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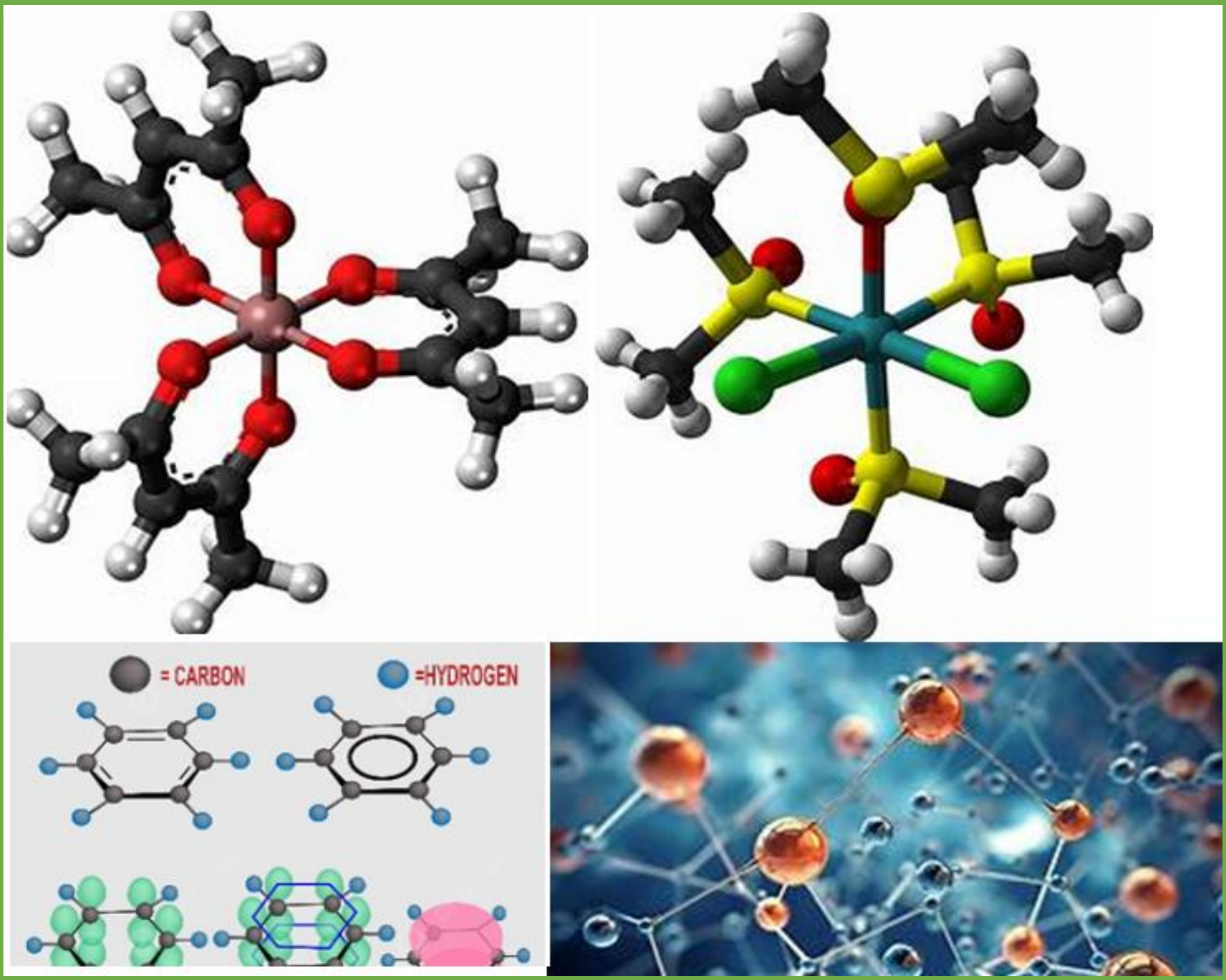
B.Sc. IInd Semester

FUNDAMAENTAL CHEMISTRY-II



DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY
HALDWANI (NAINITAL), UTTARAKHAND-263139

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UNIT 1: CHEMICAL BONDING -III

CONTENTS:

1.1 INTRODUCTION

The solids have been classified in two different ways:

A. First kind of Classification

This classification gives two categories of solids, *viz.* true solids and pseudosolids.

(i) True solids-These have definite shape and volume which are retained even on long standing. These are rigid and hence cannot be distorted. These solids have sharp melting points. Examples are NaCl, KCl, Fe, Cu, S etc.

(ii) Pseudo solids-These do not have definite shape and volume and lose them on long standing. These are less rigid and hence can easily be distorted. These solids melt over a range of temperature. Examples are glass and pitch.

B. Second kind of classification

This classification is more appropriate and gives three categories of solids, *viz.* crystalline solids, non-crystalline or amorphous solids and polycrystalline solids.

(i) Crystalline solids- The constituent particles (atoms, ions or molecules) of these solids are arranged in a regular and definite manner in three-dimensional space. These are said to have long range order. They have sharp melting points and can be broken into pieces, e.g., NaCl, sugar, diamond, graphite, sulphur etc.

(ii) Amorphous solids- The constituent particles of these solids are not arranged in a regular manner and hence have short range order. These do not have sharp melting points, i.e., they first soften and then change to liquid state on heating. Example are glass, rubber, plastics, silica etc.

(iii) Polycrystalline solids- These solids occur as powder and resemble amorphous solids but their individual particles have all the characteristics of crystalline solids.

Based on the nature of bonding forces existing between the constituent particles of crystalline solids, these have further been categorized into five classes, *viz.* ionic crystals, covalent crystals, molecular (van der Waals') crystals, metallic crystals and hydrogen bonded crystals.

Lattice points and crystal lattice

It has been mentioned above that the constituent particles of a crystalline solid are arranged in a regular order. The position of these particles relative to one another in the solid is represented by points (·) which are called lattice points or lattice sites and the orderly arrangement of these infinite lattice points is called a crystal lattice or space lattice.

Unit cell is a small unit of lattice points which on repeating infinitely in three dimensions gives a crystal lattice. This small unit is called a unit cell of the lattice. This shows all the properties of the crystal lattice.

1.2 OBJECTIVE

The objective of writing the study material of this unit is :

- To make the readers comfortable with electrostatic attraction forces and to acquaint them with the exciting world of the ionic crystals.
- An attempt has been made to through light on the type of force that holds an extremely large number of ions together forming a bulk or cluster of ions which exists in solid state only. At the same time the text gives an idea about why are the ions in an ionic crystal arranged in a regular manner and has a definite ratio.
- It has also been tried to give a brief account of lattice defects and semi-conductors which are of immense importance industrially.

1.3 IONIC SOLIDS

In these solids, the constituent particles are the ions, both positive and negative, which are held together by strong electrostatic force of attraction. There operates a repulsive force between the ions of same charge if these are adjacent to each other, therefore, the ions of similar charge move away from one another and those of opposite charge come closer together. These ions are arranged in the crystal lattice in regular pattern where the positive ions are surrounded by a definite number of negative ions and the negative ions, in turn, are surrounded by a certain number of positive ions. The attractive forces are maximum when each ion is surrounded by the greatest possible number of the oppositely charged ions. The positive and negative ions are present in the crystal lattice in a simple whole number ratio, i.e. 1:1, 1:2, 2:1 etc. The ionic solids along with other crystalline solids have been assigned seven basic crystal systems. These systems along with types of space lattices present in the crystal system and examples have been given below (**Table 1.1**):

S. No.	**Name of the crystal system**	**Type of space lattices present in the crystal system**	**Examples**
1	Cubic	(i) Simple cubic (SC) (ii) Body-centered cubic (BCC) (iii) Face- centred cubic (FCC)	NaCl, KCl, CaF_2, $NaClO_2$ ZnS, Cu_2O, alums, diamond Pb, Au, Ag, Hg
2	Orthorhombic	(i) Simple orthorhombic (ii) Body centred orthorhombic (iii) End – centred orthorhombic	KNO_3, K_2SO_4, $BaSO_4$, $MgSO_4$ Mg_2SiO_4 Pb CO_3, α–sulphur.
3	Tetragonal	Simple tetragonal Body centred tetragonal	$NiSO_4$, SnO_2, TiO_2 $ZrSiO_4$, KH_2PO_4, $PbWO_4$
4	Monoclinic	Simple monoclinic End-centred monoclinic	Na_2 SO_4. 10 H_2O FeO_4, $CuSO_4$. $2H_2O$, $Na_2B_4O_7$. $10H_2O$
5	Triclinic	Simple triclinic	$CuSO_4.5H_2O$, $K_2Cr_7O_7$, H_3BO_3

6	Hexagonal	Simple hexagonal	AgI, ZnO, CdS, HgS, PbI_2, quartz, Mg, Cd, Zn.
7	Rhombohedral	Simple	$NaNO_3$, calcite, magnesite, Sb, Bi.

Table. 1.1 The seven crystal systems

The ions in a given ionic crystal are arranged (or packed) in different ways which are given below:

(i) **Hexagonal close-packed** (hcp) **structure,** i.e., AB AB ………packing of spheres.

This structure has the packing sequence of different layers of spheres as AB AB….. In this structure, each sphere is surrounded by 12 other nearest spheres and hence the coordination number (CN) of each sphere is 12.

(ii) **Cubic close-packed** (ccp) **or face-centred cubic** (fcc) **structure,** i.e., ABCABC……packing of spheres.

This structure has the packing sequence of different layers of spheres is ABC ABC………This structure has cubic symmetry. Each sphere is surrounded by 12 other nearest spheres in this arrangement and hence the coordination number of each sphere is 12.

In both of the above structures, the coordination number of each sphere is 12 since each sphere is surrounded by six nearest spheres lying in the same layer, three spheres lying in the layer just above it and three spheres lying in the layer just below it. Both types of the above structures have the same packing efficiency which is 74 %, i.e., 74 % of the total volume of the unit cell is occupied by the spheres.

(iii) **Body-centred cubic** (bcc) **structure-**In this arrangement, there are 8 spheres at eight corners of a cube and one sphere at the centre of the cube. Each sphere is in contact with 8 other spheres in this structure and hence the coordination number of each sphere is 8.

Interstitial sites (holes or voids) **in ionic crystals**

In an ionic crystal, the bigger ions (i.e., anions) have close packed structure which may be either hexagonal close packed or cubic close packed type. In this close-packed structure, there is some vacant space between the anions which is called interstitial site (or hole or void). These sites or voids are occupied by smaller ions, i.e., cations.

Depending on the number of anions and the pattern in which they surround a cation in a given ionic crystal, there are four types of interstitial sites, *viz.* trigonal (C.N. = 3), tetrahedral (C.N. =4), octahedral (C.N. =6) and cubic (C.N. =8), respectively.

1.3.1 Characteristics of ionic solids:

Following are the main characteristics of ionic solids:

(i) The constituent particles of these solids are the cations and the anions which are held together by strong electrostatic force of attraction known as ionic bond and these exist as crystalline solids.

(ii) The ionic bond in ionic crystals is not rigid and nondirectional, i.e., it extends equally in all directions. Hence the ionic solids neither have any definite geometry nor show stereoisomerism like covalent molecules.

(iii) Since the anions are generally larger in size than the cations, the anions have closest packing arrangement in ionic solids in which there are left some empty spaces called interstitial sites or voids. These sites may be tetrahedral, octahedral or cubic type which are occupied by the cations.

(iv) Each ionic solid is formed from a small unit called a unit cell which contains a definite number of cations and anions. This unit cell in electrically neutral.

(v) The ionic solids are poor or bad conductors of electricity because in solid state the ions are fixed in their position and cannot move even if an external electric field is applied on them.

However, in fused state or in aqueous solution they conduct electricity because under these conditions the ions are free to move. Also, the ionic solids having defects can conduct electricity due to the movement of ions from the lattice sites to the vacancies or that of free electrons present in them.

(vi) These solids are very hard and brittle due to the movement of one layer over the other along a plane on applying external force.

(vii) These have lattice energy and high melting points and boiling points.

(viii) These solids are generally soluble in water or polar solvents due to ionization and undergo ionic reactions in that medium.

1.3.2 Crystal coordination number (CCN):

We have learnt above that in ionic crystals the positive ions are surrounded by a definite number of negative ions and vice versa. The number of ions of opposite charge surrounding an ion in the ionic crystal is called the crystal coordination number or simply coordination number (C.N.)

In case of ionic crystals of AB type (e.g., NaCl, CsCl, Zns etc.) in which the number of both kind of ions is same, the C.N. of cation is equal to the C.N. of the negative ion, e.g., in NaCl crystal each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion, in turn, is surrounded by six equidistant Na^+ ions. Hence the coordination number of both Na^+ and Cl^- ions is 6. In CsCl, the C.N. of Cs^+ ion and Cl^- ion, both is 8 (due to different type of packing of ions than in NaCl).

In ionic crystals of the type AB_2 or A_2B (e.g., CaF_2, Na_2S etc.) in which the cation-anion ratio is 1:2 or 2:1, the two types of ions have different coordination numbers. For example, in Ca F_2, the C.N. of F^- ions is half to that of Ca^{2+} ions. The X-ray study has shown that C.N. of Ca^{2+} ions is 8 and that of F^- ions is 4.

1.3.3 Radius ratio (R_r):

In an ionic crystal, the arrangement of ions (packing) and their coordination number depend on the relative size of ions or the ratio of radii of the ions which is known as radius ratio. Thus, the radius ratio (R_r) is defined as "**the ratio of the radius of cation (r_{C+}) to that of anion (r_{A-}) in an ionic crystal**". This can also be shown as

$R_r = \frac{r_{C+}}{r_{A-}}$ Where r_{C+} is the radiusof cation and r_{A-} is the radius of anion, R_r is radius ratio.

The radius ratio plays an important role in determining the structure of ionic solids and predicting the coordination number of the cation or the anion.

Radius ratio effect

The effect of radius ratio in determining the coordination number and the arrangement of ions (structure or packing) in an ionic crystal is known as radius ratio effect. As the cation becomes larger with respect to the anion, i.e. R_r increases, higher number of anions can fit around the cation and hence the coordination number of the cation increases. Which C.N. will give the most stable arrangement of ions is dependent on radius ratio.

The relationship between the various ionic arrangements and the radius ratios is given below:

Limiting value of $\frac{r_{c+}}{r_{A-}}$	**Coordination number**	**Arrangement of ions**
< 0.155	2	Linear
0.155-0.225	3	Trigonal planar (B_2O_3)
0.225-0.414	4	Tetrahedral (ZnS)
0.414-0.732	4	Square planar
0.414-0.732	6	Octahedral (NaCl)
0.732-0.999	8	Body centred cubic (CsCl, CaF_2)

The R_r value can be used for predicting the ionic arrangement and C.N. in the ionic crystals as already mentioned. For example, the radius ratio for NaCl crystal is r_{Na+}/r_{Cl}-= 0.95Å/1.81Å = 0.525. This value lies between 0.414 and 0.732. Thus the C.N. should be either 4 or 6 and the arrangement should be square planar or octahedral. The X- ray study of NaCl crystal has revealed that the crystal has octahedral arrangement of ions, i.e. each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion has six equidistant Na^+ ions. The cation-anion stoichiometry is 1:1 and the C.N. is 6 for both the ions. Similarly, it can be shown for CsCl (R_r = 169/181 = 0.93) that the C.N. is 8 for both the ions and arrangement of ions in the crystal is cubic.

Let us now consider the effect of R_r on the C.N. of the ionic crystal:

(i) If the value of R_r decreases due to decreasing size of cation or increasing size of anion, the crystal will become unstable. In this arrangement all the anions will not be able to touch the outer surface of cation. To do so, anions will move closer to each other and repulsion between them will increase. This repulsion pushes away one or more anions so that remaining anions fit around the cation giving more stable arrangement and coordination number may decrease from 8 to 6 or from 6 to 4.

(ii) It R_r increases either by increasing cationic size or decreasing anionic size, the arrangement will not be stable. In such a case the outer surfaces of the anions will not touch each other. On further increasing the R_r value, anions move far apart from each other and more anions may be accommodated in the packing arrangement. As a result, the coordination number may increase from 4 to 6 or from 6 to 8 This happens with Cl^- ion in NaCl (C.N. 6) and CsCl (C.N. 8).

1.3.4 Limitations of R_r rule:

Though the radius ratio rule is applicable to a majority number of ionic crystals, yet there are exceptions also. Following are some limitations of this rule:

(i) The ionic radii measured are not accurate or reliable because the radius of an ion is not constant but changes depending on its environment. It has been observed that the radius of an ion increases about 3% when C.N. changes from 6 to 8 and decreases about 6% when C.N. changes from 6 to 4. In such cases the radius ratio rule does not apply.

(ii) The R_r rule is valid to the packing of hard spheres of known size only. The anions are not hard due to their large size and are polarizable under the influence of cations thereby forming covalent bonds which are directional in nature and may prefer other orientations.

(iii) This rule does not explain the octahedral lattice arrangement of oxides of large divalent cations such as Pb^{2+}, Sr^{2+}, Ba^{2+} etc. through they are expected to have this arrangement (structure).

(iv) Rb halides (RbX,X = Cl, Br, I) show C.N. 6 at ordinary conditions but adopt the CsCl structure at high pressure. Rr rule is unable to explain this observation.

(v) According to this rule, Li-halides should adopt 4-coordination structure but they crystallize in octahedral lattice thus violating the R_r rule. It may be due to covalent character of halides of lithium.

1.4 LATTICE DEFECTS

The packing of ions (or structure) in the ionic solids given above relate to ideal crystals. An ideal crystal is that which has the same unit cells containing the same lattice points throughout the whole of the crystal.

At absolute zero, most of the ionic crystals show well-ordered arrangement of ions and there are no defects, if the crystals are ideal. With rise in temperature, however, there is a chance that one or more of the lattice sites may remain unoccupied due to the migration of ions from their positions to the interstitial sites or out of the surface of the crystal. This constitutes a defect called lattice or point defect. The lattice defects in the ionic crystals are of three types:

(i) Stoichiometric defects
(ii) Non-stoichiometric defects
(iii) Impurity defects

(i) Stoichiometric defects

In the stoichiometric crystals of the compounds, the ratio of different atoms or ions is exactly the same as indicated by the chemical formulae of the compounds. These compounds obey the law of constant composition. If there is deviation from this ideal or perfect crystal structure, the crystal is said to have the defect or imperfection which arises due to the presence of cationic or anionic vacancies or dislocation of ions in the lattice structure. Accordingly, these defects are of two types:

(A) Schottky defects

If equal number of cations and anions are missing from their lattice sites in an ionic crystal of the type A^+B^- and the electrical neutrality of the crystal is maintained, the resulting defect is called the Schottky defect. This consists of pair (s) of holes in the crystal lattice due to missing cation (s) and anion (s).

This type of defect occurs mainly in the highly ionic compounds were

(i) The cations and anions are of similar sizes
(ii) C. N. of the ions is high, i.e., 6 or 8

Examples: NaCl, KCl, CsCl etc.

The presence of this defect decreases the density of the crystal due to missing ions.

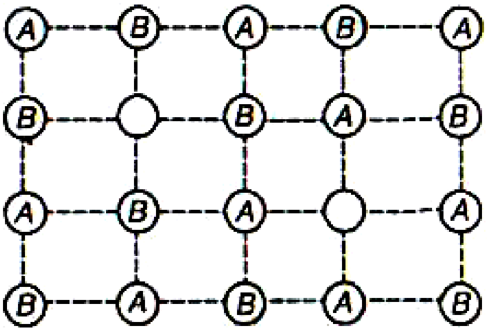


Fig. 1.1 Schottky defect showing one cation and one anion missing

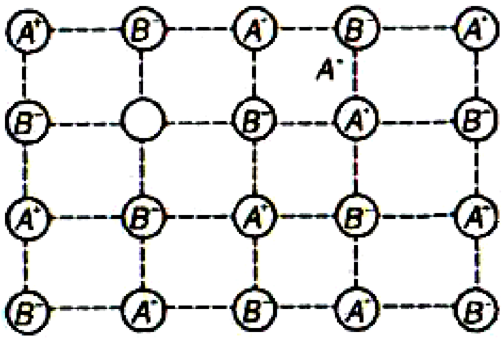


Fig. 1.2 Frenkel defect showing migration of cation to interstitial site

(B) Frenkel defects

This type of defect arises in the ionic crystals due to the departure (or migration) of an ion, usually cation due to its smaller size, from its regular position in the lattice to the vacant interstitialsite between the lattice points. This creates a hole in the lattice. The electrical neutrality and the stoichiometry of the crystal are maintained even after this defect is created. This defect occurs mainly in the compounds where;

(i) There is large difference in the cationic and anionic sizes, i.e.,ions are much larger in size than cations (R_r is low)

(ii) The C.N. of the ions is low, i.e., 4 or 6

Examples: ZnS, AgCl, AgBr, AgI etc.

Lattice vacancies (or holes) occur in almost all the ionic solids. However, Schotlky defect occurs more often than Frenkel defect. The reason being much less energy required to form a Schottky defect than needed to create a Frenkel defect. X-ray diffraction of Nacl crystal has shown that at room temp., this substance has one defect for 10^{15} lattice sites but at 500^0C 10^9 defects and at 800^0C, 10^{11} defects have been observed for the same number of lattice sites.

