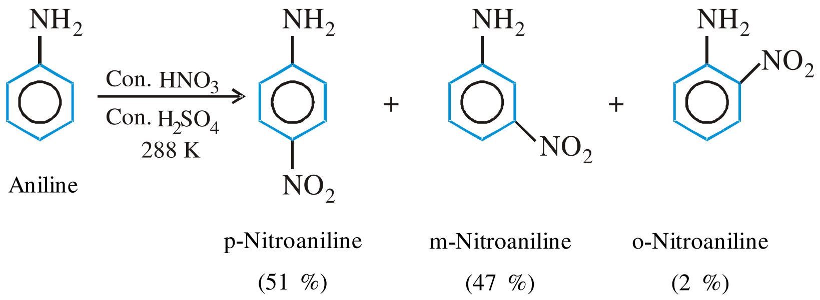


In the above reaction, in the formed acetanilide there is resonance and so the non-bonding electron pair interacts with oxygen atom.

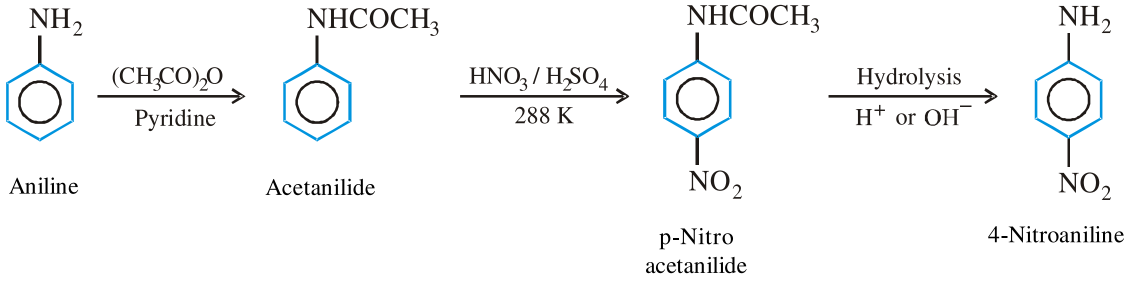


Hence, the electrons are not easily available to benzene for resonance. This functional effect of –NHCOCH$_3$ group decreases compared to –NH$_2$ group.

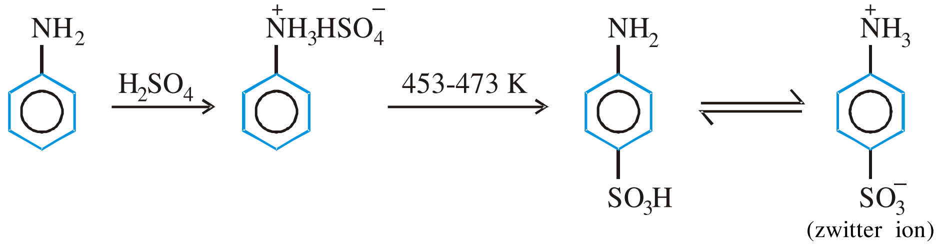
(b) Nitration : Aniline in presence of con. H_2SO_4 reacts with con. HNO_3 at 288 K temperature and mixture of p- and o- nitroaniline with m- nitroaniline are obtained by nitration because the **anilinium ion $-\overset{+}{N}H_3$ formed in acidic medium is m-directing group.**



Here also, to obtain monosubstituted derivative, first acetylation of –NH$_2$ group with acetic anhydride is carried out and then nitration is carried out.



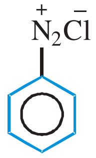
(c) Sulphonation : On reaction of aniline with con. H_2SO_4, anilinium hydrogen sulphate is obtained, which is if heated at 453-473 K temperature product, p-aminobenzene sulphonic acid (sulphanilic acid) is obtained as product.



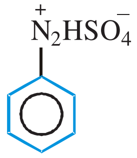
Aniline does not give Friedel-Crafts alkylation and acylation reactions because the catalyst anhydrous $AlCl_3$ used in the reaction is Lewis acid and so it forms salt by combining with aniline. Hence, **nitrogen in aniline attains positive electric charge so it acts as deactivating group for the further reaction.**

6.8 Diazonium Salt

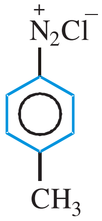
Diazonium salt is shown by general formula as Ar $\overset{+}{N}_2\overset{-}{X}$ **where** $X^- = Cl^-, Br^-, HSO_4^-, BF_4^-$ **etc.** $\overset{+}{N}_2\ (-\overset{+}{N}\equiv N)$ **group is called diazonium group.** In their nomenclature diazonium suffix is applied to original hydrocarbon and then the name of negative ion is written. e.g.,



Benzenediazonium chloride

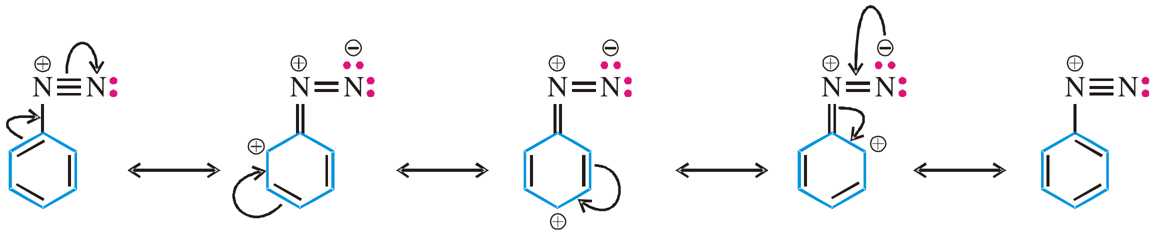


Benzenediazonium hydrogen sulphate



p-Toluenediazonium chloride

Primary aliphatic amine forms highly unstable alkyl diazonium salt while primary aromatic amine which forms arenediazonium salt, is stable due to resonance as shown below.

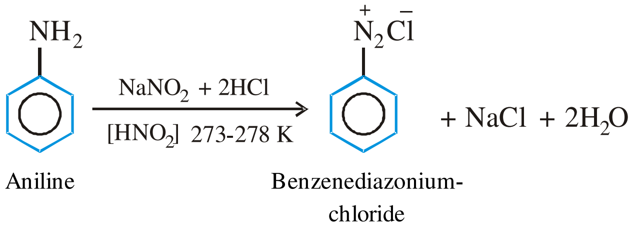


(a) Preparation of benzenediazonium chloride salt : In the reaction between primary aromatic amine and nitrous acid carried out at low temperature, diazonium salt is formed. This reaction is called diazotisation.

A solution of aniline in dilute hydrochloric acid is prepared and, it is cooled to 273-278 K temperature; On adding sodium nitrite, nitrous acid is formed and benzene diazonium chloride (salt) is obtained. As benzenediazonium salt is unstable at higher temperature, it is necessary to keep the temperature 273-278 K.

$$Ar-NH_2 \xrightarrow[{[HNO_2]}\ 273\text{-}278\ K]{NaNO_2\ +\ 2HCl} Ar-\overset{+}{N}\equiv N\cdot\overset{-}{Cl}+NaCl+2H_2O$$

As diazonium salt is unstable, it is used immediately.



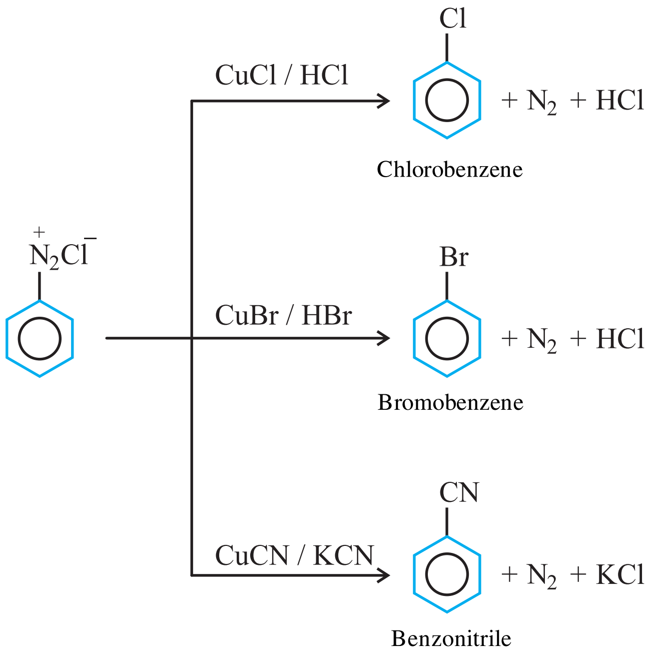
(b) Physical properties : Benzenediazonium chloride is colourless, crystalline solid. It is easily soluble in water and at low temperature becomes stable in solution; but on heating it reacts with water. It easily decomposes in dry state. Benzenediazonium fluoroborate $(C_6H_5N_2^+BF_4^-)$ named diazonium salt is insoluble in water and is stable at room temperature.

(c) Chemical reactions :

(A) Displacement of nitrogen : Diazonium group $(-\overset{+}{N}\equiv N)$ can be substituted by groups like Cl^-, Br^-, I^-, CN^-, OH^- and dinitrogen (N_2) is removed in the form of gas because of substitution reaction.

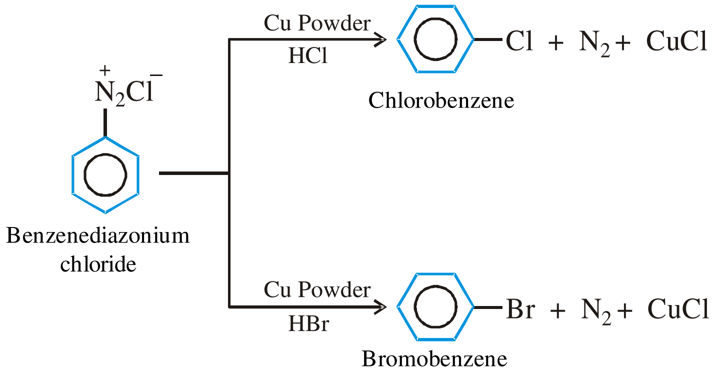
(i) Diazonium salt reacting with cuprous chloride in HCl gives chlorobenzene, with cuprous bromide in HBr gives bromobenzene and with cuprous cyanide in KCN gives benzonitrile (cyanobenzene). These reactions are called **Sandmeyer reactions.**

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow{CuX / HX\ (X = Cl^-,\ Br^-,\ CN^-)} Ar-X+N_2+HCl$$



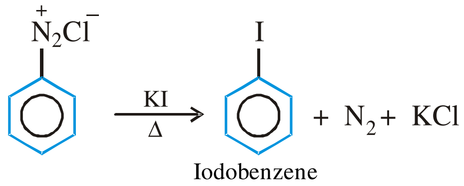
(ii) On reaction of diazonium salt in presence of copper powder with HCl or HBr, chlorobenzene or bromobenzene are respectively obtained. This reaction is called Gatterman reaction.

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow[HX\ (X = Cl,\ Br)]{Cu\ powder} Ar-X+N_2+CuCl$$



(iii) On heating diazonium salt with potassium iodide, iodobenzene is formed.

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow[\Delta]{KI}Ar-I+N_2+KCl$$

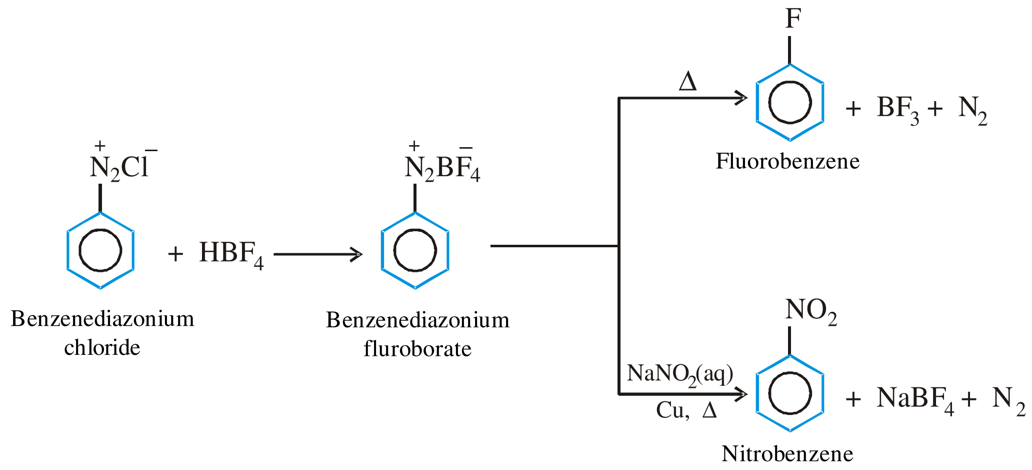


(iv) Precipitates of diazonium fluoroborate are obtained by reaction of diazonium salt with fluoroboric acid (HBF_4). On heating, it decomposes and gives fluorobenzene.

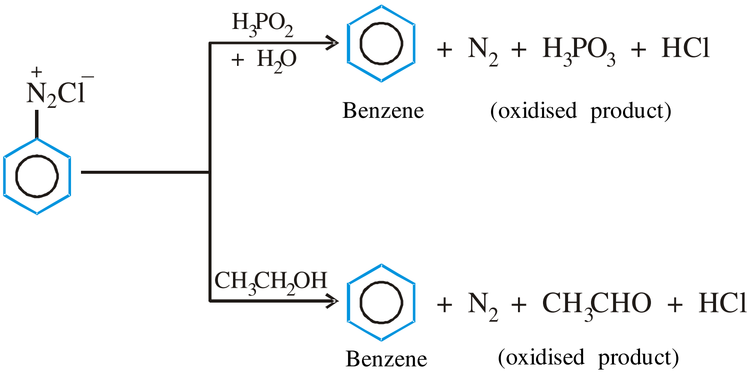
In addition, nitrobenzene is obtained by heating diazonium fluoroborate with aqueous solution of sodium nitrite ($NaNO_2$) in presence of copper metal.

$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow{\Delta}ArF+BF_3+N_2$$

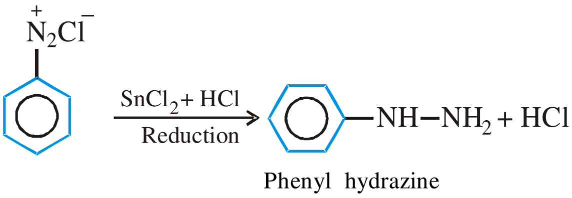
$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow[Cu,\ \Delta]{NaNO_2(aq)}ArNO_2+NaBF_4+N_2$$



(v) Benzene is obtained by reduction of diazonium salt with weak reducing agent like hypophosphorus acid (Phosphinic acid, H_3PO_2) or ethanol.

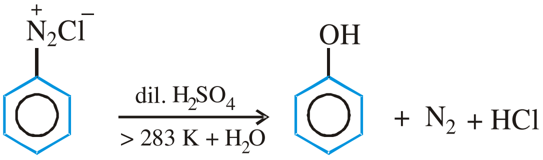


When diazonium salt is reduced with stannous chloride and hydrochloric acid, it gives phenyl hydrazine (Here diazonium group is not substituted).



(vi) Phenol is obtained by heating diazonium salt with dil. H_2SO_4 at temperature higher than 283 K.

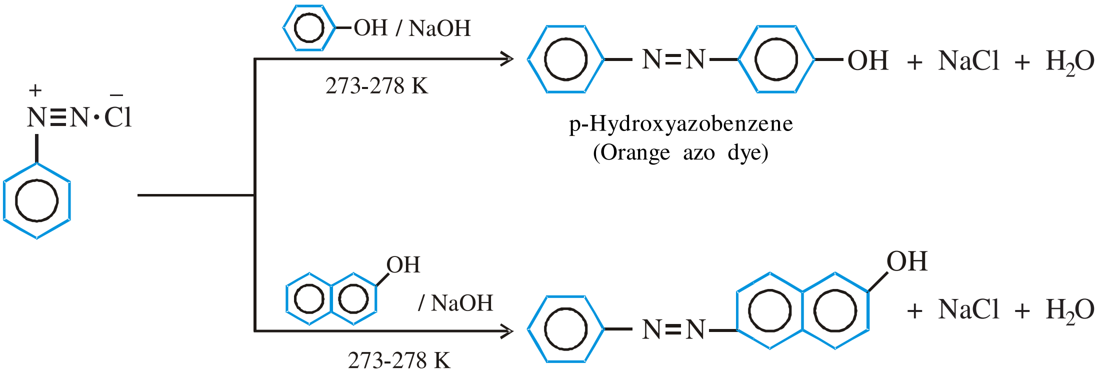
$$Ar\overset{+}{N_2}\overset{-}{X} \xrightarrow[283\ K + H_2O]{H_2SO_4} Ar-OH + N_2 + HCl$$



Benzendiazonium chloride

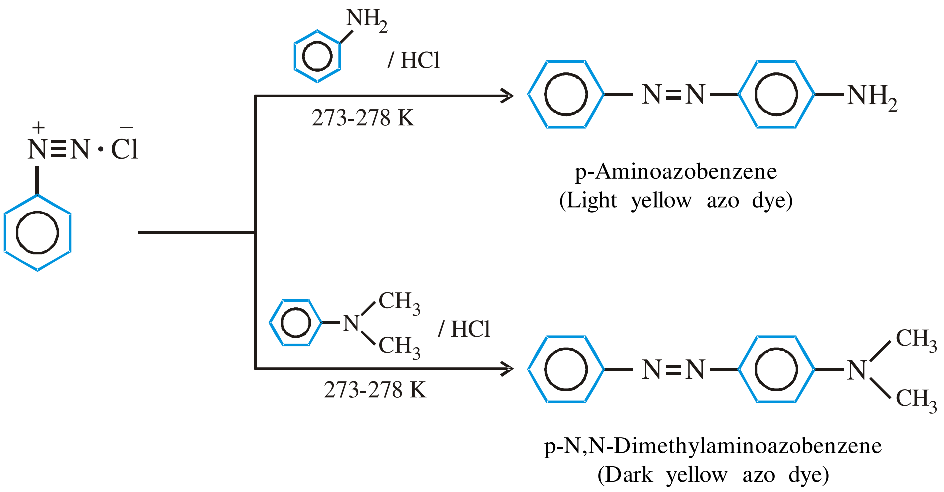
Phenol

(B) Azo coupling reaction : Solution of phenol or beta naphthol (β-naphthol) in sodium hydroxide when reacts with benzene diazonium chloride at 273-278 K temperature, orange and red colour azo dyes are obtained. Also, light yellow and dark yellow coloured azo dyes are respectively obtained when solutions of aniline or N,N-dimethyl aniline in hydrochloric acid react with benzene diazonium chloride.



p-Hydroxyazobenzene
(Orange azo dye)

β-Naphthylazobenzene
(Red azo dye)



(d) Importance of Diazonium salts in synthesis of Aromatic compounds : From the above reactions, it can be said that to introduce –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$ groups in aromatic (benzene) ring, diazonium salt is an important intermediate compound.

From aromatic (benzene) compounds, aromatic (aryl) fluoride and aromatic (aryl) iodide can not be obtained by direct halogenation reaction. **Similary benzonitrile can not be prepared by nucleophilic substitution of benzene but these compounds can be easily prepared via diazonium salt.**

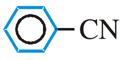
6.9 Cyanide or Nitrile Compounds

If cyano or nitrile group is present in organic compounds they are called cyanide or nitrile compounds. Carbon, hydrogen and nitrogen elements are mainly present in nitrile compounds. Its general formula is shown as $R-C\equiv N$ in which R = alkyl or aryl group.

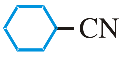
IUPAC Nomenclature of nitrile compounds : For common nomenclature, “Cyanide” word is placed at the end of the name of hydrocarbon. Viz. $CH_3-C\equiv N$ methyl cyanide, $CH_3-CH_2-C\equiv N$ ethyl cyanide etc.

For IUPAC nomenclature of nitrile compounds, the longest carbon series of original hydrocarbon is determined and then with carbon of nitrile group the longest carbon series of original hydrocarbon is determined and then at the end the word “nitrile’ is attached, viz. $CH_3-C\equiv N$ ethane nitrile; $CH_3-CH_2-C\equiv N$ propane nitrile. **If –CN group is attached with cyclic system, then for their IUPAC name the suffix “carbonitrile” is joined.**

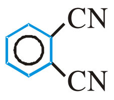
Viz.,



Benzenecarbonitrile



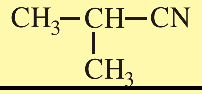
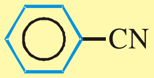
Cyclohexanecarbonitrile



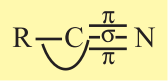
Benzene-1,2-dicarbonitrile

Structural formulas, common name, IUPAC name and boiling points of some cyanide compounds are given in table 6.3

Tabel 6.3 Structural formula, common name IUPAC name and boiling points of some cyanide compounds

Sr.	Structural formula	Common name	IUPAC name	Boiling point
1.	$CH_3–CN$	Methyl cyanide	Ethanenitrile	355 K
2.	$CH_3–CH_2–CN$	Ethyl cyanide	Propanenitrile	370 K
3.	$CH_2=CH–CN$	Vinyl cyanide (Acrylonitrile)	Prop-2-enenitrile	351 K
4.	$CH_3–CH_2–CH_2–CN$	Propyl cyanide	Butane nitrile	391 K
5.	 $CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CN$	Isopropyl cyanide	2-Methyl propane nitrile	377 K
6.		Phenyl cyanide (Benzonitrile)	Benzene carbonitrile or Benzonitrile	464 K

Electronic structure of Cyanide :



C–N one σ and two π bonds

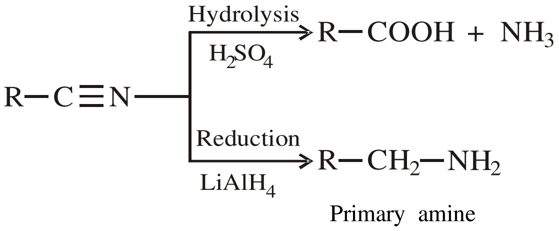
C and N sp hybridisation

R–C–N bond angle 180^0.

Physical properties of cyanides : In alkyl cyanide compounds $–C^{+\delta}\equiv N^{-\delta}$ bond being polar and absence of intermolecular hydrogen bond, the boiling points of alkyl cyanides are less than their corresponding carboxylic acids, viz. The boiling points of ethane nitrile (boiling points 355 K) and propane nitrile (boiling point 370 K) are lower than the boiling points of ethanoic acid (boiling point 391 K) and propanoic acid (boiling point 414 K) respectively

Alkyl cyanides are very weak basic compounds, having fine fragrant smell and are non-poisonous compounds. The alkyl cyanides having less molecular masses are soluble in water as well as is many other organic solvents. Ethane nitrile (acetonitrile) is the most dipolar and so it makes many types of organic reagents soluble in it. Its boiling point being normal, it can be easily removed so that it can be used again and it being inert it is useful as solvent in many most of the organic reactions.

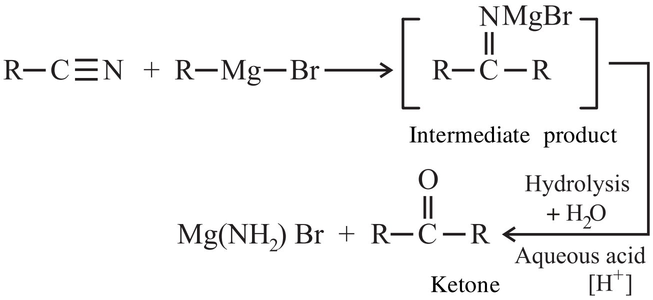
Chemical properties of cyanides : Carboxylic acids are obtained by hydrolysis of cyanide compounds in presence of sulphuric acid and ammonia is liberated. Primary amine is obtained by reduction with $LiAlH_4$.

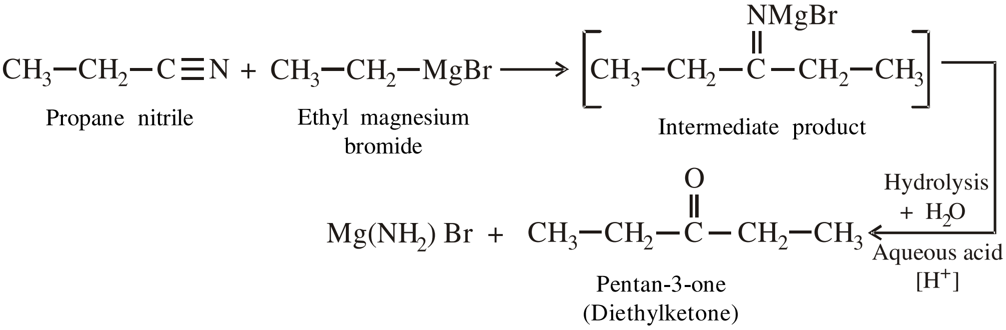


(i) Ethylethanoate (ethyl acetate) is formed when ethane nitrile and ethanol are heated in presence of concentrated sulphuric acid.

$$\underset{\text{Ethane nitrile}}{CH_3-C\equiv N} + \underset{\text{Ethanol}}{CH_3-CH_2-OH} + H_2O \xrightarrow[\Delta]{\text{Con. }[H_2SO_4]} \underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3} + NH_3$$

(ii) Ketone is obtained by hydrolysis of the intermediate product in presence of aqueous acid; the intermediate product is obtained by addition reaction of cyanide compounds with Grignard reagent (R–Mg–X) (X = Br, I)





6.10 Isocyanide Compounds

If isocyanide group is present in organic compounds, they are called isocyanide compounds. These compounds are also called isonitrile or carbylamine compounds. In isocyanide compounds, mainly carbon, hydrogen and nitrogen elements are present. **Their general formula can be shown as $R-\overset{+}{N}\equiv\overset{-}{C}$ where R = alkyl group or aryl group.** Isocyanide group is dipolar in which nitrogen possesses positive charge and carbon possesses negative charge. The characteristic of cyanide groups are opposite to those of isocyanides.

The naming of isocyanide compounds is done by placing the prefix "iso" before the name of cyanide compounds. In other method of nomeclature, carbylamine word is placed at the end of the alkyl group, viz **CH_3–NC is methylisocyanide and according to IUPAC it is called ethan isonitrile or methylcarbylamine.**

The boiling points of alkyl isocyanides are lower than their isomeric alkyl cyanides because isocyanide group is dipolar. These compounds possess very foul smell and are very poisonous and sparingly soluble in water.

When isocynide compounds are reduced with $LiAlH_4$, secondary amine is obtained as product.

$$R-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[LiAlH_4]{Reduction}R-NH-CH_3$$

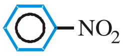
(2^0) Secondary amine

$$CH_3-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[LiAlH_4]{Reduction}CH_3-NH-CH_3$$

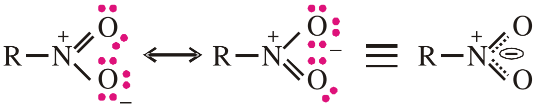
Ethanisonitrile — N-Methylmethanamine (Dimethyl amine)

6.11 Nitro Compounds

If nitro group is present in organic compounds, they are called nitro compounds. In nitro compounds mainly carbon, hydrogen, nitrogen and oxygen atoms are present. Their general formula is shown as **$R–NO_2$ where R = alkyl or aryl group.**

For IUPAC nomenclature of alkyl nitro compounds, the longest carbon series of the original alkane is determined and the prefix nitro is added. viz. $CH_3–NO_2$ nitromethane, $CH_3–CH_2–NO_2$ nitroethane etc. The nomenclature of aryl nitro compounds is done as for alkyl nitro compounds, viz.  nitrobenzene.

Nitro compounds are colourless, having odour, neutral and sparingly soluble in water. The resonance forms of alkyl nitro compounds :



The mixture of alkyl nitro compounds is obtained by nitration reaction of alkane hydrocarbon and heating with fuming nitric acid in vapour state at 673 K temperature, viz. By nitration of propane, nitro methane, nitroethane and 1-nitropropane are obtained. The industrial production of alkyl nitro compounds is carried out by this method.

$$2CH_3-CH_2-CH_3\xrightarrow[673\ K]{Fuming\ HNO_3}CH_3-NO_2+CH_3-CH_2-NO_2+CH_3-CH_2-CH_2-NO_2$$

Propane — Nitromethane — Nitroethane — 1-Nitropropane

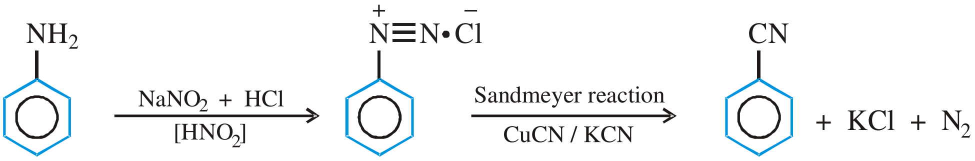
Primary alkyl amines are obtained by carrying out reduction of nitroalkane with lithium aluminium hydride ($LiAlH_4$) or with hydrogen in presence of nickel catalyst.

$$CH_3-CH_2-NO_2+3H_2\xrightarrow[or\ [Ni]]{LiAlH_4}CH_3-CH_2-NH_2+2H_2O$$

Nitroethane — Ethanamine

Some Organic Conversions :

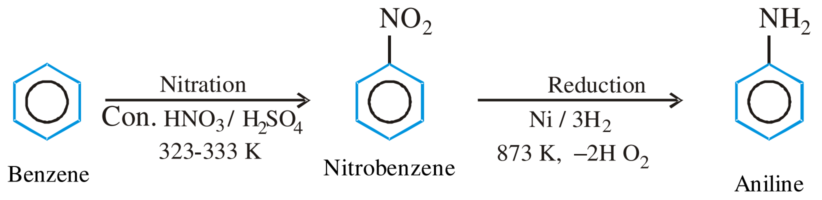
(i) Cyanobenzene from aniline :



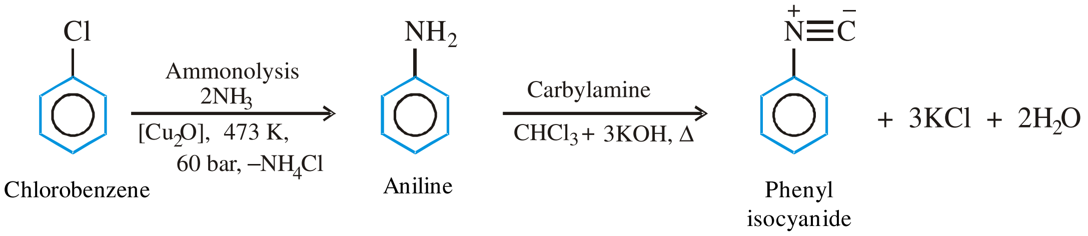
Benzenediazonium chloride

Cyanobenzene (Phenylcyanide)

(ii) Aniline from benzene :



(iii) Phenyl isocyanide from chlorobenzene :



(iv) Diethylamine from methylcyanide :

$$CH_3-C\equiv N \xrightarrow[LiAlH_4]{Reduction} CH_3-CH_2-NH_2 \xrightarrow[-HI]{Alkylation,\ C_2H_5I} C_2H_5-NH-C_2H_5$$

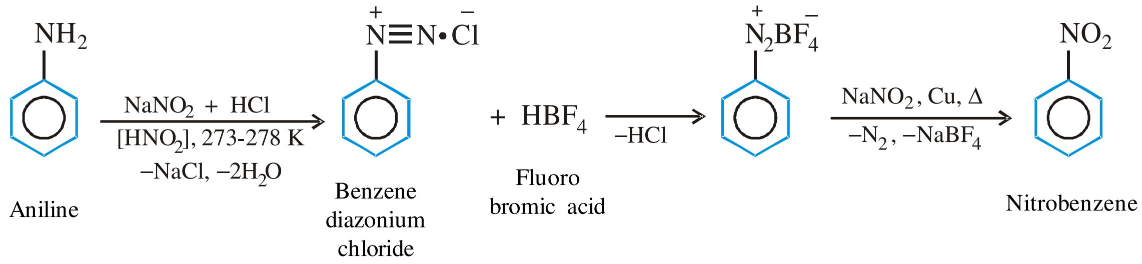
Methylcyanide Ethanamine Diethylamine

(v) N-acetyl ethylamine from acetamide :

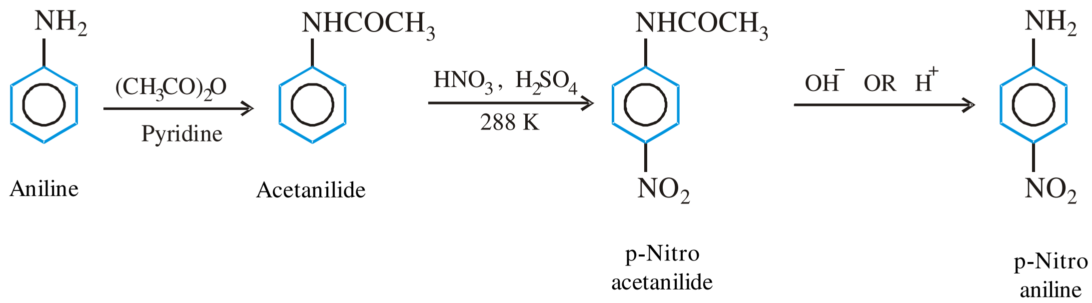
$$CH_3CONH_2 \xrightarrow[(i)\ LiAlH_4\ (ii)\ H_2O]{Reduction} CH_3-CH_2-NH_2 \xrightarrow[\substack{or\ (CH_3CO)_2O,\ -HCl \\ or\ -CH_3COOH}]{Acetylation,\ CH_3COCl} CH_3-CH_2NHCOCH_3$$

Acetamide Ethanamine N-Acetylethyle amine

(vi) Nitrobenzene from aniline :



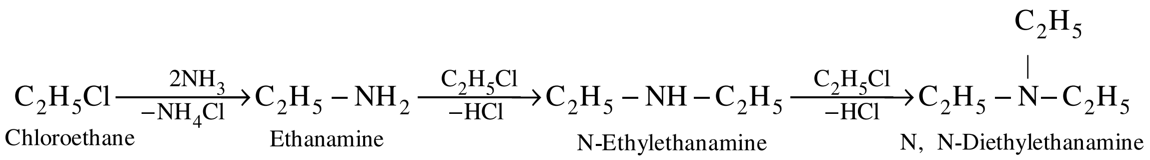
(vii) p-Nitroaniline from aniline :



(viii) Dimethyl amine from methylchloride

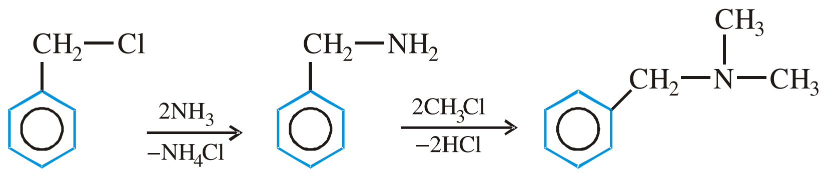
$$\underset{\text{Methylchloride}}{CH_3Cl} \xrightarrow[-NH_4Cl]{\substack{2NH_3\\ \text{Ammonolysis}}} \underset{\text{Methanamine}}{CH_3-NH_2} \xrightarrow[\substack{CHCl_3\ +\ 3KOH,\\ -3KCl,\ -3H_2O}]{\text{Carbylamine}} \underset{\substack{\text{Methyl}\\ \text{isocyanide}}}{CH_3-N\equiv C} \xrightarrow[Ni\ /\ 2H_2]{\text{Reduction}} \underset{\substack{\text{Dimethyl}\\ \text{amine}}}{CH_3-NH-CH_3}$$

(ix) N,N-Diethylethanamine from chloroethane



$$\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow[-NH_4Cl]{2NH_3} \underset{\text{Ethanamine}}{C_2H_5-NH_2} \xrightarrow[-HCl]{C_2H_5Cl} \underset{\text{N-Ethylethanamine}}{C_2H_5-NH-C_2H_5} \xrightarrow[-HCl]{C_2H_5Cl} \underset{\text{N, N-Diethylethanamine}}{C_2H_5-\overset{\overset{\displaystyle C_2H_5}{|}}{N}-C_2H_5}$$

(x) N, N-Dimethylphenylmethanamine from benzyl chloride

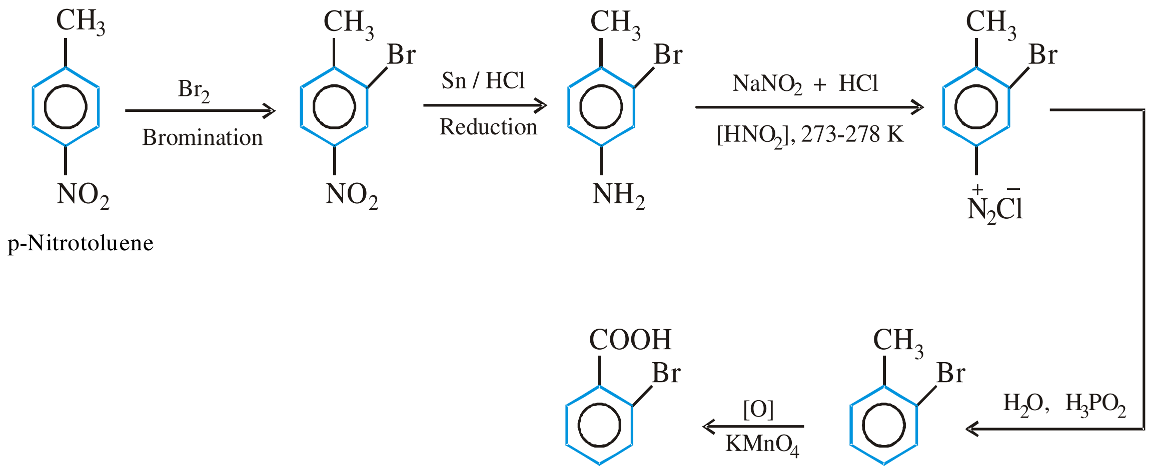


Benzylchloride Benzylamine N, N-Dimethyl phenyl methanamine

(xi) Propan-1-amine from chloroethane :

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow[KCN,\ -KCl]{\text{Ethanolic}} \underset{\text{Propanenitrile}}{CH_3-CH_2-C\equiv N} \xrightarrow[2H_2\ /\ Ni]{\text{Reduction}} \underset{\text{Propan-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

(xii) 2-Bromobenzoic acid from p-nitrotoluene



2-Bromo benzoic acid

(xiii) Ethanol from acetyl chloride

$$\underset{\text{Acetyl chloride}}{CH_3-COCl} \xrightarrow[-NH_4Cl]{2NH_3} CH_3-CONH_2 \xrightarrow[\substack{\text{(i) } LiAlH_4\\ \text{(ii) } H_2O}]{\text{Reduction}} \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} \xrightarrow[\substack{NaNO_2\\ +HCl}]{\substack{\text{Nitrous}\\ \text{acid}}} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

SUMMARY

- In nitrogen containing organic compounds there are amino (–NH_2), cyano or nitrile (–CN), isocyanide (–NC), and nitro (–NO_2) functional groups.