Consequences of the stoichiometric defects

(i) Crystalline solids having these defects are able to conduct electricity to a small extent when an electric field is applied on them. This happens through an ionic mechanism, i.e., a nearby ion under the influence of electric field moves from its lattice site to occupy the vacancy present in the crystal and creates a new hole. Another nearby ion moves to occupy this vacancy. The process in repeated many times thereby causing a hole to migrate across the crystal which is equivalent to moving a charge in the opposite direction. In alkali halides, the migration of cation only has been detected below 500^0c but both ions migrate at higher temperature thereby increasing the conduction.

(ii) The presence of holes lowers the lattice energy and hence the stability of the crystal. If too many holes are present, then it may cause a partial collapse of the lattice.

(iii)The closeness of similar charges brought about by the Frenkel defect tends to increase the dielectric constant of the crystals.

(ii) Non-stoichiomstric defects

In the non-stoichiometric crystals, the ratio of different atoms or ions present in the compound differs from that which is required by ideal chemical formula of the compound. These compounds do not obey the law of constant composition. In such cases, there is either an excess of metal ions or deficiency of metal ions (or excess of anions) which creates non-stoichiometric defect. The crystal as a whole is neutral but the crystal structure becomes irregular. These defects can exist in a crystal in addition to the stoichiometric defects. These defects are of two types:

(a) Metal excess defects

In these defects the positive ions are in excess. These may arise due to either the absence of anions, i.e., the anions are missing from the lattice sites leaving the vacancies which are occupied by extra electrons to maintain the electrical neutrality or due to the presence of extra cations occupying the vacant interstitial sites in the lattice which are counter balanced by extra electrons also present in interstitial space.

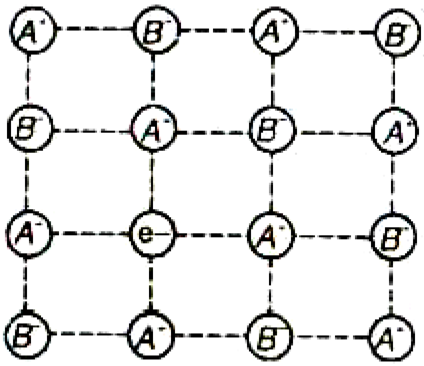


Fig. 1.3 (a) Metal excess defect due to missing of anion

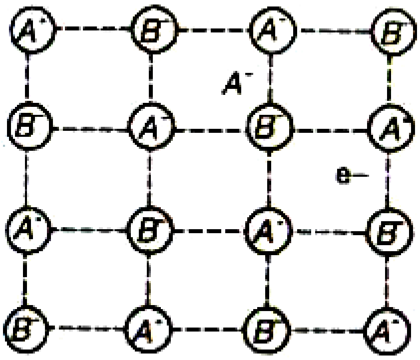
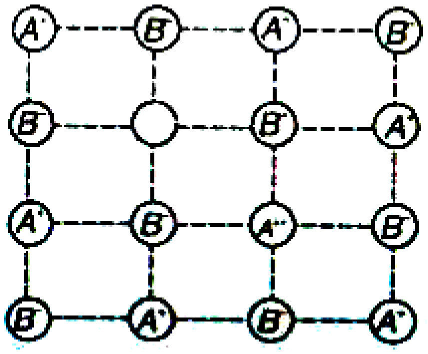


Fig. 1.3 (b) Metal exess defect due to interstitial cation

The anion sites occupied by electrons are called F-centres which are responsible for the colour of the compounds and their paramagnetic behaviour. The first type of metal excess defect is produced by heating the compound with excess of metal vapours. Examples: NaCl, KCl etc. The second type defect is observed in ZnO, CdO, Fe_2O_3, Cr_2O_3 etc.

(b) Metal deficiency defects

These defects occur in the compounds where the metal ion exhibits variable oxidation state, i.e., the compounds of transition elements. The defect is caused either due to missing cations from the regular positions in the lattice thus creating cation vacancies and to maintain the electrical neutrality, the nearby cations acquire extra positive charge (examples FeS, FeO, NiO etc.) or the defect may also be produced by the presence of extra anions in the interstitial sites. The extra negative charge is balanced by extra positive charge on some of the cations. However, due to the larger size of anions, these can hardly be adjusted in the interstitial sites. Therefore, the examples of this type of defect are rare and the defect remains merely a theoretical possibility.



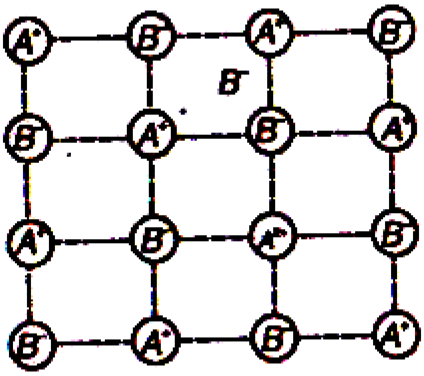


Fig. 1.4 (a) Metal deficiency defect due to missing cation

Fig. 1.4 (b) Metal deficiency defect due to an interstitial anion

Consequences of non-stoichiomtiric defects

Due to the metal excess defects the compounds show electrical conductivity because free electrons present in the crystals can migrate easily under the electric field. Since the number of defects and hence the number of electrons is small, so such compounds show lesser conductance than metals, fused salts or dissolved salts. These compounds, therefore, are termed as semiconductors. These electrons may also be excited to higher energy levels by absorption of certain wavelengths from the white light (visible range) and are responsible for colour of the compounds.

The crystals of the compounds with metal deficiency defects can also act as semiconductors due to the movement of electrons from one ion of normal oxidation state to that of higher oxidation state to create another higher oxidation at its position. This type of movement of electrons between the ions appears as an apparent movement of positive holes thereby making the crystal a semiconductor.

1.5 SEMICONDUCTORS (THERMAL DEFECTS AND IMPURITY DEFECTS)

Semiconductors are the materials which have electrical conductivity at normal temperature which is intermediate between a conductor (like metals) and an insulator. Thus, the semiconductors allow only a portion of the applied electric field to flow through them. According to the band theory which differentiates among conductors, semiconductors and insulators, the semiconductors are the solids which have only a small difference of energy between the filled valence band of electrons and an empty conduction band. This is called band gap. If this band gap can be overcome by any means, *viz.* thermal energy or impurity addition, the electrons from the filled band may go to higher energy empty conduction band in a limited number thereby making the material to conduct electric current.

This is evident from the fact that there are some materials which may be insulators at low temperature, (i.e. absolute zero) but become conductors at elevated temperatures (thermal defects) or on adding certain impurities (impurity defects). These are called semiconductors, e.g. crystals of silicon (Si) and germanium (Ge).

(i) **Intrinsic semiconductors (thermal defects)**

A semiconductor which is obtained by heating an insulator is called intrinsic semiconductor, i.e., the defect in the crystal is produced by thermal energy. Pure silicon, pure germanium or pure grey tin are some examples of materials which act as semiconductors. Actually, at elevated temperatures, sufficient amount of energy is available to break the covalent bonds in the crystal to make some electrons free. These electrons can migrate through the crystal leaving behind positive holes at the site of missing bonds. We can thus conclude that the heat energy promotes some electrons from the filled band into the next higher energy conduction band across the small energy gap and the material becomes conductor. With the rise in temperature the conductivity of semiconductors, therefore, increases.

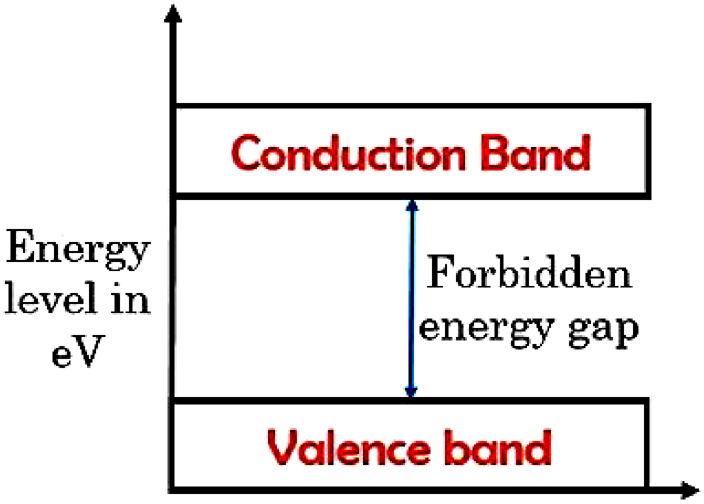


Fig. 1.5 Energy bands in semiconductor

(ii) **Extrinsic semiconductors (impurity defects); n-type and p-type semiconductors**

Certain defects in crystals arise from the presence of chemical impurities called impurity defects. Thus, the materials obtained by adding impurity atoms to the insulators and making them conductors are called extrinsic semiconductors which are said to have impurity defects. For example, the addition of phosphorus, arsenic, boron or gallium atoms to silicon or germanium crystals makes them semiconductors. These are of two types:

(a) **n- type semiconductors (n = normal)**

If a very small amount of (say) arsenic, the element of group 15th, is added as impurity to the pure crystal of silicon, the element of group 14, by a suitable means, the process is called doping and we get the so called arsenic doped silicon. During the process of doping, a minute proposition of Si atoms is randomly replaced by arsenic atoms with one extra electron in their outer shell because only four outer electrons of as are required to form bonds with neighboring Si atoms in the lattice (Si, ns^2p^2& As: ns^2p^3, i.e. Si has 4 and As has 5 valence electrons). At low temp., like absolute zero, these free electrons are located at the as atoms but at normal or elevated temperatures, these free electrons migrate through the crystal lattice to conduct the electricity in the normal way as happens in the metallic conductors. Hence this is called n-type semiconduction and the material so obtained in known as n-type extrinsic semiconductor. In these materials, the impurity atoms act as charge carriers.

(b) **p-type semiconductors (p-positive hole)**

Here the pure crystal of Si is doped with a minute quantity of gallium, an element of group 13 (Ga: ns^2p^1, i.e. 3 electrons in the valence shell) in which some of the Si atoms are substituted by Ga atoms. Each Ga atom forms three electron pair bonds with neighbouring Si atoms. Fourth neighbouring Si atom forms a weak one electron bond with Ga atom which behaves as free electron at Si atom. This creates electron deficiency or positive hole in the lattice site from where the electron is missing. There are as many positive holes as the number of Ga atoms. At absolute zero, the positive hole is located at Ga atom and free electron at Si atom. At elevated or normal temperature, these free electrons move through the crystal from one vacancy site to another thereby leaving new vacancies or positive holes behind. Thus, it appears that the positive holes are moving though actually it is the flow of electrons that takes place to conduct electric current through the crystal on applying the electric field. The flow of electrons and the movement of positive holes occurs in opposite directions. This process is, therefore, called p-type semi conduction and the material so produced in known as p-type extrinsic semiconductor.

1.6 LATTICE ENERGY OF IONIC CRYSTALS

An ionic crystal lattice consists of a large number of cations and anions which are considered to be hard spheres. These ions arrange themselves in a regular pattern to attain a close packed structure. The system gets stabilized by releasing energy during the packing process, i.e. the potential energy of the system is decreased. This released energy is called the lattice energy of the ionic crystal lattice. Similarly, if the ionic lattice has to be broken down into the constituent ions, the energy required is also known as the lattice energy of the ionic crystal. Thus, the lattice energy of an ionic crystal may be defined in two ways depending on the process of packing of ions or their separation from the crystal-

(a) **"The amount of energy released when one mole of gaseous cations and one mole of gaseous anions are brought closer together to their equilibrium position in the stable lattice, from an infinite distance, to form one mole of ionic crystal".** It is denoted by the letter U.**e.g.**

$C^+(g) + A^-(g) \longrightarrow C^+A^-(s)$ + Energy released (-U, exothermic process)

(s = ionic solid) ………… (1.1)

(b) "The amount of energy required to remove the constituent ions of one mole of a solid ionic crystal from their equilibrium position in the crystal to infinite distance".e.g. $C^+A^-(s)$ + Energy released (+ U, endothermic process) $\longrightarrow$ $C^+(g) + A^-(g)$

(s = ionic solid) ………… (1.2)

In both the processes, the magnitude of the energy is same, i.e., energy released = energy required (absorbed) but the symbol of lattice energy is associated with opposite signs. The lattice energy is a quantitative measure of the stability of any ionic solid.

Factors affecting the magnitude of lattice energy

The lattice energy of ionic crystals depends on the following factors:

(i) Charge on the two ions or the product of charges α lattice energy.Greater the charge on the cation or the anion or greater the product of charges on the ions, greater is the magnitude of lattice energy, U. Thus, the lattice energy of ionic crystals containing polyvalent ions is more than those containing monovalent ions, e.g.

Ionic solids	Na^+F^-<	$Mg^{2+}F_2$<	$Mg^2 O^{2-}$
lattice energy (kJ mol^-).	914	2882	3895

and Li^+Cl^- (845 kJ mol^{-1}) < $Ca^{2+}O^{2-}$ (3460 kJ mol^1)

(ii) Interionic distance (r) between the ions or ionic size α $\frac{1}{lattice\ energy}$

Lattice energy is inversely proportional to the interionic distance (r) between the ions. Since r = r_{C+} - r_{A}-, smaller the size of ions, smaller will be the value of r and higher will be value of lattice energy. For example, in case of alkali metal fluorides, the r_{M+} increases from Li^+ to Cs^+ hence energy of these compounds decreases from LiF to CsF:

Ionic solid	Li F >	NaF >	KF >	RbF>	CsF
Lattice energy (kJ mol^-)	1034	914	812	780	744

(iii) Electronic configuration of the cation

Pure ionic crystals are generally formed by the cations having inert gas configuration in their outershell, i.e. ns^2p^6 type. If the cation has non-inert gas/pseudo inert gas configuration in the outer shell, i.e. ns^2p^6 d^{10} type, this involves covalent character in the ionic bond of the crystal thereby increasing the lattice energy of the crystal. For example, AgCl (904kJ mol^{-1}) has larger value of lattice energy than that of NaCl (788kJ mol^{-1}). AgCl has significant covalent character while NaCl is essentially ionic because Ag^+ has $ns^2p^6d^{10}$ outer shell configuration and Na^+ has ns^2p^6 type configuration.

Effect of lattice energy on crystals

(i) **Solubility**- For an ionic solid to be dissolved in a solvent, the strong forces of attraction between its ions (i.e. lattice energy) must overcome by the ion-solvent interaction energy called solvation energy (which is released during this interaction). For non-polar solvents, solvation energy is small so ionic solids do not dissolve in them because lattice energy > solvation energy. In a polar solvent like water, generally, ionic solids dissolve because the solvation energy> lattice energy and thus ion-solvent interaction breaks the ionic solid into constituent ions which are solvated and go into the solution.

There are some ionic solids which do not dissolve in polar solvents, *viz.* water. For example, AgCl in insoluble in water. This is due to greater cohesive forces in AgCl resulting from covalent character of ionic bond. $BaSO_4$, $SrSO_4$, $PbSO_4$ etc. are also insoluble in water due to very high lattice energy of these crystals.

(ii) **Melting point** - As the lattice energy increases, the melting point also increases.

1.7 BORN-HABER CYCLE: EXPERIMENTAL DETERMINATION OF LATTICE ENERGY OF AN IONIC SOLID

Since direct experimental determination of lattice energies are not easy, there are determined by indirect method using a thermo-chemical cyclic process known as Born-Haber cycle. To illustrate this, we take example of formation of compound MX(s) from M(s) and X_2(g). The different steps involved in the formation of MX(s) in crystalline state are as given below;

(i) Sublimation of M (s) to M (g). In this step 1 mole of solid M absorbs energy equal to its sublimation energy, $(\Delta H_{sub})_M$ and is converted to gaseous state, M(g), this is an endothermic process. (Energy is absorbed)

$$\underset{(1mole)}{M\,(s)} + (\Delta H_{sub})_M \qquad \underset{(1mole)}{M\,(g)} \qquad .....(1.3)$$

(ii) Dissociation of X_2 (g) to X (g). In this step half mole of X_2 (g) absorbs energy equal to half of the dissociation energy X_2 (g), $(\Delta H_{diss.})_{X_2}$ and is converted to X (g). It is an endothermic process. (Energy is absorbed):

$$\underset{(1mole)}{X_2\,(g)} + (\Delta\, H_{diss.})_{X_2} \longrightarrow X\,(g) \qquad ....(1.4)$$

(iii) Ionisation of M (g) to M^+ (g). Each M (g) atom absorbs energy equal to its ionisation energy $(IE)_M$ and loses its outermost electron to form M^+(g). It is an endothermic process. (Energy is absorbed):

$$\underset{(1mole)}{M\,(g)} + (IE)_M \longrightarrow \underset{(1mole)}{M^+\,(g)} + e^- \qquad ....(1.5)$$

(iv) Conversion of X(g) into X^- (g). The X (g) atom gains electron given by M(g) above to its outer shell to form X^- (g). In this process X(g) releases energy equal to its electron affinity or affinity energy $(EA)_X$. This is an exothermic process (Energy is released):

$$X (g) + e^- \longrightarrow X^- (g) - (EA)_X \qquad \ldots\ldots\ldots\ldots(1.6)$$

(1mole) (1mole)

(v) Combination of M^+ (g) and X^- (g) to form MX (solid). This is the final step in which M^+ (g) and X^- (g) formed as above combine together to form MX(s). In this process energy equal to lattice energy of MX, $(U)_{MX}$ is released. This is also an exothermic process and energy is released:

$$M^+ (g) + X^- (g) \longrightarrow MX (s) - (U)_{MX} \qquad \ldots\ldots\ldots\ldots(1.7)$$

(1mole) (1mole) (1mole)

The overall change as illustrated above may be represented in one direct step, as;

$$M (s) + X_2 (g) \longrightarrow MX \text{ (crystal)} – (\Delta H_{for})_{MX} \text{ (exothermic process)} \ldots..(1.8)$$

According to Hess's Law, the heat of formation (total enthalpy change) of MX, $(\Delta H_{for})_{MX}$ must be same irrespective of the fact weather it takes place directly in one step or through a number of steps as illustrated above. Hence,

$$-(\Delta H_{for})_{MX} = (\Delta H_{sub})_M + (\Delta H_{diss})_{X_2} + (I_E)_M – (E_A)_X – (U)_{MX} \qquad \ldots\ldots\ldots.(1.9)$$

Here energy terms of endothermic processes are associated with positive sign and those of exothermic processes with negative sign. With the help of the above final equation, we can determine the value of $(U)_{MX}$ if the quantitative values of other energy terms are known and placing these values in the equation along with their algebraic signs. NaCl may be taken as an example. The whole act of above processes can also be given diagrammatically as shown below:

Applications of Born-Haber Cycle:

(i) Born-Haber cycle can be used to obtain any one of the six energy values for the six appropriate equations given above. In particular, the value of electron affinity of the non-metals which is most difficult to determine experimentally can be obtained by this method.

(ii) This cycle is useful in establishing the stability of ionic compounds. It is generally observed that the lattice energy for a compound is known but standard enthalpy of formation is not. So standard enthalpy of formation can be obtained with the help of Born-Haber cycle.

(iii) This cycle helps to understand the disproportionation reactions from lower to higher oxidation states in metal salts, i.e. most metals fail to form stable ionic compounds in low oxidation states such as MnCl, CaCl, AlO etc, If Born – Haber cycle is compared for MCl and MCl_2 (M = Mg, Ca etc). it can be shown that the formation of MCl_2 in favoured over that of MCl. The much higher lattice energy of MCl_2 over that of MCl is the answer to this question.

1.8 FAJAN'S RULES; POLARISATION OF IONS

In an ionic solid, both cation and anion are maintained at an equilibrium distance but when a cation approaches an anion closely, the net positive charge on the cation attracts the electron cloud of anion and at the same time the cation also repels the positive nucleus of anion. The combined effect of these two forces, attractive and repulsive, is that the electron cloud of anion (being larger in size) no longer remains symmetrical but is shifted towards the cation. This is called distortion or polarization of the anion by the cation and anion is said to be polarised. The ability of cation to polarise a nearby anion is called its polarising power.

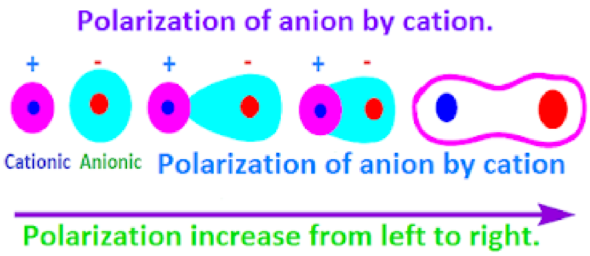


Fig. 1.6 Polarisation of anion

The anion also polarises a cation but due to the larger size of anion, it polarises a cation to a lesser extent (or almost negligible) while the polarisation of anion by a cation is appreciable, i, e. the anions are more susceptible to get polarised. Thus, in general, the cations have high polarising power and anions have more polarisability, i.e. the tendency to get polarised.

Due to the polarisation of anion by the cation, the electron cloud of anion is concentrated between the nuclei of two ions and behaves as if it is being shared by the two ions. Because of this tendency, the ionic bond in the compound passes to the covalent bond, i.e. has covalent character. There are certain factors which affect the polarisation of the ions, These are known as Fajan's rules.

Fajan's Rules: These rules are as follows:

(i) **Charge on the cation or the anion**

Generally, the polarising power of a cation increases with increasing positive charge on it. This is because a cation having higher charge can attract electrons effectively. This can be seen in the anhydrous chlorides, *viz.* NaCl, $MgCl_2$ and $AlCl_3$. With increasing polarising power of cation, the covalent character of the bond between the cation and the anion also increases. Because the covalent compounds have lower melting points, therefore in the above chlorides the polarising power increases in the order: $Na^+ < Mg^{2+} < Al^{3+}$ and accordingly the melting points decrease from NaCl to $AlCl_3$ as given below:

Compound : $Nacl < MgCl_2 < AlCl_3$ (covalent character increases)

Melting point (^0C) : 800 > 712> 575

Similarly, the polarisability of an anion increases with increasing negative charge on it because the outer electron cloud is loosely held by the nucleus of the anion and also the anion can repel its outer electrons more effectively. Thus, the oxide ions, O^{2-} in the oxides of metals are more polarised than (say) F^- ions in the fluorides of the same metals and hence the oxides are more covalent than fluorides having lower melting points.

(ii) **Size of the cation (cationic radii)**

Smaller the cationic size, closer it can go to the anion and more is its polarising power. Thus, with increasing cationic size, the power of cation to polarise an anion decreases which decreases the covalent character of the bond between the ions. This increases the melting points of the compounds. Let us take anhydrous chlorides of group 2nd elements, *viz*. $Becl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $RaCl_2$. The cationic size and melting points of these chlorides are given below:

Metal chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	$RaCl_2$
Cation present	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
Cationic size (Å)	0.31<	0.65 <	0.99 <	1.13 <	1.35<	1.40
Melting point (^{0}C)	405 <	712 <	772 <	872 <	960 <	1000

The covalent character decreases with increasing cationic size and melting point of the compound and hence ionic character increases.

(iii)**Size of the anion (anionic radii)**

Larger the anionic size, more is its polarisalility, i.e. the tendency to get polarsed. With increasing anionic size, the polarisalility also increases thereby increasing the covalent character in the bond and consequently decreasing the melting point of the compounds. Calcium halides may be taken as examples.

Calcium halide	CaF_2	$CaCl_2$	$CaBr_2$	CaI_2	The covalent character of
Anion present	F^-	Cl^-	Br^-	I^-	the halides increase.
Anionic size (Å)	1.36 <	1.81 <	1.95 <	2.16	
Melting point (^{0}C)	1392 >	772 >	730 >	575	

(iv)**Electronic configuration of the cation**

A Cation with pseudo inert gas electronic configuration (i.e., $ns^2p^6d^{10}$) in its outer most shell (18 electrons) has greater polarising power, due to greater Zeff, to polorise an anion than a cation with inert gas configuration (i.e. ns^2p^6) in its outer shell (8 electrons) even if both type of cations have the same size and charge. Thus, the first type of cation will polarise the anion to a greater extent thereby resulting in a more covalent bond with lower melting point of the compound. Let us look at two chlorides, *viz*. AgCl and KCl, Ag^+ ion has $4s^2p^6d^{10}$ outer shell electronic configuration and gives more covalent AgCl (m.p. 455^0C) than KCl (m.p. 776^0C) which has K^+ ion with $3s^2p^6$ outer shell configuration.

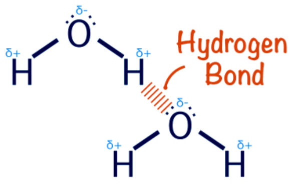
1.9 WEAK INTERACTIONS

The force that holds the atoms together in a molecule is called a chemical bond. These bonds *viz*. ionic bond, covalent bond and coordinate covalent bond are formed due to strong attraction tendency between the species. The resulting products, i.e. the molecules or their aggregates (sometimes) are stable species. But there are instances where only weak bonds exist between/amongst different species, for example within molecules. In these cases, we say that molecular forces are present between the molecules. Such species are said to have formed by weak interactions. Hydrogen bonding and van der waals' forces are common examples of such molecular forces causing weak interactions.

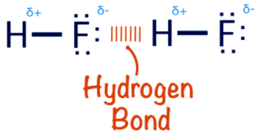
1.9.1 Hydrogen Bonding:

This is a peculiar type of bonding which has been named after an element, hydrogen and operates between the molecules containing hydrogen and an atom of the electronegative elements. It is defined as "**the electrostatic force of attraction between H-atom linked covalently to an atom of highly electronegative element like F, O, N etc. in a molecule and another atom of a highly electronegative elements of the same or different molecule**". Thus, hydrogen bond may be formed either between the molecules of same substance or between the molecules of different substances. It is a weak bond formed by the weak interaction and is represented by dotted line (……).

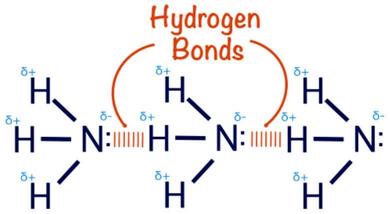
The common examples in which hydrogen bonding exists are:



H_2O (water)



HF (hydrogen flouride)



NH_3 (ammonia)

Hydrogen bonding takes place between the molecules of same substance or different substances.

Cause of hydrogen bond formation

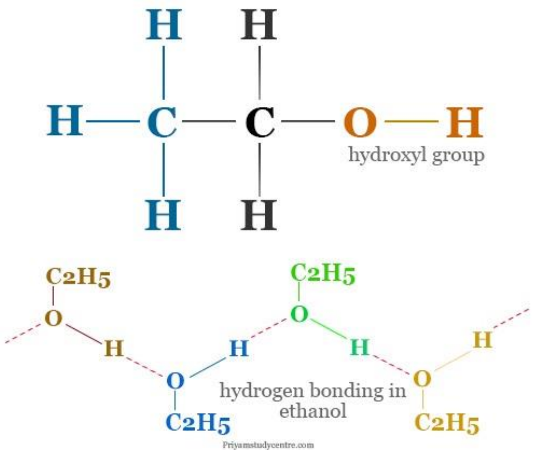
When H-atom is linked with an atom of highly electronegative element (say) A atom (Amay be F, O, N etc.) to form a polar covalent molecule HA, the molecule develops polarity like $H^{\delta+}$-$A^{\delta-}$ due to electronegativity difference between H and A-atoms. If this molecule comes closer to another such molecule, e.g. $H^{\delta+}$-$A^{\delta-}$ or$H^{\delta+}$-$B^{\delta-}$ (B may also be F, O, N etc.), the two dipoles will be linked together by a special type of bond through hydrogen atom, called hydrogen bond: A^{δ}-$H^{\delta+}$----- B^{δ}-$H^{\delta+}$ Here H-atom acts as a bridge between electronegative atoms A and B. This process may be repeated for several molecules to give a cluster of molecules where H– bond is formed between any two adjacent molecules of the aggregate or cluster.

Types of Hydrogen bonding

The hydrogen bonding in the compounds has been found of two types:

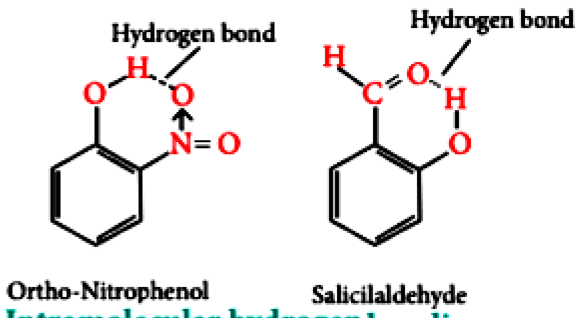
(i) **Intermolecular hydrogen bonding (molecular association)**

This type of H-bonding takes place between several molecules of the same substance or different substances. The molecules get associated as a result of H-bonding to give a large cluster. This process is known as association. The examples of this type of H-bonding are H_2O, NH_3, HF etc. which have been shown above in the beginning of this topic where association of similar type of molecules occurs. Association of C_2H_2 (acetylene)and CH_3COCH_3(acetone) has also been shown above. Other examples of intermolecular H-bonding are given below between the molecules of different substances:



(ii) **Intramolecular hydrogen bonding (**Chelating).

This type of hydrogen bond is formed between the two atoms of the same molecule, one of the atoms being H-atom. It may lead to the linking of two groups of a molecule to form a ring structure, the ring being generally, a five-membered or a six–membered chelate ring (meaning claw). The examples in which intramolecular hydrogen bonding occurs are aromatic organic molecules *viz*. o-nitrophenol, o-chlorophenol, salicylic acid, salicylaldehyde etc.



Intramolecular hydrogen bonding

Strength of H-bond

As has been stated above that this bond is a weak bond since it is merely an electrostatic force of attraction and not a chemical bond. The strength of H-bond increases with increasing electronegativity of the atom attached with H-atom by a covalent bond, i.e. N, O, and F. This bond is much stronger than van der Waals' force but about ten times weaker than a covalent bond. The order of the strength may be given as: van der Waals' forces < H-bond < covalent bond <ionicbond.

Consequences of hydreogen bonding

Hydrogen bonding largely affects a number of physical properties of H-bonded compounds. Some of them are given below:

(i) Melting and boiling points of hydrides of group 15,16 and 17 elements; the hydrides of N, O and F among those of other elements of these groups show abnormal melting and boiling points. This is attribute to the association of molecules caused by the formation of hydrogen bonds. Let us take hydrides of group 16 elements, *viz*. H_2O, H_2S, H2Se & H_2Te. The melting and boiling points of H_2O are exceptionally high in comparison to those of other hydrides which show the increasing trends in these properties, i.e. $H_2O >> H_2S > H_2Se > H_2Te$ (both m.p. and b.p.)

(ii) Density of ice and water; like every solid crystal, ice has definite lattice structure in which water molecules are arranged in such a way that every water molecule is surrounded by four other water molecules in tetrahedral fashion. The central H_2O molecule is linked to four other H_2O molecules by hydrogen bonding (See Fig. 5.7). Because H-bonds are weaker and longer than covalent bonds, this arrangement gives a three-dimensional open cage like structure with large empty space within the structure. This increases the volume and decreases the density of ice. That is way ice floats on water surface.

In liquid form water molecules lie closer together hence the same mass of water has smaller volume and its density is more than that of ice.

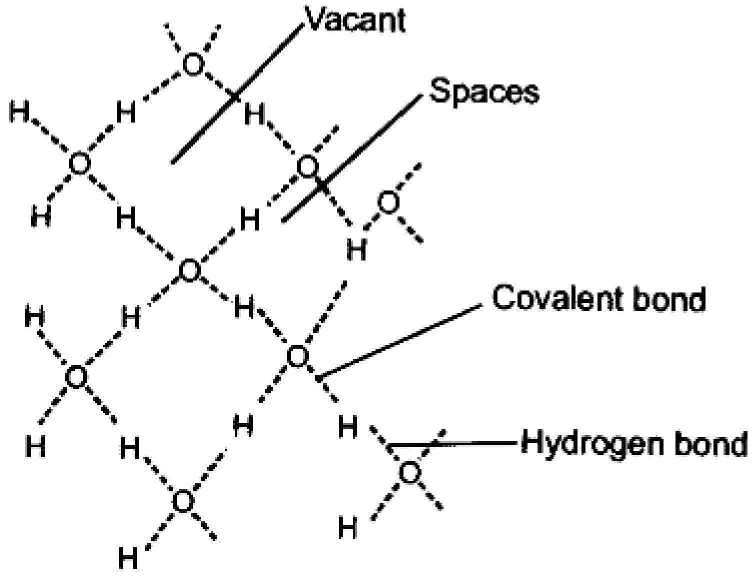


Fig. 1.7 Open cage like crystal structure of ice

(iii) Density of water is maximum a 4^0C; When ice melts, the cage like structure breaks down and the molecules of water are packed closely together, thereby decreasing the volume. The breaking of structure (i.e. hydrogen bonds) is not completed until the temperature reaches 4^0C. Above 4^0C, expansion commences thereby increasing the volume. Thus, the volume of water is minimum and density is maximum (density =) at 4^0c.

1.9.2 Van der Waals' Forces (or Intermolecular forces):

The weak attractive forces between the uncharged atoms or molecules of polar as well as non-polar substances are collectively referred to as van der Waals' forces. The magnitude of these forces is maximum for solids and decreases for liquids and minimum for gases. The crystals whose constituent particles are held together in position by these forces are called molecular crystals. These forces arise from the electrostatic attraction of the nuclei of one molecule for the electrons of a different molecule. The repulsions between the electrons of the two molecules and the nuclei of the two molecules try to counter balance the electrostatic attractions but there is always a small net attractive force. Van der Waals' forces are short range forces. These forces are due to different type of interactions which are given below:

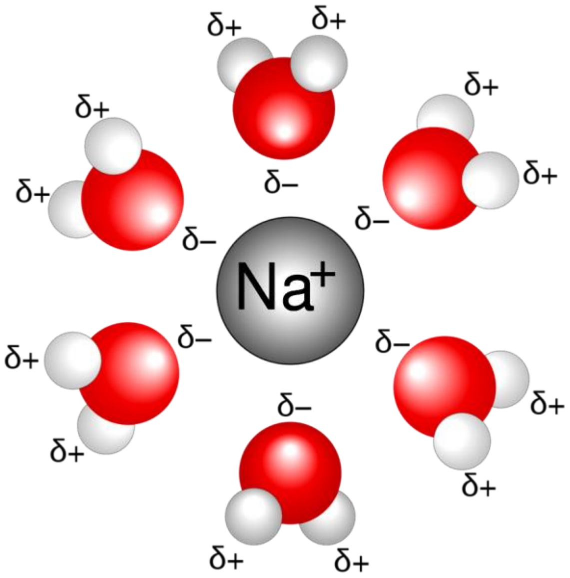


Fig. 1.8 Dipole-dipole interaction (head to tail arrangement)

(i) Dipole-dipole interaction

These interactions are present in polar molecules like NH_3, SO_2, HCl etc. (all gases). Although these molecules are neutral, they have permanent dipole moments and behave as dipoles. Larger the dipole moment of a molecule, greater is the dipole-dipole attractive force between the molecules. Actually, in the dipoles, the van der Waals' forces are due to the electrostatic interactions between the positive end of one dipole and the negative end of the other dipole.

(ii) Ion-dipole interaction

If a charged particle such as an ion is introduced into the neighbourhood of an uncharged nonpolar molecule (e.g. an atom of a noble gas), it will distort the electron cloud of the atom or molecule in the same way as a cation does on a large anion (polarisation). The polarisation of neutral species depends on its inherent polarisability and polarising field afforded by the charged ion (±). Such interactions occur only in solution of ionic compounds in non-polar solvents.

(i) **Dipole- induced dipole interaction**

A dipole can induce an uncharged non-polar species into a dipole as does an ion in ion dipole interaction. Then there occurs dipole induced dipole interaction. These are important only in solution of polar compounds in non-polar solvents.

(ii) **London or dispersion forces** (instantaneous dipole-induced dipole interactions)

These interactions are present in non-polar molecules like N_2, O_2, Cl_2, CH_4 etc. and mono atomic molecules like He, Ne, Ar etc. These molecules do not have permanent dipole moment. The average electronic distribution in a non-polar molecule is symmetric but because of continuous motion of the electrons, at any given instant, the centres of negative and positive charges may not coincide. This causes a momentary distortion of the electronic charge cloud which results in an instantaneous temporary polarity. Then this instantaneous dipole may induce polarity in another non-polar atom/molecule. These two dipoles attract each other by electrostatic forces called London forces.

Since van der Waals' forces are weak and may be easily overcome, the condensed gas readily vapourises and molecular crystals are soft and have low melting points.

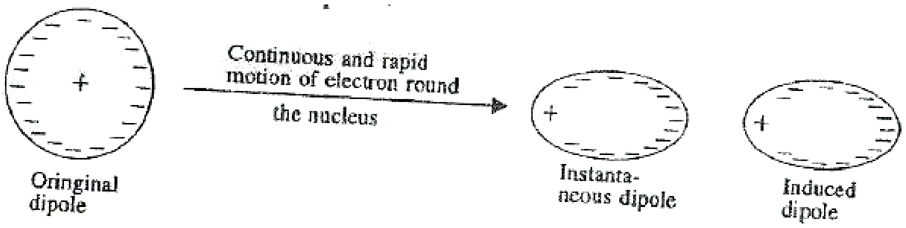


Fig. 1.9 Insanitary dipole dipole induced dipole interaction between non-polar

1.10 SUMMARY

The summary of the present unit is:

- This unit consists of a brief discussion of ionic solids, their characteristics, the interesting topic of radius ratio and its effect, crystal coordination number and limitations of radius ratio rule.
- The lattice defects have been fruitfully discussed and an elaborate account of semiconductors has been given. A concise account of lattice energy, the factors affecting its magnitude and its experimental determination has been discussed.
- The rules governing the covalent character of ionic bond, a brief discussion of H-bond and van der Waals' forces have also been taken care offor the readers.

1.11TERMINAL QUESTIONS

i. The coordiniation number of Cl^- ion in NaCl crystal is:

(a) 4 (b) 6 (c) 8 (d) 12

ii.CsCl crystal has the packing pattern of ions:

(a) Cubic (b) Tetrahedral (c) Octahedral (d) Square planar

iii. If one cation and one anion are missing from their positions in a crystal lattice, the defect produced is:

(a) Schottky defect (b) Frenkal defect (c) n-type defect (d) p-type defect

iv. Which one of the following will have covalent character?

(a) LiCl (b) NaCl (c) KCl (d) CsCl

1. How do the ionic crystals behave towards the electric field applied on them in solid state, fused state and in solution?
2. Give a brief account of n-type semi-conductors.
3. How is lattice energy of an ionic compound related with its solubility in polar solvent?
4. What is polarization of ions?
5. What is the cause of H-bonding in the compounds?
6. We have two cations. One of them has pseudo inert gas outer shell electronic configuration and the other has inert gas configuration in the outer shell. Which of these will cause more polarisation of an anion?

67. Give a brief account of London forces.

Answer

i. (b) ii. (a) iii. (a) iv. (a)

1.12 REFERENCES: LIST OF BOOKS CONSULTED

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UNIT 2: S-BLOCK ELEMENT

CONTENTS:

2.1 INTRODUCTION

The six elements of Group 1(or IA) of the periodic table, *viz.* lithium (Li_3), sodium (Na_{11}), potassium (K_{19}), rubedium (Rb_{37}), caesium (Cs_{55}) and francium (Fr_{87}) are collectively called the alkali metals. This name alkali has been derived from arabic which means ash because the ashes of plants contain the compounds of Na and K in large quantities. In addition to this, these elements form strongly alkaline oxides and hydroxides. The individual elements were named on the basis of their use, origin in plants and spectral characteristics, i.e. colours of spectral lines. The last but radioactive element francium was named after the name of the country where M. Curie worked (France) on her persistence, though she was born in Warsaw (Poland).

All these elements belong to s-block of theperiodic table because in the atoms of these elements the last or differentiating electron enters the s-subshell of the valence shell. These occupy their position at the extreme left portion of the periodic table. Every period of the periodic table commences with an alkali metal.

The alkali metals, due to their reducing nature and their oxides being too reactive to occur in nature, are generally found as cations combined with anions of the most electronegative elements. The less electropositive element (*viz.* Li) is present in nature as silicate minerals and more electropositive elements are found as chlorides. The elements are obtained from the minerals/ores by the electrolysis of their fused salts.

All these elements are metals and have less gradation in their characteristic properties.

2.2 OBJECTIVE

The objective of preparing the course material of this unit,

- On the alkali metals (the elements of Group 1) is to give a summary of the general properties and their trends in the group.

- That is to acquaint the readers with general characteristics of these metals along with their flame colouration and their uses, the nature and behaviour of their oxides and hydroxides, solubility behaviour of their salts and hydration, and complexation of alkali metal ions.
- The anomalous behavior of lithium, its dissimilarity with other alkali metals and similarity with Mg, the element of next group and next period, called diagonal relationship shall be discussed.
- The alkaline earth metals, has been written to give a summarized view of the general characteristics and their gradation in the group and to acquaint the readers about the properties as well as the uses of these metals and their salts in the light of the said properties, the preparation and properties of the halides and hydrides of beryllium, the complexation behavior of alkaline earth metal ions along with the anomalous behavior of beryllium in contrast to other group members.

2.3. GENERAL CHARACTERISTICS OF ALKALI METALS AND THEIR USES

2.3.1 Electronic configuration

The valence (or ultimate) shell electronic configuration of these elements is invariably ns^1 where n denotes the principal quantum number of the valence or outer shell and s is the subshell that receives the solitary differentiating electron while the penultimate shell contains, in general, eight $[(n\text{-}1)s^2P^6]$ electrons (Li is an exception with two electrons in its penultimate shell). On losing the solitary valence electron, the alkali metal atoms are converted into M^+ ions having inert gas configuration in the outer shell. These ions are colorless and diamagnetic in nature. The similarity in the electronic configuration of these elements is responsible for their similar physical and chemical properties. These are all monovalent elements and give colorless ionic salts.