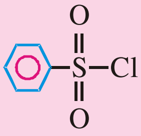
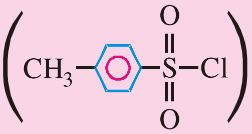
- If amino, cyano, isocyanide and nitro groups are attached to carbon in hydrocarbon series then they are called amine compounds, cyanide compounds, isocyanide compounds and nitro compounds, respectively.

- Amine is formed by substitution of hydrogen in ammonia by hydrocarbon. Like ammonia, in amine compounds, nitrogen atom is trivalent and posseses non-bonding electron pair.

- In amine compounds, the atomic orbitals of nitrogen atom possesses sp^3 hybridisation and these compounds possess pyramidal structure. The four orbitals of nitrogen possess non-bonding electron pair.

- Because of the presence of non bonding election pair, C–N–R (where R is H or C) the angle decreases slightly from 109^0 28'. In trimethyl amine the bond angle is 108^0.

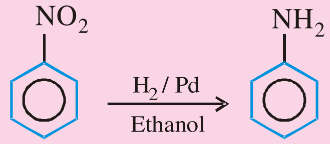
- If one alkyl or aryl group is attached with nitrogen atom then it is called primary (1^0) amine, two groups are attached then secondary (2^0) amine and three groups are attached then tertiary (3^0) amine.

- The separation of primary, secondary and tertiary amines can be carried out by Hinsberg reagent- benzene sulphonylchloride (). In the present time instead of benzene sulphonyl chloride, paratoludine sulphonyl chloride  is used.

- For common nomenclature of primary amine compounds, at the end of the alkyl group attached to nitrogen, the word amine is placed. In secondary alkyl amines, if two alkyl groups attached to nitrogen are same then the prefix di is added and then at the end amine word is placed. If the two alkyl groups are different then they are written in alphabetical order and then the word amine is placed at the end. In tertiary amine if three alkyl groups are common then the prefix tri is placed before the name of alkyl group and then word amine is placed at the end. If two alkyl groups out of three are same then the prefix di is placed before the name of that alkyl group and then the name of third alkyl group is combined and the word amine is placed at the end. If the three alkyl groups attached to nitrogen are different, then they are shown in alphabetical order and then the word amino is placed at the end. In amino compounds having more than one amine group corresponding to the number of amine groups, the words di, tri, tetra etc. are added as prefix and the position of amino group is mentioned.

- In IUPAC nomenclature of primary amine from the end of the hydrocabon attached to nitrogen the last letter ‘e’ is removed and the suffix ‘amine’ is attached. If there are more than two carbon atoms then in the longest chain of hydrocarbon the minimum number of amino group showing position is shown before the suffix amine. If there are more than two amine groups then the prefix di, tri, tetra etc. are mentioned corresponding to numbers 2, 3, 4 etc. Here the last letter ‘e’ is not removed from the name of hydrocarbon.
- For nomenclature of secondary and tertiary amines, symbol N is used to show the position of substituent of hydrogen of amine group.
- For preparation of amine compounds

(i) Reduction of nitro group



Nitro benzene

Aniline

$$CH_3{-}CH_2{-}NO_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3{-}CH_2{-}NH_2$$

Nitro ethane

Ethanamine

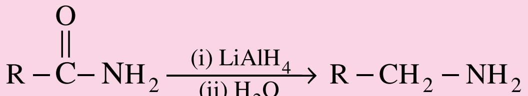
(ii) Ammonolysis of halide :

$$R{-}X + NH_3 \rightarrow R{-}NH_3{-}X \xrightarrow[-NH_4Cl]{NH_3} R{-}NH_2$$

(iii) Reduction of nitrile :

$$R{-}C{\equiv}N \xrightarrow[Na(Hg)\,/\,C_2H_5OH]{H_2\,/\,Ni} R{-}CH_2{-}NH_2$$

(iv) Reduction of amide :

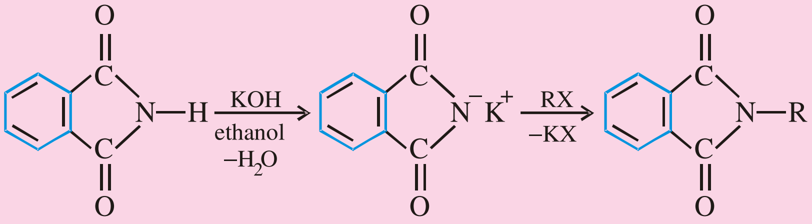


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2-NH_2$$

Amide

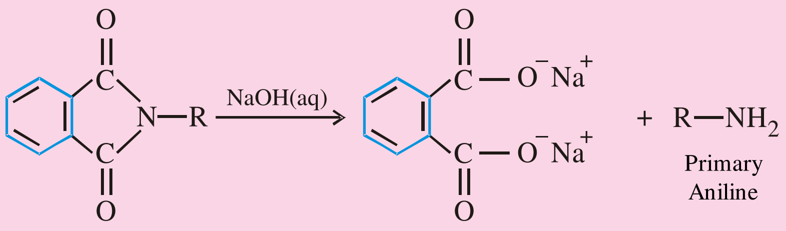
Amine

(v) Gabriel phthalimide :

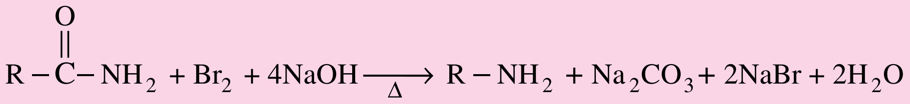


Phthalimide

N-Alkylphthalimide

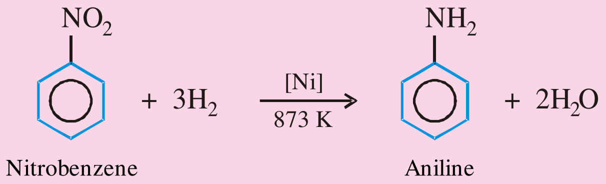


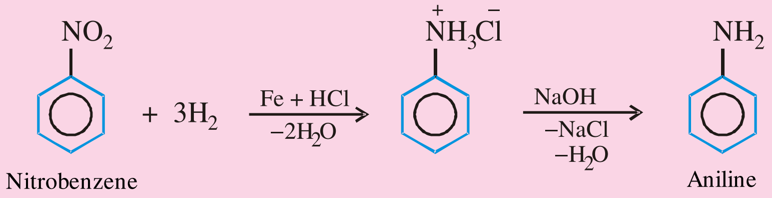
(vi) **Hoffmann reaction :**

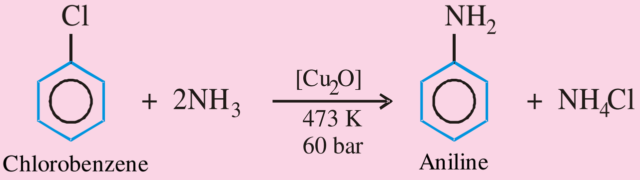


$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- **Industrial production of aniline :**







- The boiling points of primary alkylamines are higher than those of corresponding hydrocarbons. With the increase in number of carbon in primary alkylamine, the boiling point increases. In isomeric alkylamines having same molecular formula, the boiling point decreases on going from primary to tertiary.

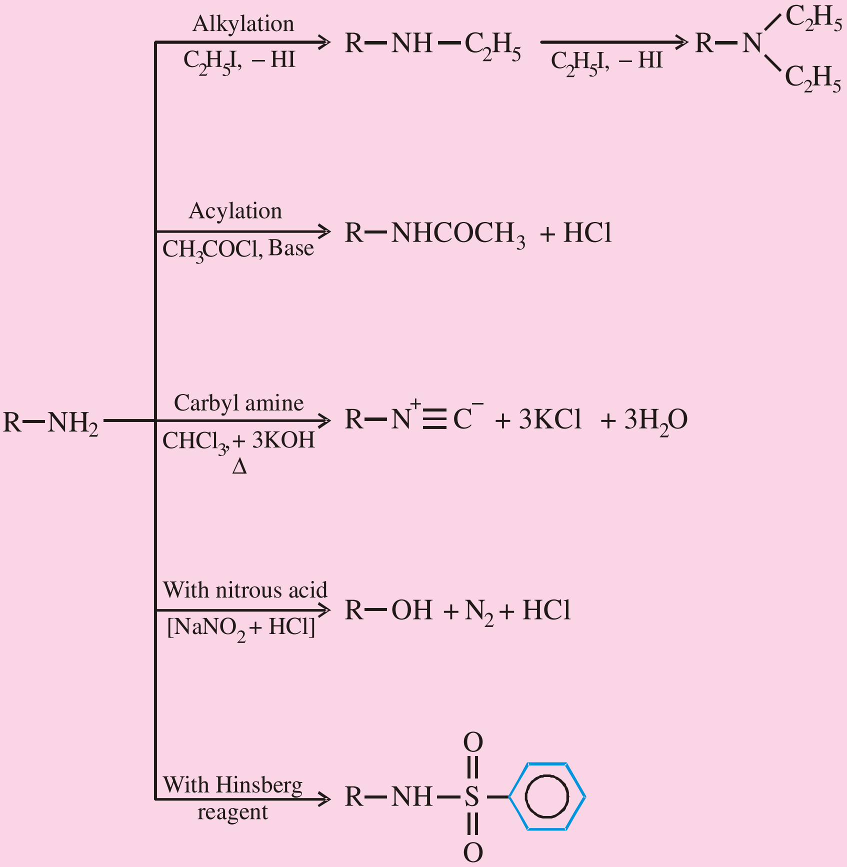
- In aqueous solutions of primary and tertiary amine compounds, hydrogen bonds are formed between molecules of amine and water and so the intermolecular attraction increases. The secondary amines are less soluble in water than the corresponding primary amines.

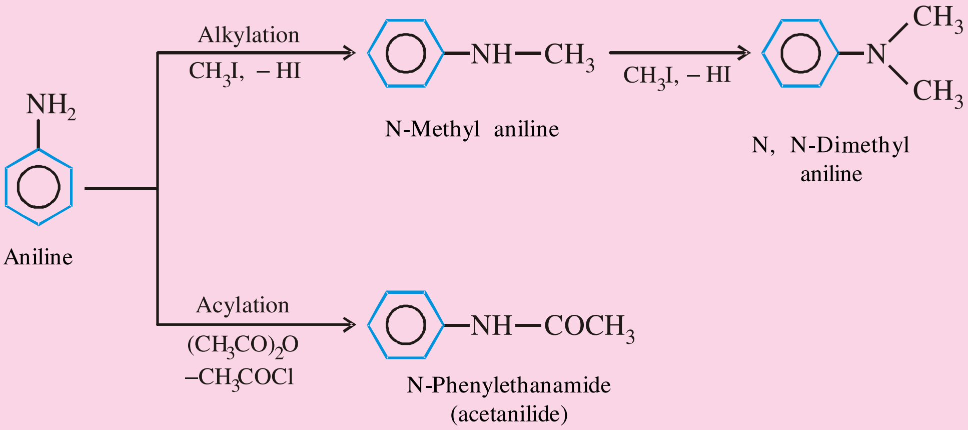
- Amines act as Lewis base because the nonbonding electron pair is on nitrogen atom of amine compounds and forms salt by reaction with acid.

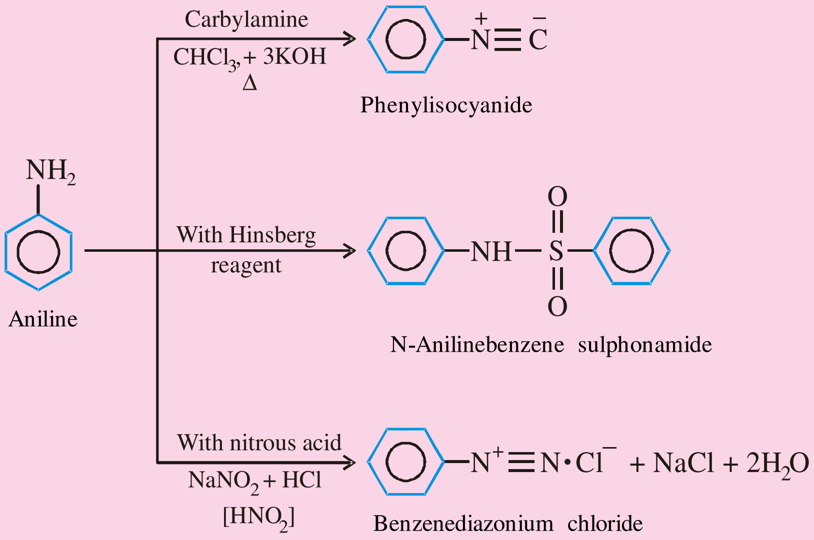
$$R-\ddot{N}H_2 + HX \rightleftharpoons R-\overset{+}{N}H_3\overset{-}{X}\ \text{(salt)}$$

Amine compounds are soluble in water but insoluble in organic solvent like ether.

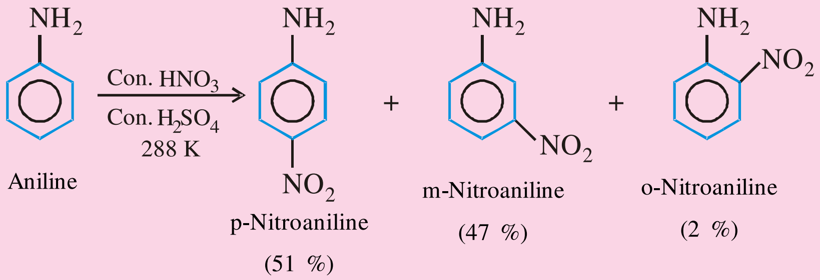
- The order of basicity of ammonia, primary amine, secondary amine and tertiary amines in gaseous state is tertiary amine > secondary amine > primary amine > ammonia.
- Order of basicity in aqueous medium : primary amine > secondary amine > tertiary amine.
- The order of strength as a base in methyl substituted amine and ethyl substituted amine is respectively $(C_2H_5)_2$–NH > $(C_2H_5)_3N$ > $C_2H_5NH_2$ > NH_3 and $(CH_3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > NH_3
- The basicity of aryl amine is less than ammonia because, in aniline there is resonance. In substituted aniline, due to the presence of electron donor groups $-OCH_3$, $-CH_3$, its strength as base increases while the strength as base decreases because of the presence of electron attracting groups like $-NO_2$, $-SO_3H$, $-COOH$, $-X$.



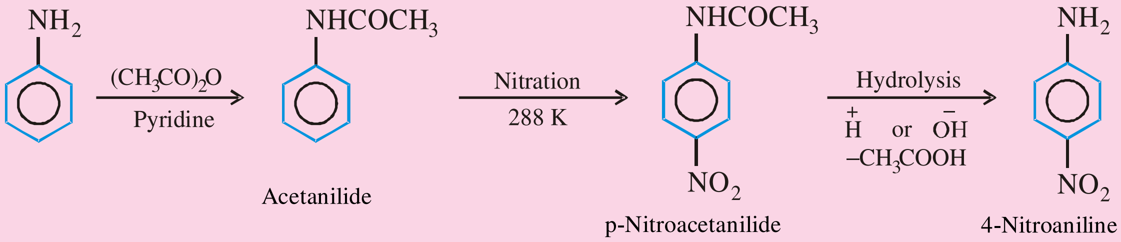




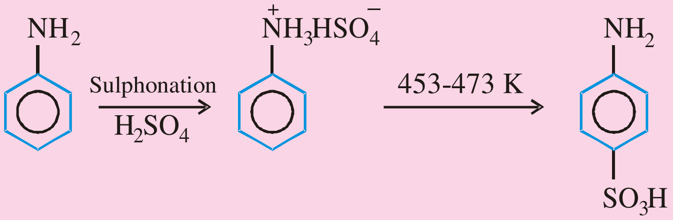
- **Nitration :**

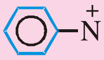


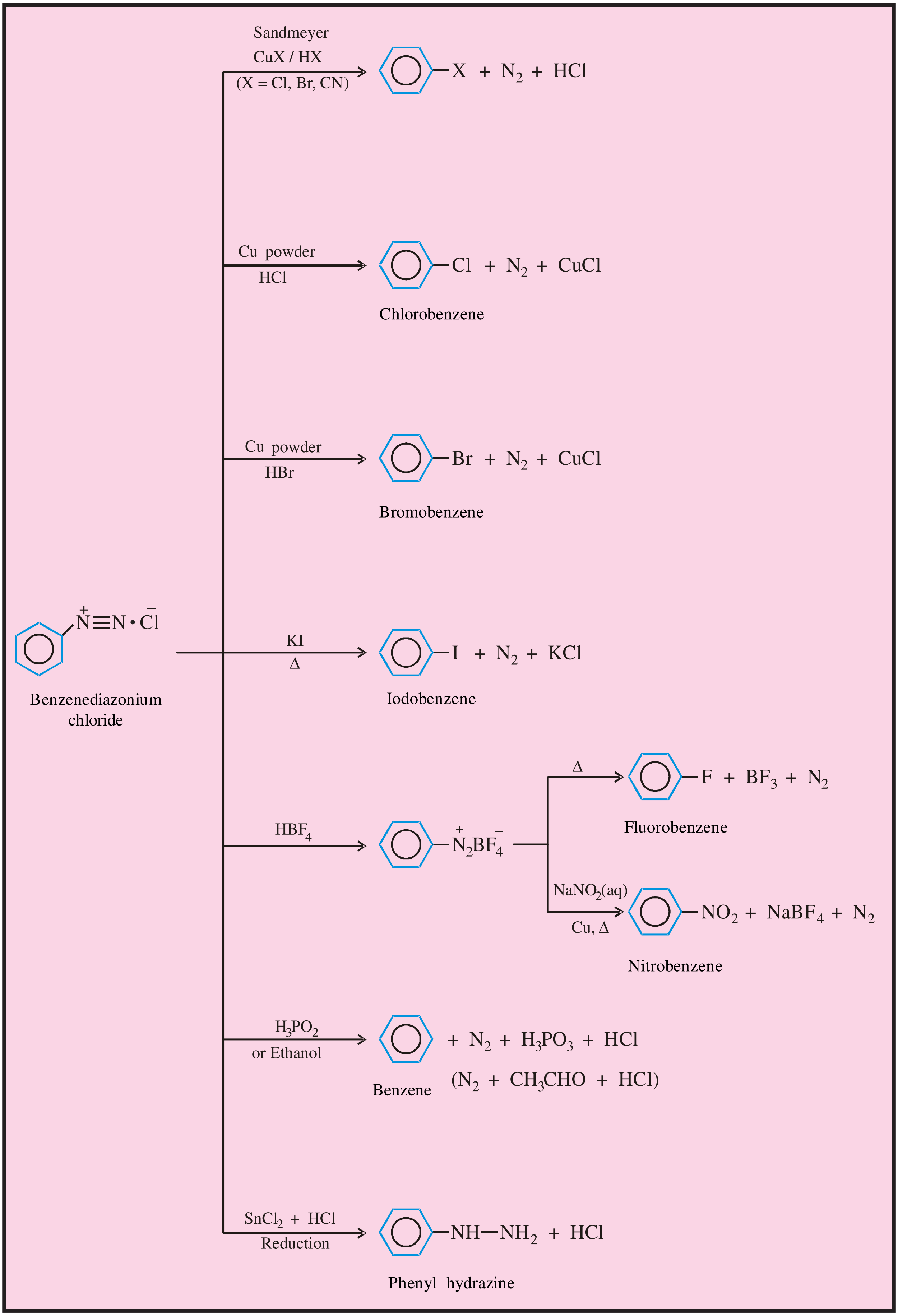
- Here, to obtain monosubstituted derivative acetylation of $-NH_2$ group is done with acetic anhydride and then nitration is carried out.

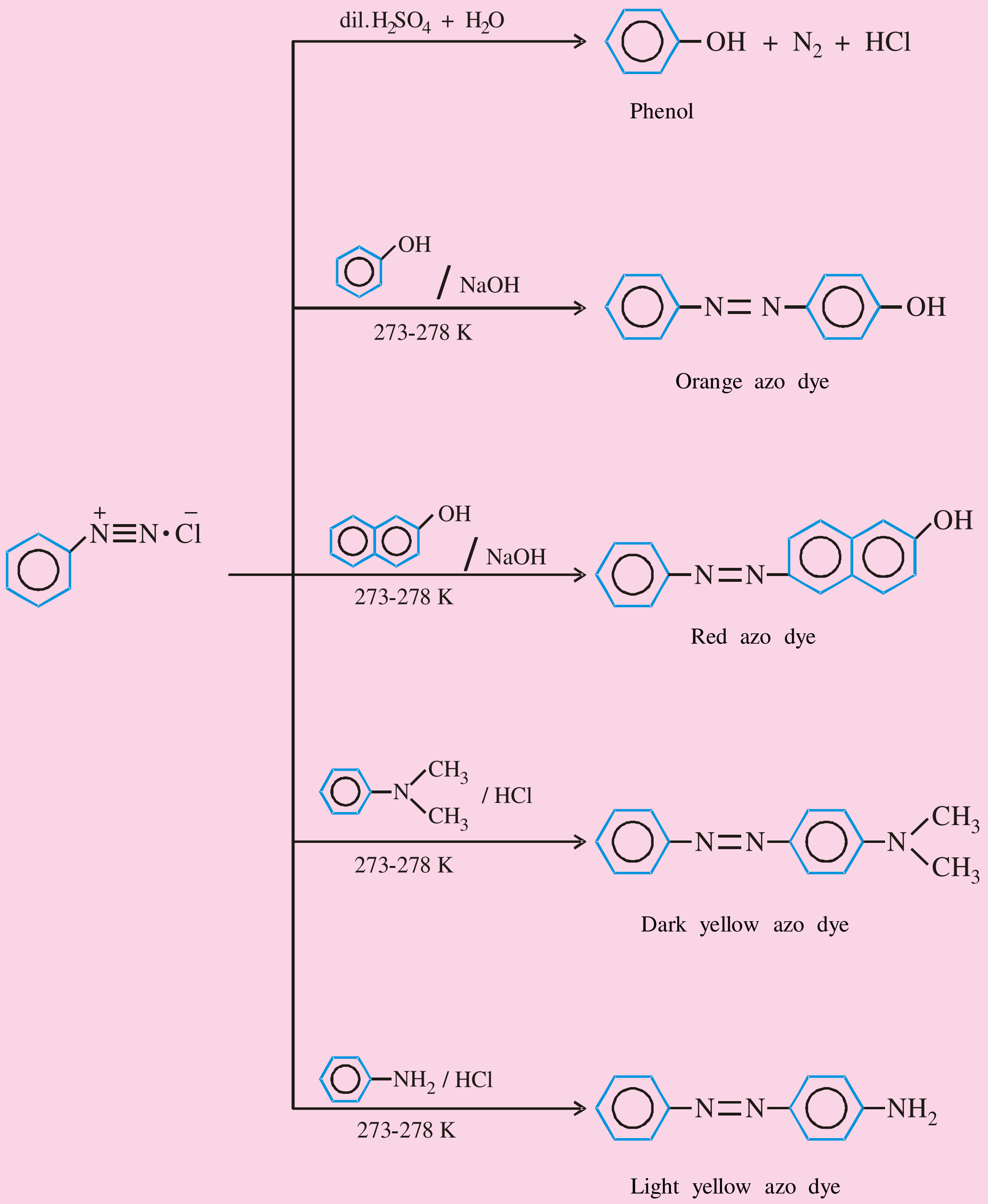


- **Sulphonation :**



- **Diazonium salt :**  $-\overset{+}{N}\equiv N\cdot\overset{-}{Cl}$ ($Ar-\overset{+}{N_2}\cdot\overset{-}{Cl}$) is colourless, crystalline solid and easily soluble in water. At low temperature it becomes stable in water. In dry state it decomposes easily. Benzene diazonium fluoroborate salt is insoluble in water and is stable at room temperature. The chemical reactions are as follows :


Sandmeyer
CuX / HX
(X = Cl, Br, CN)
—X + N2 + HCl
Cu powder
HCl
—Cl + N2 + CuCl
Chlorobenzene
Cu powder
HBr
—Br + N2 + CuCl
Bromobenzene
N≡N • Cl
Benzenediazonium chloride
KI
Δ
—I + N2 + KCl
Iodobenzene
HBF4
N2BF4
Δ
—F + BF3 + N2
Fluorobenzene
NaNO2(aq)
Cu, Δ
—NO2 + NaBF4 + N2
Nitrobenzene
H3PO2
or Ethanol
+ N2 + H3PO3 + HCl
(N2 + CH3CHO + HCl)
Benzene
SnCl2 + HCl
Reduction
—NH—NH2 + HCl
Phenyl hydrazine

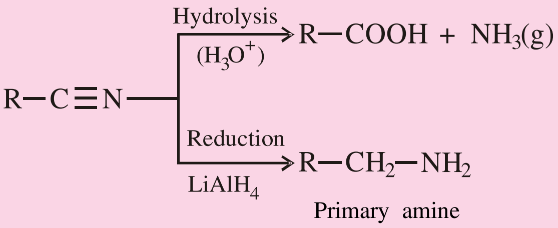


- From the reactions given above, it can be said that diazonium salt is important intermediate compound to introduce groups such as –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$.

- If cyano or nitrile group is present in organic compounds then they are called cyanide or nitrile compounds. Their general formula is R–C≡N for common nomenclature, at the end of the hydrocarbon, the word cyanide is placed. For IUPAC nomenclature, after the longest series of carbon the word nitrile is joined with end of the name of hydrocarbon. If –CN group is attached with cyclic system, then carbonitrile suffix is attached.

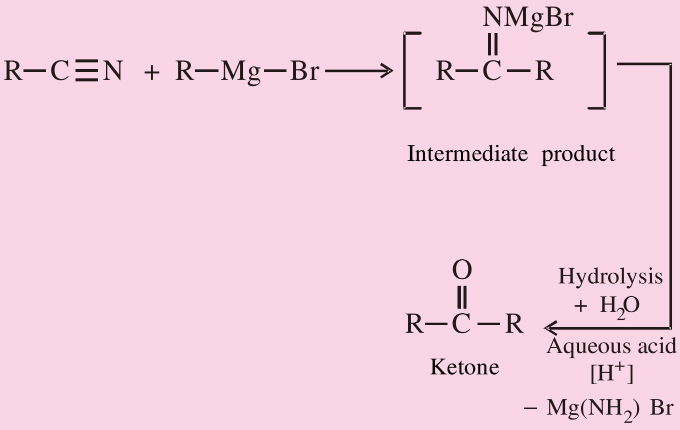
- In the electronic configuration of C–N one σ- and two π-bonds, C and N possess sp hybridisation and R–C–N bond angle is 180^0.

- In alkyl cyanide compounds the $-C^{+\delta}\equiv N^{-\delta}$ bond is polar and intermolecular hydrogen bond being not possible their boiling points are less than corresponding carboxylic acids. These compounds possess low molecular masses, and so are soluble in water and many organic solvents. Ethane nitrile (acetonitrile) being most polar it dissolves many types of organic substances.



$$CH_3-C\equiv N+CH_3-CH_2-OH+H_2O\xrightarrow[\text{Con. }[H_2SO_4]]{\Delta}CH_3COOCH_2CH_3+NH_3$$

Ethanenitrile Ethanol Ethylethanoate



- If isocyanide group is present in organic compounds, they are called isocyanide compounds. These compounds are called isonitrile or carbylamine compounds.

- Before names of cyanide compounds, the prefix 'iso' is attached for the nomenclatures of isocyanide compounds.

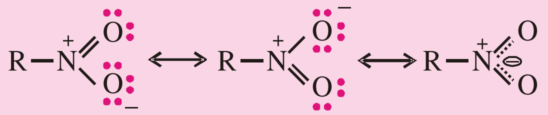
- The boiling points of alkyl isocyanides are lower than their isomeric alkyl cyanides.

$$R-\overset{+}{N}\equiv\overset{-}{C}\xrightarrow[\text{LiAlH}_4]{\text{Reduction}}R-NH-CH_3$$

(2^0) Secondary amine

- In organic compounds if nitro group is present then they are called nitro compounds. They are shown as $R\text{–}NO_2$, R = alkyl or aryl group. In IUPAC nomenclature of alkyl nitro compounds, the longest original carbon series is selected and the word nitro is placed as prefix first with alkane compounds.

- The resonance forms of alkyl nitro compounds :



$$2CH_3-CH_2-CH_3 \xrightarrow[673\ K]{\text{Fuming } HNO_3} CH_3-NO_2 + CH_2-CH_2-NO_2 + CH_3-CH_2-CH_2-NO_2$$

Propane Nitromethane Nitroethane 1-Nitropropane

$$CH_3-CH_2-NO_2 \xrightarrow[\text{or } [Ni]/3H_2]{LiAlH_4} CH_3-CH_2-NH_2 + 2H_2O$$

Nitroethane Ethanamine

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which of the following will give secondary amine on reduction ?

(A) Ethane nitrile (B) Ethyl cyanide (C) Nitro ethane (D) Ethane isonitrile

(2) Which of the following compounds gives alcohol with NaNO2 / HCl ?

(A) CH_3-NH_2 (B) $(CH_3)_2NH$ (C) $C_6H_5NH_2$ (D) $C_6H_5-NH-CH_3$

(3) Which of the following compounds will not give diazotisation reaction ?

(A) Benzenamine (B) Phenylmethanamine

(C) p-Aminophenol (D) o-Amino phenol

(4) Which of the following reactions will not give primary amine ?

(A) $CH_3CONH_2 \xrightarrow{Br_2\ /\ NaOH}$ (B) $CH_3-\overset{+}{N}\equiv\overset{-}{C} \xrightarrow{LiAlH_4}$

(C) $CH_3-C\equiv N \xrightarrow{LiAlH_4}$ (D) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

(5) Substance A + $CHCl_3$ + 3KOH $\xrightarrow{\Delta}$ isocyanide + 3KCl + $3H_2O$.

What can be A in the reaction ?

(A) Aniline (B) Dimethylamine

(C) N-Methylaniline (D) All the given

(6) Which of the following substances gives reaction with benzene sulphonyl chloride ?

(A) N, N-Dimethyl ethanamine (B) Trimethylamine

(C) Methylethyl amine (D) Dimethylethyl amine

(7) Which product will be obtained by the hydrolysis of the product obtained by reaction of ethyl cyanide with methyl magnesium bromide ?

(A) Diethylether (B) Methyl ethyl ketone

(C) Dimethyl ketone (D) Methyl ethanoate

(8) In which of the following reagents aminobenzene is soluble ?

(A) HCl (B) NaOH (C) NH_3 (D) $NaHCO_3$

(9) Mention the IUPAC name of the product obtained by reaction of ethanol and concentrated H_2SO_4 with aqueous solution of methyl cyanide.

(A) Methylethanoate (B) Ethylmethanoate

(C) Ethyl acetate (D) Ethyl ethanoate.

(10) What is the correct order of basicity of different types of amines having C_3H_9N molecular formula in non-aqueous solvent ?

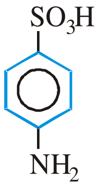
(A) $CH_3–NH–CH_2–CH_3 > (CH_3)_3N > CH_3–CH_2–CH_2–NH_2$

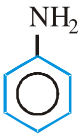
(B) $CH_3–CH_2–CH_2–NH_2 > CH_3–NH–CH_2–CH_3 > (CH_3)_3N$

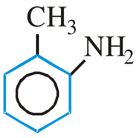
(C) $(CH_3)_3N > CH_3–NH–CH_2–CH_3 > CH_3–CH_2–CH_2–NH_2$

(D) $(CH_3)_3N > CH_3–CH_2–CH_2–NH_2 > CH_3–NH–CH_2–CH_3$

(11) Which of the following substances will give diazotisation reaction ?

(A) 

(B) 

(C) 

(D) All the given

(12) Which of the following compounds is not prepared by Sandmeyer's reaction?

(A) Chlorobenzene (B) Iodobenzene (C) Benzene nitrile (D) Bromobenzene.

(13) Which of the following is a tertiary amine ?

(A) $CH_3–NH–CH_2–CH_3$ (B) $CH_3–CH_2–NH–CH_3$

(C) $CH_3CH_2–NH–CH_2CH_3$ (D) $(CH_3)_2–N–CH_2–CH_3$

(14) Which of the following statements is in correct ?

(A) Some amines possess hydrogen bond

(B) Methylamine is more basic than ammonia

(C) Diethylamine is less basic than methylamine

(D) The boiling point of ethane is lower than that of ethylamine

(15) Which of the following amines gives alcohol or phenol by reaction with $NaNO_2$ and HCl at 273-278 K ?

(A) $C_6H_5CH_2NH–CH_3$ (B) $(CH_3)_2NH$

(C) $C_6H_5CH_2–NH_2$ (D) $C_2H_5–NH_2$

2. Answer the following questions in brief :

(1) Give structural formula and IUPAC names :

(a) Isopropyl amine

(b) Benzylamine

(c) Propyl amine

(d) Dimethyl amine

(e) Ethyl methyl amine

(f) Phenylcyanide

(g) p-Nitroaniline

(h) N, N-Dimethyl aniline

(i) Methylpropyl amine

(j) Diethyl methyl amine

(k) N, N-Diethyl aminobenzene

(l) Methyl isocyanide

(m) Phenyl isocyanide

(n) Isopropyl cyanide

(2) Write shape and bond angle of tertiary amine.

(3) Give name and structural formula of Hinsberg reagent.

(4) What is used at present for the separation of amines ?

(5) Write equation of ammonolysis of halides.

(6) Write Hoffmann reaction.

(7) Write reaction of nitrous acid with alkyl amine.

(8) Write bromination of aniline.

(9) Explain giving scientific reasons for the following :

(a) The boiling points of primary amine are higher than those of alkanes.

(b) The boiling points of primary amines are less than those of their corresponding alcohols.

(c) The boiling point of isomeric secondary amine is more than that of tertiary amine and that of primary amine is the highest.

(d) Amine compounds are basic in aqueous solutions.

(e) Aniline is less basic than methylamine.

(f) The boiling points of alkyl cyanides are lower than their corresponding carboxylic acids.

(g) The aqueous solubility of primary amine is more than that of secondary amine.

(10) Explain the following reactions giving reason :

(a) With ethanamine :

(i) Methyl iodide (ii) Ethyl chloride (iii) Nitrous acid

(iv) Hinsberg reagent (v) Acetic anhydride

(b) With aniline :

(i) Acetyl chloride (ii) Nitrous acid (iii) Ethyl iodide

(iv) $CHCl_3$ / KOH

(c) Reaction of methyl cyanide with ethanol.

(d) Ethyl cyanide with ethyl magnesium bromide.

3. Write the answers of the following questions :

(1) Write classification of amines giving examples.

(2) Write electronic configuration of amine (with figure).

(3) Explain reduction of nitrile compounds.

(4) Write Gabriel phthalimide synthesis.

(5) Explain Hoffmann reaction with example.

(6) Explain physical properties of amines.

(7) Explain alkylation of methanamine and aniline.

(8) Explain giving example the reaction to obtain monosubstituted aniline.

(9) Explain nitration of aniline.

(10) Explain preparation of benzene diazonium chloride.

(11) Explain azo coupling reactions.

(12) Write electronic structure and physical properties of cyanide.

(13) Write chemical reactions of cyanide compounds.

(14) Mention the physical properties and resonance structures of nitro compounds.

(15) Explain preparation of nitro compounds and their reduction.

4. Write the answers of the following questions in detail :

(1) Explain separation of 1^0, 2^0 and 3^0 amines.

(2) Write a note on the industrial production of amine.

(3) Explain basicity of aliphatic amines.

(4) Explain basicity of aromatic amines.

(5) Explain chemical reaction of benzene diazonium chloride.

●

Unit

7

Biomolecules

7.1 Introduction

Chemical compounds present in living systems are known as **biomolecules.** Carbohydrates, proteins, vitamins, nucleic acids, enzymes and lipids are biomolecules. These molecules mainly contain carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur elements. Biomolecules play the important role in living systems so they are called basic constituents of living systems. We have general information about these biomolecules from the study during previous standards. In this unit we will study about classification, different structures and importance of biomolecules such as carbohydrates, proteins, vitamins, enzymes and nucleic acids.

7.2 Carbohydrates

Carbohydrates are the most important class of organic compounds. Generally they are obtained from plants. They fulfil basic requirements of human life, like foods, clothes and abode. **Carbohydrates are chemically polyhydroxy aldehydes or polyhydroxy ketones or such compounds which can be hydrolysed to these compounds.** Carbohydrates contain carbon, hydrogen and oxygen elements. In formulae of these compounds, the proportion of hydrogen and oxygen elements is 2 : 1. This proportion is equal to proportion of hydrogen and oxygen elements (2 : 1) in water molecule. Therefore, initially these compounds are known as hydrates of carbon. e.g.,

Carbohydrates	**Molecular formula**
(1) Glucose	$C_6H_{12}O_6$ OR $C_6(H_2O)_6$
(2) Sucrose	$C_{12}H_{22}O_{11}$ OR $C_{12}(H_2O)_{11}$
(3) Starch	$(C_6H_{10}O_5)_n$ OR $[C_6(H_2O)_5]_n$

Thus, **general formula of carbohydrates can be written as $C_x(H_2O)_y$ but it is not utterly true.** Some members of carbohydrate class do not possess 2:1 proportion of hydrogen and oxygen in their molecule. e.g., Rhamnose ($C_6H_{12}O_5$). Moreover, some compounds are not members of carbohydrate class but their molecules contain 2 : 1 proportion of hydrogen and oxygen. e.g., formaldehyde (CH_2O), acetic acid ($C_2H_4O_2$), lactic acid ($C_3H_6O_3$) etc. Thus, molecules of some members of carbohydrate class having 2:1 proportion of hydrogen and oxygen elements is like an accidental coincidence. All types of sugars, starch, cellulose etc. compounds are known as carbohydrates. Carbohydrates are often referred to as saccharides because of the sweet taste of the simpler members of the family, the sugars (sugar means saccharum in Latin and sakcharon in Greek)

7.2.1 Classification of Carbohydrates :

Carbohydrates are classified as monosaccharide, oligosaccharide or polysaccharide on the basis of hydrolysis of their molecules.

(1) Monosaccharide : Simplest carbohydrates are included in this class. A carbohydrate that cannot be further hydrolyzed to simpler carbohydrate is called **monosaccharide.** Carbohydrates containing two to ten carbon atoms are included in this class. Their general formula is $C_nH_{2n}O_n$. Glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$) are six carbon atoms containing monosaccharide. They occur in nature.

(2) Oligosaccharide : Oligosaccharide is sugar containing two to four monosaccharide units. Oligosaccharide can be classified as disaccharide, trisaccharide or tetrasaccharide.

(A) Disaccharide : A carbohydrate that can be hydrolyzed to two monosaccharide molecules is called a **disaccharide.**

$$\text{Disaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Two monosaccharides}$$

Carbohydrates containing ten to twelve carbon atoms are included in this class. Their general formula is $C_nH_{2n-2}O_{n-1}$. Sucrose ($C_{12}H_{22}O_{11}$), maltose ($C_{12}H_{22}O_{11}$), lactose ($C_{12}H_{22}O_{11}$), cellobiose ($C_{12}H_{22}O_{11}$) etc. are disaccharides.

(B) Trisaccharide : A carbohydrate that can be hydrolyzed to three monosaccharide molecules is called a **trisaccharide.**

$$\text{Trisaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Three monosaccharides}$$

General formula of trisaccharides is $C_nH_{2n-4}O_{n-2}$. Raffinose ($C_{18}H_{32}O_{16}$) is an example of trisaccharides. Raffinose is also known as melitriose.

(C) Tetrasaccharide : A carbohydrate that can be hydrolyzed to four monosaccharide molecules is called **tetrasaccharide.**

$$\text{Tetrasaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Four monosaccharides.}$$

General formula of tetrasaccharide is $C_nH_{2n-6}O_{n-3}$. Stachyose is an example of tetrasaccharide.

(3) Polysaccharide : Polysaccharides are macromolecular substances. A carbohydrate that can be hydrolyzed to many monosaccharide molecules is called a **polysaccharide.**

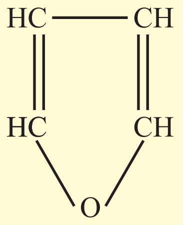
$$\text{Polysaccharide} + \text{Water} \xrightarrow{H^+ \text{ or enzymes}} \text{Many monosaccharide molecules}$$

Starch, cellulose, glycogen, dextrin etc. are common examples of polysaccharides. Starch and cellulose occur in nature.

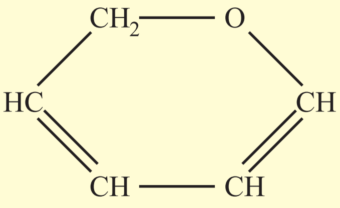
Generally monosaccharides and oligosaccharides are crystalline, water soluble and sweet in taste. They are known as sugar. Polysaccharides are amorphous, water insoluble and tasteless. They are known as nonsugar.

7.2.2 Nomenclature of Carbohydrates :

Generally the compounds of carbohydrate class contain 'ose' suffix in their names. e.g., Glucose, fructose, lactose, sucrose, maltose, cellobiose, rhamnose, raffinose, stachyose. If carbohydrate compound contains an aldehyde group it is called an aldose and that containing a keto group is called a ketose. Moreover, the number of carbon atoms present in these compounds are indicated by addition of Greek word like tri, tetra, penta and hexa before suffix 'ose' in the name of carbohydrate for three, four, five and six carbon atoms, respectively. e.g., Three carbon atoms and aldehyde group containing carbohydrate compound is called an aldotriose. Three carbon atoms and ketone group containing carbohydrate compound is called ketotriose. Glucose contains six carbon atoms and aldehyde group, so it is known as aldohexose. In the same manner fructose contains six carbon atoms and ketone group so it is known as ketohexose. Moreover, after detailed study of carbohydrate compounds we will know that they generally exist in cyclic form. Many times a proper word is used to mention the five membered or six membered cyclic compounds. e.g., **Pyranose** word is six membered (five carbon atoms and one oxygen atom) cyclic compound. **Furanose** word is used for five membered (four carbon atoms and one oxygen atom) cyclic compound.



Furan



Pyran

Cyclic structure of glucose contains six membered ring so it is known as glucopyranose. Cyclic structure of fructose contains five membered ring so it is known as fructofuranose.

7.3 Monosaccharides

As seen earlier, glucose and fructose are common examples of monosaccharide. So, in this unit, we will study about preparation and different types of structures of glucose as a representative member of monosaccharide class.

7.3.1 Glucose :

Glucose is present in ripe fruits and honey. Grapes contain 20 to 25 % glucose, so glucose is also known as grape sugar. It is also present in human blood and urine in fixed amount.

Preparation of glucose :

(1) From cane sugar : Mixture of glucose and fructose can be obtained by hydrolysis of alcoholic solution of cane sugar (sucrose) with the help of dilute hydrochloric acid or sulphuric acid as catalyst.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

After completion of this reaction, excess amount of alcohol is added to this mixture. Glucose is insoluble in alcohol so it settles down at the bottom of the vessel as precipitate and fructose is soluble in alcohol so it is present in solution. Therefore, glucose separates out easily by filtration.

(2) From starch : In industry, glucose is obtained by hydrolysis of starch with help of dilute H_2SO_4 at 393 K under 2-3 bar pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[398\text{ K, 2-3 bar}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

After completion of hydrolysis, excess sulphuric acid is neutralised by calcium carbonate. Due to this reaction insoluble calcium sulphate is formed. It is removed by filtration. Filtrate is made colourless by adsorption with charcoal. After concentrating this filtrate in absence of air, the crystals of glucose are formed.

Structure of Glucose : Structure of glucose and other aldose compounds are decided by following methods and reactions.

Open chain structure of glucose :

(1) From the analysis of glucose following results are obtained:

Empirical formula : CH_2O

Molecular mass : 180 gram mol^{-1}

Molecular formula : $C_6H_{12}O_6$

(2) When glucose is heated for a long time with hydrogen iodide results in formation of n-hexane. It indicates that all six carbon atoms of glucose are linked in linear chain.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\Delta]{HI} \underset{\text{n-Hexane}}{CH_3–CH_2–CH_2–CH_2–CH_2–CH_3}$$

Thus, C–C–C–C–C–C chain is present in the structure of glucose.

(3) Glucose gives typical reactions with reagents for carbonyl group. e.g., Glucose forms cyanohydrin with hydrogen cyanide (HCN); glucose forms oxime with hydroxylamine (NH_2OH); glucose forms phenylhydrazone with phenylhydrazine ($C_6H_5NHNH_2$). These reactions suggest that carbonyl group ($>C=O$) is definitely present in glucose molecule, because these reactions are specific reactions of carbonyl group.

(4) Oxidation of glucose by bromine water forms equal carbon containing acid-gluconic acid. Solution of ammonical silver nitrate (Tollens' reagent) is reduced to silver by glucose. Glucose can reduce Fehling's solution to cuprous oxide (precipitate) and will be self oxidized to acid. These three reactions prove the presence of aldehyde group in glucose, because all these reactions are specific tests for aldehyde functional group. As per general rule aldehyde group is attached to the end of the carbon chain.

Thus, OHC–C–C–C–C–C chain is present in the structure of glucose.

(5) Glucose is oxidized by strong oxidizing agent nitric acid to equal number of carbon atoms containing dicarboxylic acid-saccharic acid. It suggests that aldehyde group is attached at one end of carbon chain of glucose and primary alcohol ($–CH_2OH$) group is attached at the other end of carbon chain of glucose.

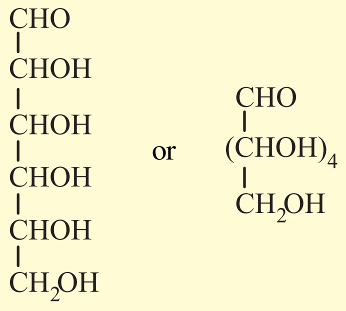
Thus, $OHC–C–C–C–C–CH_2OH$ chain is present in the structure of glucose.

(6) Glucose forms five acetyl groups containing penta acetyl glucose with acetic anhydride in presence of anhydrous zinc chloride or pyridine. It suggests that five hydroxyl groups are present in glucose molecule. Moreover these five hydroxyl groups are attached at

different carbon atoms because if two or more hydroxyl groups are attached at the same carbon atom then that compound is unstable and it loses water molecule easily. But glucose molecule does not lose water molecule and it is a stable compound.

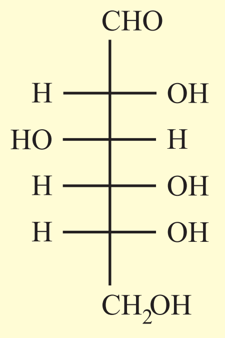
Thus, 
$OHC-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}-CH_2OH$ chain is present in the structure of glucose.

(7) In deciding the chain at point-6, the valency of second to fourth carbon atoms are satisfied by hydrogen atom, as a result structure of glucose obtained is as follows :


Glucose Glucose

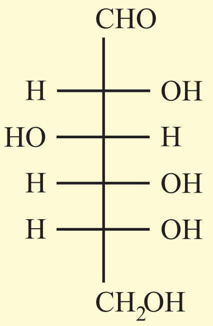
Now for understanding the structure of glucose molecule we will study about arrangement of its atoms and groups in space.

Configuration of Glucose : An arrangement of atoms or groups of molecule in space is called the configuration of that compound. Scientist Emil Fischer determined the configuration of glucose after studying many reactions. It is as following :

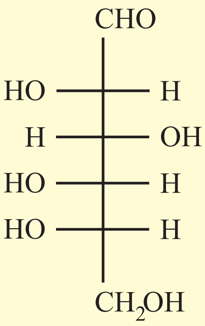

D-(+)-Glucose

Scientist Emil Fischer determined the configuration of almost all aldopentose and aldohexose in a period of only four years (1888-1891). In 1902, the Nobel prize was awarded to him for his research works in chemistry. We have learnt about D, L, d or (+), *l* or (–) in unit 6 of semester III.

In Fischer projection of carbohydrate compounds, if the –OH group is attached to the bottom most chiral carbon atom on the right side, the compound possesses D-configuration. If –OH group is attached on the left-side, the compound possesses L-configuration. D- and L-compounds are enantiomers. Optically active organic compound rotates the plane of polarized light. This value of rotation (in degree) is known as angle of rotation (α) shown by that compound. This rotation is measured by **polarimeter instrument.** If only optically active organic compound shows this rotation in a clockwise direction or on a right side direction then (+) sign is put before its rotation value. This compound is called **dextrorotatory.** It is mentioned with d or (+) sign. If any optically active organic compound shows this rotation in an anticlockwise direction or on left side direction then (–) sign is put before its rotation value. This compound is called **levorotatory.** It is mentioned with *l* or (–) sign. d or (+) (dextrorotatory) and l or (–) (levorotatory) compounds are also enantiomers. There is no direct relation of D and L with d or *l*.



D-(+)-Glucose



L-(−)-Glucose

The specific rotation $[\alpha]_{\lambda}^{T}$ can be calculated from the value of angle of rotation (α) of optically active compound. The specific rotation is required for the comparison of optical activities of two compounds.

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times C}$$

where, $[\alpha]$ = specific rotation

T = Temperature (K)

λ = Wavelength of the incident light

(D symbol is used for wavelength of sodium light)

α = Observed angle of rotation (by polarimeter)

l = Length of tube (in decimeter) (10 cm = 1 dm)

C = Concentration of compound (gram ml^{-1})

Example 1 : The observed angle of rotation of 2.0g of sucrose in 10 ml of aqueous solution in a polarimeter tube 10 cm long is $+13.3^0$. What is the specific rotation of the solution of sucrose ?

Solution : Here $C = 2.0 \text{ g}/10 \text{ ml} = 0.2 \text{ gml}^{-1}$

$l = 10 \text{ cm} = 1 \text{ dm}$

$\alpha = +13.3^0$

$$\text{Now, } [\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times C}$$

$$= \frac{+13.3}{1 \times 0.2}$$

$$= +66.5^0$$

Thus, specific rotation of sucrose is $+66.5^0$

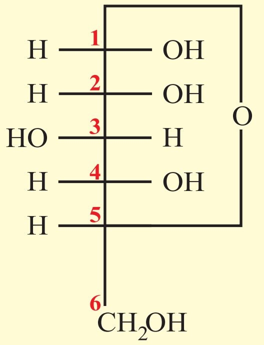
Cyclic structure of glucose : –CHO group is present in configuration of glucose, but glucose does not give some reactions of aldehyde. Moreover glucose also gives some reactions which are not given by an aldehyde.

(1) Glucose does not form addition product with sodium bisulphite ($NaHSO_3$). Generally aldehyde group containing compounds form addition product with sodium bisulphite.

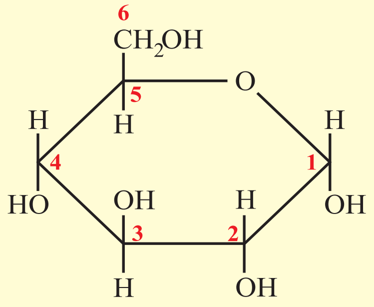
(2) An aldehyde reduces Tollens' reagent and Fehling's solutions. It also gives violet colour with Schiff's reagent. Glucose gives first two reactions but does not give violet colour with Schiff's reagent.

(3) An aldehyde does not show mutarotation property (process of changes in specific rotation) while glucose shows this property.

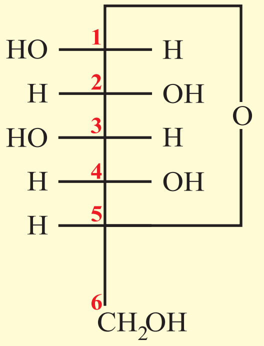
Thus, these reactions create doubt about the open chain structure of glucose. Experimental results have decided that glucose exists in two configurations α and β. Existence of these two configurations of glucose cannot be explained by its open chain structure. In 1895 scientists Fischer, Tollens and Tanret have suggested that structure of glucose should not be an open chain but it is a cyclic form. In 1925, Haworth and Hirst from experimental evidences suggested that glucose molecule may contain pyranose ring (ring contains five carbon atoms and one oxygen atom). Study of X-rays also supported this point. Thus, glucose consists of pyranose ring containing cyclic structure. It can be shown as below :



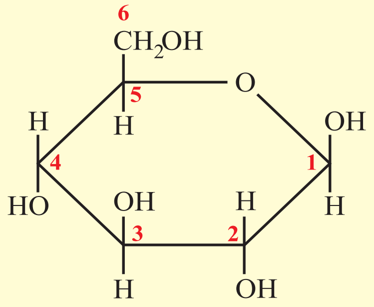
α-D-(+)-glucose
(Fischer projection)



α-D-(+)-glucose
(Haworth projection)

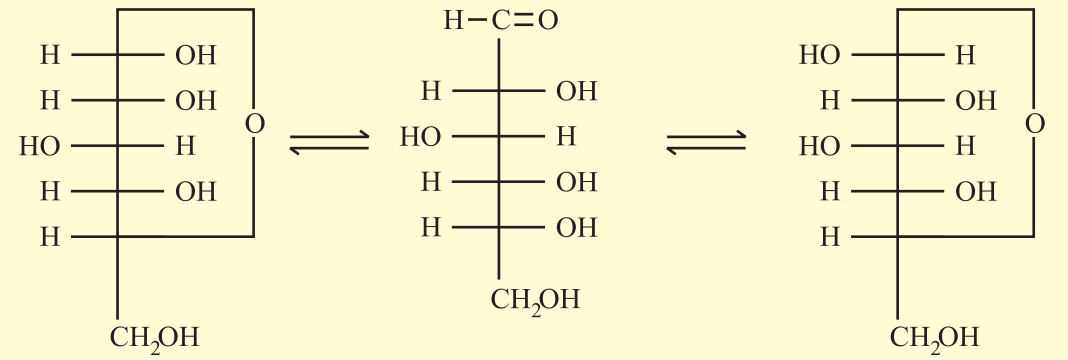


β-D-(+)-glucose
(Fischer projection)



β-D-(+)-glucose
(Haworth projection)

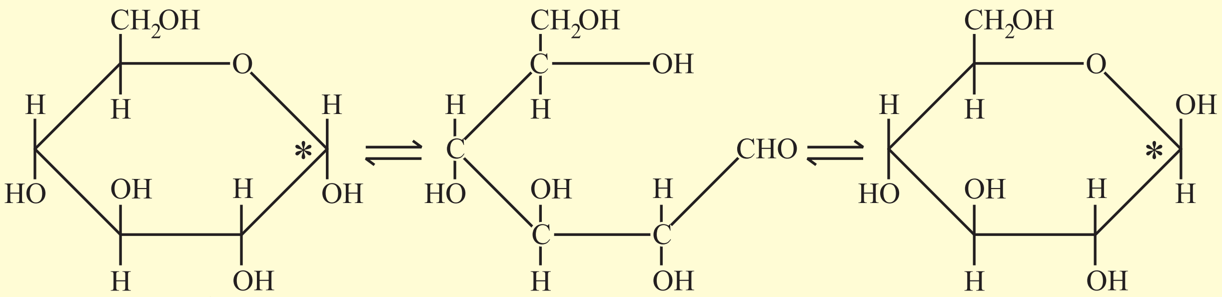
Generally the carbon of cyclic structure which is carbonyl carbon in open chain structure is called **anomeric carbon.** The first carbon atom of cyclic structure of glucose is anomeric carbon because it is a carbonyl carbon in open chain structure of glucose. The isomers differ in configuration at anomeric carbon and are called **anomers.** α-D-(+)-glucose and β-D-(+)-glucose are anomers, because the –OH group is attached at right side to anomeric carbon (C1) of Fischer projection of α-D-(+)-glucose, while the –OH group is attached at left side to anomeric carbon (C1) of Fischer projection of β-D-(+)-glucose. Atom or group on the right side in Fisher projection is below in Haworth projection. α-D-(+)-glucose can be obtained by crystallization from water at 303 K. It can also be obtained by crystallization from ethyl alcohol or glacial acetic acid. The crystals obtained in this way are dissolved in water and the specific rotation of this freshly prepared solution of glucose is $+112^0$. After some time it decreases to $+52.5^0$. β-D-(+)-glucose can be obtained by crystallization from water at 371 K. It can also be obtained by crystallization from pyridine. The crystals obtained this way are dissolved in water and the specific rotation of this freshly prepared solution of glucose is $+19^0$. After some time it increases to $+ 52.5^0$. This process of change in specific rotation is called **mutarotation.** This mutarotation is shown by glucose and it should be due to conversion of α-form to β-from and β-form to α-form. If the solution of glucose shows a specific rotation of $+52.5^0$ then mixture of α-D-(+)-glucose (36 %) and β-D-(+) glucose (64 %) is present in it. This conversion can be explained as follows :



α-D-(+)-glucose (36 %)

β-D-(+)-glucose (64 %)

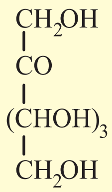
It can be easily understood by Haworth projections also.



α-D-(+)-glucose

β-D-(+)-glucose

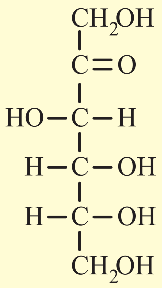
7.3.2 Fructose :



$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

Fructose

(Open chain structure)

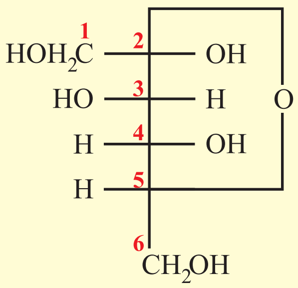


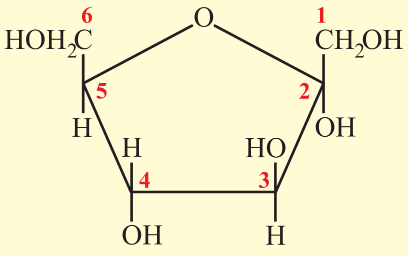
D-(–)-Fructose

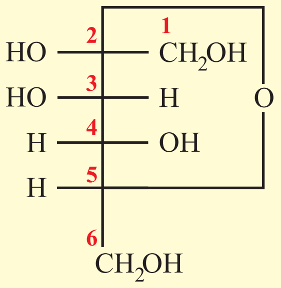
(Configuration of fructose)

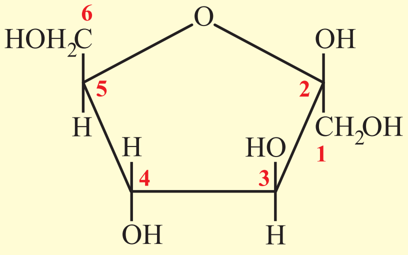
Fructose is a white crystalline substance. It is soluble in water, partially soluble in alcohol and insoluble in ether. It is levo rotatory optically active compound. It is sweet in taste. Its sweetness is higher compared to glucose, table sugar and also all other sugars. Molecular formula of fructose is $C_6H_{12}O_6$. It contains ketone group and six carbon atoms, so it is known as ketohexose. Experimentally established structures of fructose are mentioned below :

Experimental results have proved that fructose exists in two configurations α-and β-and consists of furanose ring containing cyclic structure. C2 is anomeric carbon in fructose. Fructose shows mutarotation property. Cyclic structure of fructose is as follows :


α-D-(–)-Fructose
(Fischer projection)


α-D-(–)-Fructose
(Haworth projection)


β-D-(–)-Fructose
(Fischer projection)


β-D-(–)-Fructose
(Haworth projection)

7.4 Disaccharides

Disaccharide molecule is formed by two monosaccharide units. Hydrolysis of disaccharide by diluted acid or enzyme gives same type or two different types of monosaccharides. Molecular formula of disaccharide is $C_{12}H_{22}O_{11}$.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

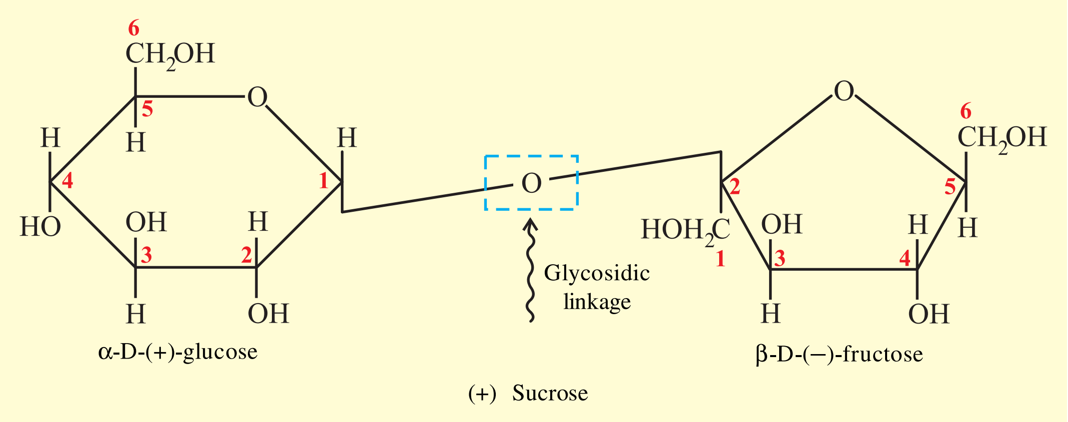
$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

In disaccharide, the linkage of two monosaccharides joined with each other by linkage of oxygen atom is called glycosidic linkage. Disaccharides are sweet in taste, crystalline and soluble in water.

(1) Sucrose : Sucrose is table sugar used in our daily life. It is mostly found in sugar cane and beets. Therefore it is called cane sugar. Sucrose is colourless, crystalline, sweet in taste and water soluble. This sugar is dextrorotatory (+). Specific rotation of its aqueous solution is $+66.5^0$. Mutarotation does not occur in it. If sucrose is boiled with dilute acid (HCl or H_2SO_4) or hydrolyzed by invertase enzyme then mixture of D-(+)-glucose and D-(–)-fructose in equal proportion (1 : 1) is obtained.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{invertase}]{\text{dilute acid or}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The aqueous solution of sucrose is dextrorotatory (+) before hydrolysis, but at the end of hydrolysis, produces aqueous solution of glucose and fructose mixture is found as levorotatory (–). The specific rotation of this solution observed is -20^0. The process of change in sign of rotation of sucrose solution is called inversion. The mixture of glucose and fructose obtained at the end of hydrolysis is called invert sugar. The specific rotation in inverted sugar during hydrolysis due to specific rotation of glucose solution is $+ 52.5^0$ and specific rotation of fructose solution is (-92^0). In this, the specific rotation of fructose is higher than that of glucose; as a result final mixture formed is levorotatory (–). Experimental results have proved that the glycosidic linkage is formed between C1 of α-D-(+)-glucose and C2 of β-D-(–)-fructose in structure of sucrose. Thus, **in sucrose, two monosaccharide units are joined to each other by C1–O–C2 linkage.**



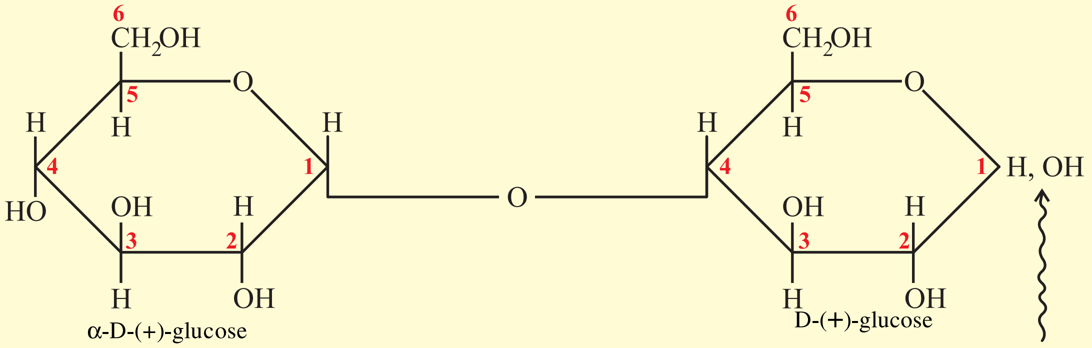
(+) Sucrose

In sucrose both monosaccharide units viz. glucose and fructose are reducing sugars. The –OH group attached to C1 in cyclic structure of glucose and to C2 in cyclic structure of fructose acts as reducing agent group. In sucrose, the reducing agent groups of two monosaccharide units are involved in glycosidic bond, because of which they are not free. Therefore sucrose does not reduce the Fehling's solution and does not form phenylhydrazone with phenylhydrazine. Thus, **sucrose is non-reducing sugar.** Sucrose is taken as a standard for comparison of sweetness of other sugars. Its sweetness index is considered as 100. As per this, glucose, fructose and lactose possess sweetness index as 74, 173 and 16, respectively. When sucrose is heated to 483 K it loses water and forms a brown amorphous substance called **caramal.** This caramal is used as a colouring agent in preparation of sweets and ice-creams.

(2) Maltose : Barley contains malt. Maltose is the main constituent of malt. Therefore maltose is known as malt sugar. Maltose is formed before alcohol is formed from the starch containing compounds. Maltose is colourless and has needle shaped crystals. It is very soluble in water but insoluble in alcohol. Maltose is dextrorotatory (+) and shows mutarotation. Its hydrolysis occurs by dilute acid or maltase enzyme and as a result D-(+)-glucose is formed.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{maltase}]{\text{dilute acid or}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Experimental results have proved that in structure of maltose, the glycosidic linkage is formed between C1 of α-D-(+)-glucose and C4 of another D-(+)-glucose unit. Thus, **in maltose two monosaccharide units are joined by C1–O–C4 linkage.**

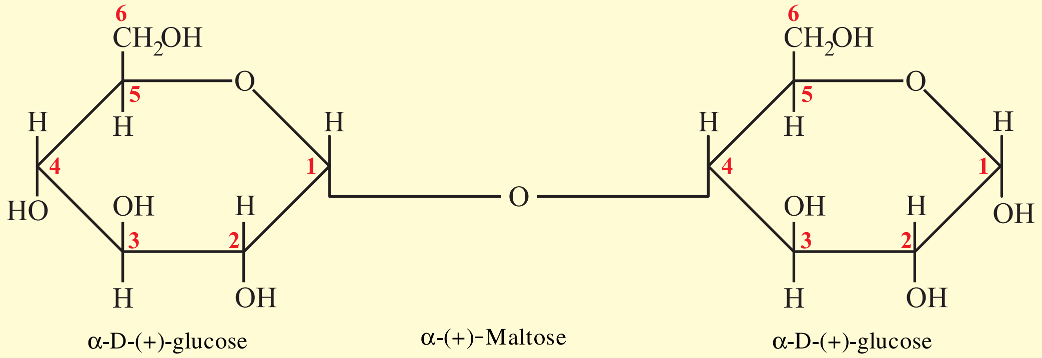


(+)-Maltose

This anomeric carbon (C1) does not have a definite configuration

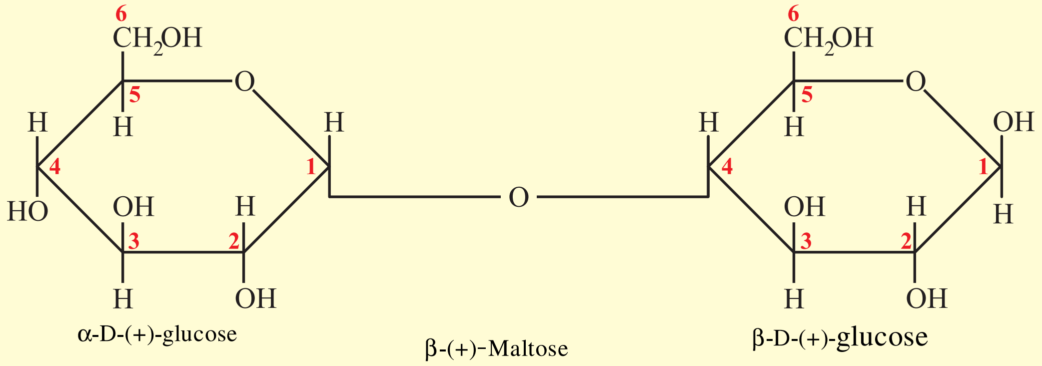
Here, anomeric carbon of one glucose unit, out of two glucose units is not involved in formation of glycosidic bond. The configuration of this anomeric carbon is changed and two forms of maltose are formed. They are called anomers of maltose. If the configuration of this anomeric carbon is similar to α-D-(+)-glucose then it is called α-maltose and if it is similar to β-D-(+)-glucose then it is called β-maltose. Thus,

α-(+)-Maltose = α-D-(+)-glucose + α-D-(+)-glucose



α-(+)-Maltose

β-(+)-Maltose = α-D-(+)-glucose + β-D-(+)-glucose



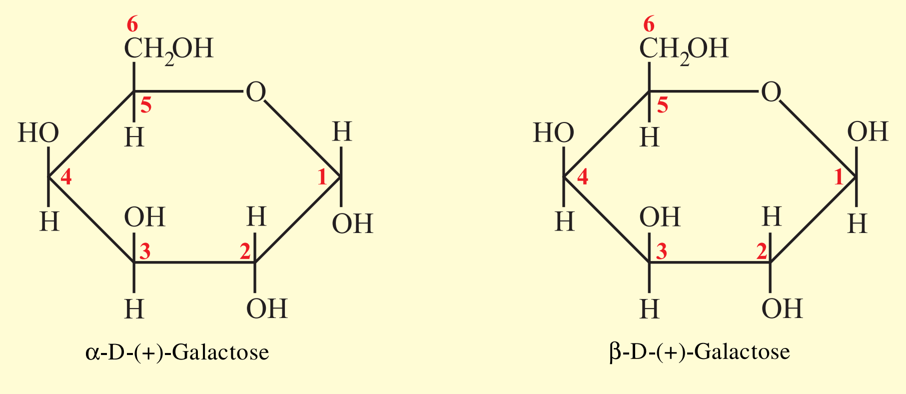
β-(+)-Maltose

In maltose, both the monosaccharide units viz. glucose are reducing sugars. In cyclic structure of glucose, –OH group attached to C1 act as reducing agent. Two glucose units are joined by C1–O–C4 linkage. Thus, reducing agent group of one glucose unit is involved in formation of glycosidic bond but reducing agent group of another glucose unit is free. Therefore maltose reduces Fehling's solution and forms phenylhydrazone with phenylhydrazine. Thus, **maltose is reducing sugar.**

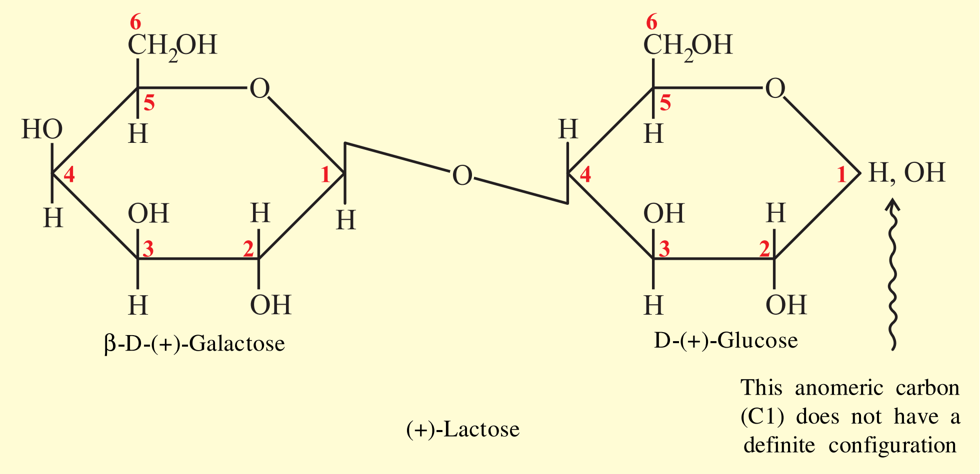
(3) Lactose : Lactose is present in the milk of animals, so it is known as milk sugar. This sugar in not present in plants. Casein is separated from milk; then after this fats are also taken out of it. Remaining milk contains lactose. Lactose sugar can be obtained by concentrating this milk in evacuated vessel. Lactose is soluble in water but insoluble in alcohol. It is dextrorotatory (+) and shows mutarotation. Its hydrolysis occurs by dilute acid or emulsin enzyme and as a result mixture of D-(+) -galactose and D-(+)-glucose in equal proportion (1:1) is formed.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{emulsin}]{\text{dilute acid or}} \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

It is necessary to know the structure of galactose before knowing the structure of lactose. Experimental results have proved the cyclic structure of galactose ($C_6H_{12}O_6$) as follows :



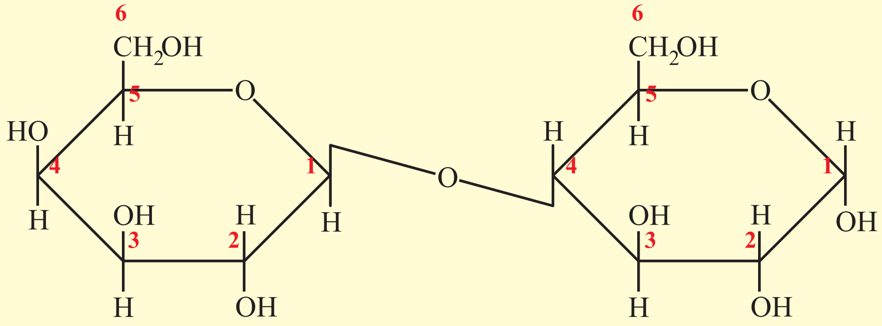
Experimental results have proved that in structure of lactose, the glycosidic linkage is formed between C1 of β-D-(+)- galactose and C4 of D-(+)-glucose. Thus **in lactose two monosaccharide units are joined by C1–O–C4 linkage.**



(+)-Lactose

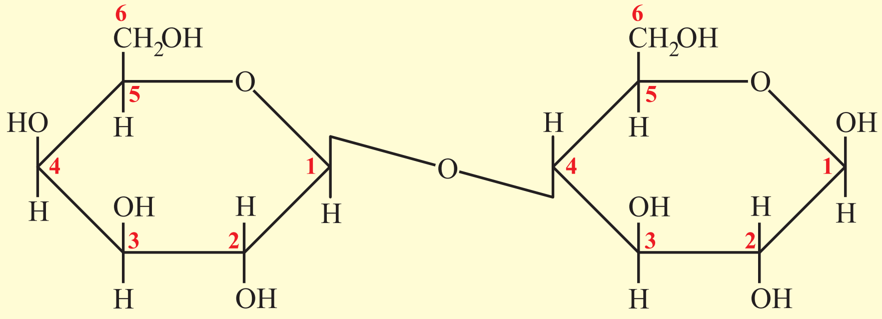
Here, anomeric carbon of D-(+)-glucose unit out of two monosaccharides is not involved in formation of glycosidic bond. The configuration of this anomeric carbon is changed and two forms of lactose are formed. They are called anomers of lactose. If configuration of this anomeric carbon is similar to α-D-(+)-glucose, then it is called α-lactose and if it is similar to β-D-(+)-glucose then it is called β-lactose. Thus,

α-(+)-lactose = β-D-(+)-galactose + α-D-(+)-glucose



β-D-(+)-galactose α-(+)-Lactose α-D-(+)-glucose

β-(+)-lactose = β-D-(+)-galactose + β-D-(+)-glucose



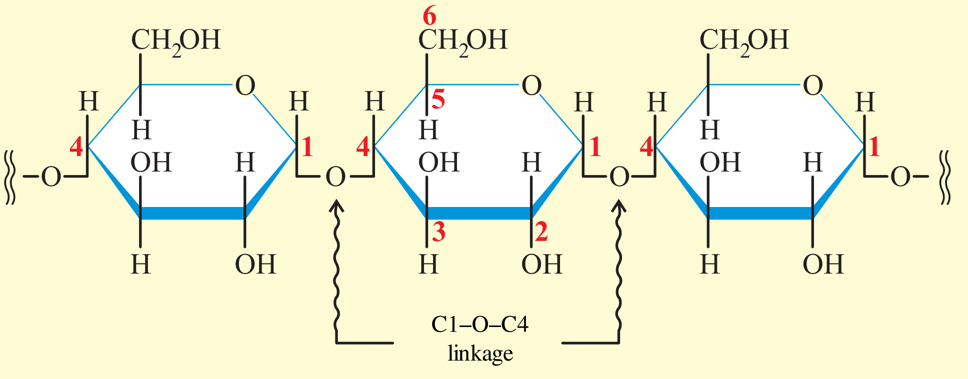
β-D-(+)-galactose β-(+)-Lactose β-D-(+)-glucose

In lactose, both the monosaccharides viz. galactose and glucose, are reducing sugars. In cyclic structures of glucose and galactose, –OH group attached to C1 acts as reducing agent. Galactose and glucose units are joined by C1–O–C4 linkage in lactose. Thus, reducing agent group of glucose unit is free. Therefore lactose reduces Fehling's solution and forms phenylhydrazone with phenylhydrazine. Thus, **lactose is a reducing sugar.**

7.5 Polysaccharides

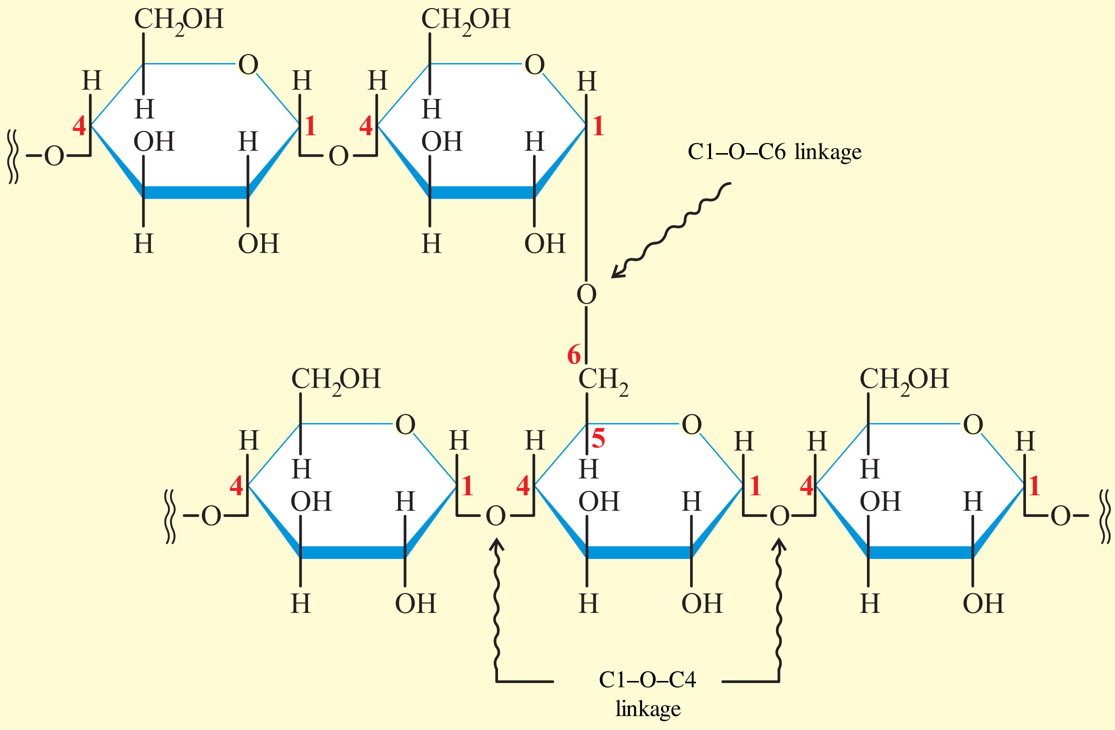
Many monosaccharide molecules are joined with one another in polysaccharide molecule. Starch, cellulose, glycogen and dextrin are examples of polysaccharide. Polysaccharide compounds possess very high molecular mass. Molecular mass of starch may be as high as 8 lakh to 10 lakh. Determination of exact molecular mass of polysaccharide compound is difficult. Therefore, their general formula of them can be written as $(C_6H_{10}O_5)_n$. These compounds are tasteless and amorphous. They are also insoluble in hot water. Hydrolysis of polysaccharide compounds by dilute acid or enzyme form disaccharide and in the end hexose and pentose are formed.