2.3.2 Physical state, hardness and density

The alkali metals, except lithium, are extremely soft solids to be cut by knife and can be readily fused. This is because of the weak metallic bonding among the atoms of the metallic crystals. They are also highly malleable and ductile, freshly cut metals have a bright lustrewhich is quickly tarnished as soon as the metal comes in contact with atmospheric air. In general, these metals have high density due to the close packing of atoms in the metallic crystals but lithium has low density due to low atomic weight. The density increases down the group because atomic weight increases.

2.3.3 Atomic and ionic radii (atomic volume)

Both the atomic and ionic radii (of M^+ ions) increase from the first (i.e., Li) to the last (i.e. Fr) element on moving down the group due to the inclusion of an extra shell of electrons at each step, i.e. in the next element. But the ionic radii are smaller than the atomic radii of the corresponding elements due to the elimination of the outer shell and greater attractive pull of nuclear charge on the outer electrons of the ions. The above statement is evidenced by the values of atomic and ionic radii for the alkali metals given below:

Elements	Li	Na	K	Rb	Cs
Atomic (i.e. metallic radii (Å)	1.55	1.90	2.35	2.48	2.67
Ionic (or Crystal) radii (Å) (for M^+ ions)	0.60	0.95	1.33	1.48	1.69

The group trend of the atomic volume is the same as that for atomic radius due to the similar reason as given above. These elements have the largest atomic radii, ionic radii and atomic volumes among the elements of the respective periods.

2.3.4 Melting points, boiling points and heats of atomization

Alkali metals have low melting and boiling points because of weak inter- atomic bonds in the crystal lattice which decrease further down the group due to increasing atomic size.

These metals also have low heats of atomization and have the same trends as the melting and boiling points due to the same reason as discussed above though the change is sharp at the beginning and a small change is observed in the higher members.

2.3.5 Ionization energies, electron affinities and electronegativities

Alkali metal atoms can lose their solitary electrons from the respective outer shells (i.e. ns^1) with relative ease because the electron in each atom in held weakly with nucleus due to the larger size of the atom. These metals, therefore, have low ionization energies. Further, the ionization energy values decrease on moving down the group from Li to Fr as shown below:

Elements	Li	Na	K	Rb	Cs
Ionisation energy (kJmol^{-1})	520	496	419	403	376

The electron affinity and electronegativity values are also very low for these metals as these have no or very low tendency to attract or accommodate the electrons. The values of these properties decrease down the group though the change is small.

2.3.6 Electropositive (or Metallic) character and reducing properties

The electropositive character of the elements depends on the ease with which the atoms of the elements lose their outermost electrons. Because of their low ionization energy values, the alkali metals have the highest electropositive character among all the elements of the periodic table. With decreasing ionization energy values, the electropositive character also increases down the group for alkali metals, i.e. Li metal is the least electropositive due to highest ionization energy and Cs, the most electropositive with the least ionization energy value among the alkali metals. The last element, Fr has been excluded because all its isotopes are radioactive with very short half-life periods to be available for their detailed study.

According to the trend of electropositive character of alkali metals, their reducing property must also increase down the group, i.e. from Li to Cs but the reverse trend is observed in the reducing properties though the basic nature of their oxides increases from the first to the last element in accordance with the electropositive character. Li has maximum reducing power and Cs has minimum reducing tendency. The anomalous trend in the reducing properties can be explained as follows:

The standard electrode potential is taken as the measure of the reducing properties of these elements. More negative is the standard reduction potential or more positive is the standard oxidation potential of the metal, greater is its tendency to lose electron (s) and stronger is its reducing power.

It has been found that Li has the highest standard oxidation potential (+3.05V) or highest negative standard reduction potential value (-3.05V) thereby making it the strongest reducing agent among all the alkali metals as it can lose the ns^1 electron most readily in aqueous condition.

Actually the conversion of an alkali metal in the solid state, M (s), in contact with water into M^+ (aq.) represents the reducing power of M in aqueous medium which takes place in three steps, i.e. sublimation, M (s) ---- →M (g) requiring sublimation energy, S, which is slightly higher for Li metal than for others, ionization, M (g) $\longrightarrow$ M^+ (g), absorbing ionization energy, I, again which is maximum for Li atom and hydration of the cation, M^+(g) + nH_2O M^+ (aq), liberating hydration energy, H. Anhydrous Li^+ ion, being the smallest in size, gets hydrated to the maximum extent releasing the highest hydration energy content.

The standard oxidation potential (E^0_{ox}) and other energy terms are related as $E^0 = H - I - S$

The hydration energy of lithium being very high, enough to compensates the values of I and S and consequently results in high electrode potential value making it the strongest reducing agent in contact with water though the reducing power of alkali metals in the dry or anhydrous conditions depends on their ionization energy values.

2.3.7 Photoelectric effect (effect of light)

The outermost ns^1 electron in the atoms of alkali metals is so loosely held with the nucleus that even the low energy photons (i.e. light) can eject this electron from the surface of these metals. This property of emitting the electron from the metal surface even on the exposure of light is called **Photoelectric effect** and permits the application of these metals (especially K and Cs) in the photoelectric cells which are sensitive particularly to blue light. Li metal with the highest ionization energy does not show this effect.

2.3.8 Flame colouration and use

The alkali metals give characteristic colour in Bunsen flame, i.e. Li- crimson red, Na- yellow, K-violet, Rb and Cs – also violet.

The reason for this flame colouration being when an alkali metal or its any compound is heated in the flame, the outer electron can be excited to higher energy levels by absorbing some energy from the flame. When the excited electron returns back to the ground or original level, the absorbed excitation energy is released in the form of light in the visible region of the electromagnetic spectrum and colour is imparted by the metal to the flame. Since for the same excitation energy, the electrons of the atoms of different alkali metals are excited to different higher energy levels depending on the tightness with which the nuclear charge holds the outer electron (s) with itself. Thus, in Li, electrons are excited up to lower levels and in other metals up to higher levels and the released energy as a consequence goes on increasing from Li to Cs and accordingly the colours are observed for them, i.e. for Li crimson- red (due to lower energy) and for Cs, violet (due to higher released energy).

This property of alkali metals to impart colouration in the Bunsen flame has been used to detect their presence in the salts by the so-called flame test and to estimate Na and K quantitatively in plant samples.

2.3.9 Polarizing power of alkali metal ions

On approaching nearer to an anion, the alkali metal cations attract the anionic charge and repel the nuclei of anions thereby distorting or polarizing the anion. This results in the passage of ionic bond in the compound to covalent bond. This effect has been found to be more pronounced in smaller alkali metal cations, i.e. Li^+ ion (all alkali metal cations have the same charge). That is why Li salts are covalent in nature and insoluble in water but soluble in organic solvents. While others form ionic compounds which are freely soluble in water.

2.3.10 Action of liquid ammonia

The alkali metals dissolve in liq. NH_3 without the evolution of H_2 to give blue colour in dilute solutions. This is due to the excitation of free electrons to higher energy level to give an absorption band in visible range of the spectrum and therefore, the solution looks blue due to transmitted light. The concentrated solutions are good conductors of electricity due to the presence of ammoniated electrons, $[e(NH_3)]^-$ and are bronze coloured.

2.3.11 Uses of alkali metals

(a) The most important use of lithium is in making alloys, e.g., on adding to the alloys of magnesium, it improves their tensile strength and resistance to corrosion.

(b) Lithium is also used as deoxidizer in the purification of nickel and copper.

(c) It is an ingredient of high energy fuels employed for the propulsion of intercontinental rockets (i.e., thermonuclear energy).

(d) Compounds of lithium are used in glass and pottery industry to increase the strength and resistance of glass and to prevent the surface cracking of pottery.

(e) Li-citrate and salicylate are used in medicine for gout.

(f) LiOH is used in making high quality lubricating greases which can withstand extreme temperature variations.

(g) Sodium is used in the laboratory as a reducing agent in the form of sodium amalgam and it is also used for detecting N, S and halogens (Cl, Br, I) in organic compounds.

(h) In metallurgy, this metal is employed for the extraction of many elements like Si, B, Mg etc.

(i) It is largely used in industry for the production of artificial rubber, dyes and drugs.

(j) Its compound, Na_2 CO_3, is used as a laboratory reagent, for laundry works and as domestic cleansing agent as well as in softening of hard water.

(k) $NaHCO_3$, another compound of Na, is used in medicine (as soda bicarb) to neutralize the acidity in the stomach and as baking soda.

(l) Potassium and caesium metals are used in photoelectric cells.

(m) The sodium-potassium alloy is used in the special thermometers employed for measuring high temperature.

(n) $KClO_3$, an important compound of potassium is used as oxidizing agent in the laboratory in fireworks as well as match industry.

2.4. OXIDES AND HYDROXIDES OF ALKALI METALS

2.4 1 Oxides

Alkali metals react with oxygen or air rapidly and get tarnished due to the formation of their oxides on the surface of the metals. That is why alkali metals are stored in kerosene or paraffin oil.

When these metals are burnt in oxygen or air, they yield either of the three types of oxides: monoxide (M_2O) or peroxide (M_2O_2) (Na, K, Rb, Cs) or super oxide MO_2 (K, Rb, Cs) depending on the nature of the metal. The oxides of these metals can also be obtained by dissolving the metal in ammonia and treating the solution with the required amount of oxygen. Lithium does not form higher oxides because Li^+ ion is too small and has much stronger positive field around it than other alkali metal ions. This strong positive field near one oxygen anion restricts the spread of negative charge towards another oxygen atom making the formation of higher oxide difficult.

Generally, under normal conditions, following oxides of different metals can be obtained:

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (Monoxide only)}$$

$$4Na + O_2 \longrightarrow 2\,Na_2O \quad \text{and}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \text{ (monoxide and peroxide both)}$$

$$M + O_2 \longrightarrow MO_2 \text{ (M = K, Rb, Cs; superoxide, generally)}$$

Since the normal oxide of alkali metals other than that of Li are not formed by the direct reaction between the metal and O_2 or air, they are obtained by indirect methods, e.g.

$$2Na_2O_2 + 4Na \rightleftharpoons 4\,Na_2O \text{ (reversible reaction)}$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

The normal monoxides are strongly basic and highly soluble in water giving alkaline solutions by proton exchange $O^{2-} + H_2O \rightleftharpoons OH^- + OH^-$ (hydrolysis of oxide ion to hydroxide) and disproportionate to peroxide and metal vapours when heated

$$2Na_2O \xrightarrow{\Delta} Na_2O_2 + 2Na \text{ (vapours)}$$

The peroxide of sodium yields H_2O_2 on treatment with dilute acids in cold and superoxide (NaO_2) by heating with O_2.

$$Na_2O_2 + 2H^+ \longrightarrow H_2O_2 + 2Na^+$$

$$Na_2O_2 + O_2 \longrightarrow 2NaO_2$$

In general alkali metal peroxides and super oxides are strongly oxidizing agents and react with water and dilute acids to H_2O_2 and O_2 :

$$O_2^{2-} + 2H_2O \longrightarrow 2OH^- + H_2O_2$$

$$O_2^{2-} + H_2SO_4 \longrightarrow SO^{2-}_4 + H_2O_2$$

` $$2O_2- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$$

$$4O_2^- + 2H_2SO_4 \longrightarrow 2SO_4^{2-} + 2H_2O + 3O_2$$

2.4.2 Hydroxides

All alkali metals form ionic hydroxides with the general formula MOH and can be prepared by treating the monoxides or metals with water:

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

$$M_2O + H_2O \longrightarrow 2MOH \qquad (M = \text{alkali metals})$$

The reaction between water and the metal, except Li, is highly explosive hence this method is not generally used for the preparation of hydroxides. These are obtained by the electrolysis of aqueous solutions of the chlorides.

These hydroxides are highly soluble in water and alcohol and ionize to yield OH^- ions and thus behave as strong bases or alkalies in solution. The solubility increases and the hydroxides become more and more basic on moving down the group, i.e. from Li to Cs due to an increasing trend in electropositive character. LiOH is less basic and less soluble in water.

The hydroxides other than LiOH are thermally stable even at very high temperature:

$$2\,LiOH \xrightleftharpoons{780^0C} Li_2O + H_2O\uparrow$$

$$2NaOH \xrightarrow{1300^0C} \text{stable but sublimes}$$

The alkali metal hydroxides are strong bases and react with acids, acidic oxides and amphoteric oxides to form salts:

$$2MOH + H_2SO_4 \longrightarrow M_2SO_4 + 2H_2O$$

$$2MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$

$$2MOH + Al_2O_3 \longrightarrow 2MAlO_2 + H_2O$$

The hydroxides absorb CO_2, even in traces, from the air to form carbonates:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

2.5 SOLUBILITY AND HYDRATION OF ALKALI METAL COMPOUNDS (IONIC HYDRATION)

The terms, solubility and hydration of compounds are related with the lattice energies and hydration energies of the compounds. The lattice energy is a direct and quantitative measure of ionic bond strength of any compound. When an ionic compound is placed in water (or any polar solvent), the ionic charges of the compound attract the polar molecules (called dipoles). The ions of the compound after separation combine with water (solvent) molecules. This process is called hydration (solvation). For example, when NaCl is placed in water the positively charged Na^+ ions attack the partially negatively charged oxygen atoms ($O^{\partial-}$) and the negatively charged Cl^- ions attract the partially positively charged hydrogen atoms ($H^{\partial+}$) of water molecules. Energy is released in this process which is known as hydration energy. If the hydration energy is more than the lattice energy of the compound, the ionic bonds will be broken and the solid compound dissolves, i.e. the ions go into solution as hydrated ions. But if the hydration energy is less than the lattice energy of the compound, the ionic compounds remain insoluble. It may be concluded that the solubility of ionic compounds depends on the difference between their lattice energies and hydration energies. The large lattice energy of LiF makes it insoluble in water. Thus, it can be said that lattice energy and ionic hydration are intimately related with each other. The alkali metal ions are hydrated to different extents, e.g. anhydrous Li^+ ion being smallest in size is hydrated to the maximum extent and anhydrous Cs^+ ion is hydrated to the minimum extent due to its largest size among these ions. After hydration $Li\ (aq)^+$ ion is the largest and $Cs\ (aq)^+$ ion is the smallest in size.

2.6. COMPLEXATION OF ALKALI METAL IONS

The alkali metal ions have the least tendency of complexation with normal ligands among the elements of the periodic table. This is mainly due to:

(i) Relatively larger ionic size of the alkali metal ions
(ii) Low charge densities (charge/size) of the ions
(iii) Non-availability of the vacant d-orbitals of right energy to accept lone pairs from the ligands
(iv) Very high basicity of the metals and
(v) Non-availability of variable oxidation states in the ions.

However, a few complexes of these elements have been formed but the complex forming ability decreases down the group from lithium to caesium. Alkali metals form complexes with oxygen containing multidentate chelating ligands such as salicylaldehyde, acetylacetone etc. (**Fig. 2.1**) given below:

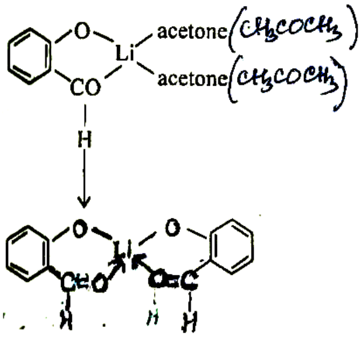


Figure 2.1

An important class of complexing agent, the crown ether, has been synthesized known as dibenzo-18-crown-6 containing two benzene rings and 18 atoms making a crown-shaped ring, six of them being oxygen atoms. These six oxygens may form complexes with a metal ion, even with a large alkali metal ion. The bonding of the metal ion to the polyether is largely electrostatic. Polyethers having different sizes are known. The size of the metal ion and that of the hole in the centre of Polyethers must be comparable for close fitting of the metal ion in the ring.

Benzo-12-crown-4 has a ring of 12 atoms, four of which are oxygens. A crown-4 polyether forms stable complex with Li^+ or Na^+ ion where as a crown-6 polyether prefers K^+ ion with unusual coordination number.

The polyethers act as ion carriers inside living cells to transport ions across cell membranes and thus maintain the balance between Na^+ and K^+ ions inside and outside cells.

The crown ethers also form some unusual complexes called electrides. These are paramagnetic such as Cs^+ (crown ether)e-. Because of very large size and hydrophobic character of the complexed cation, crown ether complexing can lead to salts becoming soluble in organic solvents containing no donor atoms, e.g. [K(crown-6)]OH and K (crown-6)]MnO_4 in benzene and toluene, respectively.

Three dimensional equivalents of crown ethers contain nitrogen atoms to obtain branching and to provide extra donor sites. They are called cryptands as they hide the cation. A typical cryptand-222 has been shown in (**Fig.2.2**) below. All the N and O atoms of this compound act as donors, the conformations at the nitrogen atoms being the ends, i.e. the lone pairs inwards cryptands shield the cations such thatthey are complexed more effectively than crown ethers. The cryptands-221 and -222 form their more stable alkali metal complexes with Li^+, Na^+ and K^+ respectively in terms of enthalpy.

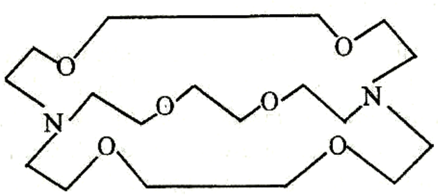


Fig. 2.2 Cryptand-222

The action of cryptand-222 on sodium in ethylamine solution produces [Na (cryptand-222)]$^+$ Na^-, a golden yellow solid. This shows the striking application of cryptand-222 in shifting the disproportionation equilibrium to the right-hand side:

$$2Na \longrightarrow Na^+ + Na^-$$

Also, the salts containing the ions K^-, Rb^- and Cs^- have also been prepared.

2.7ANOMALOUS BEHAVIOUR OF LITHIUM

Lithium, the first element of the alkali metal series, though shows most of the characteristic properties of the alkali metals (Group IA) as has been discussed above yet it also differs from them in many respects. This anomalous behaviour of lithium may be attributed to the following points:

(i) Very small size of Li and Li^+ ion as compared to those of others.
(ii) High charge density (charge/size) and high polarizing power of Li^+ ion.
(iii) Higher electronegativity and ionization energy of Li than other alkali metals and less electropositive character.

The main points of difference are summarized below:

i. Lithium is harder and more ductile metal than the other alkali metals with higher melting and boiling points.

ii. Chemically it is less reactive than other alkali metals. Thus, it is attacked by water only slowly even at 27^0C while other metals react instantly and vigorously even at lower temperature. Also, Li is not attacked by air easily and does not lose its lustre even on melting.

iii. Li is the only alkali metal which forms nitride (Li_3N) by the reaction with nitrogen. Other alkali metals do not react with N_2.

iv. On burning with O_2 or air, Li gives only monoxide (Li_2O) while other alkali metals generally give peroxides or superoxides, i.e. M_2O_2 and MO_2.

v. Lithium halides, being covalent in nature, are soluble in organic solvents while other alkali metal halides are not.

vi. Li_2O is much less basic (almost amphoteric) in nature while monoxides, M_2O, of other alkali metals are highly basic. Therefore, LiOH is a weak base, MOH of other alkali metals are strong bases.

vii. Most of the lithium salts are only sparingly soluble in water while the corresponding salts of other alkali metals are freely soluble. This is either because of high lattice energy or covalent nature of Li-salts.

viii. The carbonate and hydroxide of lithium are thermally less stable and decompose to give Li_2O:

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

The same salts of other alkali metals are stable to heat and do not decompose.

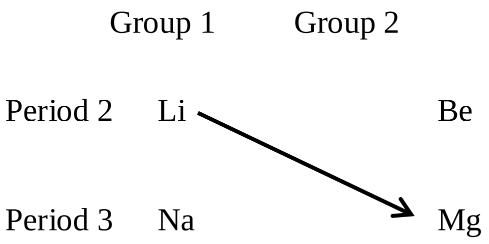
ix. Li- nitrate on heating decomposes easily to evolve NO_2 and O_2 but other metal nitrates are converted to nitrites and O_2:

$$4\ Li\ NO_3 \xrightarrow{\Delta} 2\ Li_2O + 4NO_2\uparrow + O_2\uparrow$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$$

2.7.1 Diagonal relationship of Li with Mg

Though lithium, the first element of alkali metal series and the member of Group 1 and period 2, shows a number of dissimilarities from other alkali metals yet it exhibits close resemblance with Mg, the element of the next higher group (Group 2) and the next higher period (Period 3) located diagonally opposite to it in the periodic table, in many respects. This sort of relationship between the two elements in the periodic table is called diagonal relationship:



The resemblance between these diagonal neighbours is because of:

(i). Close similarity in atomic and ionic sizes, i.e.

$$r(Li) = 1.34Å, \qquad r(Mg) = 1.36Å$$

$$r(Li^+) = 0.60Å, \qquad r(Mg^{2+}) = 0.65Å$$

(ii). On moving down the group, the periodic properties, *viz*. ioniziation energy and electronegativity decease and electropositive character increases from Li to Na But the same properties have the reverse trend on moving across the period from Na to Mg, i.e. the first two properties increase and the last one decreases. The net effect is that both Li and Mg have almost the same values of these parameters.