(1) Starch : In nature, the starch is found in all green plants, roots and seeds. Its main sources are wheat, rice, potatoes, maize and sorghum. They occur in the form of granules which vary in size and shape. Starch is colourless, odourless and solid insoluble compound in water. Starch is a mixture of amylose (about 20%) and amylopectin (about 80%) polysaccharides. Amylose structure consists of a long unbranched chain with 200 to 1000 glucose molecules. In this chain α-D-(+)-glucose units are joined by C1–O–C4 linkage.



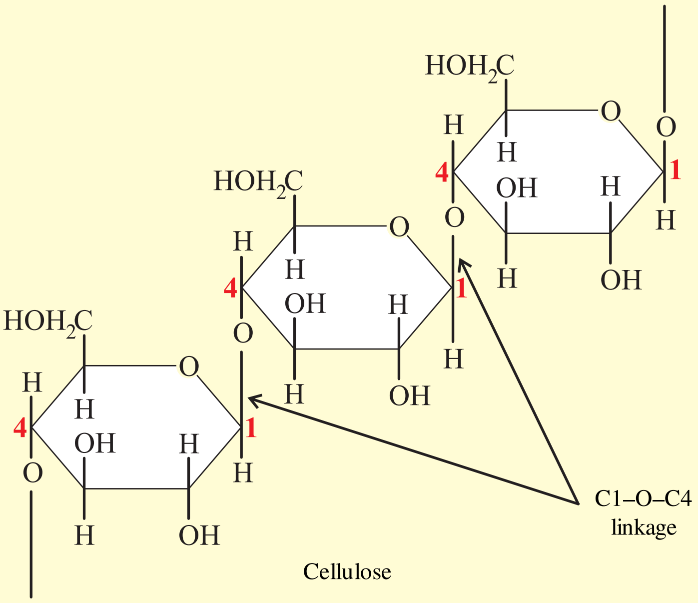
Amylose

In structure of amylopectin α-D-(+)-glucose units are joined by C1–O–C4 linkage, but some α-D-(+)-glucose units are joined by C1–O–C6 linkage and they make branches.



Amylopectin

(2) Cellulose : Cellulose is the main component of cell walls of plants. Cotton is pure form of cellulose. Moreover cellulose is obtained from wood (50% cellulose) and jute (65% cellulose) in moderate proportion. Cellulose is a colourless fibrous compound. It is insoluble in water and in most organic solvents but it is completely soluble in ammonical cupric hyroxide solution. Molecular mass of cellulose is approximately 3 lakh to 5 lakh (1800 to 3000 glucose units). Hydrolysis of cellulose by acid gives D-(+)-glucose. Experimental results have proved that cellulose consists of long chain of β-D-(+)-glucose. In this chain, the glycosidic linkage is formed between C1 of one β-D-(+)-glucose unit and C4 of next β-D-(+)-glucose unit. Thus, **in cellulose, two monosaccharide molecules are joined by C1–O–C4 linkage.**



Cellulose

7.6 Importance of Carbohydrates

- Cellwall of bacteria and plants is made up of cellulose.
- New growing plant uses the starch which is stored in seeds as food for their growth.
- The stored glycogen in animals is converted into glucose and gives energy when required.
- Major component of our food materials is carbohydrates. e.g., table sugar, jaggery, wheat, rice etc.
- Linen, rayon and acetate fibre are form of cellulose. They are used for making clothes.
- Wood is used for construction of building and furniture, wood is also cellulose.
- Carbohydrate compounds are used for preparation of paper, photographic - film, explosive substances, plastics etc.

7.7 Proteins

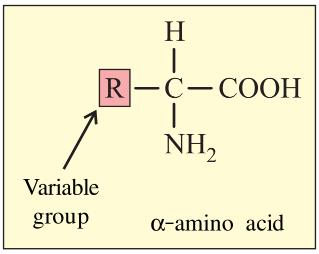
Protein compounds possess very high molecular mass (Approximate 20000 to 2 crore). They are biopolymer complexes of amino acids. They are present in all living cells. Therefore proteins are of prime physiological importance in all living cells. Enzymes, hormones, antibodies are all proteins. A large number of different amino acids are obtained by the hydrolysis of protein. All proteins contain C, H, O, N elements while some may also contain non-metal elements like S,P and metal elements like Fe, Cu, Zn, Mn in trace amount.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \text{Amino acids}$$

It is necessary to study amino acids before studying the proteins and peptides.

7.7.1 Amino Acids :

In 1901, scientist Emil Fischer had obtained several amino acids by hydrolysis of proteins. Thus, amino acids are the building block of protein structure. The name amino acid indicates that they contain both an amino ($-NH_2$) and carboxyl ($-COOH$) group. Those amino acids which are obtained from hydrolysis of protein are all α-amino acids. This means that in their structure, amino group is on α-carbon atom adjacent to carboxyl group. General structure of α-amino acid is as follows :



$$R-\underset{NH_2}{\overset{H}{C}}-COOH$$

Here –R is not restricted to alkyl group. –R may be open chain, cyclic or aromatic hydrocarbon group; amino, carboxyl, hydroxyl or sulphur containing group (table 7.1). It is necessary to note here that structures of all α-amino acid possess primary amino group, while only proline contains secondary amino group. In this compound nitrogen atom of amino group is involved in five membered ring (table 7.1). All α-amino acids are known by trivial names. From these names general properties or their sources can be known but any information about their structure is not obtained. Glycine got its name because of its sweet taste (in Greek 'Glykos' means 'sweet'). Tyrosine got its name because it was first obtained from cheese (in Greek, 'tyros' means cheese). As we know that amino acid contains one acidic group ($-COOH$) and one basic group ($-NH_2$), therefore acidic, basic and neutral nature of amino acid depends on the nature of attaching group R. Amino acids can be classified in neutral, acidic and basic forms as follows :

(1) **Neutral amino acid :** The amino acid in which the, attaching group-R possesses neutral nature it is known as neutral amino acid (table 7.1). e.g., glycine, alanine.

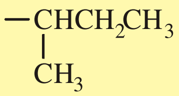
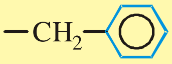
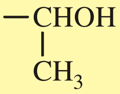
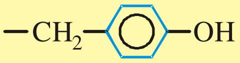
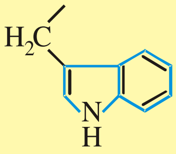
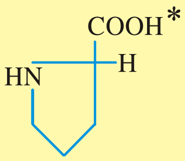
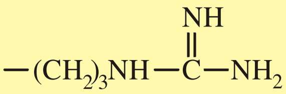
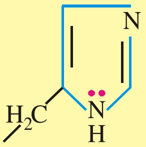
(2) **Acidic amino acid :** The amino acid in which the, attaching group-R possesses acidic nature, it is known as acidic amino acid (table 7.1) e.g., aspartic acid, glutamic acid.

(3) **Basic amino acid :** In which amino acid, attaching group-R possesses basic nature is known as basic amino acid (table7.1). e.g., lysine, arginine.

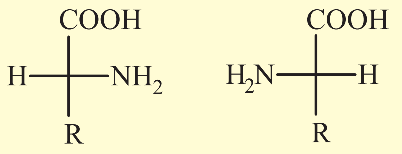
Amino acids which can be synthesised in body are known as **non-essential amino acids** and those which cannot be synthesised in the body and must be obtained through diet are called **essential amino acids.** Leucine, isoleucine, lysine, methionine, phenyl alanine, threonine, tryptophan, valine, arginine and histidine are essential amino acids. Name and structure of twenty important naturally occurring amino acids are mentioned in table 7.1.

Table 7.1 Important naturally occurring amino acids (For information only)

Sr.	Name of the amino acids	Structure of R	Three letters symbol	One letter symbol
	Neutral amino acid			
1.	Glycine	$-H$	Gly	G
2	Alanine	$-CH_3$	Ala	A
3.	Valine	$-CH(CH_3)_2$	Val	V

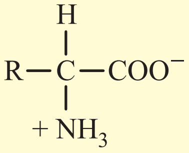
4.	Leucine	$-CH_2CH(CH_3)_2$	Leu	L
5.	Isoleucine	 $-\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	Ile	I
6.	Phenylalanine		Phe	F
7.	Asparagine	$-CH_2CONH_2$	Asn	N
8.	Glutamine	$-CH_2CH_2CONH_2$	Gln	Q
9.	Serine	$-CH_2OH$	Ser	S
10.	Threonine	 $-\underset{\underset{CH_3}{\vert}}{C}HOH$	Thr	T
11.	Cysteine	$-CH_2SH$	Cys	C
12.	Methionine	$-CH_2CH_2SCH_3$	Met	M
13.	Tyrosine		Tyr	Y
14.	Tryptophan		Trp	W
15.	Proline		Pro	P
	Acidic amino acids			
16.	Aspartic acid	$-CH_2COOH$	Asp	D
17.	Glutamic acid	$-CH_2CH_2COOH$	Glu	E
	Basic amino acids			
18.	Lysine	$-(CH_2)_4NH_2$	Lys	K
19.	Arginine	 $-(CH_2)_3NH-\overset{\overset{NH}{\Vert}}{C}-NH_2$	Arg	R
20.	Histidine		His	H

* It is not only structure of R but it is entire structure of amino acid



D-amino acid L-amino acid

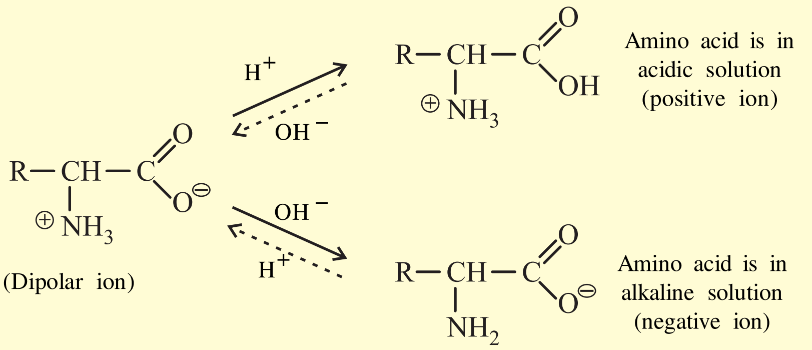
D- and L- forms of amino acids : According to table 7.1 we can say that in all amino acids α-carbon is chiral carbon except glycine. Therefore D and L forms of all these amino acids can exist. The Fischer projection of amino acid with the –COOH group on the top and –R group at the bottom of the vertical axis is a **D-amino acid** if the $-NH_2$ group is on the right of the horizontal axis and is an **L-amino acid** if $-NH_2$ is on the left. Most of the amino acids found in nature have L-configuration.



Amino acid as dipolar molecule

Amino acid as dipolar molecule : We know that amino acids contain both the acidic group (–COOH) and basic group ($-NH_2$). In dry solid form, the amino acid exists as dipolar molecule in which carboxyl group is present as carboxylate ion (COO^-) and amino group is present as aminium ion ($\overset{+}{N}H_3$). This dipolar ion is also known as **zwitter ions.**

In acidic solution, dipolar ion of amino acid exists as a positive ion while in alkaline solution it exists as a negative ion.

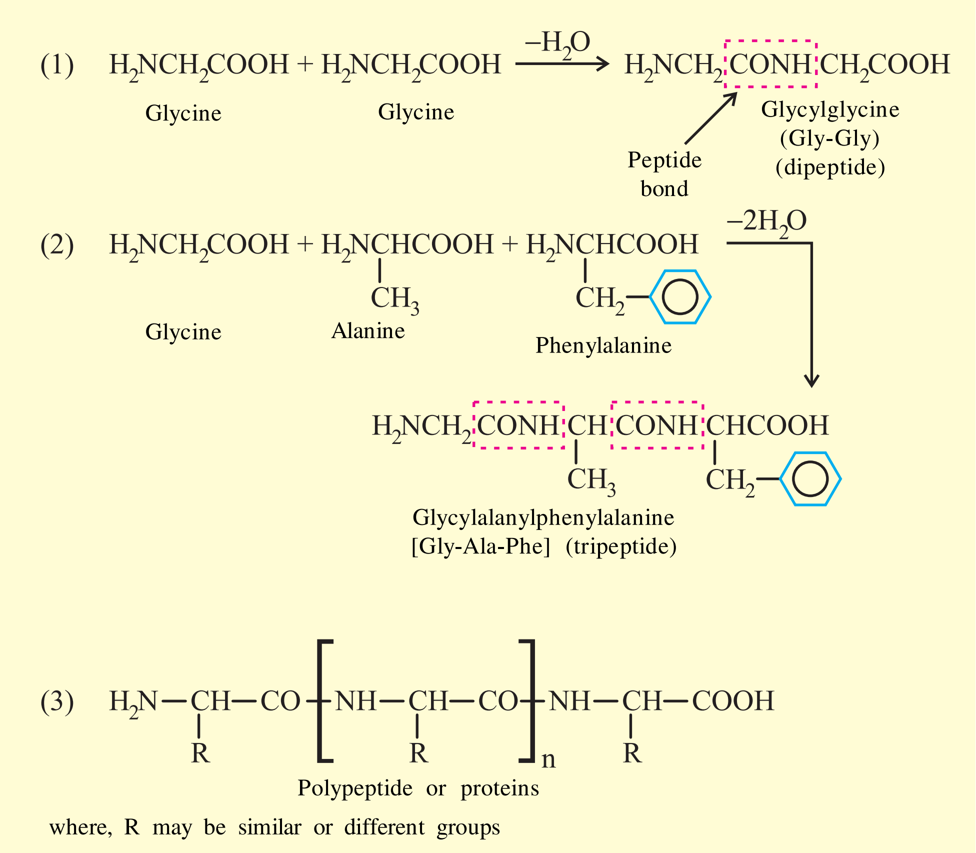


Thus, amino acids exist as positive ion (pH < 7) or negative ion (pH > 7) or dipolar ion (pH = 7) corresponding to pH of their aqueous solution. If solution of amino acid is put in an electric field then the ions present will migrate towards the specific electrode. If amino acid is present as positive ion in its solution then it will migrate towards cathode (negative electrode) and if it is present as negative ion in its solution then it will migrate towards anode (positive electrode). If amino acid is dipolar ion in its solution then it will not migrate towards anode or cathode, because of dipolar ion is neutral with respect to balancing of charge. In electric field, the pH value at which the amino acid does not migrate towards any electrode is called the **isoelectric point (pI) of amino acid.** Different amino acid have different isoelectric points.

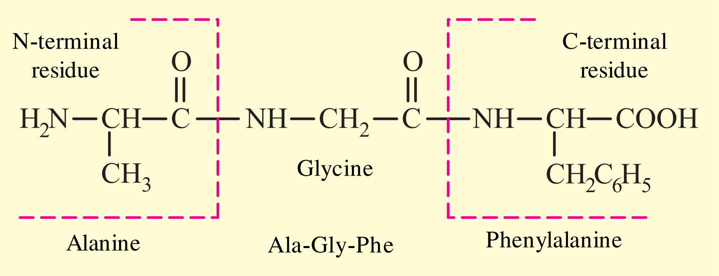
Most of the amino acids react with acid or base and form salt, so they are known as **amphoteric compounds.** A mixture of amino acids can be separated by electrophoresis and different types of chromatographic techniques.

7.7.2 Peptides :

Scientist Emil Fischer suggested that reaction between $-NH_2$ group of one amino acid and –COOH group of another amino acid loses the water molecule and forms amide. This amide bond (–CONH–) is known as **peptide bond or peptide linkage.** If two amino acids are joined by peptide bond and form a chain then it is called the **dipeptide.** If three amino acids are joined by peptide bond and form a chain is called the **tripeptide.** If four to ten amino acids are joined by peptide bond and form a long chain then it is called the **oligopeptide.** If many amino acids are joined by peptide bond and form a long chain then it is called **polypeptide or protein.** Generally peptides having molecular mass upto 10,000 are called **polypeptides** and which peptides which have molecular mass above 10,000 are called **proteins.** e.g.,



Out of two amino acids (first and last) of peptide chain, the $-NH_2$ group of one amino acid and $-COOH$ group of another amino acid are not involved in formation of peptide bond. Thus, $-NH_2$ group at one end and $-COOH$ group at other end are free in polypeptide chain. According to simple convention for representation of peptide structure, the free $-NH_2$ group containing end is written at left side in peptide chain. It is known as **N-terminal residue.** The free $-COOH$ group containing end is written at right side in peptide chain. It is known as **C-terminal residue.** According to this convention tripeptide alanylglycylphenylalanine can be mentioned as follows :



The sequence of amino acids is most important in peptide chain. If amino acids are joined with different sequences then different peptides are formed. e.g., Three amino acids A, B, C are joined in different sequences to form six different types of tripeptides A–B–C, A–C–B, B–A–C, B–C–A, C–A–B, C–B–A.

7.7.3 Structures of Proteins :

Proteins can be classified into two types on the basis of their molecular shapes: (i) Fibrous proteins (ii) Globular proteins.

(i) Fibrous Proteins : When the polypeptide chains run parallel and are held together by **hydrogen and disulphide bonds,** then fibre like structure is formed. Such proteins are generally insoluble in water. e.g., Keratin (present in hair, wool, silk) and myosin (present in muscles) etc.

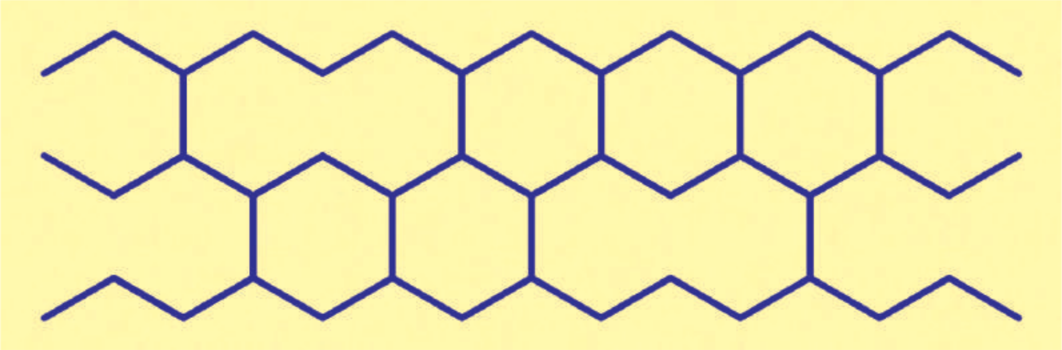


Fig. 7.1 Fibrous proteins

(ii) Globular Proteins : This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. e.g., insulin, albumins etc.

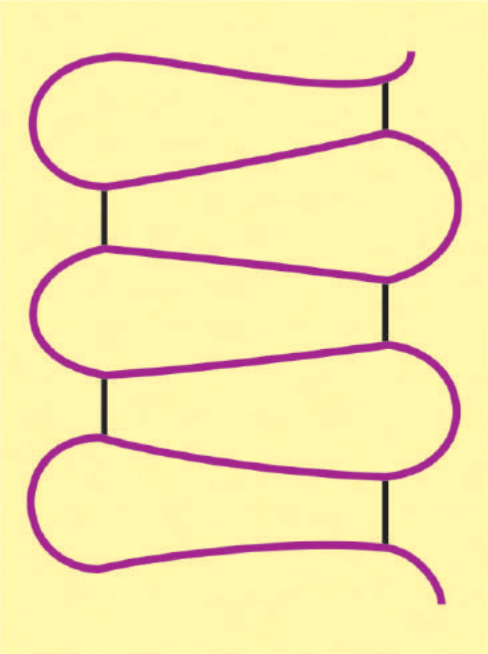


Fig. 7.2 Globular proteins

Four different types of protein structures viz. primary, secondary, tertiary and quaternary have been discovered. In 1954 scientist Linus Pauling was awarded the Nobel Prize in chemistry for work on protein-structure.

(1) Primary structure of proteins : Primary structure of proteins consists of one or more chains of polypeptides. In this, the amino acids present are joined in a specific sequence. Two polypeptide chains are joined with each other by **disulphide linkage (–S–S–)** in primary structure of insulin in human.

(2) Secondary structure of proteins : This type of structure is shown in long chain of polypeptides. Secondary structure can be explained by two different types. (a) α-helix shape (b) β-pleated sheet shape (zig zag shape)

In α-helix shaped protein, polypeptide chain is coiled in helix shape. Approximate 3.6 amino acids are included per turn of the helix. In this structure, hydrogen bond is formed between oxygen atom of $\rangle C=O$ and hydrogen atom of –NH of peptide bond. This structure is presented in Fig. 7.3.

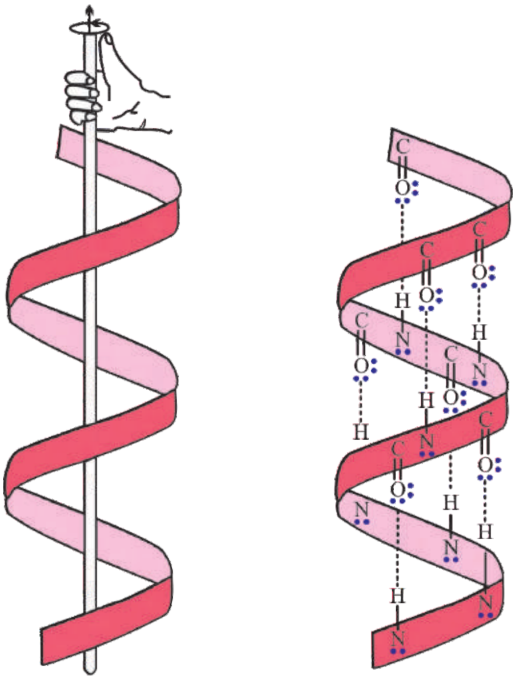
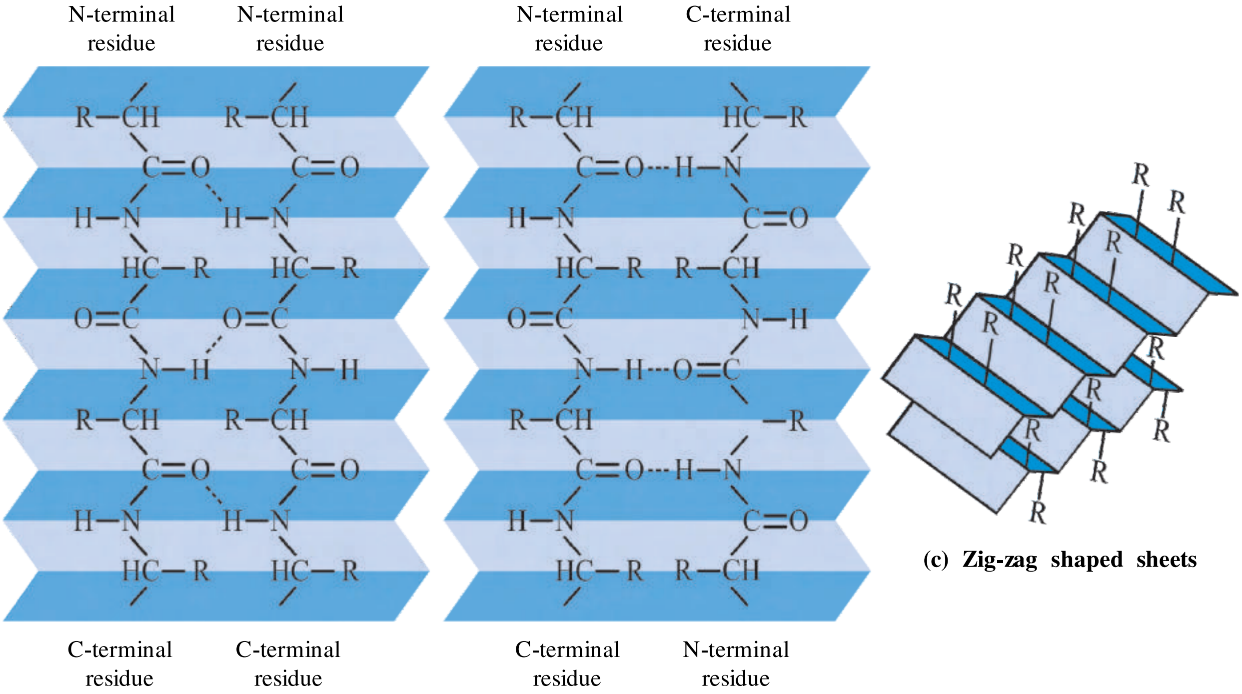


Fig. 7.3 α-Helix structure of proteins (For information only)

In β-pleated sheet shaped protein, one polypeptide chain forms intermolecular hydrogen bond (between oxygen atom of $\rangle C=O$ and H atom of $H-N\langle$) with adjacent polypeptide chain. Therefore these protein chains are formed like zig zag shaped sheet. This structure is presented in Fig. 7.4.



(c) Zig-zag shaped sheets

(a) Same terminal residue containing polypeptides

(b) Different terminal residue containing polypeptides

Fig. 7.4 β-Pleated sheet structure of proteins (For information only)

(3) Tertiary structure of proteins : The tertiary structure of a protein is the three dimensional arrangement of all the atoms in the protein. In this structure, long chain of polypeptides is folded at many points and forms coil shape. Side chains of amino acids are joined to each other by van der Waals' attraction forces, hydrogen bond, ionic bond and disulphide bond. Tertiary structure of myglobin protein is presented in Fig. 7.5.

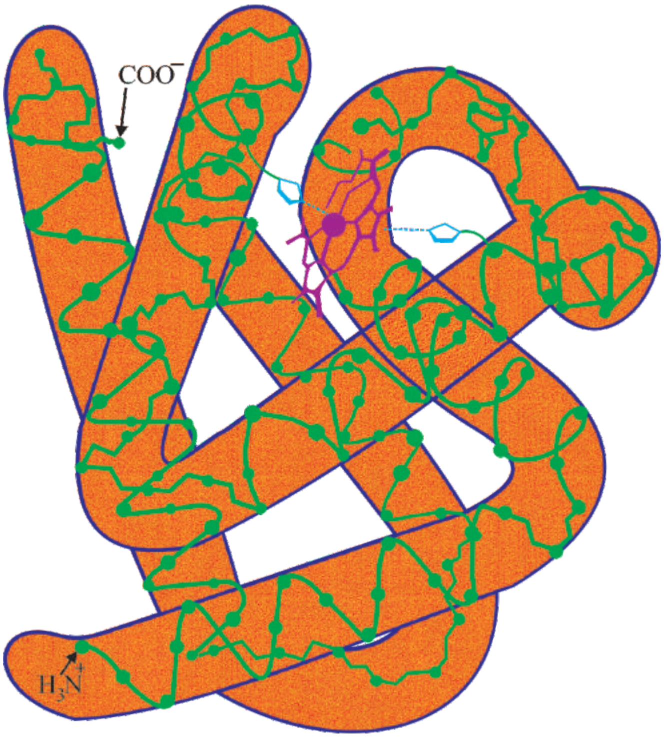


Fig. 7.5 Tertiary structure of myglobin protein (For information only)

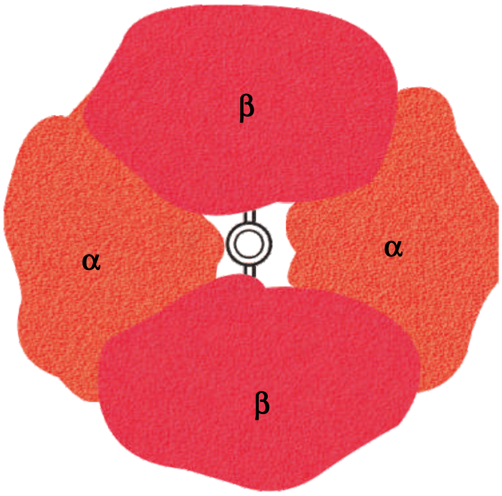


Fig. 7.6 Quaternary structure of haemoglobin protein (For information only)

(4) Quaternary structure of proteins : This quaternary structure is found in some complex proteins. These proteins are made up of two or more polypeptide chains. Non protein components may also be present in them. In this structure, chains of polypeptides are joined with each other by hydrogen bond, ionic bond and disulphide bond. Haemoglobin protein consists of quaternary structure, which is presented in Fig. 7.6. In this structure, two alpha chains and two beta chains are present. These four chains are arranged in a specific way as mentioned in Fig. 7.6.

7.7.4 Denaturation of Proteins :

Proteins found in living organisms are remarkably sensitive to changes in environment. Relatively small changes in pH, temperature or solvent composition, even for only a short period, may cause proteins to become denatured. In proteins, occurrence of this denaturing is known as denaturation of proteins. Due to this denaturation, proteins lose their biological activity. Reasons of denaturation of proteins are as follows :

(1) Increase in temperature : Most globular proteins become denatured when heated above 323 K - 333 K. e.g., If an egg is fried or boiled in water at 373 K or above then white protein becomes denatured, forming an insoluble mass.

(2) Changes in pH : Adding concentrated acid or alkali to a protein in aqueous solution causes changes in the characteristics of ionizable side chains in it and hydrogen bond and different types of attractions are broken down. In certain clinical chemistry tests removal of all protein material is first required. For this the trichloroacetic acid is added to sample and resulting protein is converted into precipitates by denaturation. They can be removed easily.

(3) Detergents : Detergent such as sodium dodecyl sulphate is associated with the non polar groups of proteins. It creates interference with the hydrophobic interactions in protein, due to which protein becomes denatured.

(4) Organic solvents : Organic solvents such as alcohol, acetone and ether denature the proteins by interference of hydrophobic interactions.

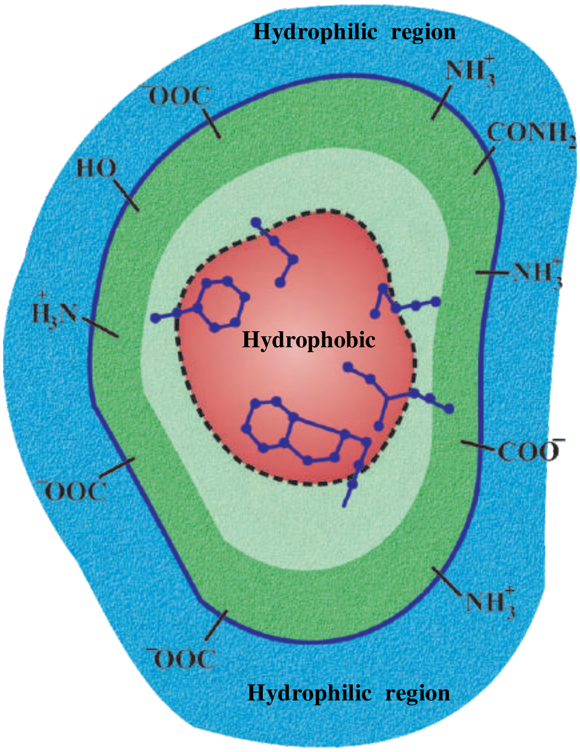


Fig. 7.7 Hydrophilic and hydrophobic regions in proteins (For information only)

7.8 Enzymes

The substance which acts as a catalyst in biochemical reactions is known as **enzyme.** Enzymes are globular proteins. Enzymes participate in biochemical reactions and increase the reaction rate. They are not utilized in reaction which means that they are obtained as such in original form at the end of the reaction. Some enzymes can increase the rate of reaction by 10^{12} times. e.g., Hydrolysis of a fat (an ester) to a carboxylic acid and an alcohol is extremely slow, but this reaction occurs rapidly in the presence of lipase enzyme. Some enzymes consist of only of proteins. Some enzymes which consist of other chemical components except proteins which are necessary for their proper functioning of them. Such a component is called a **cofactor.** Cofactors may be inorganic components such as zinc (Zn^{2+}), manganese (Mn^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+}) or copper (Cu^{2+}) metal ions. If the cofactor is organic in nature, it is called a **coenzyme.** Thus, coenzyme is a non-protein. It is necessary to note here that if inorganic component is cofactor in enzyme then it is not called coenzyme. The protein part of an enzyme is called **apoenzyme.** Both the coenzyme and the apoenzyme must be present for enzymatic activity to take place.

Coenzyme	+	**Apoenzyme**	→	**Enzyme**
(Non-protein) (inactive)		(Protein) (inactive)		(Active)

Working mechanism of enzyme : Enzyme (E) and substrate (S) combine to form an enzyme-substrate intermediate (E–S) complex. This intermediate decomposes to give product (P) and regenerate the enzyme (E).