Some points of similarity between Li and Mg are as follows:

a. Both the elements have almost similar polarizing power due to small size and high charge density of the ions.

b. Both Li and Mg decompose water only slowly liberating H_2.

c. Both the elements combine with nitrogen to give nitrides:

$$6Li + N_2 \longrightarrow 2Li_3N$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

d. The chlorides of both these elements are deliquescent and are separated from aqueous solutions as hydrated crystals, i.e. $LiCl.2H_2O$ and $MgCl_2\,6H_2O$

These chlorides are also hydrolyzed in the similar way in water unlike those of other alkali metals.

e. The nitrates, carbonates and hydroxides of both Li and Mg decompose on heating to evolve O_2 & NO_2 (nitrates), CO_2 (carbonates) and H_2O vapours (hydroxides):

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2\uparrow + O_2\uparrow$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2\uparrow$$

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$$

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

2.8 ALKALINE EARTH METAL

The alkaline earth metals, the members of Group 2 (or IIA) of the modern periodic table, consist of the six elements, *viz.* beryllium (Be_4), magnesium (Mg_{12}), calcium (Ca_{20}), strontium (Sr_{38}), barium (Ba_{56}) and radium (Ra_{88}). The name alkaline earth metals was taken from the fact that in old days the word 'earth' was applied for the metallic oxides and the oxides of three of these metals, *viz.* calcium, strontium and barium were known much earlier than the metals themselves and occurred in nature as lime (CaO), strontia (SrO) and baryta (BaO). These oxides were called alkaline earths since they were alkaline in nature and produced alkaline solution in water as well as they existed in nature as the earths (oxides).

Later when these elements were discovered, they were named as alkaline earth metals. After the discovery of other members of this group, v*iz*. Be, Mg and Ra, this term was used to include all the elements of the group (Group 2).

However, because radium corresponds to the alkaline earth metals in its chemical properties but it is a radioactive element, therefore, it is studied separately along with other radioactive elements. These elements are also said to belong to s-block of the elements because in the atoms of these elements too, like group IA elements (or alkali metals), the differentiating or last electron enters the s-subshell of the ultimate shell. These elements are also placed at the extreme left portion of the periodic table after the alkali metals.

These metals are never found free (in metallic form) in nature because of their active reducing behaviour like alkali metals and react readily with a variety of non-metals. Magnesium is the second most abundant metallic element in the sea water and also occurs in a variety of silicate minerals. Beryllium occurs as beryl minerals. Calcium is found abundantly as carbonate in marble, lime stone and chalk. Strontium and barium are found most frequently as the sulphates. Radium is a member of decay chain of U^{238}. All these metals can be prepared by the electrolysis of their halides or by the reduction of their oxides with the available strong reducing agents.

2.9 GENERAL CHARACTERISTICS OF ALKALINE EARTH METALS AND THEIR USES

The general characteristics of alkaline earth metals can be summarized as follows:

2.9.1 Electronic configuration

The valence (or ultimate) shell electronic configuration of the metals of the group IIA is invariably ns^2 where n is the principal quantum number or the shell number of the ultimate shell and s denotes the subshell which receives the last electron. The penultimate shell, like alkali metals, except Be has eight, i.e. $(n-1)s^2p^6$, electrons in these elements. Be has two electrons i.e. $(n-1)s^2$ in the penultimate shell. If the valence electrons are ejected from the metal atoms of these elements, they are converted to M^{2+} ions having the inert gas configuration in the outer shell. These ions are colourless and diamagnetic in nature, i.e. the elements form colourless ionic salts and are bivalent. Due to their alike electronic structure, these elements resemble closely in their physical and particularly in chemical properties.

2.9.2 Physical state, hardness and density

All these metals are silvery white solids exhibiting grayish white metallic lustre when freshly cut but tarnish soon after their exposure to air. They are also malleable and ductile but less than alkali metals and are harder than alkali metals. This is because of stronger metallic bonding in the crystal lattice. The hardness of these metals increases with increasing atomic number. They have high electrical as well as thermal conductivity because the two valence electrons can move easily through the crystal lattice.

These metals have higher density than alkali metals because they can be packed more tightly due to greater charge and smaller radius. The density first decreases up to calcium and then increases, i.e., there is irregular trend due to different crystal structures of the metals.

2.9.3 Atomic and ionic radii and atomic volume

The atomic radii of these elements, though large enough, are smaller than those of the neighbouring alkali metals in the same period due to higher nuclear charge of the atoms which tends to draw the valence electrons inwards. The atomic radii increase down the group from Be to Ra due to the inclusion of an extra shell of electrons at each step.

The ionic radii of M^{2+} ions of these elements are smaller than those of the alkali metal ions and larger than those of other elements of the respective periods (with the same charge). These radii also have the increasing trend as that of atomic radii down the group. This is clear from both atomic and ionic for these elements as given below (Table 2.1):

Elements	Be	Mg	Ca	Sr	Ba	Ra
Atomic radii (Å)	1.12	1.60	1.97	2.15	2.22	----
Ionic radii (Å)	0.31	0.65	0.99	1.13	1.35	1.40

(of M^{2+} type ions)						

Table 2.1 Atomic and Ionoc radii of alkaline earth metals

The atomic volume of these elements has been found to increase on moving down the group from Be to Ra as happens in the case of atomic radii.

2.9.4 Melting and boiling points and heat of atomization

Both the melting and boiling points do not show regular trend. These are, however, higher than those of the neighbouring alkali metals due to smaller size as compared to those elements and much stronger bonds in solid state due to the presence of two electrons in the valence shell. Heat of atomization decreases from Be to Ra. Though it falls considerably from Be to Mg but the difference is small in the subsequent elements. This reveals that the metallic bond strength is maximum in the case of beryllium among all the alkaline earth metals.

2.9.5 Ionization energies and oxidation states

These elements have higher ionization energy values (1st ionization potential) than those of the neighbouring alkali metals. This is due to the smaller size and greater nuclear charge of the atoms of these elements as compared to alkali metals which exert stronger pull-on outer electrons. The outer ns^2 electrons of these elements are removed from their atoms one by one in steps on supplying energy and thus two ionization energy values are observed for each element. The first as well as the second ionization energy values of these elements decrease on going down the group from Be to Ba as expected because of increasing atomic size in the group. However, the ionization energies of Ra are slightly higher than those of Ba but no satisfactory explanation is available for this anomaly. Thus, beryllium has the highest values and barium has the lowest values of ionization energies among these elements. It has been noticed that the second ionization energy is approximately double to the first ionization energy for each element as is evident from the following table:

Elements	Be	Mg	Ca	Sr	Ba	Ra
Ionization $IE_{(1)}$ Energies $IE_{(2)}$ (kJmol^{-1})	899.5	738	590	549.5	503	509.5
	1757	1451	1145.5	1064	965	979

Table 2.2 First and Second Ionization Energies of Alkaline Earth Metals

It is interesting to note that in view of the much higher second ionization energy values of these elements than the first ionization energy values, it appears that these metals would prefer to form M^+ ions rather than M^{2+} ions. However, in actual practice, these metals form only M^{2+} ions, *viz*, Be^{2+}, Mg^{2+} etc. If ionization energy were the only factor involved, they would have formed only M^+ ions rather than M^{2+} ions but actually they only form M^{2+} ions. This anomaly has been explained by the fact that the M^{2+} ions are excessively hydrated and a large amount of energy known as energy or enthalpy of hydration is released in the process which more than counterbalances the higher value of the second ionization energy in each case. The hydration energy values have been given below and could be compared with IInd I.E. values of the elements:

Elements	Be	Mg	Ca	Sr	Ba	Ra
Enthalpy of hydration (kJ mol^{-1})	-2455	-1900	-1565	-1415	-1275	-

Table 2.3 Enthalpy of hydration of Alkaline earth metals

2.9.6 Electropositive character and reducing property

Because of their large size and having comparatively low ionization energies, the alkaline earth metals are strongly electropositive elements as the change $M \longrightarrow M^{2+} + 2e^-$ can be brought about fairly readily. However, these are less electropositive than group IA elements of their respective periods. That is why these metals do not show photoelectric effect on exposure to light. Among these elements beryllium has the least electropositive character and hence also has least tendency to form Be^{2+} ions. That is why its compounds with nitrogen, oxygen, sulphur and halogens are covalent whereas the corresponding compounds of other members of this group are ionic. Also, the hydroxides of these elements become more and more basic as we move from Be to Ba.

The reducing properties (based on values of standard electrode potential) are also high for these elements which increase down the group from Be to Ba though this property is lower than that exhibited by alkali metals. This infers that these metals are less electropositive and weaker reducing agents than the alkali metals of the corresponding periods inspite of high enthalpy of hydration because of their higher sublimation and ionization energies.

2.9.7 Flame colouration

The alkaline earth metals and their salts impart characteristic colours to the Bunsen flame, *viz*. calcium-brick red, strontium-crimson red, barium-apple green and radium-crimson red. The reason for this is that when energy is supplied to these elements or their compounds by putting them in the flame, their outer electrons are excited to higher energy levels by absorbing energy. On returning back to the ground or original level, the electrons emit or release the absorbed energy in the form of visible light of a particular wavelength which appears in the form of characteristic colours as given above.

In the atoms of Be and Mg elements and their salts because of their smaller size and stronger force of attraction between the outer electrons and the nuclear charge, these electrons are not excited to the higher levels by the energy of the flame which is unable to overcome the attractive force. Therefore, they do not give any colour to the Bunsen flame.

2.9.8 Polarizing power of alkaline earth metal ions

The polarizing power of bivalent cations of the group IIA metals for a given anion goes on decreasing from Be^{2+} to Ra^{2+} due to increasing ionic size. This results in the formation of covalent compounds by smaller cations, as expected, with an anion. This is the reason why most of the Be-compounds are covalent in nature.

2.9.9 Hydration of alkaline earth metal ions

The M^{2+} ions of alkaline earth metals are extensively hydrated to form the hydrated cation, $[M(H_2O)x]^{2+}$ and in this process a large amount of energy called energy or enthalpy of hydration is released as has already been discussed (see subsection **v**). The hydration energy values and extent of hydrationof the cations decrease with increasing ionic radii of anhydrous M^{2+} ions, i.e. Be^{2+} to Ba^{2+} ion.

The hydration energy values for alkaline earth metals are higher than those of the alkali metals in the respective periods and hence the alkaline earth metal compounds are hydrated to the larger extent. For example, magnesium and calcum chlorides exist as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$, respectively while NaCl and KCl do not form hydrates.

2.9.10 Solubility in liquid ammonia

Like alkali metals, alkaline earth metals also dissolve in liquid ammonia yielding coloured solutions. On evaporation, the metal-ammonia solutions give hexa-ammoniates, $[M(NH_3)_6]$. These ammoniates are good conductors of electricity and decompose at high temperature. The tendency of ammoniate formation is decreased with increasing size of metal atom, i.e., down the group.

2.9.11 Uses of alkaline earth metals

(a) Beryllium (pure) is used in the nuclear reactors as the source of neutrons.

(b) Due to high permeability to X-rays, Be-sheets are used for windows of X-ray tubes. It is also used for imparting hardness to alloys, e.g., Cu-Be alloy.

(c) Mg is used as a structural metal because of its lightness and alloying property with other metals.

(d) Being a powerful reducing agent, Ca is used in the extraction of Be, Cr and Th metals from their oxides which are otherwise difficult to be reduced by carbon.

(e) When alloyed with lead, Ca is used as cable covering.

(f) Since, Ca and Ba have great affinity for oxygen and nitrogen, these are used for removing air from vacuum tubes and as deoxidizer in the manufacture of steel.

(g) Sr and Ba are also used as scavengers for removing last traces of air in steel production and from vacuum tubes.

(h) Various Ca-salts are used industrially as follows:

(i) CaO: manufacture of bleaching powder, calcium carbide and as basic lining in furnaces.

(ii) Ca $(OH)_2$: preparation of sodalime $[Ca(OH)_2 + NaOH]$ which is a good adsorbent for a number of gases and as a decarboxylating agent in organic chemistry.

(iii) Gypsum: manufacture of plaster of paris.

(iv) $CaCO_3$: manufacture of cement.

(i) Ba salt, $BaSO_4$ is used to prepare white pigment-lithopone $(BaSO_4 + ZnS)$

(j) Ra-salts are used in radiotherapy for the treatment of cancer and in luminous paints.

2.10 HALIDES AND HYDRIDE OF BERYLLIUM

2.10.1 Preparation and properties of Be-halides:

Beryllium reacts directly with halogens at appropriate elevated temperatures to form halides, Be X_2:

$$\mathrm{Be} + \mathrm{X}_2 \xrightarrow{\text{Heat}} \mathrm{Be\ X}_2$$

BeF_2, though covalent, yet is more soluble in water than other alkaline earth fluorides.

Anhydrous $BeCl_2$ is made by the action of carbon tetra chloride on BeO at high temperature of about 800^0C (This is a standard method for preparing metal chlorides).

$BeCl_2$ has lower melting and boiling points as well as much lower electrical conductivity in the fused state than other alkaline earth metal chlorides because of its covalent nature (due to high polarization power of Be^{2+} ions). This is hygroscopic and fumes in air, is soluble in some organic solvents. $BeCl_2$ is hydrolysed in aqueous solution and makes it an acidic solution.

$$BeCl_2 + 2H_2O \xrightarrow{\text{Heat}} Be\,(OH)_2 + 2HCl$$

In the gas phase, $BeCl_2$ is a linear symmetric molecule which is consistent with a description of the bonding in terms of sp-hyprid orbitals around the Be-atom. In the solid state, beryllium chloride displays the Be-Cl-Be bridged structure in which each Be atom is tetrahedrally surrounded by four Cl-atoms through covalent bonds as shown below:

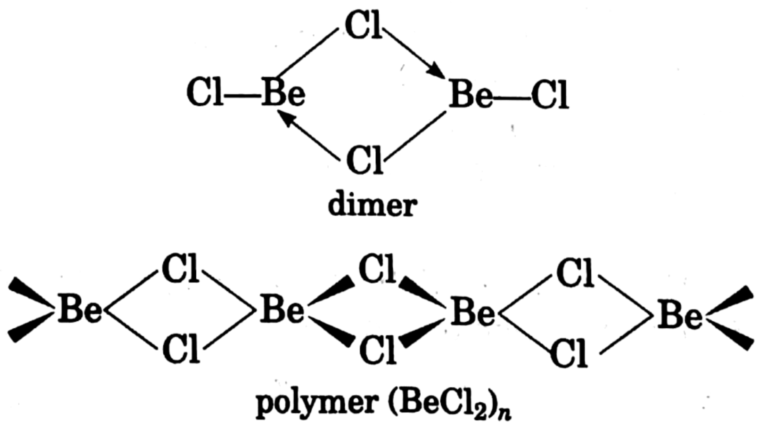


Fig.2.3 Structure of polymeric beryllium chloride

The two Be-Cl covalent bonds in the polymeric solid $BeCl_2$ are normal covalent bond and rest two bonds are coordinate covalent bonds with each chlorine donating a lone pair of electrons to the Be-atom (2c-2e bonds). This compound sometimes taken as a polymer involving a three centre-two electron (3c-2e) or multicentre bonds formed by the overlapping of an unpaired sp-hybrid orbital of one Be, unpaired atomic orbital of Cl-atom and an empty atomic orbital of another Be-atom.

$BeCl_2$ is sometimes used as a Friedel –Crafts catalyst.

2.10.2 Preparation and properties of Be-hydride (BeH_2):

Beryllium shows only a slight tendeny to react with hydrogen, hence BeH_2 cannot be prepared by direct combination of Be and H_2. Therefore, this is prepared by reducing $BeCl_2$ with LiH or $LiAlH_4$ in ethereal medium.

$$\mathbf{BeCl_2 + 2\,LiH \xrightarrow{\text{Ether}} BeH_2 + 2\,LiCl}$$

$$\mathbf{2\,BeCl_2 + LiAlH_4 \xrightarrow{Ether} 2BeH_2 + LiCl + AlCl_3}$$

Beryllium hydride is a covalent compound and reacts very slowly with water liberating hydrogen, hence used as reducing agent.

$$\mathbf{BeH_2 + 2H_2O \longrightarrow Be(OH)_2 + 2H_2\uparrow}$$

It is a polymeric hydride $(BeH_2)_n$ and exists as a solid. It contains hydrogen bridges between Be-atoms forming three centre-two electron (3c-2e) bonds in which a banana shaped molecular orbital covers three atoms i.e., Be-----H----Be and contains two electrons.

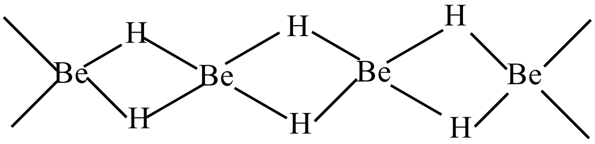


Fig.2.4 Structure of polymeric beryllium hydride

The formation of three centre two electron or multicentre bonds in this polymeric hydride can be explained in the similar way as has been done for the polymeric $BeCl_2$. The only difference being H atom in place of Cl- atom (see above). There is no possibility of the existence of a coordinate bond as in case of $BeCl_2$.

2.11 COMPLEXATION BEHAVIOUR OF ALKALINE EARTH METALS

The complex formation by a metal is favoured mainly by the small size, highly charged ion and availability of suitable empty orbitals. The cations of group IIA elements do not possess these characteristics, hence are not having a significant tendency to form complexes, however the tendency is more than those of alkali metals by virtue of their higher charge density.

However, Be forms a number of complexes with many oxygen and nitrogen containing organic compounds. It also gives stable complexes with F^- ion due to its small size, e.g. $[BeF_3]^-$, $[BeF_4]^{2-}$ etc. in which Be F_2 accepts electron pairs from F^- ions:

$$\mathbf{BeF_2 + F^- \longrightarrow [BeF_3]^-}$$

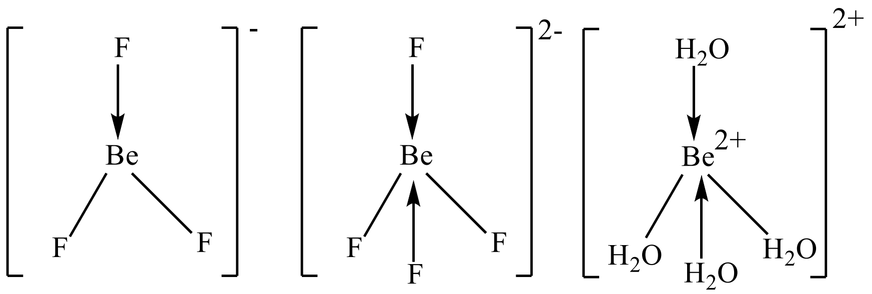
(Be is sp^2hybridised and contains two normal covalent bonds and one coordinate bond.)

$$BeF_2 + 2F^- \longrightarrow [BeF_4]^{2-}$$

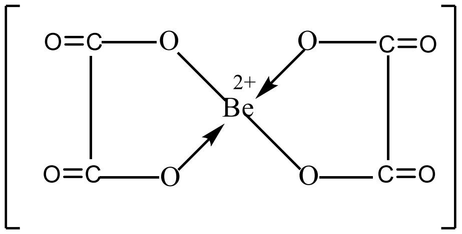
(Be is sp^{3}hybridised and contains two normal and two coordinate bonds: $F^- \longrightarrow BeF_2$)

Be^{2+} ion also gives $[Be(H_2O)_4]^{2+}$ complex with four coordinate bonds of $H_2O \rightarrow$ Be type and $[Be(oxalate)_2]^{2-}$ type complex with oxalic acid.

It gives $M^I{}_2[BeCl_4]$ with alkali metal chlorides which are decomposed by water. In aqueous medium, Be forms stronger complex with fluoride than chloride ions. The fluoride, aquo and oxalate complexes may be shown as:



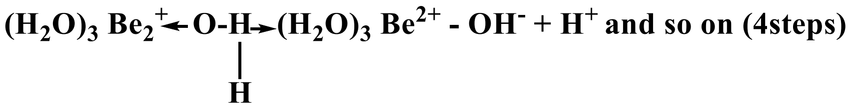
Trigonal Tetrahedral Tetrahedral



Tetrahedral

Fig. 2.5

In $[Be(H_2O)_4]^{2+}$ complex, Be^{2+} ion withdraws electronic charge from oxygen atoms of water towards itself and facilitates the removal of protons forming $[Be(OH)_4]^{2-}$ complex ion.



$$\mathbf{(H_2O)_3\ Be_2{}^{+} \leftarrow \underset{\substack{|\\ H}}{O}\text{-}H \rightarrow (H_2O)_3\ Be^{2+} - OH^- + H^+ \text{ and so on (4steps)}}$$

Thus $[Be\ (H_2O)_4]^{2+}$ is an acid and $[Be(OH)_4]^{2-}$ is a base.

Be has been found to have a unique property of forming a series of stable and volatile molecular oxide-carboxylate complexes of general formula $[OBe_4(RCOO)_6]$ where R = H, Me, Et, Pr, Ph etc. These are white crystalline compounds readily soluble in organic solvents but are insoluble in water or lower alcohols.