E	+	**S**	→	**E-S**	→	**E**	+	**P**
(Enzyme)		(Substrate)		(Enzyme-substrate complex) intermediate compound		Enzyme		Product

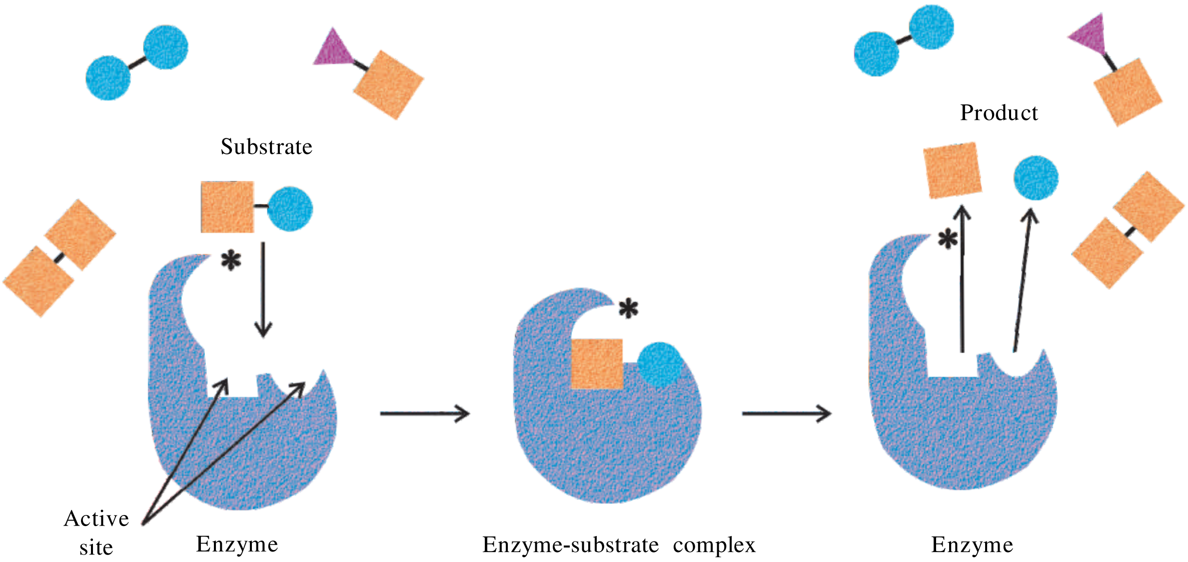


Fig. 7.8 Working mechanism of enzyme (For information only)

The substrate must fit in portion of the enzyme, called the **active site.** The specific amino acids which are present in protein part of enzyme bind the substrate. Therefore this protein part acts as an active site. Mostly an enzyme binds to specific substrate suitable with its active site. It does not bind with other substrate. For example, maltase hydrolyses the maltose but it is not useful in hydrolysis of other disaccharides-lactose or sucrose. Lactose is hydrolysed by emulsin and sucrose is hydrolysed by invertase enzyme. Thus, **each enzyme is specific for each specific reaction.** This type of working mechanism of enzyme can be explained by the lock and key model. Specific lock (substrate) is opened only by the specific key (enzyme) which is suitable for that lock. You have learnt in detail about lock and key model in unit 2 : on surface chemistry.

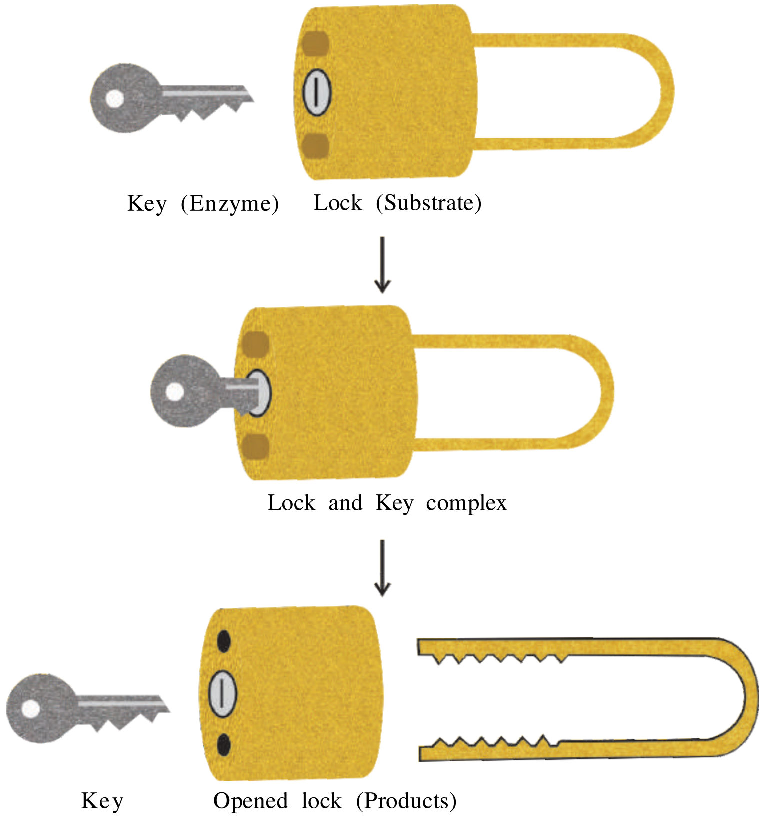


Fig. 7.9 Working mechanism of enzyme (Lock and Key model) (For information only)

Names of enzyme can be assigned in two ways. Enzyme can be named by adding the suffix 'ase' to the root of its substrate name. e.g., one which affects maltose is called maltase and which affects lipid is called lipase. In another way, the name of enzyme is decided by the type of reaction on which enzyme is affected. e.g., Enzyme that catalyses the hydrolysis is called hydrolase and enzyme that catalyses the oxidation is called oxidase.

7.9 Vitamins

Certain organic compounds are required in small amounts in our diet. The deficiency of these compounds causes specific diseases in our body. These organic compounds are called **vitamins.** The word vitamine was coined from the word vital + amine, because the earlier work showed that these organic compounds contained amino group. But later work showed that most of these compounds did not contain amino group, so the letter 'e' was dropped and the term vitamin is familiar nowadays. Most of the vitamins cannot be synthezised in our body but plants can synthesise them. Therefore vitamins are considered as essential food constituents. Vitamins are designated by alphabets A,B,C,D etc. Some of them are further named as sub-groups e.g., B_1, B_2, B_6, B_{12} etc. Human body synthezises vitamin A from carotene and it also synthezises vitamin D in skin with the help of sunlight. Vitamin B complex and vitamin K are formed by microorganism in intestine. High proportion of vitamin is harmful to us, so we should not use pills of vitamins without the advice of the doctor.

Vitamins are classified as two types **(1) Fat soluble : e.g., Vitamin A, D, E, K (2) Water soluble : e.g., Vitamin B complex, C. Vitamin H (biotin) is insoluble in both water and fat.** Important vitamins, their sources and diseases caused by their deficiency are presented in table 7.2.

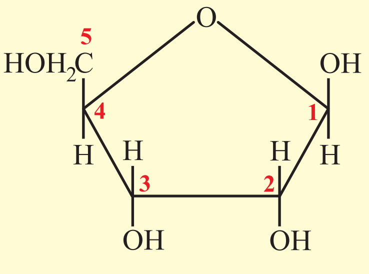
Table 7.2. Vitamins, sources and diseases caused by their deficiency

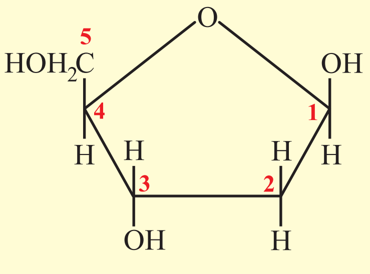
No.	Vitamin	Source	Diseases caused by their deficiency
1.	Vitamin A (Retinol)	Liver oil of fish, carrot, butter, cheese and milk	Xerophthalima
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri-Beri
3.	Vitamin B_2 (Riboflavin)	Milk, egg white, liver, kidney	Dark-red tongue and skin diseases
4.	Vitamin B_6 (Pyridoxine)	Cereals, gram, milk, yeast, egg white	Skin diseases and convulsions
5.	Vitamin B_{12} (Cyanocobalamine)	Egg, fish, liver, meat (not found in plants)	Pernicious anemia
6.	Vitamin C (Ascorbic acid)	Tomato, green pepper, orange, citrus fruits and green vegetables	Scurvy
7.	Vitamin D (Calciferol)	Sunlight, fish, egg white	Bone deformation in children and soft bones and joint pain in adults
8.	Vitamin E (α-Tocopherol)	Vegetable oil, green vegetables, egg white, meat	Sterility
9.	Vitamin K (Phylloquinone)	Green vegetables	Haemorrhage
10.	Vitamin H (Biotin)	Milk, yeast, liver	Loses of hair, skin diseases, paralysis

7.10 Nucleic Acids

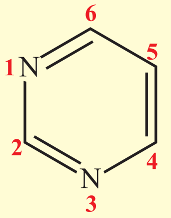
Every generation of each and every species shows similarity with its ancestors in many ways. The process of transmission of these characteristics from one generation to the next generation is called heredity. For this, chromosomes are responsible which are present in nucleus of living cell. These chromosomes are made up of proteins and nucleic acids. Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA) are two types of nucleic acids. **Nucleic acids are long chain polymers of nucleotides, so nucleic acids are also called polynucleotides.** Complete hydrolysis of nucleic acids (DNA and RNA) forms a pentose sugar, nitrogen containing heterocyclic compounds and phosphoric acid. It indicates that nucleic acids are formed of these three constituents. Thus, it is necessary to know structure of these three constituents for understanding the structure of nucleic acid.

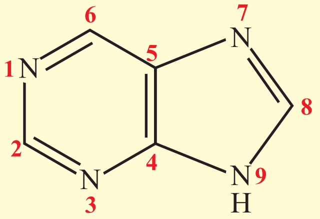
(1) Sugar : β-D-ribose sugar is present in RNA and β-D-2-deoxyribose sugar is present in DNA.


β-D-Ribose


β-D-2-deoxyribose

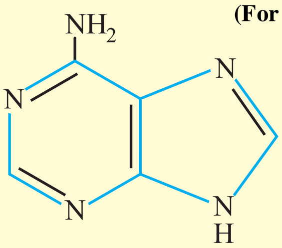
(2) Heterocyclic base : In nucleic acids, purine and pyrimidine heterocyclic systems act as base. Pyrimidine is monocyclic compound whereas purine is dicyclic compound.

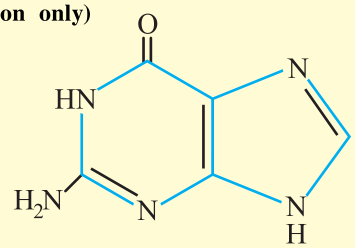

Pyrimidine

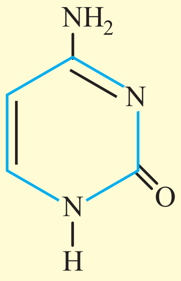

Purine

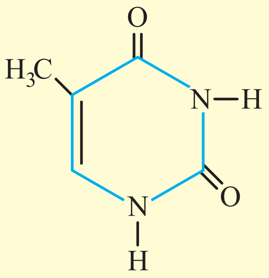
Adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U) are present in nucleic acids as heterocyclic bases. Out of them A and G are purine derivatives and C, T and U are pyrimidine derivatives, they are known as purine bases and pyrimidine bases, respectively. **DNA contains A, G, C and T bases, while RNA contains A, G, C and U bases.**

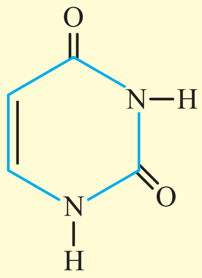
(For information only)


Adenine

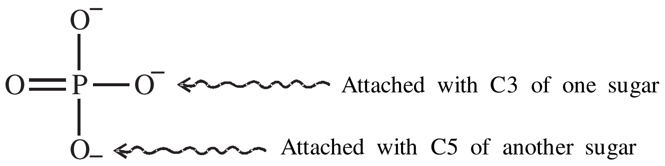

Guanine


Cytosine


Thymine

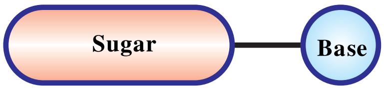

Uracil

(3) Phosphoric acid : In nucleic acid, sugars are joined together by phosphate ion (PO_4^{3-}) of phosphoric acid

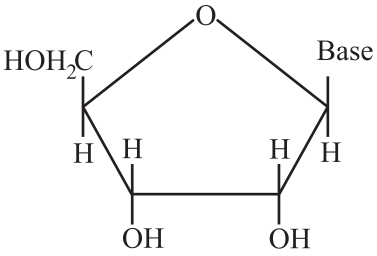


$$O{=}P(O^-)(O^-){-}O^-$$

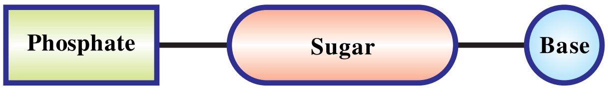
A unit formed by the attachment of a base to first position of sugar is known as **nucleoside.** A unit formed by the attachment of a nucleoside to phosphate ion is known as **nucleotide.**



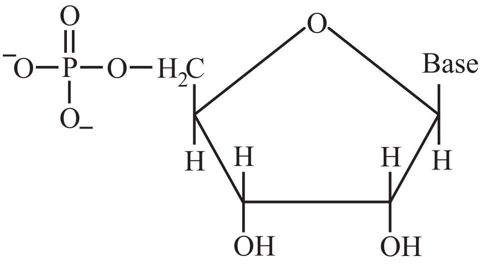
Nucleoside



Nucleoside



Nucleotide



Nucleotide

Two nucleotides are joined together by **phosphodiester linkage.** This linkage is formed between C3 of one sugar and C5 of another sugar. Formation of dinucleotide is shown in Fig. 7.10.

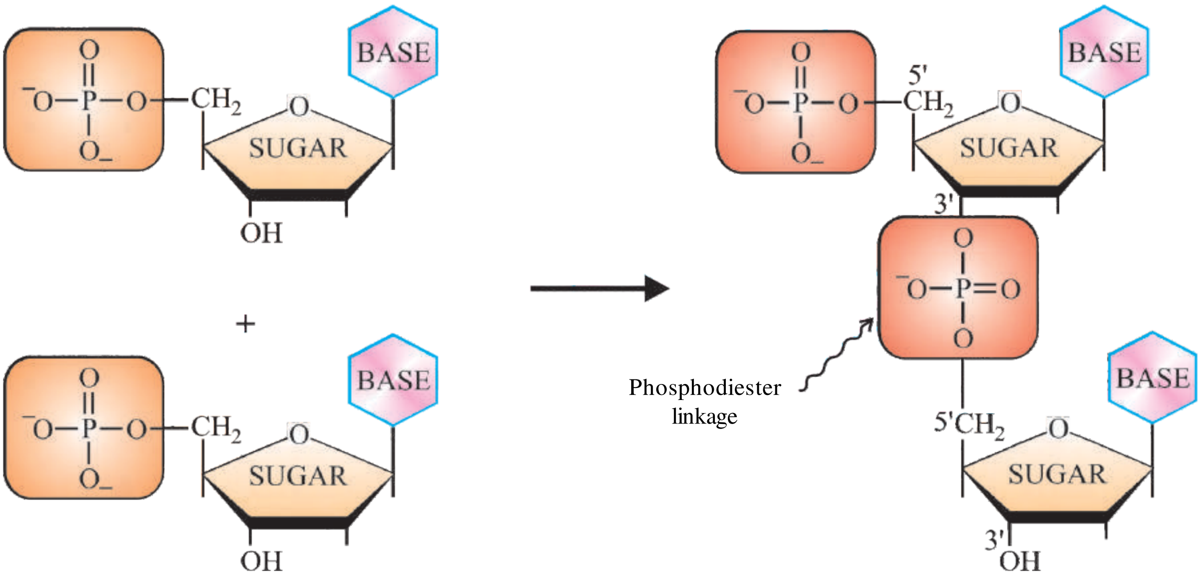
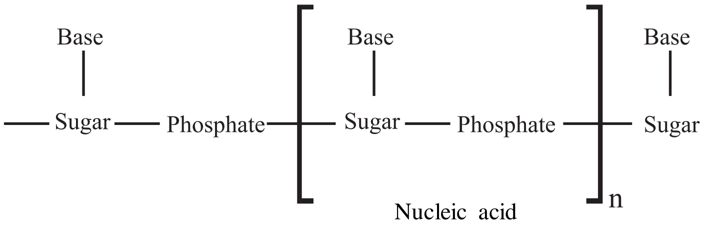


Fig. 7.10 Formation of dinucleotides (For information only)

Many nucleotides join together and form polynucleotides. It is known as nucleic acid. Structure of nucleic acid can be shown in an easy way as follows.



7.10.1 Double Helix Structure of DNA :

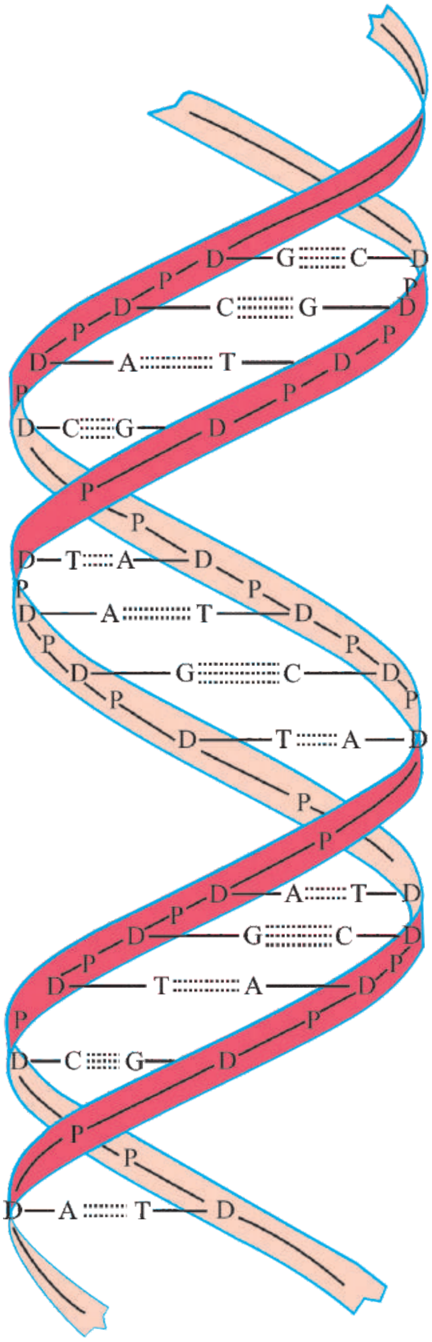


Fig. 7.11 Double helix structure of DNA
(For information only)

It is proved that the molecular shape of DNA is like a twisted rope which is shown in Fig. 7.11. It contains **phosphoric acid units on outer side and base compounds in central part.** In the nucleus of the cell, the these nucleic acids are divided, which are present in gene of chromosomes during reproduction. These nucleic acids are arranged similarly in new cell. Due to this heredity, characteristics are transmitted from one generation to next generation. In 1953 J.D. Watson and H.C. Crick proposed a double helix structure for DNA from X-ray diffraction studies of DNA. This structure looks like a spiral staircase. In connection of two polynucleotide chains, purine base of one nucleotide is joined with pyrimidine base of opposite nucleotide by hydrogen bond. In this adenine (A) base is always joined with thymine (T) and guanine (G) is always joined with cytosine (C). **A and T are joined together with two hydrogen bonds and C and G are joined together with three hydrogen bonds.**

P = Phosphate

D = Deoxyribose

A = Adenine

T = Thymine

C = Cytosine

G = Guanine

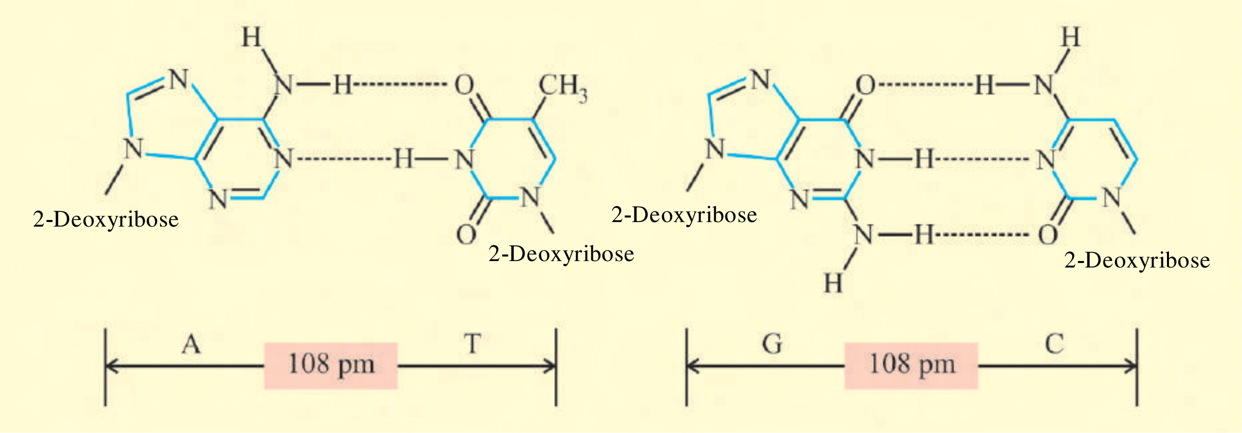


Fig. 7.12 Hydrogen bonds between A and T / G and C (For information only)

7.10.2 Biological Importance of Nucleic Acids :

DNA is the responsible chemical for heredity. It reserves the genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to new cell. Another function of nucleic acids is the protein synthesis in the cell. Actually, the proteins are synthesised by various RNA molecule in the cell but the message for the synthesis of a specific protein is present in DNA.

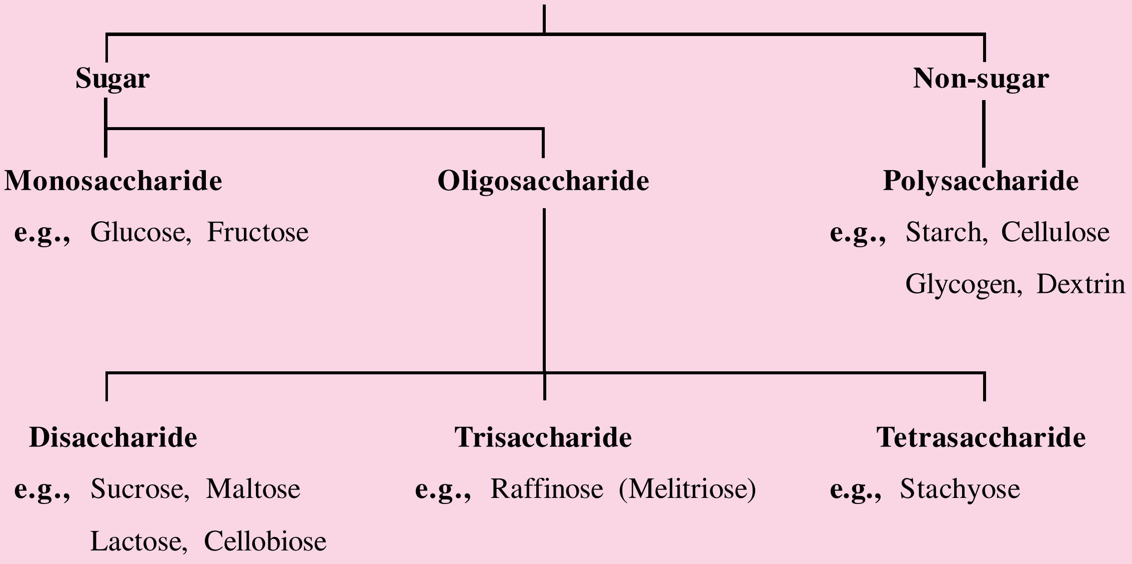
SUMMARY

- Chemical compounds present in living systems are known as biomolecules.
- Carbohydrates, proteins, vitamins, nucleic acids enzymes and lipids are biomolecules.

Carbohydrates

- Carbohydrates are chemically polyhydroxy aldehydes or polyhydroxy ketones or such compounds which can be hydrolysed to these compounds.

Carbohydrates



Monosaccharides

Monosaccharide	**General class**	**(+) or (–)**	**Does it show mutarotation ?**	**Anomers**	**Is it reducing sugar ?**
Glucose	Aldohexose	(+)	Yes	α-D-(+)-glucose β-D-(+)-glucose	Yes
Fructose	Ketohexose	(–)	Yes	α-D-(–)-fructose β-D-(–)-fructose	Yes

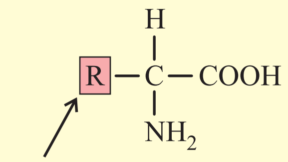
Disaccharides

Disaccharide	**(+) or (–)**	**Monosaccharide unit**	**Glycosidic linkage**	**Does it show mutarotation ?**	**Anomers**	**Is it reducing sugar ?**
Sucrose	(+)	Glucose Fructose	α-D-(+)-glucose(C1)-O-(C2)-β-D-(–)-fructose	No	No	No
Maltose	(+)	Glucose Glucose	α-D-(+)-glucose(C1)-O-(C4)-D-(+)-glucose	Yes	α-(+)-Maltose β-(+)-Maltose	Yes
Lactose	(+)	Galactose Glucose	β-D-(+)-galactose(C1)-O-(C4)-D-(+)-glucose	Yes	α-(+)-Lactose β-(+)-Lactose	Yes

Polysaccharides

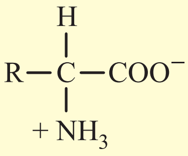
Polysaccharide	**Monosaccharide unit**	**Glycosidic linkage**
Starch		
Amylose	Glucose	α-D-(+)-glucose(C1)-O-(C4)-α-D-(+)-glucose
Amylopectin	Glucose	α-D-(+)-glucose(C1)-O-(C4)-α-D-(+)-glucose and α-D-(+)-glucose(C1)-O-(C6)-α-D-(+)-glucose
Cellulose	Glucose	β-D-(+)-glucose(C1)-O-(C4)-β-D-(+)-glucose

Amino acids



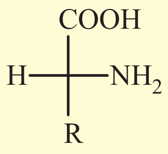
$R-\underset{NH_2}{\overset{H}{C}}-COOH$

General structure of α-amino acid



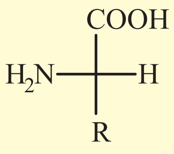
$R-\underset{+NH_3}{\overset{H}{C}}-COO^-$

Amino acid as dipolar ion



$H-\underset{R}{\overset{COOH}{C}}-NH_2$

D-amino acid



$H_2N-\underset{R}{\overset{COOH}{C}}-H$

L-amino acid

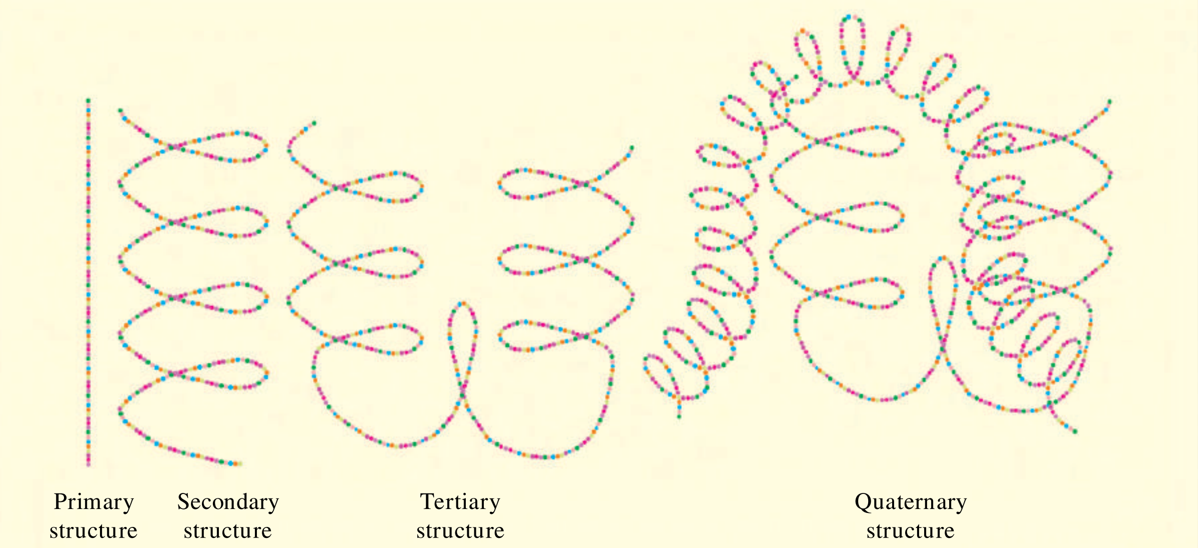
Proteins

- Proteins $\xrightarrow{\text{Hydrolysis}}$ Peptides $\xrightarrow{\text{Hydrolysis}}$ Amino acids
- Amino acid + amino acid → Dipeptide

  Amino acid + amino acid + amino acid → Tripeptide

  Amino acid + amino acid + amino acid + amino acid → Tetrapeptide

  n (Amino acid) → Polypeptide or proteins



Structures of Proteins

Enzymes

- The substance which acts as a catalyst in biochemical reaction is known as enzyme.
- **Coenzyme** + **Apoenzyme** → **Enzyme**

  (Non Protein) (inactive) (Protein) (inactive) (active)

- **E** + **S** → **E-S** → **E** + **P**

  (Enzyme) (Substrate) (Enzyme-substrate complex) Enzyme Product

(Working mechanism of enzyme)

Vitamins

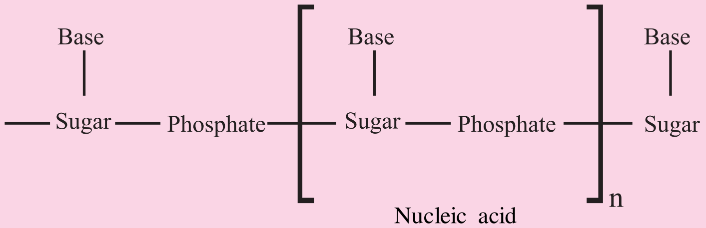
- Vitamin A, B_1, B_2, B_6, B_{12}, C, D, E, K and H are known.
- All vitamins are most important for human body. Deficiency of specific vitamin causes specific diseases.

Nucleic acids

- Two types of nucleic acids are

  (i) Deoxyribonucleic acid (DNA) and (ii) Ribonucleic acid (RNA)

- Nucleic acid means polynucleotides
- Nucleotide means nucleoside + phosphate
- Nucleoside means sugar + base
- DNA is the responsible chemical for heredity



Nucleic acid

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which compound from the following is a disaccharide ?

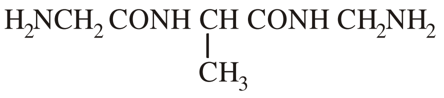
(A) Glucose (B) Fructose (C) Maltose (D) Melitriose

(2) What is the name of total four carbon atoms and one aldehyde group containing carbohydrate ?

(A) Aldotetrose (B) Aldopentose (C) Ketotetrose (D) Ketopentose

(3) Which sugar from the following is not a reducing sugar ?

(A) Glucose (B) Sucrose (C) Maltose (D) Lactose

(4) Which type of peptide chain is present in  ?

$H_2NCH_2CONH\underset{\underset{CH_3}{|}}{CH}CONHCH_2NH_2$

(A) Dipeptide (B) Tripeptide (C) Tetrapeptide (D) Polypeptide

(5) Which structure of protein is having β-pleated sheet shape?

(A) Primary (B) Secondary (C) Tertiary (D) Quaternary

(6) Which of the following statements is true ?

(A) Enzymes are carbohydrates

(B) Enzymes are not obtained at the end of reaction

(C) Enzymes are obtained in the changed form at the end of reaction

(D) Enzymes are obtained in the original form at the end of reaction.

(7) Which vitamin is insoluble in water and fat ?

(A) A (B) B complex (C) C (D) H

(8) Which of the following statements is incorrent ?

(A) A, G, C and T bases are present in DNA

(B) A and T are joined together by two hydrogen bonds in DNA

(C) A and C are purine bases.

(D) T and U are pyrimidine bases.

(9) By which linkage, two monosaccharides are joined together in disaccharide ?

(A) Peptide (B) Phosphodiester (C) Glycosidic (D) Disulphide

(10) Which of the following units are present in α-(+) -lactose ?

(A) β-(D)-(+)-galactose + α-D-(+)-glucose

(B) β-(D)-(+)-galactose + β-D-(+)-glucose

(C) α-(D)-(+)-galactose + α-D-(+)-glucose

(D) α-(D)-(+)-galactose + β-D-(+)-glucose

2. Write the answers of the following questions in brief :

(1) Write two examples of disaccharide.

(2) Write two examples of trisaccharide.

(3) Write two examples of polysaccharide.

(4) Write one example each of aldohexose and ketohexose.

(5) Write the empirical formula and molecular formula of glucose.

(6) Draw the Haworth projections of anomers of glucose.

(7) Draw the Fischer and Haworth projections of α-D-(–)-fructose.

(8) Which enzymes hydrolyse sucrose and maltose ?

(9) Mention the general structure of amino acid.

(10) Write two examples of neutral amino acids.

(11) Write two examples of acidic amino acids.

(12) Write two examples of basic amino acids.

(13) Write general structure of D- and L-amino acids.

(14) Write two names of separation techniques for amino acid mixture.

(15) Which two amino acids form glycylalanine dipeptide chain ?

(16) Based on the molecular shape which two types of protein are there ?

(17) Mention two factors for denaturation of protein.

(18) Mention the names of fat soluble vitamins.

(19) Mention the names of water soluble vitamins.

(20) At which position is the base joined with sugar in nucleoside ?

(21) By which linkage are two nucleotides joined to each other ?

(22) Which two bases are joined together with two hydrogen bonds in DNA ?

(23) Which three bases are joined together with three hydrogen bonds in DNA ?

(24) At which side N-terminal residue is written in peptide chain ?

(25) Which forms of dipolar ion of amino acids are present in acidic and basic medium ?

(26) In the following compounds, glycosidic linkage occurs between which monosaccharide molecules and at which position :

(i) Sucrose
(ii) Maltose
(iii) Lactose
(iv) Amylose
(v) Amylopectin
(vi) Cellulose

(27) **Write definitions :**

(i) Carbohydrate
(ii) Dextrorotatory
(iii) Levorotatory
(iv) Anomeric carbon
(v) Anomers
(vi) Mutarotation
(vii) Caramal
(viii) Zwitter ion
(ix) Isoelectric point of amino acid
(x) N-terminal residue
(xi) C-terminal residue
(xii) Enzyme
(xiii) Cofactor
(xiv) Coenzyme
(xv) Active site of enzyme
(xvi) Vitamin
(xvii) Nucleoside
(xviii) Nucleotide

3. Write the answers of the following questions :

(1) Write the formula of calculation for specific rotation of optically active compound and explain all the terms involved.

(2) Draw the open chain structure of D-(+)-glucose and L-(–)-glucose.

(3) Draw the open chain structure of D-(–)-fructose and L-(+)-fructose.

(4) What are essential amino acids ? Mention their names.

(5) Most amino acids are amphoteric in nature. Why ?

(6) Draw the structure of any dipeptide and mention the position of peptide linkage, N-terminal residue and C-terminal residue in it.

(7) Draw the simple structure of nucleic acid.

(8) Draw the structures of the following compounds. Give the proper number carbon atoms present in each monosaccharide and mention the position of glycosidic linkage in the structure of the following compounds :

(i) (+)-Sucrose
(ii) α-(+)-Maltose
(iii) β-(+)-Lactose
(iv) Amylose
(iv) Amylopectin
(vi) Cellulose

Match the following (Q.9 to 11) :

(9)

A	B
(a) Glucose	(i) Malt sugar
(b) Maltose	(ii) Cane sugar
(c) Lactose	(iii) Grape sugar
(d) Sucrose	(iv) Milk Sugar

(10)

A	B
(a) Vitamin A	(i) Biotin
(b) Vitamin B_2	(ii) Ascorbic acid
(c) Vitamin C	(iii) Riboflavin
(d) Vitamin D	(iv) Retinol
	(v) Calciferol

(11)

A	B
(a) Vitamin B_1	(i) Sterility
(b) Vitamin C	(ii) Xerophthalima
(c) Vitamin E	(iii) Scurvy
(d) Vitamin B_{12}	(iv) Beri-Beri
	(v) Pernicious anemia

(12) Encircle ○ on the differing compound from the following groups of compounds :

(i) Starch, Cellulose, Cellobiose, Glycogen

(ii) Sucrose, Lactose, Glucose, Maltose

(iii) Cytosine, Adenine, Thymine, Uracil

(iv) Vitamin A, Vitamin C, Vitamin D, Vitamin E

Explain with reasons (Q.13 to 15)

(13) Sucrose is a non-reducing sugar.

(14) Maltose is a reducing sugar.

(15) Why lactose has anomers ?

4. Write the answers of the following questions in detail :

(1) Write classification of carbohydrates.

(2) Discuss the two methods for preparation of glucose.

(3) Describe chemical reactions for proving the open chain structure of glucose.

(4) Describe the importance of carbohydrates.

(5) Explain the primary, secondary, tertiary and quaternary structure of protein.

(6) Discuss the reasons for denaturation of proteins.

(7) Explain working mechanism of enzyme.

(8) Discuss the constituents of nucleic acid structure.

(9) Describe the double helix structure of DNA.

(10) Solve the problems :

(i) The specific rotation of 3.0 g of maltose in 20 ml of aqueous solution in a polarimeter tube 2.0 dm long is + 136^0. What is the observed angle of rotation of solution of maltose ?

(ii) Fructose has a specific rotation of (-92.4^0). An aqueous solution of a fructose has an observed angle of rotation of (-27.7^0) when placed in a polarimeter tube 10 cm long. How much amount of fructose is dissolved in 100 ml of aqueous solution ?