Basic beryllium acetate, R = CH_3, is a common and typical example. They are best prepared by refluxing the oxide or hydroxide with the carboxylic acid. Mixed oxide carboxylates can be prepared by reacting a given compound with another organic acid or acid chloride. The structure of the acetate complex (**Fig. 2.1**) features a central oxygen atom surrounded tetrahedrally by four Be-atoms. The six edges of the tetrahedron so formed are bridged by the six acetate groups in such a way that each Be atom at the corner of tetrahedron is also coordinated tetrahedrally by four oxygen atoms.

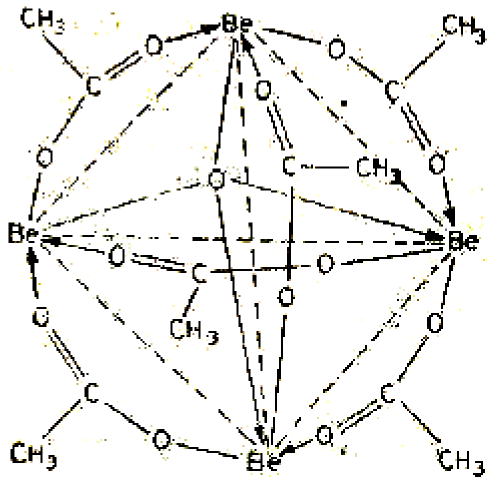


Fig. 2.6 Structure of basic beryllium acetate

Be also forms numerous chelating and bridge complxes with ligands such as the oxalate ion given earlier, alkoxides, β-diketonates and 1,3- diketonates.

The tendency to form complexes goes on decreasing when we move down the group which is attributed to increasing size of the metal ions. However, Mg^{2+} and Ca^{2+} form complexes with multidentate, ethylene diammine tetra acetate ion and Mg^{2+} alone with 8-hydroxy guinoline (oxine) etc. This property is used in quantitative analysis for the estimation of these metal ions.

2.11.1 Anomalous behaviour of beryllium

Beryllium, the first element of the alkaline earth metals, though shows various chemical similarities with other group members, yet also differs from them in many respects. This anomaly has been attributed to its small size, high charge density (charge/size) and high electronegativity as compared to other members of the group. The main points of difference are as follows:

(i) Beryllium is the hardest metal of all the elements of the group with the highest melting and boiling points.

(ii) It has the tendency to form covalent compounds with anions due to its high polarizing power and high electronegativity. At the same time its highest ionization energy among the group IIA elements does not allow it to form Be^{2+} ions easily to give the ionic compounds.

(iii) It does not react with water even at high temperatures. Other alkaline earth metals decompose water to liberate H_2 as given below:

$$M + H_2O \longrightarrow MO + H_2 \quad \text{(M = alkaline earth metals except Be)}$$

(iv) Beryllium has the lowest standard oxidation potential among all the group members and hence has the least electropositive character. This is evident from the nature of its oxide and hydroxide which are amphoteric, i.e. they dissolve both in acids and alkalies to form salts and beryllates respectively:

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

The corresponding compounds of other alkali earth metals are basic in nature, the basicity increasing down the group.

(v) BeO is covalent and has 4:4 types ZnS (wurtzite) structure but other elements give (MO type) oxides with 6:6 type NaCl structure and are ionic.

(vi) Beryllium does not react directly with hydrogen while other elements of the group IIA do so easily. Further, BeH_2 and MgH_2 are covalent but other elements give MH_2 compounds which are electrovalent.

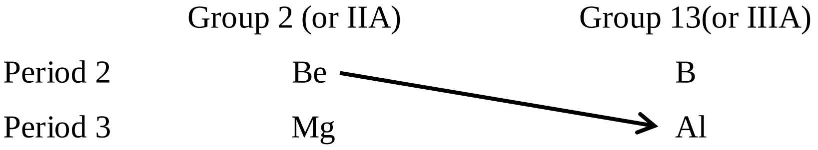
(vii) Beryllium on heating with carbon forms Be_2C type carbide which when treated with water evolves methane. The other members of the family form ionic carbides of the type MC_2 if the metals or their oxides are heated with carbon. These ionic carbides when treated with water evolve acetylene.

$$Be_2C + 2H_2O \xrightarrow{\qquad} 2BeO + CH_4 \uparrow$$

$$CaC_2 + H_2O \xrightarrow{\qquad} CaO + C_2H_2 \uparrow$$

2.12 ANOMALOUS BEHAVIOR OF BERYLLIUM (SIMILARITIES BETWEEN Be AND Al)

Be shows similarities in some of its properties with aluminum, the element of Group 13 (or IIIA) and period 3 situated diagonally opposite to it. This is called diagonal relationship.



The main points of similarities are given as follows:

(i) Both the elements (Be and Al) have strong tendency to form covalent compounds due to high polarizing power which is based on the small size and high charge density of the metal ions (charge/radius ratio: Be^{2+} = 6.45 and Al^{3+} = 6.0).

(ii) Both of them have the same value of electronegativity (1.5).

(iii) Both have almost similar values of standard oxidation potential:

$$Be = + 1.70 \text{ V}, Al = + 1.67\text{V}$$

(iv) The oxides of both the elements are amphoteric in nature, i.e. dissolve in acids as well as alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2Na\,OH \longrightarrow Na_2BeO_2 + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

(v) The Carbides of both Be and Al evolve methane (CH_4) on treatment with water.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4\uparrow$$

$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4\uparrow$$

(vi) Both the metals on reacting with dilute mineral acids or caustic alkalies liberate hydrogen gas.

$$Be + 2HCl \longrightarrow BeCl_2 + H_2\uparrow$$

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2\uparrow$$

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

$$2Al + 2NaOH + 2H_2 \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$

(vii) Both Be and Al are rendered passive on treating with conc. HNO_3 due to the formation of protective oxide coating on the metal surface.

8.7SUMMARY

The course material of this unit deals with the:

- General characteristics of the alkali metals such as their electronic configuration, physical state, density, hardness, atomic and ionic radii along with their atomic volume, their melting and boiling points as well as heats of atomization, ionization energies, electron affinities and electronegativity, their electropositive or metallic character and reducing properties, the photo electric effect and flame colouration along with its use in qualitative and qualitative analysis.

- A brief account of their polarizing power and the uses of alkali metals and their compounds have also been taken care of. The general discussion of oxides and hydroxides of alkali metals with their preparation and properties has been given in short. An account of the cause of solubility of alkali metal compounds and its connection with hydration has also been given.

- The complexation of alkali metal cations, anomalous behaviour of lithium and its diagonal relationship with magnesium have been discussed with appropriate reasoning.

- In the text of this unit, a detailed description of the general characteristics such as their electronic configuration, hardness, density, atomic and ionic radii, ionization energies, reducing property and electropositive character, melting and boiling points, flame colouration, polarizing power, hydration property and solubility in ammonia along with the uses of alkaline earth metals and their salts has been given.

- A detailed account of the halides and hydride of beryllium has also been given in the light of their preparation, properties and structural details. The complexation behaviour of the alkaline earth metals in general and that of beryllium in particular has been discussed with example.

- The anomalous behaviour of beryllium and its diagonal relationship with aluminum, the element of the next higher group and period has also been taken care of.

7.9. Terminal questions.

MCQs Type Questions

1. The element used in photoelectric cells is?

(a) Li (b) Na (c) Mg (d) Cs

2. Which one of the following has maximum reducing power in aqueous solution?

(a) Li (b) Na (c) K (d) Cr

3. The element imparting crimson red to Bunsen flame is?

(a) Li (b) Na (c) K (d) Rb

4. The least stable among the following is?

(a) $RbNO_3$ (b) KNO_3 c) $NaNo_3$ (d) $LiNO_3$

5. Which one of the following is more basic?

(a) $Be(OH)_2$ (b) $Mg(OH)_2$ (c) $Ba(OH)_2$ (d) $Ca(OH)_2$

6. Which oxide of the following is amphoteric?

(a) BaO (b) SrO (c) CaO (d) BeO

7. The metal used in nuclear reactors is

(a) Be (b) Ca (c) Ba (d) Ra

8. The alkaline earth metal having the lowest ionization energy value is

(a) Be (b) Ca (c) Ba (d) Ra

9. The two alkaline earth metals imparting crimson red flame colouration are

(a) Be and Mg (b) Mg and Ca (c) Ca and Sr (d) Sr and Ra

Short type questions

1. Write a note on reducing property of alkali metals?
2. What is photo electric effect?
3. How does the electropositive character of the alkali metals vary in the group and why?
4. Li gives only monoxide but not higher oxides Explain?
5. What happens when alkali metal nitrates are heated?
6. Differentiate between lattice energy and hydration energy?
7. How does Li_2CO_3 differ from K_2CO_3?
8. Salts of lithium, in general, are covalent while those of other alkali metals are ionic.

Explain.

10. Explain.why do Be and Mg not give any colour in the Bunsen flame?

11. Why are these metals used as deoxidizers?

12. Discuss briefly the bonding in BeH_2.

13. Discuss the structural aspects of basic beryllium acetate.

14. How do Be and Al react with acids and alkalis?

15. What factors are responsible for anomalous behaviour of Be in contrast other group members?

Answer

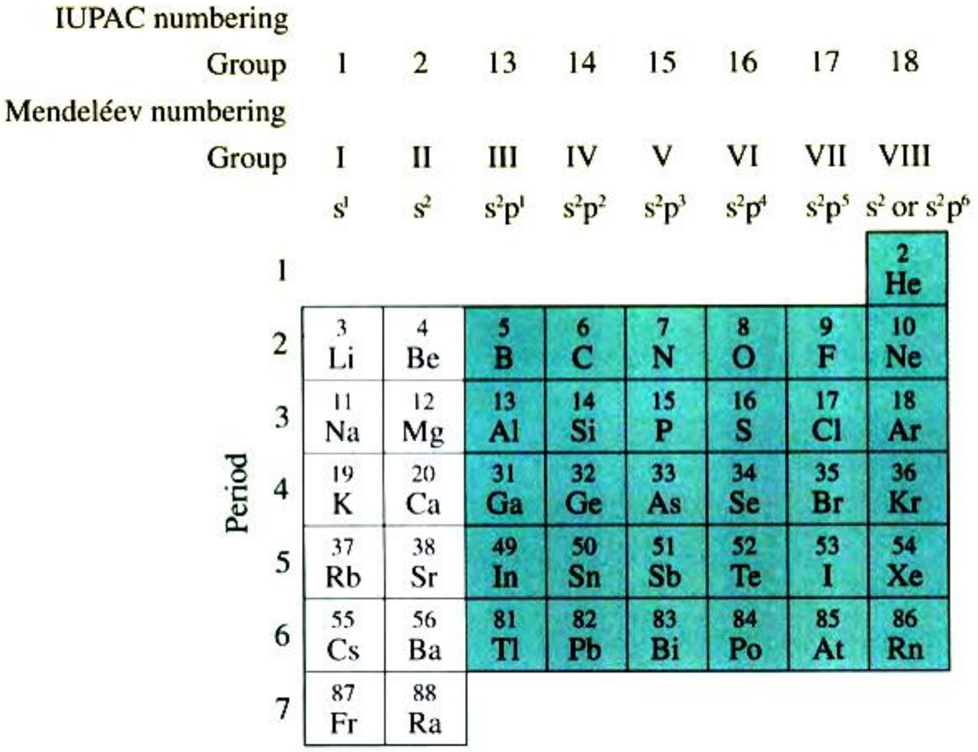
1. d 2. a 3. a 4. d 5. c 6. d 7. a 8. c 9. d

UNIT-3 p-BLOCK ELEMENTS

CONTENTS:

3.1 INTRODUCTION

Chemistry is an immensely diverse subject. Nowhere is this more evident than in the properties of the p-Block elements, those in which the outer electronic configuration is s2px. In this Book, we will study the typical elements, focusing on the p-Block elements (Figure 1.1). Much of the chemistry of the metallic +Block elements is consistent with an ionic model. With the p-Block elements, this is no longer the case: the proportion of obviously covalent substances is much larger. Before we begin our study of these elements, it is necessary to introduce some essential principles, mainly concerning bonding and thermochemistry, which apply particularly to covalent substances. Following this, we consider the chemistry of the Groups of p-Block elements, beginning with the halogens and noble gases, as these Groups most clearly display covalent properties. These are the two Groups that contain no metallic elements.



Element belonging to group IIIA, IVA, VA, VIA, VIIAand zero is which p-orbitals are being progressively filled are collectively known as p-block elements. It means that the outmost p-subshell of these elements is incompletely.

3.2 OBJECTIVES

The objective of the present chapter is:

- In this unit you learn able to general characteristics and uses of the p-block elements.
- You will also know about the chemistry of hydrides, halides, oxides and oxyacids of p-block elements, Silicates, Boron nitrogen compounds (borazene and boron nitrides), interhalogen compounds.
- And end of this unit you will be able to general introduction,general characteristics and uses of Zero group elements. Compounds of Noble gases- Preparation, Properties and structures.

3.3GENERAL CHARACTERISTICS OF p-BLOCK ELEMENTS

3.3.1 Electronic configuration:

The general electronic configuration of outmost shell of p-block elements is ns^2np^{1-6}. *The electronic configuration of elements belongs* IIIA, IVA, VA, VIA, VIIA and zero are given below:

Group	IIIA	IVA	VA	VIA	VIIA	Zero
Ele. Confi.	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6

3.3.2 Size of the Atoms and Ions:

Size of the atoms in p-block elements decreases from to left to right across a period. The size of atoms increases on descending a group in the periodic table. The ionic radii decrease on moving from left to right in a periodic and increasing on moving down a group.

3.3.3 Ionization Energy:

First ionization energies of p-block elements increases as we move across a period from left to right and decreases on descending a group.

The increases along the period, however, is not uniform. Ionization energy of group III A elements is less than that of their neighbors of group IIA elements on their left. Similarly,ionization energy of group VIA elements is less than that on VA elements on their left. It is due to high I.E., of a stable completely filled electronic configuration of II A elements and half-filled configuration of VA elements.

3.3.4 Electron Affinity:

Electron affinity generally increases as we move from left to right along the period and decreases on descending a group. Exceptions are noted in the case of nitrogen, Phosphorus and noble gases. It is due to the stable electronic configuration of these elements.

3.3.5 Electronegativity:

Electronegativity increases from left to right across a period and decreases as we descend a group.

3.3.6 Metallic character:

metals are electropositive in nature and have a tendency to lose electrons and form positively charged ions.

$$M \longrightarrow M^+ + e^-$$

On moving from left to right across a period the metallic character of the elements decreases and their oxides become less basic

Group	IIIA	IVA	VA	VIA	VIIA
Oxide	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
Nature	Amphoteric	Acidic	More Acidic	More Acidic	Most acidic

On descending a vertical group in the periodic table, the metallic character increases. In fifth group, Nitrogen is nonmetallic while bismuth is metal. The oxide of nitrogen is less basic than oxide of bismuth.

3.3.7 Oxidizing and Reducing Properties:

Some p-block elements can easily supply electrons and thus bring about electronation. These are good reducing agents.

Some other elements towards the right (like halogen) with high electron affinity can easily accept an electron and thus about de-electronation. These are good oxidizing agents. Ionization energy decreases down the group and increase along the period, the reducing property of these elements increases on going down the group and decreases as we move along the period from group III A to group VIIA.

Electron affinity decreases on descending the group and increases from left to right across a period, the oxidizing property of the elements decreases on descending a group and increses from left to right across the period.

3.3.8 Oxidation States:

p-block elements show a variety of oxidation states both positive and negative.

Group	IIIA	IVA	VA	VIA	VIIA	Zero
Elements	B	C	N	O	F	Ne
O. S	+3	+4	+5	-2	-1	0

It is notes that while positive oxidation state increases, the negative oxidation state decreases on moving from left to right across the period. Variable valency in heavier membes of group III A, IV A, VA are noted due to inert pair effect.

3.3.9 Oxides and Oxyacid's:

The oxides of p-block elements may be basic (in case of metallic elements) amphoteric (in case of metalloid) or basic (in case of nonmetal) also form a number of oxyacid. In any group the acidic character of the oxide decreases as we move down the group while the acidic character increases in the same period form left to right.

Basic oxides : Bi_2O_3

Amphoteric oxides :SnO, SnO_2, PbO, Pb_2O_3

Acidic oxides : SO_3, Cl_2O_7

Oxyacids : HNO_3, H_2SO_4

Basic character increases down a group

CO_2 SiO_2 $GeO_2SnOPbO$

Acidic Less acidic Amphoteric Basic More Basic

3.3.10 Hydrides:

Many of the p-block element form hydrides. The hydrides of non-metals are more stable. Thus, in any group the stability of the hydride decreases from top to bottom, its strength as an acid also increases in this order. The order of stability hydrides of fifth group is as follows.

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

3.3.11 Halides:

Out of p-block elements, the non-metals form covalent halides Metallic halides show a graduation from an ionic character to essentially covalent character. As we move from left to right across the period, ionic character of the halides decreases and the covalent character increases. For example, $SbCl_3$, is partially ionic whereas $TeCl_4$, is essentially covalent.

In case of a metal forms halides in more than one oxidation states halides in lower oxidation state are largely ionic and those in higher oxidation state are largely covalent.

3.4VARIATION IN PROPERTIES OF p-BLOCK ELEMENTS

3.4.1 ionization Potential Variation in p-block Elements

It is defined as, "The energy required to pull out an electron from the outer most shell of an atom in its lowest energy state (ground state)"

For example, the energy required for the following reaction is

$$\underset{\text{Atom}}{A} \longrightarrow \underset{\text{ion}}{A^+} + e^- \quad \text{(First I.P)}$$

$$A^+ \longrightarrow A^{2+} + e^- \quad \text{(Second I.P)}$$

$$A^{2+} \longrightarrow A^{3+} + e^- \quad \text{(Third I.P)}$$

called the ionization potential and is determined from spectra. The ionization power is thus the measure of the firmness with which an electron is held by an atom. alkali metals have low ionization potential and are therefore strongly electropositivethe nonmetals as have high ionization potentials they do not lose electrons readily are consequently strongly electro negative. The value of I.P. is expressed in electron volts; when expressed as Kcal atom it is known as ionization energy.

Important points regarding the variation of this property are:

(i) The ionization potential increases with increase of atomic number in any period. It is due to the fact that with increase of nuclear charge of the atom it becomes more difficult to pull out the electron.

Li	Be	B	C	N	O	F	Ne
6.4	9.8	8.3	11.3	14.3	13.6	17.4	21.6 eV

(ii) The ionization potential decreases as the atomic number increase in the same group. It is due to the fact that atomic volume too increases of nuclear charge.

Li	Na	K	Rb	Cs	
5.4	5.1	4.3	4.2	3.9	eV

(iii) The ionization potentials of all inert gases are greater than those of other immediate neighbors. It is due to the fact that they contain the most stable arrangement s^2p^6in their outermost shell.

IP for the removal of first, second or third electrons are determined separately. The value of first I.P. is small while it is higher for second or third since removal of subsequent electrons is done against greater nuclear influence on the remaining electrons.

Ionization potential depends on (i) distance of electrons from nucleus (ii) charge on the nucleus (iii) screening effects of inner electron shell (iv) types of electrons involved i.e., s, p, d and f. Generally, all these factors are interrelated; 's' electrons are nearer the nucleus than p, d or f of any principal level and are more tightly held (LP. decreases in order s>p>d>f).

3.4.2 Electronegativity Variation of p-block Elements

It is defined as, "The tendency of an atom in a compound to attract electrons towards itself is known as the Electronegativity of an atom".

Generally small atoms attract electrons more than large ones hence are more electronegative. Ionization potential and electron affinity may be regarded as measures of electronegativity, Mullikan regarded electronegativity as the I.P. + EA/130(I.P and E.A. are in Kcal/mole). But values of E.A. are known only for few hence to measure electronegativity Pauling's scale is used (this is derived from a consideration of the energies required to break the chemical bonds in molecules). It is highest value in case of F (4) while Cs has lowest (0.7) value. On this scale elements of zero group have no electronegativity value. In periods it increases with the rise of atomic number.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0

while value of electronegativity decreases in group from top to bottom, due to increase of atomic size.

Li	Na	K	Rb	Cs
1.0	0.9	0.8	0.7	0.7

Higher I.P. and greater E.A. will point higher value for electronegativity. For example, since the elements of I.A. have lowest value for I.P. and E.A, they have lowest electronegativity. On the other hand, elements of VII group have highest values for I.P. and E.A. they have highest electronegativity. In other words, the higher the value of electronegativity, the more nonmetallic is the element.

If two atoms have similar values for electronegativities ie, similar tendency to attract electrons, the bond between them will be covalent. Similarly, a large difference in values leads to an ionic bond e.g.,

Li	F	(Ionic bond)
1	4	
C	H	(Covalent Bond)
2.5	2.1	

i.e. the greater the separation of two elements on electronegativity scale, the greater is the strength of the bond between them.