●

Unit

8

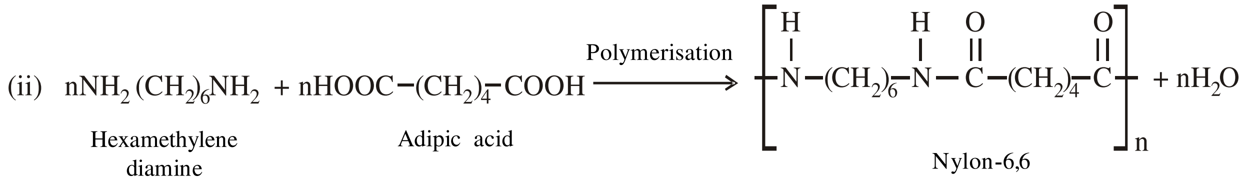
Polymers

8.1 Introduction

Polymer is part of our daily life. Daily requirement is incomplete without its usage. Thinking about universe without polymer is impossible. Polymer is a compulsory need for the physical comfort and for making our life easier. Any material of plastic, like toys for children, polythene shopping bags for purchase or synthetic clothes, tyres of vehicles or the spare parts of machines, insulated (nonconductor) wires of electric cable, or electric shock proof, devices interiors of vehicles or houses, medical field or pharmacy; in each of these polymer has established its dominance. There is a possibillity that polymer will replace the metal in future.

For daily requirement or industrial growth polymer has been used all over. In industries polymer is used in manufacturing of plastic, elastomer fiber, paint and varnish. Polymer word is formed by combination of two Greek words "poly" and "mer" in which 'poly' means many and 'mer' means unit, part or section. Polymer means huge molecule (10^3–10^7 u) containing higher molecular masses and many simple molecules combined. In general, polymer is represented by the name of macromolecules. The simple unit or molecule which is repeated many times in the polymer is known as **monomer.** Such simple units or active molecules are joined together with each other in large amount by covalent bond and form a huge molecule (polymer). This process is called **polymerisation.** The unit which is repeated several times in a huge molecule is called **repeating unit. This number of repeating unit 'n' in polymer molecule is called "degree of polymerization".** e.g., innumerable molecules of ethene monomer combined with each other by polymerisation reaction which forms a huge molecule is called polythene. Polymer molecule containing huge volume is formed by intereaction between innumerable molecules of hexamethylene diamine and adipic acid, which is called nylon-6,6.

(i) $$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow{\text{Polymerisation}} n\underset{\text{Repeating unit}}{\left[CH_2-CH_2 \right]} \longrightarrow \underset{\text{Polythene}}{\left[CH_2-CH_2 \right]_n}$$



(ii) $$\underset{\substack{\text{Hexamethylene}\\ \text{diamine}}}{nNH_2(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{nHOOC-(CH_2)_4-COOH} \xrightarrow{\text{Polymerisation}} \underset{\text{Nylon-6,6}}{\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n} + nH_2O$$

If the value of repeating unit ‘n’ is less than 25 (n < 25) then that polymer is called **oligomer.** Generally oligomer is in liquid state. Liquid polymers used in fevicol like adhesives paints are oligomers. If the value of repeating unit ‘n’ is more than 25 then that polymer is called **heavy polymer.** Generally heavy polymers are in solid state.

8.2 Classification of Polymers

Classification of polymers is possible on some acceptable bases which are shown as under :

8.2.1 Classification based on source :

Polymers are classified in three types on the basis of their availability (source) :

(1) Natural Polymers : Polymers present in nature are obtained from plants or animals, e.g., protein, cellulose, starch, nucleic acids, resins, rubber, etc., are examples of natural polymers.

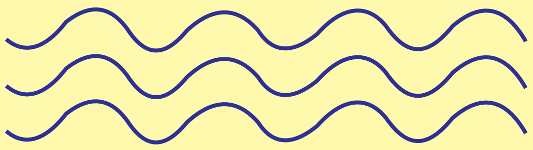
(2) Semisynthetic polymers : Polymers which are formed by chemical reaction with the polymers present in nature are called semisynthetic polymers. By changing the properties of natural polymers according to their requirement, polymers like explosive cellulose nitrate are formed by nitration of cellulose; Cellulose diacetate (rayon) is obtained by acetylation reaction of cellulose with acetic anhydride in acidic medium. Vulcanised rubber obtained by vulcanisation of natural rubber can be included in these type of polymers.

(3) Synthetic polymers : It is totally man-made polymer because synthetic polymer possesses large series of man-made polymers. In this type of polymers plastic (polythene, PVC, teflon) synthetic fibers (terylene, nylon, polyester orlon), synthetic rubber (Buna-S, Buna-N) etc are included.

8.2.2 Classification based on structures :

Polymers are classified into three types according to their structures.

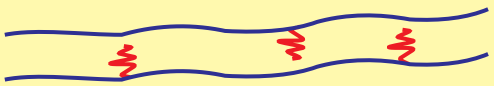
(1) Linear polymers : This type of polymers contain long straight chain in their constitution. There is no branch in their straight chain. Monomer units combine with each other, forming a long straight chain and linear polymer is obtained. Fibers are included in linear polymers. Linear polymers are obtained from natural cources like cotton, silk, wool, linen whereas synthetic linear polymers are terylene, nylon, polyesters, orlon etc. Linear polymers are arranged in a long chain as shown in fig. 8.1.



Linear polymer

Fig. 8.1

(2) Branched chain polymers : This type of polymers contain branch inbetween the long straight chain in their constitution. Monomer units combine with each other, make a long straight chain and if this chain contains brachning inbetween, then it is called branched polymer. This type of thermoplastic polymer contains low density polymer (LDP). For example, polystyrene, PVC, teflon, etc are branched polymers. Branched polymers in long chain possess branches as shown in fig 8.2.



Branched polymer

Fig. 8.2

(3) Cross linked polymers : In this type of polymers, bifunctional or trifunctional monomer combines with covalent bond inbetween the long polymer chain. Long polymer chain is joined by strong covalent bond and forms a net like structure. This type of thermosetting polymer contains high density polymer. For instance, Bakelite, Melamine are crossed linked polymers. Long chain at certain distances joined by strong binding which is shown in fig 8.3.

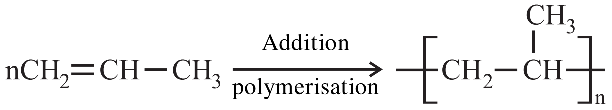
Crossed linked polymers

Fig. 8.3

8.2.3 Classification based on reaction mode of polymerisation :

On the basis of polymerisation reaction, polymers are classified into two categories

(1) Addition Polymers : Due to addition reaction, when double bond or triple bond containing innumerable monomer molecules combine with each other by chemical bond, then they form addition polymer, like polythene formed from ethene. Polypropene formed from propene and polystyrene formed from styrene are addition polymers. e.g., innumerable molecules of propene monomers are joined with each other by addition polymerisation reaction and form polypropylene polymer.



$$nCH_2{=}CH{-}CH_3 \xrightarrow[\text{polymerisation}]{\text{Addition}} \left[CH_2{-}\overset{\overset{\large CH_3}{|}}{CH} \right]_n$$

Propene monomer — Polypropene (polymers)

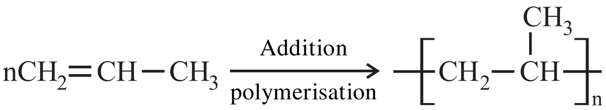
(a) Homopolymers : When same type of innumerable monomers combine with each other in addition polymerisation reaction, and form a polymer, it is known as Homopolymer. Polythene, polystyrene, polyvinyl chloride, teflon, orlon, butyl rubber, neoprene etc are hompopolymers. For example,

(i) When same kind of innumerable molecules of ethene monomers are joined by addition polymerisation reaction, then they form homopolymer polythene.

$$nCH_2{=}CH_2 \xrightarrow[\text{polymerisation}]{\text{Addition}} \left[CH_2{-}CH_2 \right]_n$$

Ethene — Polythene (homopolymer)

(ii) Innumerable molecules of propene monomer are joined by addition reaction to form polypropene.



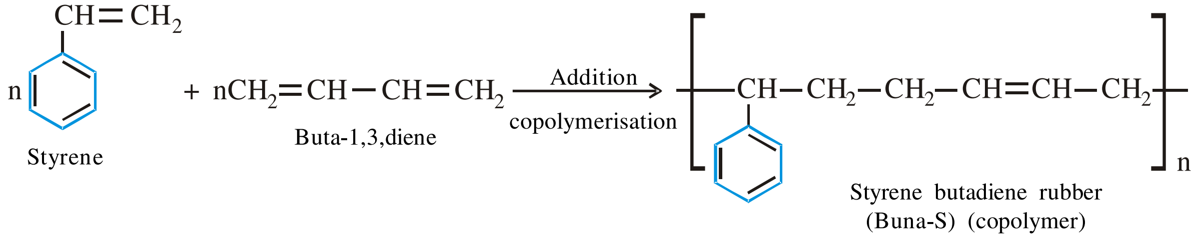
$$nCH_2{=}CH{-}CH_3 \xrightarrow[\text{polymerisation}]{\text{Addition}} \left[CH_2{-}\overset{\overset{\large CH_3}{|}}{CH} \right]_n$$

Propene — Polypropene (Homopolymer)

Here same kind of innumerable molecules (ethene or propene) combine with one another by addition reaction to form polymer, so it is called Homopolymer. In homopolymer, which is formed by the addition reaction, the repeating unit is totally based on the monomer. Naming of these homopolymers is based on the name of monomer unit.

(b) Copolymer : In addition polymerisation reaction when two or more than two different types of innumerable monomers combine with each other to form polymer then it is known as copolymer. Nylon-6,6, Terylene, Bakelite, Melamine, PHBV, etc are copolymers. For example,

Innumerable molecules of two different types of buta-1,3-diene and styrene combine by addition polymerisation reaction to form a copolymer type of rubber, Butadiene, styrene.



Here two different types of innumerable monomers of 1,3-butadiene and styrene combine with each other by addition reaction to form polymers. Hence, it is called copolymer. Repeating unit of this copolymer formed by addition reaction is dependent on the functional group of two different monomers. Names of these copolymers are represented on the basis of two different monomer units.

(2) Condensation polymer : In polymerisation reaction, two different types of innumerable monomer units containing equally bi or tri functional groups combine with each other in equal proportion by condensation reaction to form polymer. Hence, it is called condensation polymer. This type of polymerisation reaction is known as condensation polymerisation. During this condensation polymerisation reaction; water, ammonia, alcohol or hydrogen chloride molecule is released. Certain types of repeating units in condensation polymerisation depend on functional group present in two diffirent types of monomer. Its name is given by the functional group present in repeating unit. **Polyamide** condensation polymer contains –CONH– functional group and condensation polymer containing –COO– functional group is called **polyester.** For example terylene (dacron) nylon-6, nylon-6,6 are condensation polymer substances. e.g.,

Polymerisation reaction between adipic acid and hexamethylene diamine forms a condensation polymer nylon-6,6.

$$\underset{\text{Hexamethylene-diamine}}{nNH_2-(CH_2)_6-NH_2} + \underset{\text{adipic acid}}{nHOOC-(CH_2)_4-COOH} \xrightarrow[\text{polymerisation}]{\text{condensation}}$$

$$\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO \right]_n$$

Nylon-6,6

In above reaction hexamethylenediamine monomer, contains two similar functional groups $-NH_2$. Another monomer adipic acid possesses two similar functional group –COOH. When equal proportion (n : n) of inumerable units of two monomers are combined by chemical reaction, then nH_2O

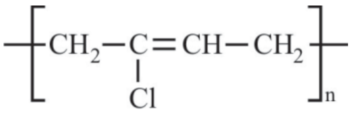
molecules are released. Due to the presence of amide (–CONH–) functional group, the obtained condensation polymer nylon-6,6 is called polyamide series polymer.

8.2.4 Classification based on molecular forces :

Polymers are used in different fields according to its characteristics. Polymers are classified by its mechanical properties, such as tensile strength, elasticity and toughness. These properties are shown with the help of intermolecular attraction forces and hydrogen bonding in polymers. Due to this attraction forces, variation is observed in long chain and branches in polymers.

It is classified on the basis of intermolecular attraction forces present in the polymer in four subcategories as under :

(1) Elastomers : This rubber is a solid substance, possessing elastic property. In elastomeric polymers, long chain of polymers are held together by weak intermolecular attraction forces. Due to weak intermolecular binding forces elastomer can be streched. A few cross linked molecules are observed in this long chain of polymers which help the polymer to retract to its original position when the force is removed. Natural rubber, Neoprene, Isoprene, Buna-S, Buna-N etc can be included in the examples of elastomers.



$$-\!\!\left[CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2\right]_n\!\!-$$

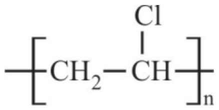
Neoprene

(2) Fibers : Those polymeric compounds which possess high tensile strength and high modulus are known as **fibers.** Because of strong intermolecular forces and hydrogen bonding, this property is seen in fibers. These strong intermolecular forces lead to close packing of long chains. As a result, crystallising property is added to it. Nylon, Terylene (polyesters) are examples of fibers.

$$-\!\!\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right]_n\!\!-$$

Nylon-6,6

(3) Thermoplastic polymers : In this type of polymers slightly branched configuration is seen in long chain of huge molecule. This polymer becomes soft on heating at higher temperature than normal temperature and again becomes infusible on cooling. Its structure changes at higher temperature. In these type of polymers, intermolecular forces are more than elastomers and less than fibers. Thermoplastic polymer is soft (fusible) and less strong than thermosetting polymer. Some examples of thermoplastics are polythene, polyvinyl chloride (PVC), polystyrene etc.



$$-\!\!\left[CH_2-\overset{\displaystyle Cl}{\overset{|}{CH}}\right]_n\!\!-$$

Polyvinyl chloride (PVC)

(4) Thermosetting polymers: The constitution of this polymer is a large molecular structure of cross linked type of polymers, or the structure is seen like long chain containing many branches. These polymers are heated at higher temperature than normal temperature and their cross linked binding is increased, yet they do not become soft. In these polymers, even at higher temperature, there are no changes in its structure. Thermosetting polymers are hard and strong. They are resistant toward scratch. They are good insulator of electricity and heat. Bakelite and melamine are this type of polymers.

8.2.5 Classification based on growth of polymerisation reaction :

Nowadays structure of polymer molecules can be changed by changing the reaction mechanism of polymerisation. The method of polymerisation reaction can be developed by chain growth or step growth.

Types of polymerisation reactions : Mainly there are two types of polymerisation reactions : (A) Addition polymerisation or chain growth polymerisation (B) Condensation polymerisation or step growth polymerisation

(A) Addition polymerisation or chain growth polymerisation : In this type of polymerisation reaction polymer is formed by addition reaction of unsaturated monomers containing double bond combined with each other by chemical bond. Innumerable monomers containing same type of double bond or innumerable monomers containing two different types of monomers, combined with each other form a polymer. So it is called **addition polymerisation** reaction. This addition polymerisation reaction is represented in various forms based on their mechanism.

Addition homopolymerisation : Where same type of monomer, containing one or more than one double bond, are combined with each other by chemical bonding; then addition polymerisation takes place. Polythene from ethene, polypropene from propene, polystryrene from styrene, butyl rubber from isobutylene, polyvinyl chloride from vinyl chloride, polyacrylonitrile (orlon) from vinyl nitrile, polytetrafluoro ethene (Teflon) from tetrafluoro ethene etc. are the examples of polymers obtained by homopolymerisation addition reaction.

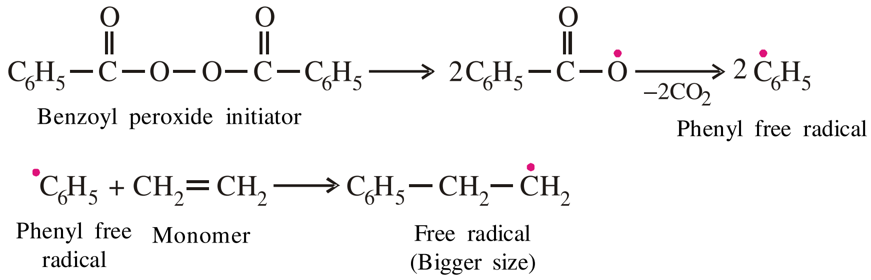
This reaction takes place by free radical or carbocation, or carbanion reactive intermediate which is produced by monomer.

Free radical addition polymerisation : Addition polymerisation reaction takes place by free radical reactive intermediate in unsaturated compounds and its derivatives, like alkene or diene.

Free radical reactive intermediate is produced by the use of initiators like benzoyl peroxide, acetyl peroxide, 3^0 butyl peroxide in the first step of this reaction with the help of proper temperature and pressure.

For example in polymerisation reaction of ethene, ethene is heated with trace amount of benzoyl peroxide as initiator at high temperature and phenyl free radical is obtained in initial stage of reaction. This phenyl free radical monomer combines with double bond of ethene molecule and forms a bigger size free radical.

First step of chain reaction :



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \xrightarrow[-2CO_2]{} 2\,\dot{C}_6H_5$$

Benzoyl peroxide initiator

Phenyl free radical

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

Phenyl free radical

Monomer

Free radical (Bigger size)

This new bigger size free radical combine alternatively with many ethene molecules and at every step longer chain of new free radicals is formed.

Second step of chain reaction :

At the end, on the basis of reaction condition, long chain of free radicals combine with each other in different ways to form polythene; out of which one of the combinations is represented as below :

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\Big\downarrow \text{n } CH_2=CH_2$$

$$C_6H_5-\left(CH_2-CH_2\right)_n-CH_2-\dot{C}H_2$$

Last step of chain reaction :

$$C_6H_5-\left(CH_2-CH_2\right)_n-CH_2-\dot{C}H_2 + C_6H_5-\left(CH_2-CH_2\right)_n-CH_2-\dot{C}H_2$$

$$\Big\downarrow$$

$$C_6H_5-\left(CH_2-CH_2\right)_n-CH_2-CH_2-CH_2-CH_2-\left(CH_2-CH_2\right)_n-C_6H_5$$

Industrial manufacturing, properties and uses of some important homo addition polymers :

(a) Polythene : According to the reaction conditions, two types of polythene can be prepared which are as under.

(i) Low Density Polythene (LDP) : Preparation : Low Density Polythene (LDP) is obtained by free radical homo addition polymerisation reaction of ethene monomer in presence of dioxygen or tertiary (3^0) butyl peroxide initiator, at 350-570 K and 1000 to 2000 bar pressure.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[\text{350 K to 570 K / 1000 to 2000 bar}]{\text{[Dioxygen / tertiary butyl peroxide]}} \underset{\text{Homopolymer polythene}}{\left[CH_2-CH_2\right]_n}$$

Properties :

- Low density polythene possesses branching structure.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is water resistant.
- It has more number of polymer molecules containing less molecular mass.
- Its boiling point and melting point are lower due to its low density.
- It is insulator towards electricity and is flexible.

Uses :

- Low density polythene is used in insulation of wires carrying electricity.
- It is useful in manufacturing of toys and packing of instruments, flexible pipes and squeeze bottles.

(ii) High Density Polythene (HDP) :

Preparation : For the preparation of high density polymer, free radical homo addition polymerisation reaction of ethene monomer in organic solvent in presence of triethyl aluminium ($(C_2H_5)_3Al$) and titanium trichloride ($TiCl_3$) or titanium tetrachloride ($TiCl_4$) (Ziegler-Natta catalyst) at 333 to 343 K temperature and under 6 to 7 bar pressure is carried out. German scientist G. Natta and Karl Ziegler were awarded the Nobel prize in 1963 for the invention of Ziegler-Natta catalyst.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow[\text{333 K to 343 K, 6 to 7 bar}]{\substack{\text{Free radical homo-addition} \\ \text{polymerisation [Ziegler-Natta]}}} \underset{\text{Polythene (Homopolymer)}}{\left[CH_2-CH_2 \right]_n}$$

Properties :

- In high density polythene, the density is higher as the molecules are arranged closely packed with each other in a branch.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is quite hard and stronger than low density polymer.
- It has more number of molecules having higher molecular mass of polymers.
- It has higher boiling point and melting point as it has higher number of polymerisation.
- They are non-conductors of electricity.

Uses :

- High density polythene is used in preparation of unbreakable instruments.
- Buckets, dustbins, bottles and pipes are manufactured from it.

(b) Polytetrafluoroethene (Teflon) PTFE :

Preparation : On heating tetrafluoro ethene, teflon is obtained by the homo addition polymerisation reaction at high pressure and in presence of free radical or persulphate catalyst.

$$\underset{\substack{\text{Tetrafluoro} \\ \text{ethane}}}{nCF_2{=}CF_2} \xrightarrow[\Delta\text{, and High temperature}]{\substack{\text{Free radical addition polymerisation} \\ \text{[Free radical or persulphate catalyst]}}} \underset{\text{Teflon}}{\left[CF_2-CF_2 \right]_n}$$

Properties :

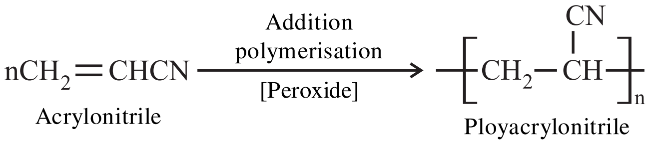
- Teflon is chemically inert.
- It is resistant towards corrosion.
- Teflon can bear high temperature so it is a type of thermoplastic and in some cases it is thermosetting.
- Teflon coating gets decomposed at temperature higher than 573 K.

Uses :

- It is used as lubricant in machines to resist scratching.
- It is used in making instruments for insulation of electricity.
- Teflon is used in munufacturing of seat and gasket.
- Teflon is used in manufacturing of non-stick kitchen vessels and tensile surface.

(c) Polyacrylonitrile (Orlon) PAN :

Preparation : Polyacrylonitrile polymer is obtained by addition polymerisation reaction of acrylonitrile monomer in presence of peroxide catalyst.



$$nCH_2{=}CHCN \xrightarrow[\text{[Peroxide]}]{\text{Addition polymerisation}} \left[CH_2-\overset{\overset{\displaystyle CN}{|}}{C}H \right]_n$$

Properties :

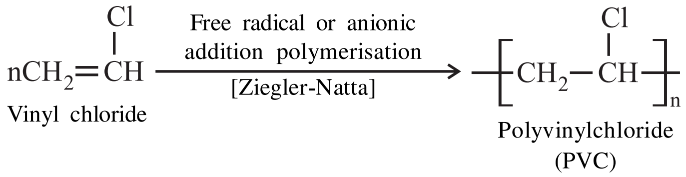
- Orlon is a branched polymer.
- It behaves like linear polymer such as natural rubber.
- It is a type of thermoplastic polymer.
- It is chemically inert.
- Acrylic fibers made out of it have good tensile strength. There is no effect of fungi and micro insects on it.

Uses :

- It is useful in making synthetic wool as a substitute of natural wool.
- Used in preparation of synthetic fibers.
- Used in making of acrylic fibers.

(d) Polyvinyl chloride (PVC)

Preparation : Polyvinyl chloride is formed by free radical addition polymerisation reaction of vinyl chloride monomer in presence of triethyl aluminium and titanium trichloride or titanium tetrachloride (Ziegler-Natta) catalyst. If reaction condition changes then ionic reactive intermediate is formed from vinyl chloride monomer. As a result polyvinyl chloride is obtained by addition polymerisation reaction.



$$nCH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}H \xrightarrow[\text{[Ziegler-Natta]}]{\text{Free radical or anionic addition polymerisation}} \left[CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}H \right]_n$$

Properties :

- PVC is a branched polymer.
- It is a kind of thermoplastic polymer.
- It is water resistant.

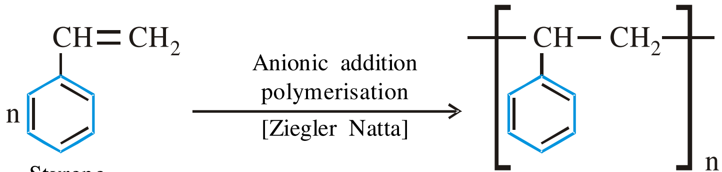
- It is resistant towards electricity.
- It is chemically inert.
- It is stronger than polythene.

Uses :

- As it is water resistant, it is useful in making rain coats, carpets, purses, etc.
- PVC is useful in making pipes, bottles, ragzin footware.

(e) Polystryrene :

Preparation : Polystyrene polymer is obtained by anionic addition polymerisation reaction of stryrene monomer in presence of triethyl aluminium and titanium trichloride titanium or tetrachloride (Ziegler-Natta) catalyst.



Styrene

Polystyrene

Properties :

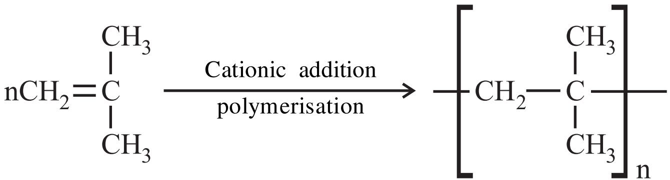
- Polystyrene is a branched polymer.
- It is a kind of thermoplastic polymer.
- It is chemically inert.
- It is lighter in weight than polythene.
- It is heat resistant and non-conductor of electricity.

Uses :

- Polystyrene is used in making cabinets of radio, friedge and T.V.
- Polystyrene is useful in making utensils as non-conductor of heat such as hot water conducting pipes, buckets, bottles etc.

(f) Butyl Rubber :

Preparation : Butyl rubber is obtained by cationic addition polymerisation reaction of iso-butylene monomer.



$$nCH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} \xrightarrow[\text{polymerisation}]{\text{Cationic addition}} \left[CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} \right]_n$$

Isobutylene

Butyl rubber

Properties :

- Butyl rubber is a branched polymer.
- It is a kind of thermoplastic polymer.

- It has a characteristic of more elasticity than natural rubber.
- It is inert towards water.

Uses :

- It is used in place of natural rubber.

Addition Copolymerisation : When polymer substance is formed by addition reaction, when two different types of monmers combine alternatively with each other, by chemical bond, then copolymer substance is formed. This reaction is called addition copolymerisation reaction. Copolymer styrene butadiene rubber is obtained from styrene and butadiene monomer whereas nitrile rubber is obtained from acrylonitrile and butadiene are polymers.

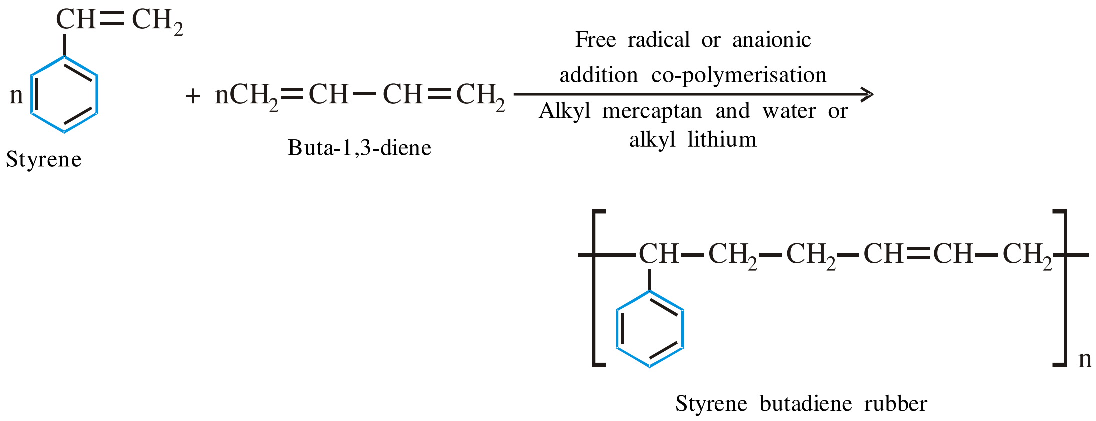
Industrial manufacturing, properties and uses of some important additon copolymer substances :

(a) Styrene Butadiene Rubber (Buna-S), SBR

Preparation : By addition reaction of two monomers-styrene and butadiene combined one by one with each other by chemical bond, styrene butadiene rubber forms a series of copolymers. Two types of products are obtained by this reaction.

(1) If addition reaction takes place between styrene and butadiene with free radical reactive intermediate alkyl mercaptan and water, then mercaptan controls the molecular mass of polymer and forms a small size and high viscosity molecules of polymer. As a result emulsion type of styrene butadiene rubber is obtained.

(2) If addition reaction takes place between styrene and butadiene at higher pressure in presence of ionic intermediate alkyl lithium and in absence of water, then ionic addition polymerisation reaction takes place where more styrene molecules combine and higher molecular mass containing hard and less flexible solution type of styrene butadiene rubber is obtained.



Properties :

- It is a synthetic rubber.
- Buna-S is reactive towards oil, waste water and ozone.
- It possesses higher viscosity than natural rubber.
- It possess high tensile strength and strong extensive property.

- Strong intermolecular H-bonding exists between their molecules.
- At higher temperature, it maintains its elastic character.
- It has higher electric capacity.

Uses :

- Its elastomer form is used in chewinggum, rubber coating and paints.
- Its solution form is used in tyres, shoes sole, gaskets etc.

(B) Condensation polymerisation or step growth polymerisation : In this type of polymerisation condensation reaction repeatedly takes place between two different types of monomers possessing two similar functional groups. As a result of this condensation polymerisation reaction, simple molecules such as water, ammonia or alcohol are removed and condensation polymer containing high molecular mass is obtained.

In condensation polymerisation reaction, repeating unit obtained in first step again reacts with bifunctional species in the second step and forms a new repeating unit. These repeating units formed possess different functional groups; then the functional group in both monomers in each step, and these repeating unit are independent from each other. Hence, this polymerisation is also called as step growth polymerisation as there is addition of repeating units.

Polymers obtained from the condensation polymerisation reaction are classified on the basis of their functional groups in repeating unit. If there is –CONH– group in repeating unit then it is called polyamide and if there is –COO– group in repeating unit, then it is called polyester. Some examples of condensation polymers are as under :

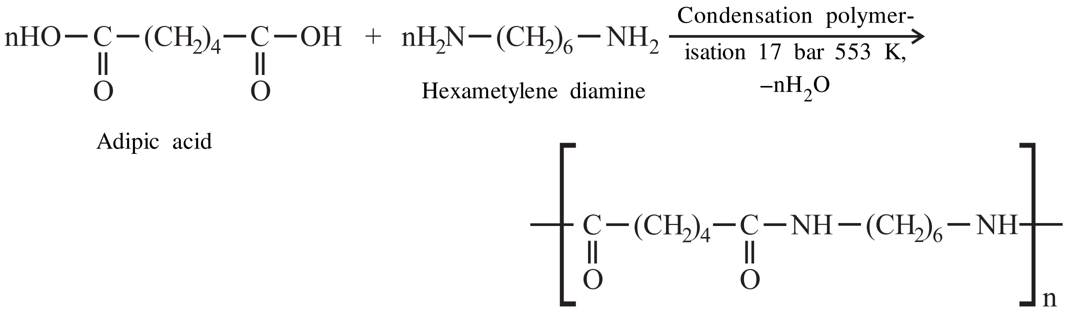
Industrial preparation, properties and uses of some important condensation polymers :

(a) Nylon 6,6 :

Preparation : Two monomers used in preparation of nylon 6,6 are (i) adipic acid containing two –COOH– functional groups and (ii) hexamethylene diamine containing two $-NH_2$ functional groups.

By condensation polymerisation reaction of mixture of two different monomers. adipic acid and hexamethylene diamine at 17 bar pressure and 553 K temperature by heating in closed vessels and on release of water molecule, Nylon-6,6 is obtained.

It is a series of polyamide polymer due to –CONH– amide group in repeating unit of nylon-6,6, and repeating units of nylon-6,6 contain 6 carbon of adipic acid and 6 carbon of hexamethylene diamine, therefore it is called nylon-6,6.



$$nHO-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-OH + nH_2N-(CH_2)_6-NH_2 \xrightarrow[\text{isation 17 bar 553 K,}\ -nH_2O]{\text{Condensation polymer-}}$$

Adipic acid

Hexametylene diamine

$$\left[\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_6-NH \right]_n$$

Nylon-6,6

Properties :

- Nylon-6,6 is the chief polymer of polyamide class.
- Nylon-6,6 is a linear polymer.
- –CONH– amide group is a repeating unit of nylon-6,6.
- Nylon-6,6 is a kind of thermoplasitc polymer.
- Fibers of Nylon-6,6 are hard, strong elastic and water resistant.

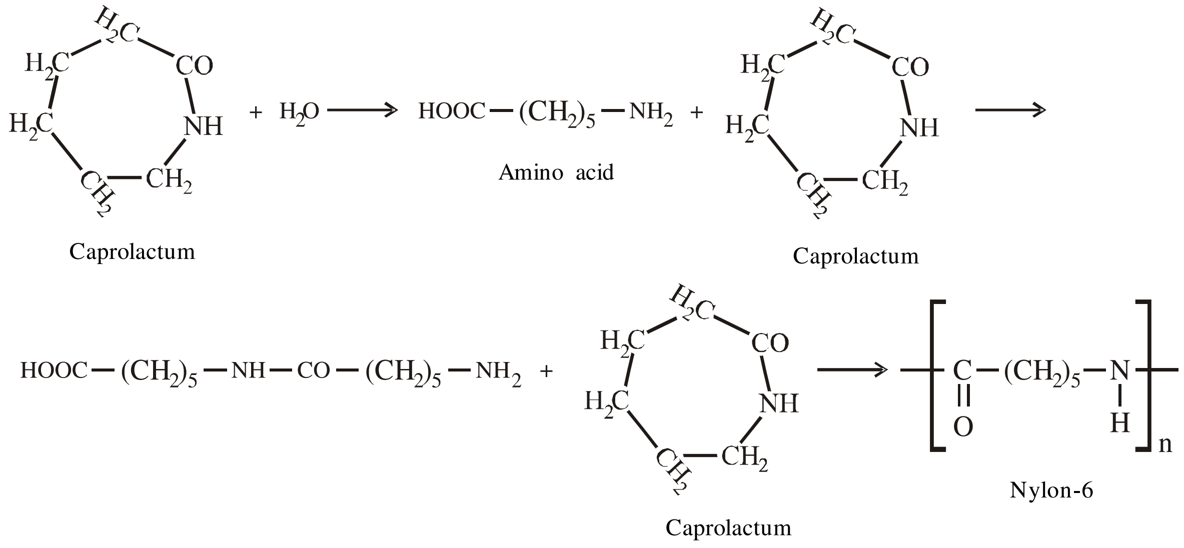
Uses :

- It is used in textile industry, preparation of fishing net, ropes and tyre industries.

(b) Nylon-6 :

Industrial preparation : On hydrolysis of one molecule of caprolactum in presence of water gives an amino acid, which reacts one by one with other caprolactum molecules by self condensation polymerisation reaction giving nylon-6.

The repeating unit of polymer nylon 6 is monomer caprolactum which contains 6 carbon atoms, therefore it is called nylon 6.



Properties :

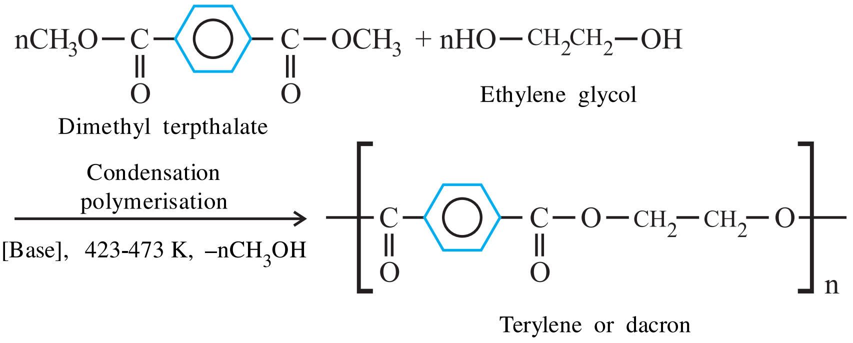
- It is the chief polymer of polyamide class.
- ⟊CONH⟊ amide is repeating unit in Nylon-6
- The fibers of Nylon-6 are insoluble in common solvents and are very strong.
- It is a linear polymer.
- It is a kind of thermoplastic polymer.

Uses :

- It is useful in carpet, ropes and tyre industries.

(c) Terylene (Dacron) :

Industrial Preparation : The mixture of two different monomers dimethyl terpthalate and ethylene glycol on heating in presence of basic catalyst at 423 to 473 K temperature, by condensation polymerisation reaction gives terylene or dacron.



Properties :

- It is the chief polymer of polyester group.
- Terylene is a linear polymer.
- (–COO–) ester is a repeating unit in terylene
- Terylene is a kind of thermoplastic polymer.
- Fibers of terylene are less elastic than nylon fibers.

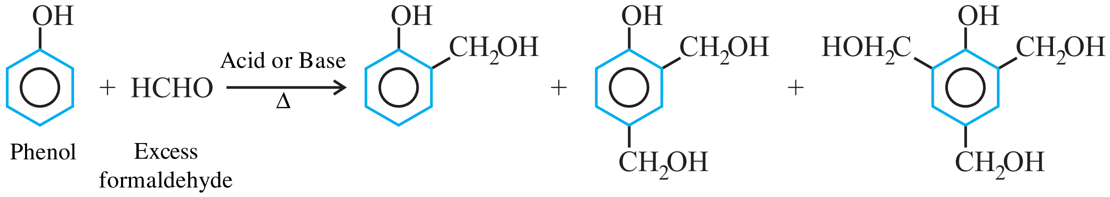
Uses :

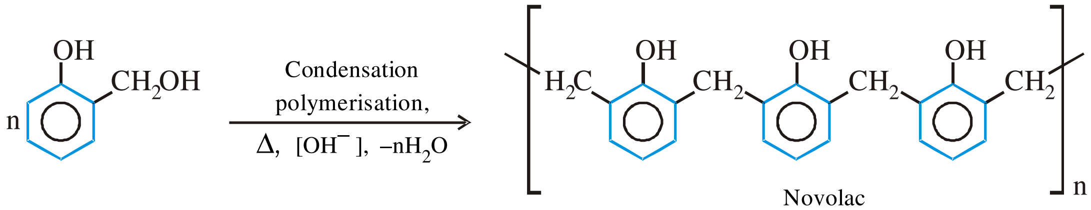
- In textile industries.
- In preparation of rope.

(d) Bakelite :

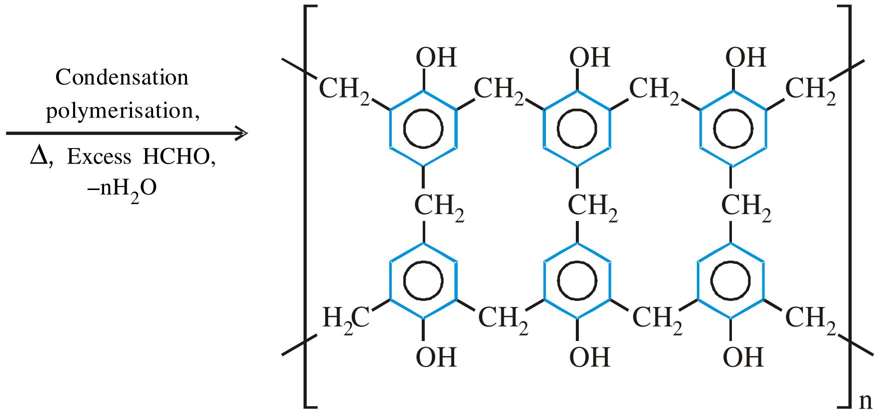
Industrial preparation :

- The mixture of phenol and formaldehyde on heating in presence of acid or base catalyst, the condensation polymerisation reaction takes place in ortho and para positions and Bakelite is obtained.
- In the begining reaction of phenol with excess formaldehyde takes place and ortho and para hydroxy methyl derivatives are obtained.
- In the begining Novolac linear polymer obtained by polymerisation reaction of hydroxy methyl phenol which on heating at higher temperature with excess of formaldehyde, the condensation takes place in p-position of Novolac and gives Bakelite.





Novolac



Bakelite (cross linked polymer)

Properties :

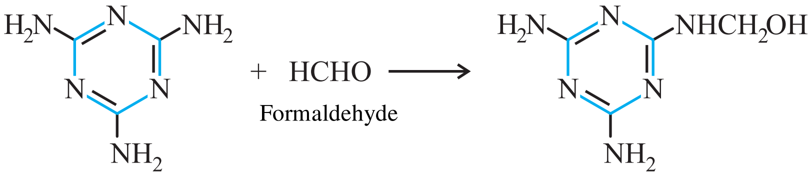
- Bakelite is a synthetic polymer of phenol formaldehyde class.
- It is a cross-linked polymer.
- It is a kind of thermosetting polymer.
- Bakelite does not fuse even on heating.
- It is water resistant, hard, brittle and scratch resistant.
- As it is brittle it cracks or breaks on striking or dropping.
- It possesses very good property as non-conductor of electricity.

Uses :

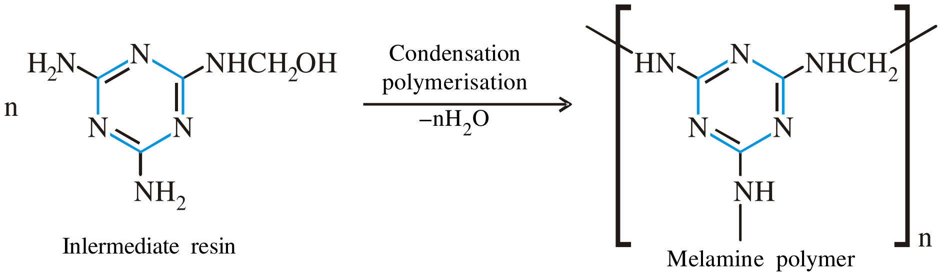
- It is used in making combs, gramophone records, handles of kitchenware and electrical appliances like plug, pin, switches.

(e) Melamine :

Preparation : Melamine polymer is formed by condensation polymerisation reaction of melamine and formaldehyde on heating.



Melamine Intermediate resin



Properties :

- Melamine is synthetic polymer of formaldehyde class.
- It is a kind of thermosetting polymer.
- It is a cross linked polymer.
- It is hard and strong.
- It does not fuse or its structure does not change at higher temperature.
- It is resistant towards scratching.
- The melamine appliances do not crack or break on striking or dropping.

Uses :

- Melamine is useful in preparation of unbreakable crokery.

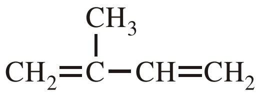
8.3 Rubber

Rubber is available in three forms : (1) Natural rubber (2) Vulcanised rubber and (3) Synthetic rubber.

8.3.1 Natural rubber :

Structure :

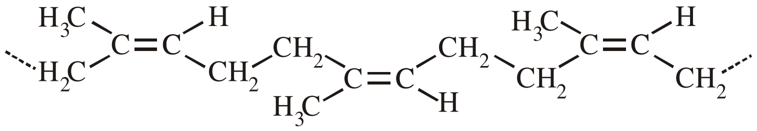
- Rubber trees are found in forests of India, Sri-Lanka, Indonesia, Malaysia and South Africa.
- By making incision in the trunk of rubber trees, the colloidal suspension of milky rubber in water, called latex is obtained. The natural rubber is obtained by physical and chemical processes.
- Natural rubber is linear polymer of isoprene monomer.
- Isoprene (2-methyl buta-1,3-diene) is also called a 1,4-polyisoprene.
- Its geometrical isomerism is cis due to which it is called cis-1,4-polyisoprene.
- During polymerisation reaction of innumerable molecules of isoprene monomers C1 = C2 and C3 = C4 breaks and bond between C2 = C3 is formed. Hence there is double bond between C2 = C3 in its repeating unit.
- Linear molecules of cis-1,4-polyisoprene are held together by weak van der Waals interaction forces and has a coiled structure. As a result, in natural polymer, elastic property is observed.



$$CH_2{=}\overset{\displaystyle CH_3 \atop |}{C}{-}CH{=}CH_2$$

Isoprene

(2methyl buta-1,3-diene)



Natural rubber

cis-1,4-polyisoprene

Properties :

- This rubber is a natural polymer.
- Natural rubber can be streched like spring and possesses elastic property.
- In it, if force is applied, even for longer time, then retension force is maintained.
- In natural rubber, this property of elasticity is maintained at 273 to 335 K temperature.
- It becomes brittle at temperature less than 273 K.
- At temperature, higher than 335 K, it becomes fusible.
- Its water absorbing capacity is higher.
- It is soluble in non-polar solvents.
- It is non-resistant against the attack of oxidising agents

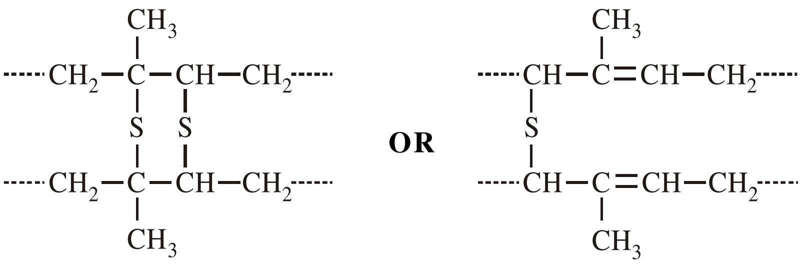
Uses :

- Natural rubber is used in many fields because of its elastic character. like in preparation of eraser, rubber band and hand gloves etc.

8.3.2 Vulcanised rubber :

Preparation :

- In 1893, Charles Goodyear discovered that mixture of natural rubber and sulphur when heated at temperature 373 to 415 K, its physical properties can be necessarily improved to a spectacular manner. This process is called vulcanisation.
- This process is slow but by adding zinc oxide as additive substance, the rate of reaction becomes fast.
- During vulcanisation process, repeating unit cis-1, 4-polyisoprene in natural rubber C2–C3 double bond of unit and adjacent $-CH_2$ groups become reactive. Therefore, bonding of these two reactive positions take place in cross through sulphur, between the two molecules of rubber and becomes hard.



Linear polymer of rubber molecules (cis-1, 4-isoprene)

Properties :

- Vulcanised rubber possesses very good elasticity.
- It does not melt (fuse) at higher temperatures and does not break at lower temperatures.
- It has very low water absorbing capacity.
- It is insoluble in organic solvents.
- It resists oxidation reaction.

Uses :

- During vulcanisation process, 5 % sulphur is used in making rubber for tyres.
- During vulcanisation process 30 % sulphur is used in making rubber for battery-cases.

8.3.3 Synthetic rubbers :

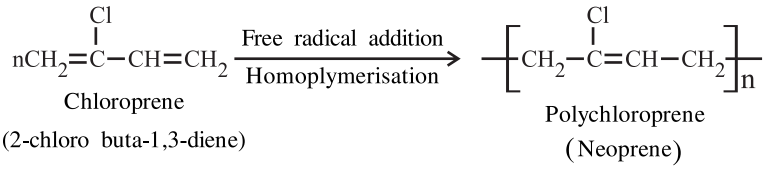
Synthetic rubber is vulcanisable rubber like polymer. On giving external stretching force, to the synthetic polymer or stretching it to twice its length, it regains its original shape and size.

Generally synthetic rubber is copolymer of buta-1,3-diene or hompolymer of buta-1,3-diene derivatives or it is a polymer of buta-1,3-diene derivatives with its unsaturated monomers.

Preparation, properties and uses of synthetic rubber :

(1) Neoprene :

Preparation : Polychloroprene (neoprene) homopolymer is obtained by addition polymerisation reaction of innumerable molecules of chloroprene (2-chloro buta-1,3-diene)



$$nCH_2{=}\overset{Cl}{\overset{|}{C}}-CH{=}CH_2 \xrightarrow[\text{Homoplymerisation}]{\text{Free radical addition}} \left[CH_2-\overset{Cl}{\overset{|}{C}}{=}CH-CH_2\right]_n$$

Properties :

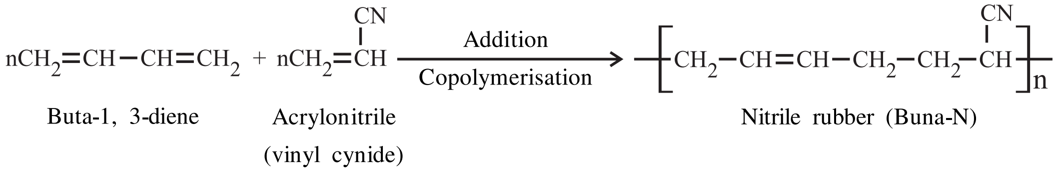
- Neoprene is a synthetic rubber of homopolymer class.
- It has superior resistance to vegetable and mineral oils.

Uses :

- Neoprene is used in conveyor belts, hose pipes, gaskets, printing rollers and as an insulator.

(2) Nitrile rubber (Buna-N)

Preparation : Nitrile rubber is obtained by addition copolymerisation reaction of mixture of two different monomers buta-1,3-diene and acrylonitrile in presence of peroxide catalyst.



$$nCH_2{=}CH-CH{=}CH_2 + nCH_2{=}\overset{\overset{\displaystyle CN}{|}}{CH} \xrightarrow[\text{Copolymerisation}]{\text{Addition}} \left[CH_2-CH{=}CH-CH_2-CH_2-\overset{\overset{\displaystyle CN}{|}}{CH} \right]_n$$

Properties :

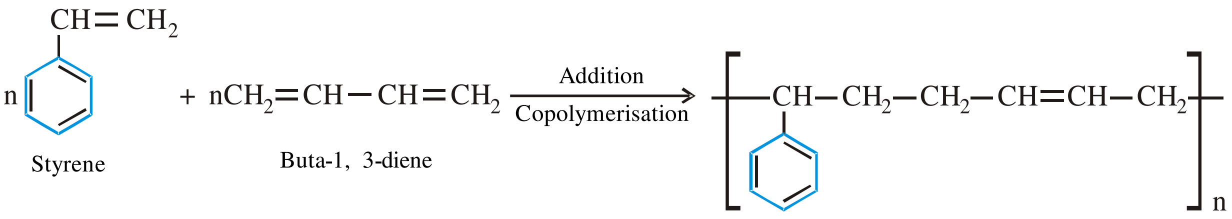
- Nitrile rubber is a copolymer obtained by addition reaction.
- Nitrile rubber has superior resistance towards lubricant oil and organic solvents.
- It does not react with petrol.

Uses :

- Nitrile rubber is used in oil seals, hose pipes and petrol tank linings.

(3) Styrene Butadiene Rubber (Buna-S, SBR)

Preparation : Two different types of innumerable molecules of styrene and buta-1,3-diene monomer joined with each other by addition copolymerisation reaction and forms copolymer named styrene butadiene rubber.



Styrene butadiene rubber
(Buna-S) (copolymer)

Properties :

- Styrene butadiene rubber is a copolymer obtained by addition reaction.
- It possesses good elasticity.
- At higher temperature, its shape does not change.

Uses :

- Styrene butadiene rubber is used in making tyres and footwears.

8.4 Molecular Mass of Polymers

Polymer being an amorphous solid substance; there is no regular arrangement of atoms and molecules. Number of monomers present in different molecules of same polymer means number of repeating unit is different. Thus its molecular mass is always taken as average molecular mass because of different branch lengths in any sample of polymer.

- The highly modern techniques used to determine the molecular mass of polymer are classical light scattering, Quasi-Elastic Light Scattering (QELS) and Dynamic Light Scattering (DLS).

- In determining the molecular mass of polymer substances, some chromatographic mode methods are used such as High Performance Liquid Chromatography (HPLC), Size Exclusion Chromatography (SEC), Gel-Permeation Chromatography (GPC). In addition to these Ultra-centrifuge technique is also used. To find out the molecular mass of polymer by calculation, the following symbols are used.

- Number average molecular mass = $\overline{M}_n$

- Weight average molecular mass = $\overline{M}_w$

- Number average molecular mass $\overline{M}_n = \dfrac{\sum_{i=1}^{\infty} N_iM_i}{\sum_{i=1}^{\infty} N_i} = \dfrac{\text{Total mass of polymer}}{\text{Total number of polymer molecules}}$

- Weight average molecular mass $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_iM_i^2}{\sum_{i=1}^{\infty} N_iM_i}$

  where N_i = Number of species molecules of each polymer,

  M_i = Molecular mass of each polymer species.

- **Calculation of $\overline{M}_n$:** $\overline{M}_n$ is determined by the method which depends upon the number of molecules present in the polymer sample.

- **Calculation of $\overline{M}_w$:** Molar mass of single molecule present is polymer substance and is calculated on the basis of light scattering, chromatographic and ultracentrifuge methods as indicated above.

- **PDI :** The ratio of mass and number moleular mass $\left(M_w/M_n\right)$ is called polydispersity Index (PDI)

- Natural polymers are generally monodispersed, therefore PDI = 1. This means is $\overline{M}_w = \overline{M}_n$.

- PDI > 1 means that $\overline{M}_w > \overline{M}_n$. Because synthetic polymer is always polydispersed.

8.5 Biopolymer

- The polymer substances present in the nature such as polysaccharide, protein and nucleic acid, which are very useful for the human life are called **Biopolymer.**

8.5.1 Biodegradable polymers :

- **The degradation of those polymers which takes place mainly by enzymes, bacteria like microorganisms, hydrolysis and to some extent by oxidation are called Biodegradable polymers.**
- Biodegradable polymers are active towards environmental processes.
- Due to the easy degradation of these polymers, after there usage, there is no issue of its disposal. As a result, there is no environmental pollution.
- After the degradation of these polymers, they can be converted into the life essential products.
- During the usage, the degradation of this polymer takes place and can be used in various fields like medical and industries.
- Synthetic biodegradable polymers can be synthesized which are convenient to living system and helpful to enviornmental cycles.
- Using some aliphatic substances as monomer, many polymers are industrially prepared such as PolyHydroxy Butyrate-co-β-hydroxy Valerate (PHBV), PolyGlycolic Acid (PGA), PolyLactic Acid (PLA), Dextran, Nylon 2 Nylon 6, etc.
- The polymers present in nature are called biopolymers. They are biodegradable polymers.

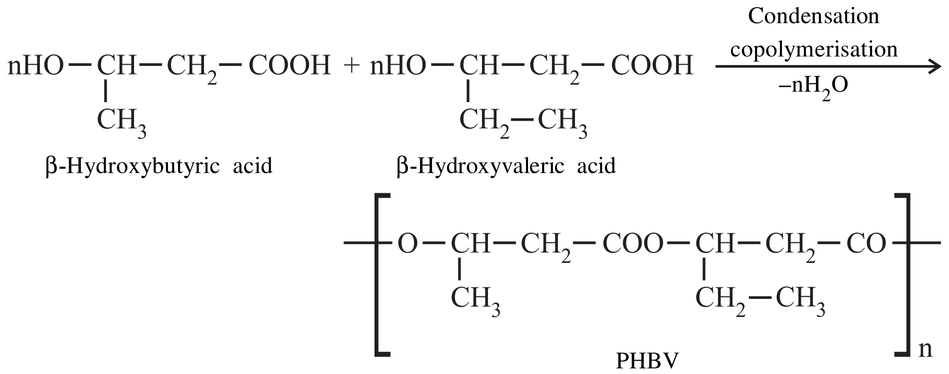
8.5.2 Non-biodegradable polymers :

- **Those synthetic polymers which do not get degraded by enzymes, bacteria like microorganism or by hydrolysis and oxidation reaction; are called non-biodegradable polymers.**
- Non-biodegradable polymer shows inertness towards the environmental process.
- As these polymers cannot be easily degraded, in everyday usage therefore disposal of polymeric waste is an acute problem. As a result environmental problems such as global warming, green house effect have been created.
- The degradation reaction does not take place; it is not converted into life essential products.
- Nowadays mostly synthesised polymer substances prepared are nonbiodegradable polymers.
- Largely used non biodegradable polymers incude polythene, polystyrene, PVC, Teflon, Orlon, Butyl rubber, Neoprene, Stryrene Butadiene Rubber, Nitrile rubber, Nylon-6, Nylon-6,6, Terylene, Bakelite, Melamine etc.

Information of some important synthetic biodegradable polymers is given below :

Poly-HydroxyButyrate-Co-β-Hydroxyvalerate (PHBV)

Preparation : PHBV is the polymer of polyester class prepared from β-hydroxy butyric acid monomer and β-hydroxy valeric acid monomer by copolymerisation condensation reaction and on release of H_2O molecule.



$$n\,HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH + n\,HO-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-COOH \xrightarrow[-nH_2O]{\text{Condensation copolymerisation}} \left[O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COO-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-CO\right]_n$$

β-Hydroxybutyric acid β-Hydroxyvaleric acid

PHBV

Properties :

- This polymer is of polyester class.
- It possesses biodegradable character.
- There is stiffness property of β-hydroxy butyric acid and has flexibility property of β-hydroxy valeric acid.
- PHBV also undergoes bacterial degradation in enviornmental conditions.

Uses :

- PHBV is used in special types of packaging
- In orthopaedic devices
- In capsules for filling controlled release of drugs.

Nylon-2 Nylon-6 : Nylon-2 Nylon-6 copolymer of polyamide series is obtained by condensation polymerisation reaction of two different types of monomer glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N–(CH_2)_5–COOH$).

$$\underset{\text{Glycine}}{n\,H_2N-CH_2-COOH} + \underset{\text{Amino caproic acid}}{n\,H_2N-(CH_2)_5-COOH} \xrightarrow{\text{Condensation copolymerisation}} \underset{\text{Nylon-2 Nylon-6}}{\left[HN-CH_2-CONH-(CH_2)_5-CO\right]_n}$$

- Nylon-2 Nylon-6 is a biodegradable polymer.
- Nylon-2 Nylon-6 is of polyamide class.

PGA and PLA :

- They are prepared industrially.
- They are biodegradable polymers used for post operation stiches.

Dextran :

- Dextran is the first biodegradable polyester polymer used for post operative stitches.
- It is biodegradable polymer of polyeseter class.

SUMMARY

- Our modern life style is incomplete without polymers.
- The biological requirements of human body are fulfilled by biopolymers, while physical requirements are fulfilled by natural and synthetic polymers.
- Polymer is a group of molecules having giant (macro) size and high molecular mass.
- Innumerable molecules of one type or two or more than two types simple organic molecules combine with one another and form a giant molecule (macro), is called polymer.
- The molecules of only one type which combine through chemical bond is called monomer. In polymerisation reaction, first of all two monomers combine and dimer is formed. On combining third molecule, trimer is formed. Thus by combination of one by one molecule, polymer is formed.
- In each polymer series, the definite part which is repeated and this repeating part is called "Repeating unit"
- The number of this repeating unit is called 'Degree of polymerisation' (n).
- If the value of degree of polymerisation 'n' is less than 25 ($n < 25$), then that polymer is called oligomer.
- Generally oligomer is in liquid state. Fevicol like adhesives and liquid polymers used in paint are oligomers.
- If the value of degree of polymerisation 'n' is more than 25 ($n > 25$) then that polymer is called heavy polymer. Generally heavy polymer is in solid state.
- The classification of polymers is as follows :

Polymers

On the basis of source	On the basis of structure	On the basis of polymerisation reaction	On the basis of molecular forces	On the basis of growth of polymerisation reaction
(1) Natural polymers	(1) Linear	(1) Addition polymer	(1) Elastomer	
(2) Semisynthetic polymer	(2) Branched	(2) Homopolymer	(2) Fibers	
(3) Synthetic polymers	(3) Cross linked	(3) Copolymer	(3) Thermoplastic	
		(4) Condensation polymer	(4) Thermosetting	

- Polymerisation reaction is mainly classified in to two classes (1) Addition polymerisation and (2) Condensation polymerisation.
- The addition polymerisation reaction occurs from the monomer through free radical or carbocation or carbonium ion mechanism. In both these methods, if polymer is obtained from only one type of monomer, it is called homopolymer and if polymer is obtained from two different types of monomers, it is called co-polymer.
- In the addition hompolymers obtained by addition reaction of only one monomer are included as polythene, teflon, orlon PVC, polystyrene, butyl rubber etc.
- In the addition copolymer obtained by addition reaction of two or more different monomers, styrene butadiene rubber can be included.
- The polymerisation reaction during which water, ammonia, alcohol, or hydrochloric acid is liberated and polymer is formed, then that reaction is called condensation polymerisation reaction.
- Nylon 66, nylon 6, terylene, bakelite, melamine etc can be included in the polymers obtained by condensation polymerisation.
- In the polymer obtained by polymerisation reaction, if the functional group ester (–COO–) is present, then it is called polymer of polyester class and if the functional group is amide (–CONH–), then it is called polymer of polyamide class
- Terylene is polymer of polyester class, whereas nylon 6 and nylon 6,6 is polymer of polyamide class.
- Natural rubber possesses unique property of elasticity, which cannot be destroyed at high or low temperatures, sulphur can be added to it and vulcanised rubber can be prepared.
- Vulcanised rubber maintains its property of elasticity at high or low temperatures. In addition, synthetic rubber containing more strength viz. neoprene, nitrile rubber, styrene butadiene rubber could be prepared which are inert towards the organic solvents.
- To determine molecular mass of polymer, different methods have been developed, and yet, its correct molecular mass cannot be determined because in the same polymer, the value of degree of polymerisation of its any two molecules is not same.
- To find molecular mass of polymer, in addition to colligative methods, light scattering and chromatographic methods have been proved more effective.
- To determine molecular mass of polymer, number average molecular mass $\overline{M}_n$ and mass average molecular mass $\overline{M}_w$ formulas can be used.
- The ratio of mass average molecular mass $\overline{M}_w$ and number average molecular mass $\overline{M}_n$ is called polydispersity index (PDI).

- The polydispersity index of natural polymer or biopolymers is PDI = 1, while for synthetic polymers it is PDI > 1.
- Polymers found in living beings are biopolymers. The decomposition of biopolymer by microorganisms like bacteria is possible. While using them, its transformation occurs in simple components and so they are called biodegradable polymers. Biodegradable polymers are friends of environment.
- The polymers which are not decomposed by microorganisms like bacteria, and the simple components are not obtained during their use, are called non-biodegradable polymers. Many problems are created in the environment by use of non-degradable polymers.
- To care of environmental problems, it is necessary to increase the use of biodegradable polymers. In some synthetic biodegradable polymers, PHBV, PGA, PLA, dextran, nylon-2 nylon-6 are included.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Those simple organic molecules which chemically combine with one another and form a polymer, is called ....

(A) Monomer (B) Tetramer (C) Dimer (D) Trimer

(2) The number 'n' of repeating unit in polymer molecule is called ....

(A) Degree of polymerisation (B) Oligomer

(C) Heavy polymer (D) Repeating unit

(3) Which functional group is present in polyester ?

(A) –COO– (B) $-CH_2-CH_2-$ (C) –CONH– (D) $-CH_2-CN$

(4) What type of polymer can be considered novolac ?

(A) Linear (B) Branched (C) Cross linked (d) (A) and (B)

(5) Which of the following substances is an elastomer ?

(A) Nylon 6 (B) Nylon 6,6

(C) Vulcanised rubber (D) Melamine

(6) Which of the following polymers is obtained by condensation polymerisation ?

(A) PVC (B) Polythene (C) Polystyrene (D) Nylon 6,6

(7) Light Scattering method is used ....

(A) to find concentration (B) to find molecular mass of polymer

(C) to test elements (D) to find number of molecules

(8) HDP is used in preparation of ....

(A) Light and soft devices (B) Hard and durable devices

(C) Cotton and wool (D) Light and cheap devices

(9) Which monomer is used for preparation of orlon ?

(A) $CF_2=CF_2$ (B) $CH_2=CH–CN$ (C) $CH_2=CHCl$ (D) $CH_2=CH–OH$

(10) From the following .... is the example of biopolymer ?

(A) Teflon (B) Neoprene (C) Nylon-6,6 (D) DNA

(11) Which of the following two monomers are used in preparation of nylon-6,6 ?

(A) Hexamethylene diamine and ethylene glycol

(B) Adipic acid and hexamethylene diamine

(C) Dimethyl terphthalate and ethylene glycol

(D) Adipic acid and ethylene glycol

(12) .... possesses biodegradable property

(A) PTFE (B) PAN (C) SBR (D) PHBV

(13) Which choice is correct for synthetic polymer substance ?

(A) $\overline{M}_n = \overline{M}_w$ (B) $\overline{M}_n \geqslant \overline{M}_w$ (C) $\overline{M}_w > \overline{M}_n$ (D) $\overline{M}_w < \overline{M}_n$

(14) Which is the formula to find mass average molecular mass ?

(A) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i^2 \cdot M_i}{\sum_{i=1}^{\infty} N_i \cdot M_i}$ (B) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$

(C) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i^2}$ (D) $\overline{M}_w = \dfrac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$

(15) What can be obtained by ultracentrifuge method in polymer chemistry ?

(A) Concentration (B) Molecular mass (C) Precipitation (D) Solution

2. Write answers of the following questions in brief :

(1) Give definitions :

(i) Degree of polymerisation

(ii) Repeating unit.

(2) Give examples of natural polymer.

(3) When is called that the condensation polymer has occurred ?

(4) What is meant by addition polymerisation reaction ?

(5) Mention the types of addition reaction on the basis of their methods.

(6) Mention the uses of high density polythene (HDP).

(7) Upto which temperature the layer of teflon does not decompose ?

(8) What type of polymer is polystyrene ?

(9) Which rubber is used in place of natural rubber ?

(10) Give equation of chemical reaction for preparation of nylon 6.

(11) Mention repeating unit of bakelite.

(12) What is PDI ?

(13) What is meant by biopolymer ?

(14) Give example of natural elastomer.

(15) The capsules used for filling controlled drugs is prepared from which polymer ?

(16) Mention the repeating unit in PTFE.

3. Answer the following questions :

(1) Give information about semisynthetic polymer substances.

(2) What are oligomers and heavy polymers ?

(3) Explain elastomers.

(4) Mention characteristics of thermoplastic polymers.

(5) Explain the preparation of any one polymer obtained by addition co-polymerisation reaction.

(6) Give properties and uses of nylon-6,6.

(7) How is melamine prepared ?

(8) Give difference between natural rubber and vulcanised rubber.

(9) Mention methods to find molecular mass of polymer.

(10) Mention the formulas of weight average molecular mass and number average molecular mass.

(11) Give differences between biodegradable and non-biodegradable polymers.

(12) Mention characteristics of PGA, PLA, dextran.

4. Answer the following questions in detail :

(1) Give classification of polymers and give one example of each.

(2) What is meant by monomer, polymer and degree of polymerisation? Explain with example.

(3) Explain condensation polymerisation reaction.

(4) Explain steps of free radical addition polymerisation reaction.

(5) Mention preparation, properties and uses of high density polythene (HDP).

(6) Explain stepwise polymerisation reaction.

(7) Mention properties and uses of bakellite.

(8) Write a note on vulcanised rubber.

(9) Write a note on 'PHBV'

(10) Explain oligomer and heavy polymer.

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Unit

9

Chemistry in Everyday Life

9.1 Introduction

Development of chemistry improves quality of human life. Contribution of chemistry is seen in each and every field of human life. Some compounds, such as foods, clothes, potable water, abode, soaps, detergents, drugs, dyes etc. which we are using regularly are mostly made from organic compounds. Moreover, fertilizers and pesticides used in agriculture, polymers, oils, papers, glass, cement, various types of fuels etc. are gifts of chemistry. Synthesis of creative and destructive explosives used in security of nation have become possible through chemistry. In this way, directly or indirectly, chemistry is closely associated with our everyday life. In this unit, we will understand uses of chemistry in three important areas – drugs, foods and cleansing agents.

9.2 Drugs

Up to 19th century, plant based natural drugs were used in crude form e.g., powder or boiled drink of bark, roots and leaves of tree etc. available in nature. The bark of cinchona tree and quinine obtained from it, were used for malaria; but for certain diseases no natural or synthetic drug was available during 19th century. Research about applications of such compounds resulted in chemical compounds which were used for treatment of diseases in 20th century. In 1904, a German chemist Paul Ehrlich realized that certain chemicals were more toxic to disease causing organisms to human cells, so these chemicals could be used to control or cure infectious diseases. Ehrlich found certain dyes that used to stain bacteria to make them more visible under a microscope. These dyes stain the nerve cells of bacteria. From this, the idea arose in his mind that if it can be made toxic for organisms, then they could be used as effective drug for these microorganisms. In this way Ehrlich synthesized arsenic containing compounds (Salvarsan and neo salvarsan) for skin disease like syphilis and for sleeping sickness. For this Ehrlich was awarded the Nobel prize in 1908. Ehrlich gave chemotherapy term for such compounds used in treatment of diseases. Thus, treatment of diseases in which parasites live (virus, fungi, yeast, bacteria, protozoa, worm) are killed and their growth is inhibited by chemicals in body is called **chemotherapy.** Due to successive efforts of Ehrlich about chemotherapy, he is known as father of chemotherapy.

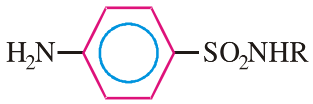
9.3 Classification of Drugs

Due to development of chemistry, many drugs are synthesized for various diseases. These drugs can be classified in four types as follows.

(1) On the basis of pharmacological effect : Drugs can be classified on basis of their pharmacological effect. This classification is most useful for doctors because they are known as drugs for specific treatment. For example, body pain relieving drugs can be classified as analgesic drugs and the drugs, killing or inhibiting the growth of microorganisms that cause harmful effect on wound or injury can be classified as antiseptic drugs.

(2) On the basis of drug action : Drugs can affect particular biochemical process. Drugs can be classified on the basis of specific action of them. Some problems occur in body due to release of histamine such as common cold, acidity, swelling, redness of skin and itching. Therefore, the drugs used to stop the release of histamine are classified as separate class of antihistamines.

(3) On the basis of chemical structure of drugs : Drugs can be classified on the basis of chemical structure. Drugs containing similar chemical structure are included in same class. Mostly, drugs containing similar chemical structure have similar drug action. e.g., sulphonamides have common structure as follows :



where, R = aromatic or heterocyclic group

(4) On the basis of molecular targets of drugs : Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These biomolecules are called target molecules of drugs. Similar target molecules containing drugs can be put in the same class.

9.4 Working Mechanism of Drugs

Macromolecules perform various functions in the body. For example, some proteins perform the role of biological catalysts in the body called **enzymes.** Some proteins are crucial to communication system in the body called **receptors.** Nucleic acids have coded genetic information for the cell. Lipid and carbohydrates are structural parts of the cell membrane.

Enzymes and receptors play an important role in our body. If these two substances show negative effect, then various systems get disturbed in our body, as a result a human being suffers from various diseases. We use specific drugs for protection of these diseases. These drugs stop negative effect of enzymes and receptors by interacting with them.

9.4.1 Drug-Enzyme Interaction :

Detailed information about enzymes is given in unit-7. Generally substrate is bound with active site of enzyme. At the end of this reaction product is formed and enzyme is obtained in original form. Information about lock and key model of enzyme, which explains the mechanism of enzyme can be found in unit-2 and 7. Drugs stop this reaction of enzymes; for this, drugs stop the substrate from binding with active site of enzyme. These drugs are called **enzyme inhibitors.** Drugs stop the substrate to bind with active site of enzymes in two ways.

(1) Drugs compete with natural substrate for their attachment on the active site of enzymes as shown in Fig. 9.1; such drugs are called **competitive inhibitors.**

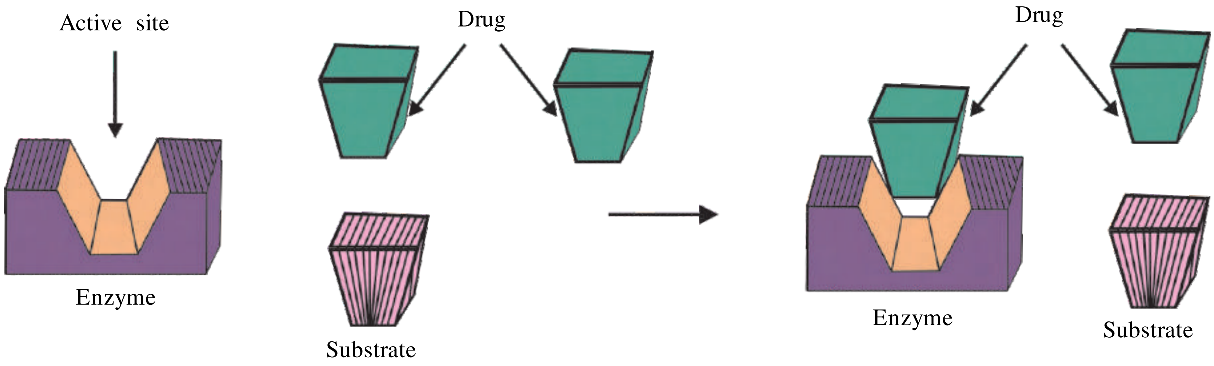


Fig. 9.1 Competition between drugs and substrate for binding with active site of enzyme

(2) Some drugs do not bind to the active site of enzyme but bind to a different site. This site is called **allosteric site.** This type of binding of drug with enzyme results in the change in shape of active site as shown in Fig. 9.2, therefore substrate cannot bind with it. If the binding between enzyme and drug is formed by strong covalent bond then it cannot be broken easily, so this enzyme is blocked permanently when body degrades the enzyme-inhibitor complex, and new enzyme is synthesised.

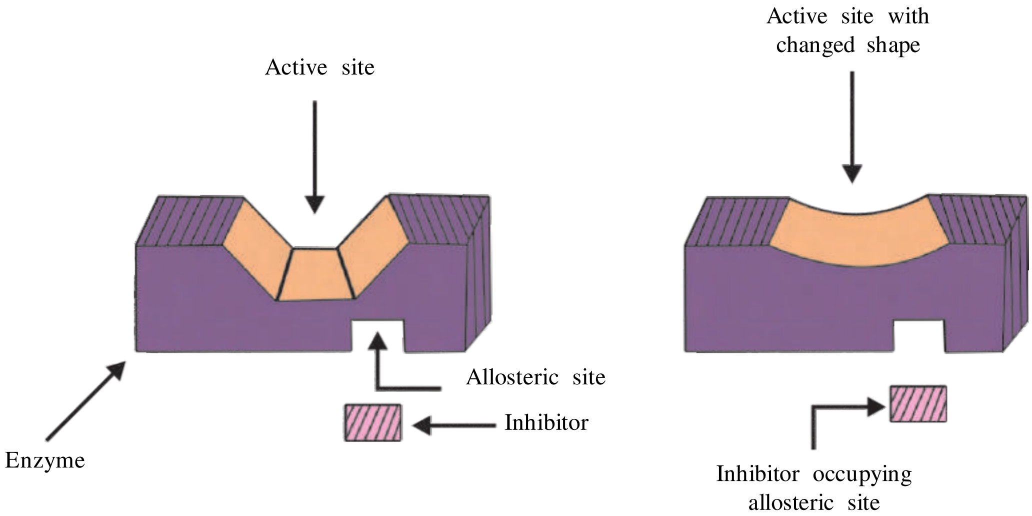


Fig. 9.2 Change in shape of active site of enzyme and allosteric site

9.4.2 Drug-Receptor Interaction :

Receptors are made from proteins. They play key role in communication process of body. Most of receptors are embedded in cell membrane as shown in Fig. 9.3.