3.4.3 Electron Affinity Variation of p-block Elements

The energy released when an extra electron is added to neutral gaseous atom to form an anion is known as electron affinity.

$$A\,(g) + e^- \longrightarrow A^-(g)$$

Generally, one electron is added (uninegative ion). But for the further addition of two or more electrons energy is needed thus the value of electron affinity will be negative for polynegative ion.

$$A^- + e^- \longrightarrow A^{2-}(g)$$

The magnitude of electron affinity depends mainly on (i) atomic size (ii) nuclear charge (iii) screening effect. In general electron affinity decreases with the increasing atomic radius while increases with increasing nuclear charge. E.A. also depends to some extent upon the type of orbital that the added electron enters. The value of E.A. is greatest for an electron entering s-orbital and decreases for p, d and f orbitals.

$F \longrightarrow F^-$ -3.62 eV

$Cl \longrightarrow Cl^-$ -3.3 eV

$Br \longrightarrow Br^-$ -3.56 eV

$I \longrightarrow I^-$ -3.28 eV

In CO_3^{2-}, SO_4^{2-}, PO_4^{3-} (molecular ions) the total negative charge is distributed over several atoms and repulsion between the charge and added electron is small; hence complex negative ions with very high charges may exist (*if the ions is large*). In periods its value increases with increase of atomic number, while in group value decreases from top to bottom.

H							He
0.7							0
Li	Be	B	C	N	O	F	Ne
0.54	0	0.3	1.13	0.2	1.48	3.62	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.74	0.4	0.4	1.9	0.8	2.07	3.79	0
						Br	Kr
						3.56	0

Be, Mg N, P and inert gases behave differently (Le have completely filled sub-shells and the new electron will have to go to sub-shells p of considerably higher energy).

3.4.4 Variation of Size of Atom and ion of p-block Elements

size of atom or ion may be the space limit upto which its electrons extend but this boundary cannot be sharply defined. Hence the more accepted view of atomic size is the shells of most probable occurrence of the outer most electrons of the atom. With the increase of number of charges on nucleus all the orbital electron are pulled in closer to the nucleus thus decreasing the size of atom in periods etc.

Na	Mg	Al	Si	P	S	CI
1.57 Å	1.36	1.25	1.17	1.10	1.04	0.99

i.e. values of alkali metals is high while it is small for halogens. On the other hand values increase in the group from top to bottom.

Li	Na	K	Rb	Cs
1.23 Å	1.57	2.03	2.16	2.33

due to the effect of extra shells of electrons being added, this out weights the effect of increased nuclear charges.

The removal of one or more electrons from an atom forms a positive ion. In this way, generally, the whole of the electrons of outer shells is removed and since the remaining inner shell do not extend so far in space, the cation, is much smaller than the metal atom. Further, the ratio positive charges on the nucleus to the number of orbital electrons is also increased hence the effective nuclear charge is increased and the electrons are pulled in. Thus, a cation is smaller than the corresponding atom e.g.,

Na	1.57 Å	Na^+	0.09 Å
Fe	1.17 Å	Fe^{++}	0.76 Å

On the other hand, in the formation of negative ions electrons are added to the atom. (The effective nuclear charge is reduced) hence electrons cloud expends. Thus, anion will be bigger than the corresponding atom.

Non-bonded Cl=0.99Å Ionic radius Cl =1.11 Å

Elements	Ionic radius	Ion	Covalent radius
H	0.29 Å	H^+	0.37 Å
	0.08	H^-	
Li	0.60	Li^+	1.225
B	0.20	B^{3+}	0.08
C	0.15	C^{4-}	0.77
	2.60	C^{4+}	
F	1.36	F^-	0.72

3.4.5 Atomic volume

Gram atomic volume of element is the volume occupied in the solid state by one gm atom of the element. Gram atomic volume first decreases and then increases in a period.

Na	Mg	Al	Si	F	S	CI	Ar
24	14	10	12	17	17	17	24

It increases in group from top to bottom.

Li	Na	K	Rb	Cs
13	26	45	56	71

3.4.6 Hydrides

Hydrogen possesses a unique property by virtue of which it may combine directly or indirectly with metals and non-metal. These binary compounds of hydrogen are known as hydrides. The most common examples of hydrides are H_2O, HCl, NH_3, NaH, CaH_2, AlH_3etc.

3.4.7 Classification of Hydrides

Hydrides have been classified in three catagories:

(i) Saline or salt-like hydrides

(ii) Covalent or molecular hydrides

(iii) Metallic hydrides.

(i) Saline or Salt-like Hydrides: The elements of IA and IIA groups from hydrides of this type. These elements are of low electronegativities. The general composition of these hydrides is MH, x is the valency of the metal.

(ii) Covalent Hydrides or hydrides of p-block elements: These hydrides are formed by all the truly non-metallic elements (except inert gases) and Al, Ga, Sn, Pb, Sb and Bi which are normally more metallic than non-metallic. Except for B, Al and Ga, others give mononuclear hydrides of formula XH_{8-n}, where is the number of valency electrons present in the neutral atom X. The simplest hydrides of B and Ga are B_2H_6 and Ga_2H_6 respectively, and for aluminium it is $(AlH_3)_2$.

Preparation: Covalent hydrides are prepared by the following methods:

(i) By direct combination of elements with hydrogen

$$F_2 + H_2 \longrightarrow 2HF$$

$$O_2 + 2H_2 \longrightarrow 2H_2O$$

(ii) By the action of hydrogen on metal or its compound.

$$AsCl_3 + 6H \longrightarrow AsH_3 + 3HCl$$

$$SbCl_3 + 6H \longrightarrow SbH_3 + 3HCl$$

(iii) By the hydrolysis of boride, silicide, carbide and nitride with water or dilute acids.

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

Magnesium Boride

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4 \uparrow$$

Magnesium silicate

$$Al_4C_3 + 12\,H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow$$

Magnesium nitride

$$Mg_2N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$$

(iv) By the action of $LiAlH_4$, on certain halides.

$$SnCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3, + SnH_4$$

$$GeCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + GeH_4$$

Properties: The covalent hydrides are characterized by molecular lattices made up of individual saturated covalent molecules. They are insoluble in water, but dissolve in organic solvents, have low melting and boiling points. They are nonconductors and volatile. The chemical properties of these hydrides vary from one periodic family to another. They all undergo thermal decomposition to hydrogen and the other element.

$$2H_2O \xrightarrow{\text{Heat}} 2H_2 + O_2$$

$$2NH_3 \xrightarrow{\text{Heat}} N_2 + 3H_2$$

The thermal stability of hydrides increases with decreasing electronegativity of the non-metal. The hydrides of the heavier elements in any periodic family is less stable than those of the highter elements.

Boron hydrides are decomposed by aqueous alkali.

$$B_2H_2 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

Similarly, boranes are decomposed by water.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

Structure: These hybrides are covalent and exist in same molecular form in all

states of aggregation. In the solid state; they are made up of molecular crystals of individual molecules held together by weak Vander Waal attractions. Same of these hydrides, such as boron hydrides, are electron-deficient in character. In B_2H_6, the B-H-B bond is a three-centre-two-electron (3C-2e) bond, ie, one electron pair binds three atoms, B, H and B. Similar structures by been proposed for higher boron hydrides.

Uses: Some of the covalent hydrides have found applications as catalysts in polymerization reactions, as reducing agents for organic reactions, and for conversions into substances which are used as high energy fuels and propellants.

(iv) **Metallic Hydrides:** The transition elements and length anides combine with hydrogen to form hydrides of variable compositions. These are called metallic hydrides. These compounds are metallic in appearance. Some of the examples of this class of hydrides are PdH_{0-6}; $TiH_{1.98}$; $LaH_{2.79}$, $CeH_{2.2}$ etc.

3.5 ELEMENTS OF GROUP-13

Group 13 (or group IIIA) of the long form of periodic table contains five elements, namely boron (B_5), aluminum (Al_{13}), gallium (Ga_{31}), indium (In_{49}) and thallium (Tl_{81}). This group is also known as boron group. All these elements are said to belong to the p-block of elements as the differentiating electron in the atoms of these elements enters the p-subshell of the outermost or the valence shell. The first element boron is semimetal while other members of this group are metals as is indicated by their properties, i.e., boron is closer to non-metals is its properties but the rest of the members show metallic properties.

Boron occurs rather sparsely, aluminum is the third most abundant element found in earth’s crust, i.e., it is the most abundant element of these all, gallium, indium and thallium are not found in concentrated deposits and do not find much of commercial applications.

3.6 GENERAL CHARACTERISTICS

The inclusion of these elements in the same group of the periodic table is justified by the following general characteristics of these elements but these have been found to show a wider range of variations and also notable contrast in their properties.

3.6.1 Electronic configuration

These elements are characterized by three electrons in the valence shell, two of which are s-electrons and one a p-electron, i.e., the valence shell configuration of the atoms of these elements is ns^2np^1, n being the principal quantum number, the ultimate shell which varies from 2 for boron to 6 for thallium. Unlike the s-block elements, the electronic configuration of the penultimate shell of the atoms of these elements varies from inert gas to pseudo inert gas type. Boron has helium configuration (i.e.$1s^2$), aluminum has octet ($2s^2p^6$) and rest of the elements have $(n-1)s^2p^6d^{10}$ type configuration (i.e. n-1 = 3 for Ga, 4 for In and 5 for Tl) in the penultimate shell. This difference in the electronic configuration in the penultimate shell, though the valence shell has the same configuration, is responsible for the abrupt variation in the properties of these elements.

3.6.2 Density, melting and boiling points and heat of sublimation

The density, in general, increases on moving down the group, however, Al has exceptionally low density. Melting point decreases considerably from B to Ga and then increases up to Tl but boiling point shows a regular decreasing trend down the group. Similar trend is observed in heats of sublimation also indicating that the atoms of the elements are held less and less closely as we move down the group. Very low melting point of Ga (30^0C) which is about ten times less than that of Tl and about seventy times less than that of B is explained on the basis that its structure contains Ga_2 molecules.

3.6.3 Ionization energy

The first ionization energy of these elements corresponds to the removal of np^1 electron which is invariably held with nucleus less tightly and has low value. Its value decreases, as expected from B to Al because Al has larger size but then increases slightly in Ga. This is because from Al to Ga though atomic size increases but d-electron in the penultimate shell (with $s^2p^6d^{10}$ configuration) in Ga not able to shield the nuclear charge effectively and the valence electrons in this element are more firmly held to the nucleus thereby having slightly higher ionisation energy value. Thallium has unexpectedly higher ionisaton energy due to the inclusion of f-electrons as well as d-electrons in the inner shells and their low shielding effect.

These elements have been assigned three successive ionization energies (i.e. I_1, I_2 and I_3), the first belonging to the removal of p-electron and last two to the ejection of s-electrons one by one for each elements $I_3 > I_2 > I_1$. Boron has the highest values of all the three ionisation energies among these elements. Though the nuclear charge of these elements is larger and their size is smaller than those of Group 2 elements, yet their first ionisation energies are unexpectedly lower than those of the alkaline earth elements in the respective periods. This is due to the fact that the p-electrons are less penetrating and lie at larger distance from the nucleus than the s-electrons and hence can be removed more easily.

3.6.4 Oxidation state

Boron gives mainly covalent compounds and has least tendency to from B^{3+} ion which is unstable because of very small size and very high ionization energy of its atoms but it may be arbitrarily assigned +3 oxidation state in its compounds with more electronegative elements. Aluminium has high charge density due to small size and high charge of Al^{3+} ion, hence its compounds, in general, are ionic in solution (having high hydration energy) and are covalent in gaseous phase. In solid state, its compounds have high lattice energy. In general sense it can be assigned + 3 oxidation state.

The higher elements exhibit both +1 and +3 oxidation states, +1 state becoming more and more stable down the group from Ga to Tl. Thus, in Ga, +3 state has been found more stable than +1 state but in Tl, +1 state is more stable. This peculiar property of these elements is due to the **inert pair effect** which increases from Ga to Tl down the group. In the compounds of Ga, In and Tl with +1 oxidation state, the np^1 electron only takes part in combination and ns^2

electron pair remains inert due to its penetration in the inner shell and strong attractive force operating between nucleus and ns^2 electrons.

The relative stability of +1 and +3 oxidation states in the last three elements can be shown as follows:

$$Ga^{3+} > In^{3+} > Tl^{3+} \quad \text{and } Ga^{+} < In^{+} < Tl^{+}$$

3.6.5 Electropositive character

The electropositive or metallic character of these elements increases form B to Tl down the group. Boron is a semi-metal and all the other elements are distinctly metallic and good conductors of electricity having almost equal electropositive character as well as close ionisation energy values.

3.6.6 Tendency to form ionic or covalent compounds

From the electronic configuration of these elements, all of them would be expected to form M^{3+} type ions and the compounds would be ionic. However, the second and third ionisation energies of boron are so high that it has little tendency to form B^{3+} ion and other elements have higher tendency to form such ions under suitable conditions due to lower ionisation energies. Thus, these elements form ionic compounds.

Further if trivalent ions are formed, the smaller ions will have more polarising power and will tend to give covalent compounds. This tendency goes on decreasing down the group. That is why B gives covalent compounds, Al forms both covalent and ionic compounds and the higher members result mainly in ionic compound formation.

3.6.7 Oxidation potential

With the exception of B, the standard oxidation potential values for the elements corresponding to the conversion; $M \longrightarrow [M\ (aq)]^{3+} + 3e^-$, are quite high because of large quantity of hydration energy associated with the $[M_{aq}]^{3+}$ ions in solution inspite of their large values of ionization energies. These high potential values for these elements may be attributed to the high charge and small radii of M^{3+} ions (i.e. high charge density).

3.6.8 Gradation in chemical properties

Some chemical properties of these elements along with their gradation in the group are discussed below:

(a) Action of air and water

Boron is almost unreactive at ordinary temperature but when heated it reacts with air (O_2). It does not react with water but is attacked by hot conc. acids, e.g. H_2SO_4.

Aluminium readily reacts with air even at ordinary temperature to form a protective layer of the oxide which protects it from further action of air. It decomposes cold water.

Galium and Indium do not react with water in absence of O_2. Thallium forms an oxide coating on the surface when treated with air.

(b) Nature of oxides and hydroxides

All the elements form oxides and hydroxides. B_2O_3 and $B(OH)_3$ both are acidic. This is because hypothetical B^{3+} ion, being very small, has very high positive charge density. Hence when placed in water, it tends to pull off electrons from water molecule towards itself sufficiently strongly by rupturing the O-H bond in water molecule. This results in the rapid hydrolysis of hypothetical B^{3+} ion by H_2O releasing H^+ ions. $B(OH)_3$ dissolves in strong alkalies to form metaborates, e.g.

$$B(OH)_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$$

The Trivalent Al^{3+} and Ga^{3+} ions, being relatively larger have smaller capacity to rupture the O-H bond in H_2O molecule by pulling off electrons. Consequently, they are hydrolyzed to a smaller extent than the hypothetical B^{3+} ion. Hence the oxides and hydroxides of Al and Ga are amphoteric. The In^{3+} and Tl^{3+} ions are very large and their interaction with water is very slow. The O-H bond in water is hardly affected by these ions. This makes the oxides and hydroxides of In and Tl distinctly basic. It can be concluded from above that on moving down the group of these elements, the oxides and hydroxides change from acidic through amphoteric to basic in character.

(c) Halides

All the elements of this group react with halogens to form the trihalides. B-halides are covalent due to its small size and high charge density.

The fluorides of other elements of the group are ionic and have high melting points while the other halides are covalent when anhydrous. For example, anhydrous $AlCl_3$ is covalent but in water it is hydrolyzed to give Al^{3+}(aq) ions. This is due to the high hydration energy of Al^{3+} ions.

The normal trihalides are planar triangular in shape (sp^2 hybridization). One vacant unhybridised p-orbital is present in the central atom of these halides which can accommodate one electron pair from the donor molecules or ligands, thus acting as Lewis's acids. Boron trihalides have strong tendency to form complexes of BX_3L type where L is a neutral molecule or anionic donor (i.e. ligand). These complexes are tetrahedral with three normal and one coordinate bonds.

Boron trihalides exist as discrete molecules while trihalides of other elements exist as dimers both in vapour state and in non-polar solvents making use of vacant p-orbital.

(d) Hydrides

These elements do not react directly with hydrogen to form hydrides. Howener, hydrides of all these elements have been prepared by indirect methods. Boron forms a large number of covalent polymeric hydrides called boranes. Aluminium forms only one high molecular weight polymeric hydride, $(AlH_3)_n$ containing Al-atoms octahedrally surrounded by six H-atoms. Gallium gives only one volatile and unstable liquid hydride-gallane (Ga_2H_6). Indium forms polymerized solid hydride, $(InH_3)_n$ but Tl hydrides are unstable. These elements also form the complex anionic hydrides with alkali metal hydrides like $Li^+[BH_4]^-$, $Li^+[AlH_4]^-$ etc. where H^- ion acts as electron pair donor. These complex hydrides are used as reducing agents.

3.6.9 Uses of Group 13 elements

Boron and aluminium are more commonly used elements.

(i) Boron is used as deoxidiser, in the casting of copper, for making boron steels which being very hard are employed as control rods in atomic reactors, in the manufacture of thermo regulators etc.

(ii) Its hydrides are used as fuels for rockets, borides and boron carbide are used as abrasives.

(iii) Boric acid is used in antiseptics and eye lotions etc.

(iv) Aluminium-alloys find extensive use in industry, Al itself for making utensils, frames, coils for motors and cable wire for electrical transmission, in the extraction of chromium and manganese.

(v) Aluminium-powder is used in making silvery white paints, in fireworks, flash light powders and thermite welding.

(vi) Ga, In and Tl elements do not find important applications but their salts are sometimes used for various purposes.

3.6.9 Boron nitrogen compounds

3.6.9.1 Borazine or borazole ($B_3N_3H_6$)

This compound is also sometimes known as inorganic benzene and is isoelectronic with benzene.

A. Preparation:

(i) Heating a mixture of B_2H_6 and NH_3:

As has been given earlier in the properties of diborane, this compound is formed when diborane and ammonia are reacted at high temperature in 1:2 molar ratio.

$$3B_2H_6 + 6NH_3 \xrightarrow{\text{high temp.}} 2B_3N_3H_6 + 12H_2$$

Diammoriate of diborane formed at low temperature by mixing B_2H_6 and NH_3 may also be converted to borazine by heating at high temperature.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{low temp.}} B_2H_6.2NH_3$$

$$3(B_2\,H_6.2NH_3 \xrightarrow{\text{high temp.}} 2B_3N_3H_6 + 12H_2$$

(ii) Reaction of Li [BH_4] on NH_4Cl:

This reaction is carried at high temperature.

$$3NH_4Cl + 3Li[BH_4] \longrightarrow B_3N_3H_6 + 3LiCl + 9H_2$$

(ii) Heating BCl_3 with NH_4Cl:

When BCl_3 is heated with NH_4Cl in chlorobenzene (C_6H_5Cl) in presence of a catalyst (e.g. Fe, Ni, Co etc) at 133^0C, trichloroborazine is obtained which on being reduced by Li[BH_4] in polyether gives borazine (yield by this method is about 50-60%).

$$3BCl_3 + 3NH_4Cl \xrightarrow{\Delta,\ C_6H_5Cl} Cl_3B_3N_3H_3 + 9HCl$$

$$2Cl_3B_3N_3H_3 + 6Li[BH_4] \xrightarrow{\substack{\text{(Fe cata.} \\ \text{Redu.}}} 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

B. Properties:

Borazine is a colourless and volatile liquid. Its important chemical properties are;

a. Hydrolysis:

(i) It is slowly hydrolysed by water to produce boric acid, H_3BO_3, ammonia and H_2 which is favoured by increasing temperature.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$$

(ii) It has also been reported that under certain conditions, borazine reacts with three molecules of water to produce tri-hydroxylbora-zine, $(OH)_3B_3N_3H_3$, in which OH groups are attached with B-atoms.

$$B_3N_3H_6 + 3H_2O \longrightarrow B_3N_3H_3(OH)_3 + 3H_2$$

b. Addition reactions:

(i) It has been found that one molecule of borazine adds three molecules of H_2O, CH_3OH, CH_3I, HCl or HBr in the cold without a catalyst. Since B-atom is less electronegative than nitrogen atom in B-N bond, more negative groups or atoms of these molecules are generally attached with boron. HCl derivative of this compound when heated at 50-100^{0}C, loses H_2 molecules to gives B-trichloro borazine (Cl-atoms attached to B-atoms).

$$B_3N_3H_6 + 3HCl \longrightarrow B_3N_3H_9Cl_3 \longrightarrow B_3N_3H_3Cl_3$$

(ii) One molecule of borazine also adds three molecules of Br_2 at 0^{0}C giving B-tribromo-N- tribromoborazine which on heating at 60^{0}C, loses three molecules of HBr to form B-tribrimoborazine.

$$B_3N_3H_6 \xrightarrow{+3Br_2} B_3N_3H_6Br_6 \xrightarrow{60^0C} B_3N_3H_3Br_3 + 3HBr$$

3.7 ELEMENTS OF GROUP-14

Group 14 (or Group IVA) of the long form of periodic table contained five elements, *viz.* carbon (C_6), silicon (Si_{14}), germanium (Ge_{32}), tin (Sn_{50}) and lead (Pb_{32}). This group is also known as carbon group. All these elements belong to p-block of elements as the last electron in the atoms of these elements enters the p-subshell of the valence or ultimate shell. The first element carbon is distinctly non-metal, Si is non-metal with the characteristics of a semi-metal, Ge is a semimetal. The last two elements, Sn and Pb, are distinctly metals. Carbon occurs up to 0.1% in the earth's crust. However, combined with oxygen and hydrogen it occurs in all living tissues of plant or animal kingdom and also in petroleum and coal deposits. Silicon is the most abundant element, next to oxygen, in earth's crust (~28%) present as silica and silicates.