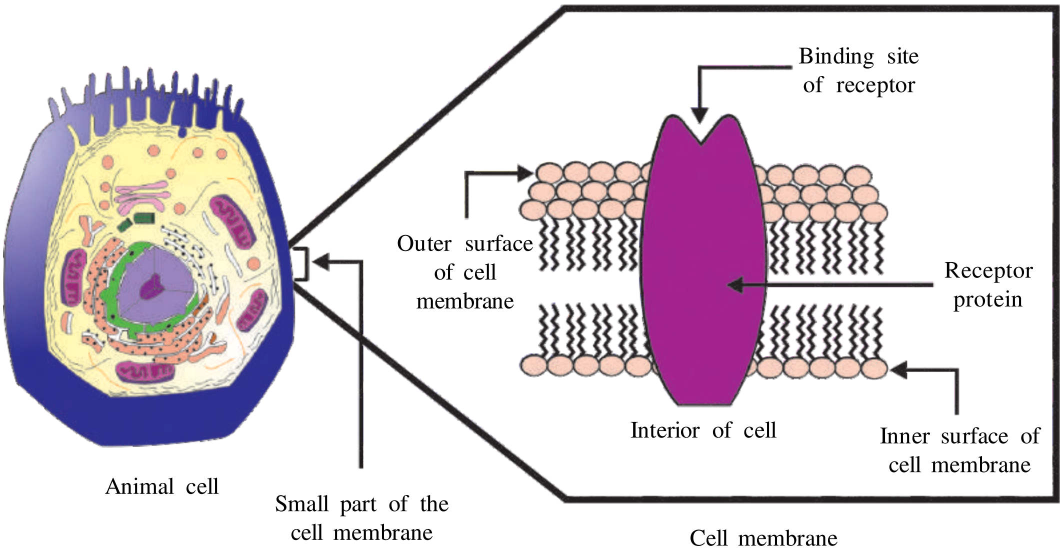


Fig. 9.3 Receptor in membrane of animal cell

Small active part of receptor is present on outside region of cell membrane. It is called binding site. In the body, message between two neurons or that between neurons to muscles is communicated through certain chemicals. These chemicals are called **chemical messengers.** When a chemical messenger comes near the binding site of receptor, then the receptor changes shape of its binding site to accept chemical messenger. Messenger gives its message to cell, and it moves away from receptor. Thus, messenger gives message to the cell without entering into the cell as shown in Fig. 9.4

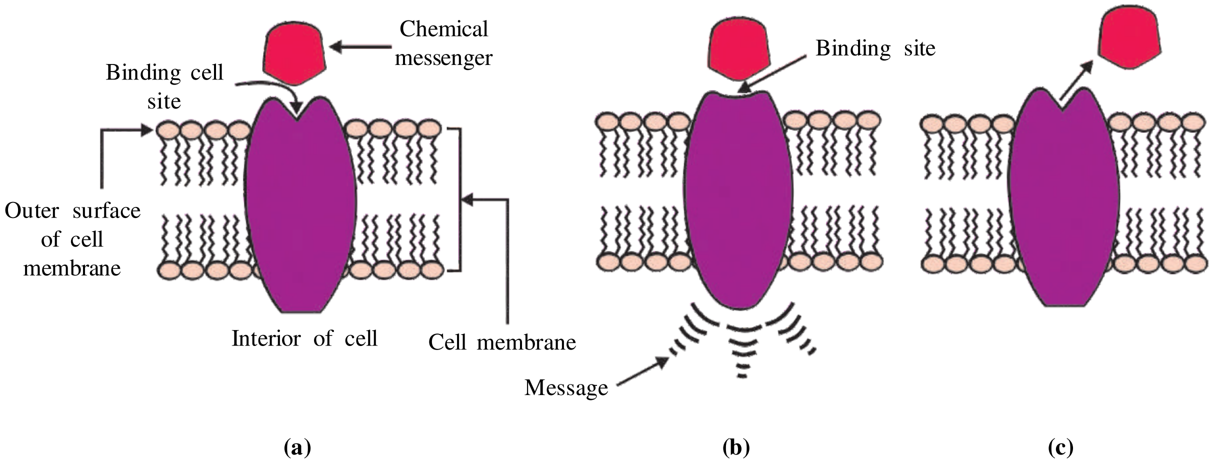


Fig. 9.4 (a) Receptor receiving chemical messenger

(b) Shape of the receptor changed for attachement of messenger

(c) Receptor regains structure after removal of chemical messenger

Many receptors are present in body. They interact with various chemical messengers. Receptors react with specific messenger due to specific shape of its binding site. Instead of messengers, drugs bind to receptor site and stop communication process of cell. These drugs are called **antagonists.** Sometimes, due to defect in natural chemical messenger, the communication process is stopped. At this time, if the messenger shaped drug is used, then receptor accept it, and under the impression of natural messenger the communication process occurs. These drugs are called **agonists.**

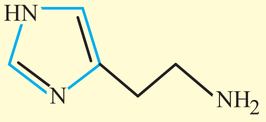
9.5 Therapeutic Action of Different Classes of Drugs

Let us discuss therapeutic action of some important classes of drugs :

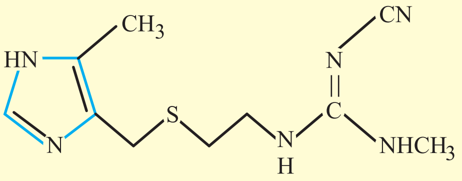
(1) Antacids : Due to overeating or indigestion, much acid is released in stomach. It is known as acidity. Acidity causes irritation and pain in stomach. In severe cases, ulcers are developed in stomach. Sodium hydrogen carbonate or mixture of aluminium hydroxide and magnesium hydroxide are used as **antacids** for treatment of acidity. Metal hydroxides are insoluble so they do not increase the pH higher than neutral value in stomach. While excessive sodium hydrogen carbonate can make the stomach fluid alkaline; due to this side effects can occur in stomach. Antacids give relief only from the symptoms but they do not control the causes, so they are not called drugs.

(2) Antihistamines : In our body, release of histamine stimulates the secretion of pepsin and hydrochloric acid in stomach, therefore, acidity develops in stomach. The drug cimetidine (Tegamet) prevents the interaction of histamine with the receptors present in stomach wall. It results in release of lesser amount of acid. Thus, this drug acts like antacid and prevents the causes of release of acid. Moreover, similar type of drug- ranitidine (zantac) is more used nowadays.

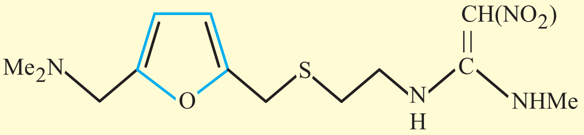
(For information only)



Histamine



Cimetidine



Ranitidine

Histamine causes common cold, redness of skin and allergy like itching in body. For this synthetic drugs brompheniramine (Dimetapp) and terfenadine (seldane) are used as antihistamines. These drugs are also known as **antiallergenic drugs.** These drugs prevent interaction between histamine in binding with receptor. Thus, these drugs protect the body from negative effect of histamine. We cannot use the antacids as antiallergenic drugs or antiallergenic drugs as antacids because both types of drugs work on different receptors.

(3) Neurologically active drugs : Tranquilizers and analgesics are neurologically active drugs. These drugs affect mainly the message transfer mechanism between nerve and receptor.

(A) Tranquilizers : Tranquilizers are a class of chemical compounds used in treatment of stress, mild and severe mental diseases. They relieve anxiety, stress, irritability or excitement. They are essential components in sleeping pills. There are various types of tranquilizers. Their functions are also different. For example, noradrenaline is one of the neurotransmitter that means neuro messenger. It changes the mood of person. If the level of noradrenaline is low for some reason then the message signal sending activity becomes slow, due to this person feels depressed. In such situation antidepressant drugs are required. These drugs inhibit catalytic effect of enzyme for degradation reaction of noradrenaline. Thus, these drugs act as enzyme inhibitors. Therefore important neurotransmitter noradrenaline is released and after a long period it activates its receptor. Thus, person comes out of depression gradually. Iproniazid and phenelzine are this type of drugs.

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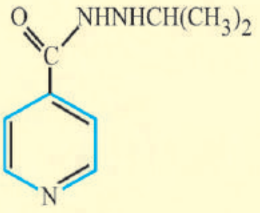
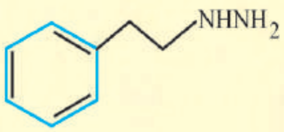


Iproniazid



Phenelzine

Some tranquilizers namely chlordiazepoxide and meprobamate are relatively mild tranquilizers. They relieve tension. Equanil drug relieves from depression and hypertension.

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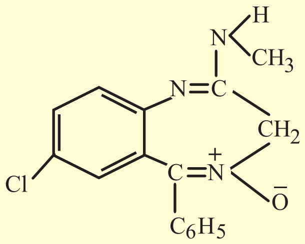
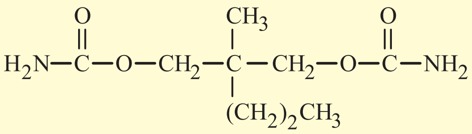
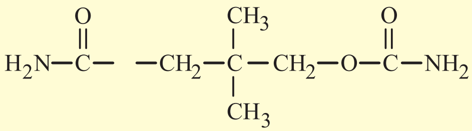


Chlordiazepoxide



$H_2N-\overset{\overset{O}{||}}{C}-O-CH_2-\underset{\underset{(CH_2)_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{||}}{C}-NH_2$

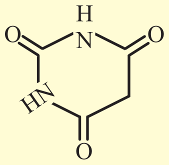
Meprobamate



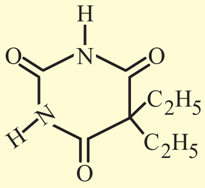
$H_2N-\overset{\overset{O}{||}}{C}-\quad -CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{||}}{C}-NH_2$

Equanil

(For information only)



Barbituric acid



Veronal

Derivatives of barbituric acid such as veronal, amytal, nembutal, luminal, seconal are important tranquilizers. These barbituric acid derivatives are called barbiturates. They are sedatives (sleep producing agents).

(B) Analgesic drugs : Physical pain reducing compounds are known as **analgesic drugs.** These drugs can be classified in to two classes as follows :

(i) Non-narcotic analgesic drugs

(ii) Narcotic analgesic drugs

(i) Non-narcotic analgesic drugs : Aspirin and paracetamol are well known examples of non-narcotic analgesic drugs. Due to these drugs, a person does not suffer from sleepiness or excitement, so they are called **non-narcotic analgesic drugs.** In body, released prostaglandins chemical causes inflammation and pain in the tissue. Aspirin inhibits synthesis of prostaglandins in body, which results in removal of pain in body. These drugs relieve from skeletal pain such as that caused by arthritis. These drugs reduce body temperature which means they are fever relievers. Therefore, these drugs are known as **antipyretics.** Aspirin prevents coagulation of blood, due to this it is more useful to patient of heart diseases.

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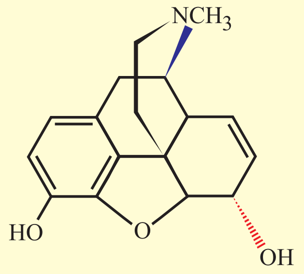

Morphine

(ii) Narcotic analgesic drugs : When morphine and many of its homologues are used as drugs, then they relieve pain and produce sleep. Due to these drugs, excitement occurs before sleep. It is called euphoria. If a person starts enjoying this situation frequently, then person has to take it regularly and becomes an addict. This is the most negative side of such drugs. These drugs produce excitement and sleep. Due to this, they are called **narcotic analgesic drugs.** If large amount of morphine is used, then it acts as poison instead of drug. Large amount of morphine produces stupor, coma, convulsions and ultimately death. These drugs are used when there is no option for them. Many efforts have been made to find out alternative of morphine and these efforts are continuing till today.

(4) Antimicrobial drugs : Diseases occur in human being and animals due to different types of microorganisms such as bacteria, virus and fungi. The drugs which are used to prevent and to inhibit the pathogenic action of these microorganisms are called **antimicrobial drugs.** The specific chemical is used to prevent and to inhibit the pathogenic action of bacteria, fungi, virus and other parasite is called antibacterial agent, antifungal agent, antiviral agent and antiparasitic agent, respectively. Generally, antibiotics, antiseptics and disinfectants are called antimicrobial drugs.

(A) Antibiotics : The chemical substances produced by living organisms to inhibit the growth or to kill microorganisms are called **antibiotics,** e.g., penicillin, tetracycline, chloramphenicol, etc. Penicillin produced by microorganisms is first antibiotic that acts as drug. In 1945, Alexander Fleming, Howard Florey and Ernst Boris Chain were awarded the Nobel prize in the field of physiology and medicine, to encourage their joint efforts in this field. Antibiotics that kill microorganisms are called **microbicidal** and antibiotics that inhibit the growth of microorganisms are called **microbiostatic.** For example, penicillin, aminoglycosides, ofloxacin etc. are bactericidal and erythromycin, tetracycline, chloramphenicol etc. are bacteriostatic.

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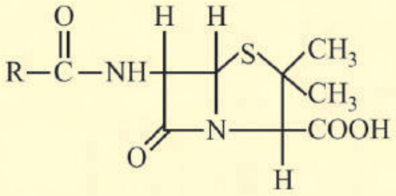
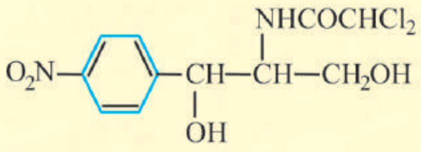


General structure of Pencillin



Chloramphenicol

Nomenclature methods of antibiotics is also interesting. Names of some antibiotics were derived from the names of bacteria, e.g., Pencillin from penicillium notatum, streptomycin from streptomyces griseus. Some names were decided from name of place from where soil samples were first collected e.g., Angolamycin from Angola. Some names were decided from name of laboratory or factory, e.g., Hemycin from Hindustan Antibiotics Ltd. Some names were derived from the names of relatives, patients, secretary of discoverer-scientist. e.g., Halinin from name of a scientist's wife, seramycetin from name of mother-in-law, vernamycin from name of secretary, bacitracin from a patient named Tarcey (microorganisms were collected from wound of Tracey).

(B) Antiseptics and disinfectants : Antiseptics and disinfectants are such chemicals that kill or inhibit the growth of microorganisms. **Antiseptics are useful in making tissues free from microorganisms.** Antiseptics are used in making mouth free from microorganisms by gargling and they can be used by applying on wounds. Potassium permanganate, furacine and soframycine are the examples of antiseptics. Like antibiotics it does not take them in abdomen. Dettol used as an antiseptic is a mixture of chloroxylenol and terpineol. Bithionol is added to soaps to develop the antiseptic properties. Iodine is a powerful antiseptic. Its 2-3 % solution prepared in alcohol-water mixture is known as tincture of iodine. It is applied on wounds for making them free from microorganisms. Dilute aqueous solution of boric acid act as weak antiseptic. It is used as washing solution for eyes to free them from microorganisms.

Generally, **disinfectants are applied to inanimate objects for making them free from microorganisms.** 0.2 to 0.4 ppm concentration containing aqueous solution of chlorine and very low concentration of sulphur dioxide can act as disinfectants. Activity of disinfectants is expressed by **phenol coefficient.** If the value of this coefficient is 10, then it means it has 10 times more disinfectant activity than phenol. Generally, this type of activity is checked on salmonella typhosa bacteria. Same compound acts as antiseptic or disinfectant at its different concentrations. e.g., 0.2% of phenol solution acts as antiseptic and 1% of phenol solution acts as disinfectant.

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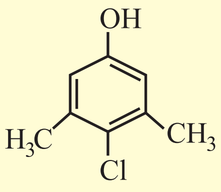
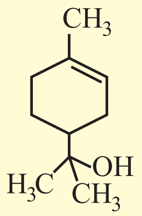
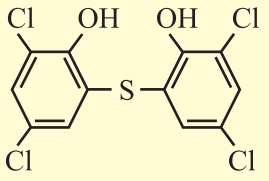


Chloroxylenol



Terpineol



Bithionol

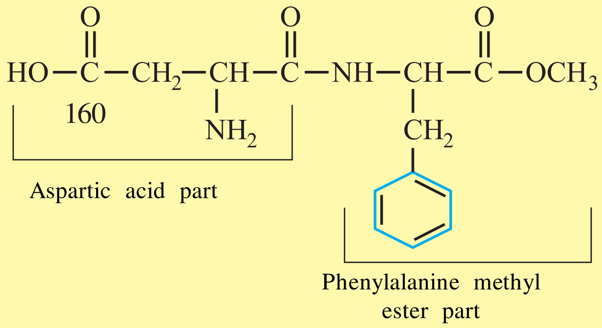
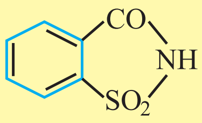
(5) Antifertility drugs : Average human life has increased due to modern drugs and good health, therefore, population increases. Increased population causes social problems such as limited resources of foods, clothes and abode, pollution and unemployment. Due to this, each and every person has to worry about how to control the population. For this, remedies should be used to control births. The chemicals used for prevention of impregnation are called **antifertility drugs.** Estrogen and progesterone possess this type of ability. For this, mixture of estrogenic and progestogenic compounds are used in pill form. They are known as antifertility pills or birth control pills. Females can take these pills in orally. In such type of compounds, mixture of mestranol (estrogenic) and norethindrone (progestogenic) is used.

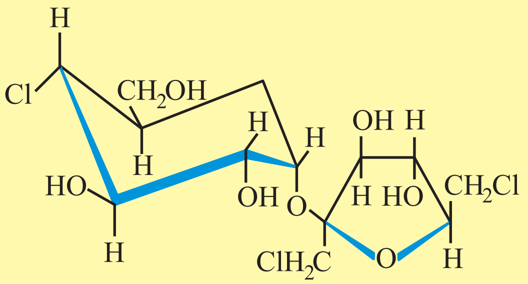
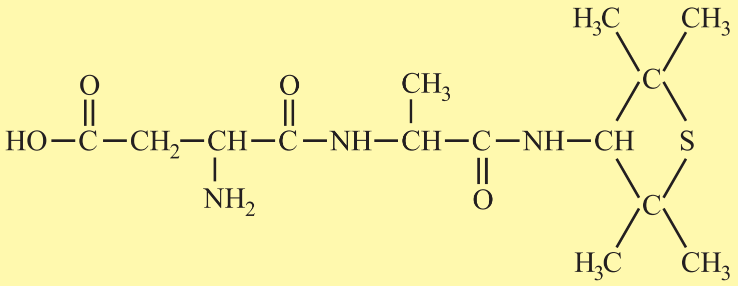
9.6 Chemicals in Food

Specific chemicals are added to foods for their preservation, enhancing their appeal and improving nutritive value in them. These compounds are food colours, flavours and sweeteners, fat and stabilising agents, antioxidants, preservatives, nutritional supplements such as minerals, vitamins and aminoacids. Let us study about some important compounds in this topic.

(1) Artificial sweetening agents : Many people suffer from fatness or obesity. Obesity causes many diseases. To reduce the obesity, use of non-caloric artificial sweeteners instead of sugar in food has increased. Aspartame, saccharin, sucrolose and alitame are well known artificial sweetening agents. Their sweetness values are 160, 550, 600, 2000 times more, respectively than that of sucrose but they give less calories to body. Aspartame is used only for cold foods and soft drinks because they are unstable at cooking temperature. Appearance and taste of sucrolose are like sugar. It is stable at cooking temperature. Structures of important artificial sweeteners are given in table 9.1

Table 9.1 Artificial sweeteners

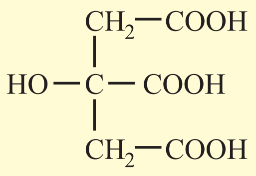
Artificial sweetener	Structural formula (For information only)	Sweetness value in comparison to sucrose
Aspartame		160
Saccharin		550

Sucrolose		600
Alitame		2000

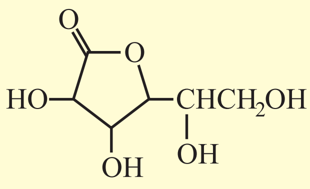
(2) Food preservatives : The chemicals used to prevent food from spoiling by microorganisms like fungi or to preserve food for a long time, are called **food preservatives.** Generally, we use table salt, table sugar and vegetable oil as food preservative in daily life for domestic purposes. Moreover, sodium benzoate, sodium metasulphite and salts of propionic acid or sorbic acid are used as preservatives in food industry.

(3) Antioxidants : Addition of some chemical compounds to food causes slow activity of oxygen; so that the food is preserved for a long time. These types of chemical compounds are called **antioxidants.** Antioxidants are more active towards oxygen. Due to this, the foods are preserved. Citric acid, ascorbic acid, butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA) are important antioxidants.

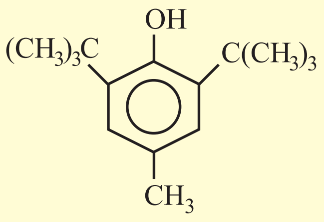
(For information only)



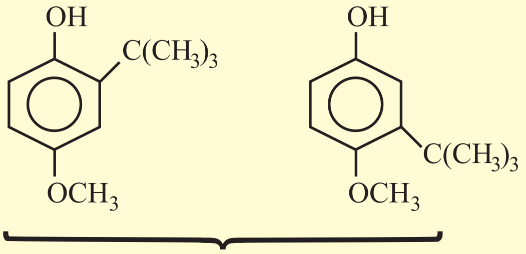
Citric acid



Ascorbic acid



Butylated hydroxy toluene (BHT)



Butylated hydroxy anisole (BHA)
(BHA is mixture of two isomers)

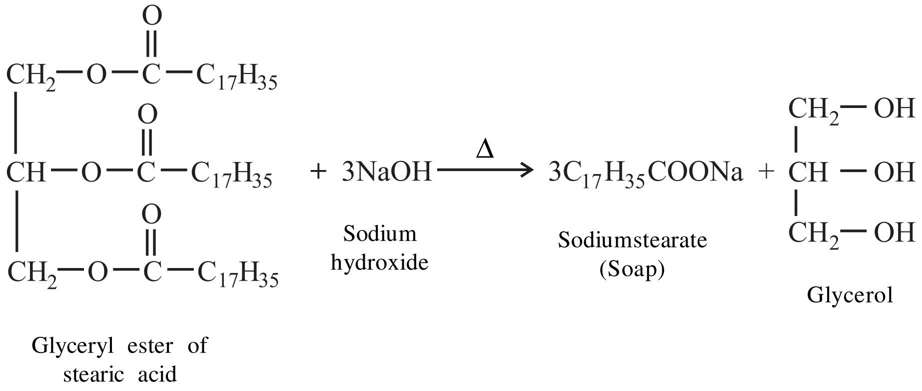
(4) Food colours : Some chemical compounds added to food are dyes and as a result food becomes colourful. These type of chemical compounds are called **food colours.** β-carotene, caramel, tetrazine, arneto are food colours.

9.7 Cleansing Agents

The chemical compounds used to remove dirt or oily materials from surfaces are called **cleansing agents.** These compounds also improve cleansing property of water.

9.7.1 Soap :

Soap is sodium or potassium salt of fatty acid (stearic acid, oleic acid, palmitic acid). Vegetable oils or animal fats are glyceryl ester of the fatty acids. They are heated with aqueous solution of sodium hydroxide or potassium hydroxide which results in formation of sodium salt of fatty acid and glycerol. This reaction of formation soap is called **saponification.**



We use various types of soaps every day, for example, bath soap, washing soap, shaving soap, medicated soap, etc. In preparation of these types of soaps, some specific chemicals are additionly added to main reactants (fats and alkali). For preparation of bath soap, fat or oil having good quality and potassium hydroxide as alkali are used, because this type of soap is soft and they make the soap smooth in comparison to sodium soap. Care should be taken about the removal of excess alkali during preparation of bath soap. Moreover, colours and fragrant materials are also added to it. Glycerol is added during preparation of shaving soap, due to this, soap and its foam do not dry up rapidly. Additionally rosin is added while preparing them. It forms sodium rosinate which foams well. Deodorants are added during preparation of medicated soap. It prevents the body odour due to sweat. **Quality of bath soap can be decided on the basis of presence of TFM (Total Fatty Matters).** If a soap has high proportion of TFM, then its quality is good. Very low proportion TFM containing soap makes skin dry and produces burning sensation. BIS (Bureau of Indian Standards) has established standard values of TFM for deciding the quality of bath soap. As per BIS, grade-1 is given to soap if it contains 76 % or more TFM, grade-2 is given to soap if it contains 65 % or more but less than 76 % of TFM, grade-3 is given to soap if it contains 60 % or more but less than 65 % of TFM. The percentage value of TFM or grade of soap is compulsory to mention on bath soaps. Dear students, kindly read this information on wrapper of a soap that you use and decide its quality yourself.

Limitations of soap :

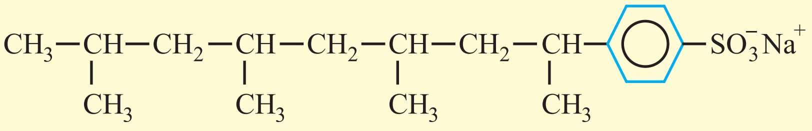
- Soap is converted to free fatty acids in acidic medium. This fatty acid is insoluble in water and it does not act as cleansing agent.

  $$\underset{\text{(Soap)}}{C_{17}H_{35}COONa} + H^+ \rightarrow \underset{\text{Fatty acid}}{C_{17}H_{35}COOH} + Na^+$$

- Soap does not produce foam with hard water, because it reacts with calcium and magnesium present in hard water and forms calcium and magnesium salts of fatty acid. Thus, soap is wasted when it is used with hard water, and does not satisfy the purpose of cleanliness.

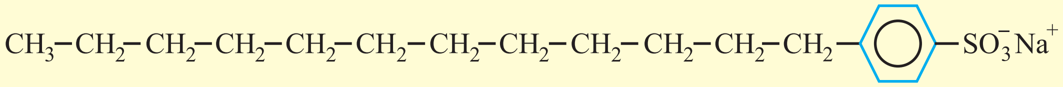
9.7.2 Synthetic Detergents :

To combat with the limitations of soap, the compounds are developed possessing similar cleanliness ability of soap called synthetic detergents. **Chemically synthetic detergents are sodium salts of organic sulphonic acid.** Synthetic detergents show the cleanliness ability in acidic medium or even with hard water. Sodium salts of branched alkyl benzene sulphonate (ABS) and linear alkyl benzene sulphonate (LAS) are examples of synthetic detergents. These detergents contain 10 to 14 carbon atoms in chain attached to aromatic ring.



Branched sodium dodecylbenzene sulphonate

(ABS detergent)



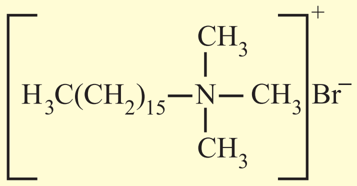
Linear sodium dodecylbenzene sulphonate

(LAS detergent)

Classification of Detergents : Detergents are classified into three categories depending upon the structural position of their molecules in aqueous medium (i) anionic detergents (ii) cationic detergents and (iii) non-ionic detergents.

(i) Anionic detergents : The detergents which are in negative ion (anionic) form in their aqueous solutions are called anionic detergents. They are effective also in dilute acidic medium. These type of detergents are used more for domestic purposes. ABS and LAS are **anionic detergents.**

(ii) Cationic detergents : The detergents which are in positive ion (cationic) form in their aqueous solution are called cationic detergents. These type of detergents being germicidal are used in hospitals and in preparation of cosmetics. Cetyl trimethyl ammonium bromide and its similar quaternary amines are **cationic detergents.** They are used in hair conditioner.



$$\left[H_3C(CH_2)_{15}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]^{+}Br^{-}$$

Cetyltrimethyl
ammonium bromide

(iii) Non-ionic detergents : The detergents which are neither in cationic nor in anionic form in their aqueous solution are called **non-ionic detergents.** They are used for cleaning the glass and ceramic wares. Polyethylene glycol and ester of stearic acid are these type of detergents.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethylene glycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} \underset{\text{Non-ionic detergents}}{CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH}$$

Biosoft and Biohard Detergents : Detergents used in everyday life are collected through gutters in the sewage farm. Microorganisms degrade organic compounds of sewage farm. Due to this degradation, organic compounds are converted into simple inorganic molecules and ions. The detergents easily degraded by microorganism are called **biosoft detergents.** The detergents not easily degraded or very slowly degraded by microorganisms are called **biohard detergents.** LAS is easily degraded by microorganisms because it contains linear alkyl group, therefore it is known as biosoft detergents; while ABS contains branched alkyl group so it is not degraded by microorganisms, therefore it is known as biohard detergent. Biohard detergents cause water pollution.

SUMMARY

- Directly or indirectly, chemistry is closely associated with our everyday life. By now we have understood applications of chemistry in drugs, foods and cleansing agents.

Drugs

- Research about applications of chemical compounds resulted in chemical compounds which were used for treatment of diseases during the twentieth century.
- The treatment in which diseases causing parasites (virus, fungi, yeast, bacteria, protozoa, worm) are killed and inhibited their growth by chemicals in body is called chemotherapy.
- Ehrlich has synthesized arsenic containing compounds for skin diseases like syphilis and for sleeping disorder. For this work Ehrlich was awarded the Nobel prize in 1908.
- Due to successive efforts of Ehrlich about chemotherapy, he is known as father of chemotherapy.
- Drugs can be classified (1) on the basis of pharmacological effect (2) on the basis of drug action (3) on the basis of chemical structure of drugs and (4) on the basis of molecular targets of drugs.
- Enzymes and receptors play an important role in our body. Drugs stop negative effect of enzymes and receptors by interacting with them.

Therapeutic action of different classes of drugs

Sr.	Drug	Uses	Example	Note
(1)	Antacids	Prevents acidity	Sodium hydrogen carbonate, mixture of aluminium hydroxide and magnesium hydroxide	Give relief only for the symptoms but do not control the causes
(2)	Antihistamine Drugs	In treatment of acidity	As antacids : cimetidine, ranitidine. As antiallergenic drugs : brompheniramine, terfenadine	Act as antihistamine drugs, the antacids cannot be used as antiallergenic drugs or the antiallergenic drugs cannot be used as antacids.
(3)	Neurologically Active Drugs			They affect mainly the message transfer mechanism between nerve and receptor.
	(A) Tranquilizers	Relief from anxiety, stress, irritability.	Iproniazid, phenelzine, chlordiazepoxide, meprobamate, derivatives of barbituric acid such as veronal, amytal, nembutal, luminal, seconal	These drugs are sedative (sleep producing)
	(B) Analgesic drugs			
	(i) Non-Narcotic	In treatment of body pain, fever, coagulation of blood	Paracetamol, aspirin	Patient does not suffer from sleepiness or excitement.
	(ii) Narcotic	In treatment of body pain	Morphine	Patient suffers from sleepiness and excitement
(4)	Antimicrobial Drugs			To prevent and to inhibit the pathogenic action of microorganisms
	(A) Antibiotics	To prevent and inhibit the growth of microorganism	Penicillin, tetracycline chloramphenicol, amino glycosides, ofloxacin, erythromycin	

	(B) Antiseptic Drugs	In making tissues free from micro-organisms	Potassium permanganate, tincture iodine, furacine, soframicine, boric acid, 0.2% aqueous solution of phenol	
	(C) Disinfectants	In making inanimate objects free from micro organism	Chlorine water having 0.2 to 0.4 ppm concentration, dilute solution of sulphur dioxide, 1% of aqueous solution of phenol	
(5)	Antifertility Drugs	Prevention of impregnation	Mixture of mestranol (estrogenic) and norethindrone (progestogenic)	These drugs are for females, these pills are taken orally.

Food

- Specific chemicals are added to food for their preservation, enhancing their appeal and improving nutritive value.

Some important compounds are added to food

Sr.	Compounds	Examples	Importance
(1)	Artificial sweetening agents	Aspartame, saccharin, sucrolose, alitame	Their sweetness is higher than table sugar but they give less calories to body
(2)	Food preservatives	Table salt, table sugar, vegetable oil, sodium benzoate, sodium metabisulphite, salt of propionic acid, salt of sorbic acid	To prevent food from spoilage by microorganisms
(3)	Antioxidants	Citric acid, ascorbic acid, butylated hydroxy toluene (BHT), butylated hydroxy anisole (BHA)	They cause slow activity of oxygen and resulting food is preserved for long time.
(4)	Food colours	β-Carotene, caramel, tetrazine, arneto	They make food colourful.

Cleansing Agents

- The chemical compounds used to remove dirt or oily materials from surfaces are called cleansing agents.
- Soaps and synthetic detergents are important cleansing agents.

- Vegetable oil or Animal fat + Sodium hydroxide or Potassium hydroxide $\xrightarrow[\text{Saponification}]{\Delta}$ Sodium salt of fatty acid (Soaps) + Glycerol
- Soaps produce insoluble compounds in acidic medium and with hard water. In these cases soap is wasted and it does not satisfy the purpose of cleansing.
- Sodium salt of organic sulphonic acid is called synthetic detergents. e.g., sodium salts of branched alkyl benzene sulphonate (ABS) and linear alkyl benzene sulphonate (LAS).

Synthetic detergents

Anionic detergents e.g.,
- Sodium salt of branched alkyl benzene sulphonate
- Sodium salt of linear alkyl benzene sulphonate

Cationic detergents e.g.,
- Cetyl trimethyl ammonium bromide

Non-ionic detergents e.g.,
- Ester formed from the polyethylene glycol and stearic acid

- The detergents easily degraded by microorganism are called biosoft detergents e.g., LAS detergents.
- The detergents not easily degraded or very slowly degraded by microorganisms are called biohard detergents. e.g., ABS detergents. These detergents cause water pollution.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Who is known as the father of chemotherapy ?

(A) Alexander Fleming (B) Howard Florey

(C) Paul Ehrlich (D) Ernst Boris Chain

(2) What are the drugs called that kill or inhibit the growth of microorganisms which cause bad effect to wounds or injury ?

(A) Tranquilizers (B) Antibiotics (C) Antiseptics (D) Disinfectants

(3) Which statement is true from the following ?

(A) Drugs bind to receptor site instead of messengers and stop communication process of cell are called agonists.

(B) The receptors which accept drugs in impression of natural messenger and communication process occurs are called antagonists.

(C) Drugs bind to different sites instead of active site of enzyme; this site is called allosteric site.

(D) Drugs helped in binding of substrate with active site of enzyme are called enzyme inhibitors.

(4) Which type of class of drugs does ranitidine belong to ?

(A) Antihistamines	(B) Neurologically active drugs
(C) Antimicrobial drugs	(D) Antifertility drugs.

(5) Which of following solutions acts as disinfectant ?

(A) Aqueous solution containing 1 % of phenol

(B) Aqueous solution containing 0.2 % of phenol

(C) Aqueous solution containing 2-3 % of iodine

(D) Dilute aqueous solution of boric acid

(6) Which order from the following is true on the basis of sweetness values ?

(A) Aspartame > Sucrolose > Alitame > Saccharine

(B) Aspartame > Saccharine > Sucrolose > Alitame

(C) Alitame > Sucrolose > Saccharine > Aspartame

(D) Saccharine > Aspartame > Alitame > Sucrolose

(7) Which of the following two pairs are proper ?

(a) Food preservative - Sodium benzoate

(b) Antioxidant - Propionic acid

(c) Food colour - β-carotene

(d) Artificial sweetening agent-Arneto

(A) a, b (B) a, c (C) a, d (D) b, d

(8) LAS is ....

(A) Cationic detergent	(B) Nonionic detergent
(C) Biosoft detergent	(D) Biohard detergent

(9) ABS is ....

(A) Anionic detergent	(B) Cationic detergent
(C) Nonionic detergent	(D) Biosoft detergent

(10) Which of the following drugs is analgesic drug ?

(A) Barbiturates (B) Penicillin (C) Ranitidine (D) Paracetamol

2. Write the answers of the following questions in brief :

(1) Which chemical produced in body causes inflammation or pain in the tissue ?

(2) What is tincture of iodine ?

(3) Write the example of weak antiseptic.

(4) Write the example of powerful antiseptic.

(5) How can the activity of disinfectant be expressed ?

(6) Mention the name of artificial sweetening agent which is stable at cooking temperature.

(7) Which compound is added in shaving soap as a well-foam maker ?

(8) Write definition of following terms :

(i) Chemotherapy
(ii) Enzyme inhibitor
(iii) Competitive inhibitors
(iv) Allosteric site
(v) Chemical messenger
(vi) Antagonists
(vii) Agonists
(viii) Antacids
(ix) Non-narcotic analgesic drug
(x) Narcotic analgesic drug
(xi) Antipyretics
(xii) Antimicrobial drugs
(xiii) Antibiotics
(xiv) Microbicidal
(xv) Microbiostatic
(xvi) Antiseptics
(xvii) Disinfectants
(xviii) Antifertility drugs
(xix) Food preservatives
(xx) Antioxidants
(xxi) Food colours
(xxii) Cleansing agents
(xxiii) Soaps
(xxiv) Synthetic detergents
(xxv) Anionic detergents
(xxvi) Cationic detergents
(xxvii) Nonionic detergents
(xxviii) Biosoft detergents
(xxix) Biohard detergents
(xxx) Antivirus agents

3. Write the answers of the following questions :

(1) Mention two points of difference :

(i) Narcotic – Non narcotic analgesic drugs
(ii) Antiseptic drugs – Disinfectants
(iii) Soap – Synthetic detergents
(iv) Anionic – Cationic detergents
(v) Biosoft – Biohard detergents

(2) Write two examples of each of the following compounds :

(i) Antacids
(ii) Antiallergenic drugs
(iii) Tranquilizers
(iv) Antibiotics
(v) Artificial sweetening agents
(vi) Food preservatives
(vii) Antioxidants
(viii) Food colours

4. Write answers of the following questions in detail :

(1) Which four points are taken into consideration in classifying the drugs ? Explain.

(2) Explain drug- enzyme interaction.

(3) Describe drug- receptor interaction.

(4) Discuss about food preservatives and antioxidants added in food.

(5) What is saponification ? Write its chemical equation. Mention the names of compounds which are added during the preparation of bath soap, washing soap and medicated soap.

(6) Explain classification of detergents with examples.

APPENDIX

Atomic Number and Molar Mass of Elements

Element	Symbol	Atomic Number	Molar mass(g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Cesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copernicium	Cn	112	(277)
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Darmstadtium	Ds	110	(271)
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50

Element	Symbol	Atomic Number	Molar mass(g mol^{-1})
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass(g mol^{-1})
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Proactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Roentgenium	Rg	111	(272)
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96

Element	Symbol	Atomic Number	Molar mass(g mol^{-1})
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununtrium	Uut	113	(284)
Ununquadium	Uuq	114	(289)
Ununpentium	Uup	115	(288)
Ununhexium	Uuh	116	(289)
Ununseptium	Uus	117	(290)
Ununoctium	Uuo	118	(293)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

(The Value given in parenthesis is the molar mass of the isotope of largest known half-life)

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
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18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
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26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
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30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
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32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
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36	5563	5575	5587	5566	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
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40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6238	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6345	6454	6464	6474	6484	6494	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7769	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9843	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	3	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1289	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2380	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6715	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	112	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	12	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	5	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9