3.8 GENERAL CHARACTERISTICS

These elements have been included in the same group of the periodic table and this is justified by the following general characteristics of these elements. There occurs an appreciable extent of variation also in their properties.

3.8.1 Electronic configuration

The atoms of these elements have four electrons in their valence or ultimate shell, two of which are in s-orbital while the remaining two are in p-orbitals with ns^2np^2 type configuration, n being the principal quantum number (the valence shell). Like the elements of Group 13, atoms of these elements also have different arrangements of electrons in the penultimate shells, i.e. varying from inert gas to pseudo-inert gas configuration. Thus carbon has helium configuration (i.e. $1s^2$), silicon has an octet (i.e. $2s^2p^6$) and rest of the elements from Ge to Pb have (n-1) $s^2p^6d^{10}$ type arrangement of electrons in their respective penultimate shells. This difference in the configuration in the last but one shell, though the valence shells have the same configuration, is responsible for the variation in the properties of these elements. Thus carbon differs from Si and these two (i.e. C & Si) from other members of the group.

3.8.2 Occurrence

Only Carbon occurs in the free state as diamond, graphite and coal. In the combined state it occurs as hydrocarbons, carbohydrates and carbon dioxide (in the atmosphere). Silicon is a major constituent of rocks. Germanium is a rare element. Tin is found as tin stone, SnO_2 while lead is present in nature as galena (PbS).

3.8.3 Density, atomic and ionic radii, atomic volume

The density, atomic radii and atomic volumes of these elements show a regular increasing trend as usual. The ionic radii (of the ions with similar charge) also show the same trend as other physical properties given above.

3.8.4 Melting and boiling points

These properties generally decrease down the group though the trend is not regular. These values for C and Si are high because of their tendencies to form giant molecules.

3.8.5 Metallic and non-matallic character

The best illustration of the change from non-metallic to metallic character with increasing atomic number is provided by this group. The first two elements are non-metals, though Si shows some properties of metalloids, Ge is a semi-metal and the last two elements are metals.

3.8.6 Ionisation energy and electronegativity

As expected, the ionization energy values decrease down the group from C to Pb, though in an irregular manner. This is due to the presence of d-orbitals in case of Ge and Sn and f-orbitals in Pb in the penultimate shell which are not able to screen the valence electrons effectively in these elements.

The electronegativity also shows the same trend but the change is abrupt in the first two elements and then only a slight change is observed among other elements.

3.8.7 Valency and oxidation state

All the elements show a covalency of 4 and are tetra covalent involving sp^3hybridisation. Due to high ionisation energy values, the existence of simple M^{4+} ions are unlikely. Their low electronegatity also makes them unavailable for the formation of M^{4-} ions. The elements, C and Si, being non-metals do not have the tendency to form electrovalent compounds but Ge, Sn and Pb, the higher congeners of these elements, exhibit tetra and bi-electrovalency forming both M^{2+} and M^{4+} ions. Thus, the oxidation state of +2 and + 4 is shown by them in their compounds. The stability of tetravalent ions (+4 oxidation state) goes on decreasing from Ge to Pb. i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$ and that of +2 oxidation state (bivalent ions) increases down the group, i.e. $Ge^{2+} < Sn^{2+} <$ Pb2+. This behaviour of the ions of Ge, Sn and Pb is attributed to the inert pair effect which is more prevalent in the heavier p-block elements, i.e. maximum for Pb in this group. That is why Sn (II) salts are used as reducing agents while Pb (IV) salts are strong oxidising agents, i.e. $Sn^{2+} < Sn^{4+}$and $Pb^{2+} > Pb^{4+}$.

The nature of the compounds of M^{2+} and M^{4+} cations can be predicted by Fajan's rules, according to which the smaller cations cause more polarization of anions and make the compounds more covalent in nature. For example, Sn^{4+} ion is smaller than Sn^{2+} ion, hence Sn (IV) compounds are covalent while Sn (II) compounds are ionic in nature, similarly Pb (IV) compounds are covalent and those of Pb (II) are ionic.

3.8.8 Catenation or Self-linkage

This depends on the tendency of the elements to form homo-chains. The atoms of all the elements of this group have this tendency of linking with themselves to form long chains called homo-chains. This property of the elements is known as catenation or self-linkage which decreases down the group from C to Pb. Thus, carbon has maximum property of catenation while tin and lead hardly show this tendency, i.e. C > Si > Ge > Sn > Pb. This is because of decreasing M-M bond energy values for these elements (C= 348 $kJmol^{-1}$, Pb = 155 $kJmol^{-1}$). The result is that it is easy to prepare compounds containing C-C chains up to twenty or even more carbon atoms while for Si and Ge, it is not possible to extend Si-Si or Ge-Ge chains beyond six units. For Sn and Pb, the Sn-Sn or Pb-Pb chain cannot be extended beyond two units.

3.8.9 Allotropy

All the elements, except Pb, of this group show allotropy, i.e. exist in different forms, e.g. carbon exists in the two forms: crystalline-diamond and graphite, and amorphous- coal, coke, charcoal etc. Silicon and Ge also exist in two forms: crystalline and amorphous. Tin has three allotropic forms: white tin, grey tin and rhombic tin.

3.8.10 Formation of oxides

These elements form three types of oxides, *viz.* mon-oxides (MO type), dioxides (MO_2 type) and other oxides such as C_3O_2, Pb_3O_4, Pb_2O_3 etc.

3.8.11 Formation of hydrides

All the dements of this group form hydrides which are covalent in nature though the number of stable hydrides and the ease with which these are formed decreases as we move from C to Pb. The MH_4 type hydrides (monomers) are in the gaseous state. The thermal stability of these hydrides decreases steadily from CH_4 to PbH_4, as is evident from their decomposition temperature: $CH_4 = 800^0C$, $SiH_4 = 450^0C$, $GeH_4 = 285^0C$, $SnH_4 = 150^0C$ and $PbH_4 = 0^0C$ and decreasing M-H bond energy. This infers that the hydrides of higher elements are thermally unstable.

3.8.12 Formation of halides and halo complexes

All the members of this group form halides either of simple type, MX_4 (e.g. CCl_4, $SiCl_4$ etc.) or MX_2 (e.g. $SiCl_2$, SiI_2 etc.) or those in which H-atoms are also present, MH_3X (e.g. CH_3Cl), MHX_3 (e.g. $CHCl_3$, $SiHF_3$ etc.) or catenated type halides (e.g. $Si_{10}Cl_{22}$).

The tetra halides of these elements can be prepared by a common method which employs the heating of element with appropriate halogen. These trahalides are having decreasing thermal stability down the group, i.e. CX_4 is most stable and PbX_4 is least stable. The tetra halides, MX_4 of Si, Ge, Sn and Pb when reacted with X^- ions, form the hexahalo complex ions, e.g.

$$SiF_4 + 2F^- \longrightarrow [Si\,F_6]^{2-}$$

Other examples are: $[GeX_6]^{2-}$, X = F, Cl; $[Sn\,X_6]^{2-}$, X = F, Cl, Br, I and $[Pb\,Cl_6]^{2-}$

3.8.13 Acid formation

All the elements give acids of H_2MO_3 type whose sodium salts are stable. The elements, Carbon and Silicon also form acids of $(MOH)_2$ type, e.g. $(COOH)_2$: oxalic acid, $(SiOOH)_2$: silico oxalic acid.

3.8.14 Uses of group 14 elements

(a) Carbon is an essential element of the plant and animal kingdom. All fuels also contain carbon. SiC is an important compound of C used as an abrasive and B_4C is the hardest artificially made abrasive used for cutting diamonds.

(b) Si and Ge containing an impurity of Group 13 or Group 15 elements are used as the semiconductors. Silica (SiO_2) is an essential material for glass industry. Silicones are important polymers.

(c) Sn is used in the preparation of a number of useful alloys, in tin plating of iron sheets and tin amalgam for making mirrors.

(d) Pb is used for making cable covering, protective sheets for roofs and drains, water pipes and lining of the chambers in sulphuric acid manufacture and many important compounds, alloys etc.

3.8.15 Silicates

The most common elements on Earth's surface are oxygen, silicon, and aluminum. More than 80% of the atoms in the solid crust are either silicon or oxygen, primarily in the form of silicates. Silicates are minerals made up of silicon and oxygen arranged in tetrahedral SiO_4^{4-} units that are connected in various ways. Aluminosilicate clays, silica, and silicate minerals make up around 95% of the earth's crust. Because the chemical composition of silicates is essential to the cement, ceramic, and glass industries, they are highly valued. Because the minerals contain silicates, silicates are frequently produced as waste products or slag during the metallurgical extraction process.

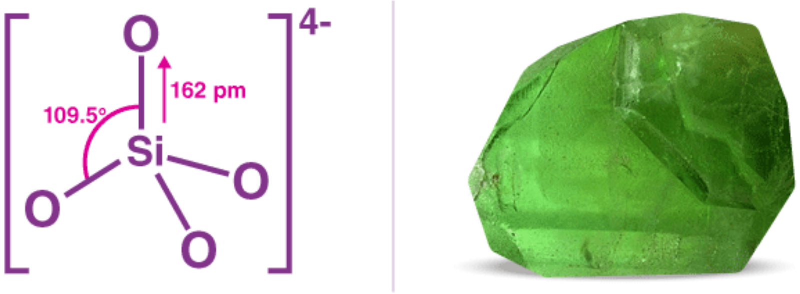


Fig. 3.1 Structure of the Silicates

The basic principle of silicate structure is suggested by the X-ray crystallographic method.

- The discrepancy in electronegativity between silicon and oxygen (3.5-1.8 = 1.7) indicates that there are 50% covalent and 50% ionic bonds between the two elements.
- The radius ratio of Si^{4+}/O^{2-} = 0.29 indicates that silicon is surrounded by four oxygen atoms at the corners of a tetrahedron and is four coordinated.
- By sharing corners with oxygen atoms, the SiO_4^{4-}tetrahedral can either exist as discrete units or polymerize into massive units.
- The oxygen atoms come together to form a dense structure with octahedral and tetrahedral voids. For one kind of vacancy, the majority of metal ions are the perfect size. Al, on the other hand, can occupy octahedral and tetrahedral voids.

3.8.15.1 Preparation of Silicates

Sicates can be prepared by fusing an alkali metal carbonate with sand in anelectric furnace at about 1400^0C.

$$Na_2CO_3 \xrightarrow{1400^0C} CO_2 + Na_2O \xrightarrow{+SiO_2} Na_4SiO_4$$

3.8.15.2 Classification of silicates

Depending on the way the tetrahedral units are linked, the silicates are classified into the following types.

(i) Orthosilicates

(ii) Pyrosilicates

(iii) Cyclic silicates

(iv) Chain silicates

(v) Double chain silicates

(vi) Sheet silicates

(vii) Three-dimensional silicates

3.9 ELEMENTS OF GROUP-15

The group 15 (group VA) of the extended or long form of periodic table contains five elements, namely nitrogen (N_7), phosphorous (P_{15}), arsenic (As_{33}), antimony (Sb_{51}) and bismuth (Bi_{83}). This group is also known as nitrogen group. All the elements of this group belong to p- block due to the filling of p- orbital (or subshell) of the valance shell by the last electron of the atoms of these elements.

The first two elements (N and P) are distinctly nonmetals.

The next two elements (As and Sb) are semi- metals and the last element Bi, is metallic in nature.

These elements, except phosphorous, do not occur very abundantly in nature. Nitrogen constitutes only about 0.0045%, phosphorous 0.116%, As, Sb and Bi nearly 10^{-4} % of the rocks of earth. The phosphorous ranks tenth in abundance among all the elements known, nitrogen constitutes nearly 78 percent by volume of the atmosphere.

3.10 GENERAL CHARACTERISTICS

The inclusion of nitrogen group elements in the same group of modern periodic table is justified by the following general characterstics of these elements. These elements furnish another example in which there is a systematic gradation of properties and there is a change of character from a true nonmetal like nitrogen to a nearly true metal, e.g., bismuth.

3.10.1 Electronic configuration

There are five electrons in the valance or ultimate shell of the atoms of these elements, i.e., ns^2p^3 where n is the principal quantum number of the valance shell. Two of these electrons are in the s- subshell and the rest three are occupying the p- subshell according to the Hund's rule among the three p- orbitals. Because of exactly half- filled orbitals, the elements are fairly stable and not so reactive. The penultimate shells have variation in the number of electrons. The first element, N, has helium configuration s^2, P has inert gas octet s^2p^6 and other elements have pseudo inert gas, $s^2p^6d^{10}$, configurations, respectively in the penultimate shells of their atoms. This variation in the configuration is responsible for gradation of properties in the group.

3.10.2Occurrence

Nitrogen occurs in the free State as the diatomic gas in nature while all the remaining elements occur in the combined state. In the combined state it occurs mainly as nitrates. Being very reactive, phosphorous does not occur in the native state, rather it occurs as phosphates in its ores. As, Sb and Bi are less abundant and occur chiefly as sulphide ores.

3.10.3Physical state and elemental structure

Nitrogen is a gas, phosphorous is a soft, lusterless solid, others are hard solids, Sb and Bi having characteristic metallocluster. Nitrogen gas exists as a diatomic molecule, N_2 while P, As and Sb exist as tetratomic molecules, P_4, As_4 and Sb_4. These are not capable of forming diatomic molecules like N_2 because they do not form $p\pi$ - $p\pi$ bonds as their larger atoms cannot come closer to each other to form such bonds as well as due to the increased repulsions from the non-bonding electrons of penultimate shell. The repulsion from the electrons of penultimate shell, $1s^2$, in nitrogen atoms is not appreciable. Further, formation of π bonds in the N_2 molecule satisfies the valency requirements of N- atoms while non formation of such bonds in other elements compels them to join with more atoms hence M_4 molecules are formed. These elements thus form giant lattices in which the bonding changes from covalent to metallic from P to Bi.

3.10.4 Metallic and non-metallic character

The change from non- metallic to metallic character with increasing atomic number in the same group, exhibited by group 14, is observed equally well in this group also, the only metallic element being Bi, the last element of the family which has the lowest value of ionization energy. This is revealed by the variation in the properties both physical and chemical.

3.10.5 Density, hardness, atomic radius, and atomic volume

Ongoing from P to Bi (N- being a gas excluded) these properties increase regularly and markedly. The atomic radius and atomic volume also increase down the group with the exception of atomic volume of as which has low value.

3.10.6 Ionization energy, electro negativity and heat of atomization

With increasing size from N to Bi, the values of first ionization energies decrease on descending the group. Similar is the trend in the electro negativity and heat of atomization. This gradation confirms the gradual increasing metallic character of the elements.

3.10.7 Melting and boiling points

The melting points (expect for Sb and Bi) and the boiling points both increase with increasing atomic number. The melting point of Bi is unusually low perhaps because of non-availability of ns^2 electron pair for bonding in the metallic crystal. The elements of this group are more volatile than their immediate neighbours of group14.

3.10.8 Oxidation states

(i) Formation of M^{5+} and M^{3+} cations

M^{5+} cations are formed when all the valance electrons, ns^2p^3, are used by the elements for bonding. N and P cannot lose all the five valance electrons due to prohibited energy considerations, i.e., because they have high ionization energies and electronegativities and hence do not form M^{5+} ions. These elements also do not form M^{3+} ions as such but these oxidation states, i.e.,+3 and +5 can be assigned to them arbitrarily in their compounds with more electronegative elements, *viz*. O and F if formed. M^{3+} cations are formed by the elements if they lose only p- electrons from ns^2p^3 configuration of the valence shell and ns^2 electron pair remains inert (inert pair effect). Since this effect increases down the group, the heavier elements, *viz*. Sb and Bi are expected to form M^{3+} ions by losing three p- electrons only and retaining the ns^2 electron pair, though they can form M^{5+} ions as well. Thus, only As and Sb will give salt with +5 and +3 oxidation states and Bi gives only Bi^{3+} ions.

(ii) Formation of M^{3-} anions

In order to achieve noble gas configuration, these elements accept three electrons from electropositive elements and form M^{3-} ions, e.g., N in NH_3 has -3 oxidation state. As the size of the atoms increases on moving down the group, the ionization energy and electronegativity values decrease and hence the attraction of the nucleus for the newly added electrons decreases. Thus, the tendency of the elements to give M^{3-} ions also decreases. In fact, N-atom, being smallest in size, has strongest tendency to form N^{3-} ion, P forms P^{3-} ions less readily and Bi, the last member of the group, hardly exhibits negative oxidation state.

(iii) Covalency of 3 and 5

Each of these elements has two paired s- electrons and three unpaired p- electrons in the valence shell. If these elements form three covalent bonds using only the p- electrons, they attain the noble gas configuration (ns^2p^6). This gives the covalency of 3 to these elements. Except nitrogen, these elements also have vacant d- orbitals in the valence shell. Under suitable conditions of energy, one of the electrons of s level may be promoted to the vacant d–orbital, thus possessing five unpaired electrons. These five unpaired electrons may be used to form five covalent bonds, thereby giving the covalency of 5 to these elements. This covalency is common among P, As and Sb. That is why N forms only trihalide and other elements form tri as well as pentahalides.

3.10. 9 Electron donor – acceptor properties

All the elements in the trivalent state have a tendency to act as electron pair donors. Nitrogen having this tendency to the maximum extent. For example, NH_3 and PH_3 molecules act as Lewis bases towards H^+ to form NH_4^+, PH_4^+ etc. due to presence of lone pair of electrons on N and P- atoms, thereby N showing a maximum covalency of 4, P, As and Sb show a covalency of 6 in [PCl_6]$^-$, [AsF_6]$^-$and [SbF_6]$^-$ complex ions in which their salts act as electron pair acceptors.

$$PCl_5 + Cl^- \rightarrow [PCl_6]^-$$

3.10. 10 Allotropy

All the elements, except Bi, show allotropy. Nitrogen in solid state exists in two allotropic forms *viz.* α-nitrogen and β – nitrogen. Phosphorous exists in various forms such as white, red, scarlet, α–black, β–black and violet. Arsenic exists in grey, yellow and black allotropic forms while antimony in the forms as yellow, black, β- and explosive.

3.10.11Catenation (Self linkage)

Although the catenation is considered to be a property peculiar to carbon, yet it is shown to some extent, by the elements lying close to carbon in the periodic table. The elements of this group have been found to show this property but to a much smaller extent than carbon. Thus, unstable compounds containing chains of upto eight N- atoms have been prepared but stable azide ion has a chain of three N- atoms, i.e. (N-N-N)$^-$ skeleton and $H_2N–NH_2$ has two N- atoms. In case of phosphorous, P-P links are limited to two atoms (e.g.P_2H_4). Other elements of the group have no tendency of self-linkage. Thus, tendency for catenation decreases on moving down the group because of gradual decrease in bond energies of M-M bonds.

3.10.12 Electrical and thermal conductivity

Both these properties increase as we move down the group because of increased delocalization of electron from nitrogen to bismuth (with a metallic crystal lattice). Thus Nitrogen and Phosphorus are non-conductors, As is a poor conductor, Sb is a good conductor and Bi is an excellent conductor.

3.10. 13 Combination with active metals

All these elements form compounds with metals, e.g., N forms nitrides: LiN, Mg_3N_2etc; phosphorous forms phosphide Ca_3P_2 etc., Arsenic gives arsenides Na_3As etc., Sb gives antimonides Mg_3Sb_2 and Bi forms bismuthides Mg_3Bi_2 etc. The nitrides among these compounds are most stable. The last two types of compounds are rare and Sb and Bi, infact, form alloys on combining with metals.

3.10.14 Chemical reactivity

These elements differ from one another appreciably in their chemical reactivity. Nitrogen is chemically non–reactive. It does not combine under ordinary conditions. It combines with elements such as Li, Al, Ca, Mg etc. to form nitrides at high temperature only and combines with oxygen only when heated in an electric arc to a temperature of the order of 2500^0C and above forming nitric oxide. On the other hand, white phosphorous, an allotropic form of P, is extremely reactive. It burns readily in oxygen forming oxides of phosphorous. The heavier elements, *viz.* As, Sb, Bi burn only when heated in air or oxygen, to form oxides. This can be attributed largely to difference in the electro negativities of the five elements.

3.10.15 Uses

(i) Nitrogen is an essential element for the growth of plants. It is generally added to the soil in the form of the fertilizers (compounds of Nitrogen) or atmospheric nitrogen is fixed by nature and this is absorbed by soil. From the soil it goes to the plants and then to the animals.

(ii) Red variety of P being non-poisonous is mostly used in match industry.

(iii) Phosphorous is also used as rat poison and in the manufacture of tracer bullets as well as in producing smoke screens.

(iv) As-Pb alloy is used in making lead shots.

(v) Antimony is mainly used in the manufacture of lead storage batteries as it is harder and acid resistant.

(vi) Bi-alloys have low melting points and are called fusible alloys. These are used in making automatic electrical fuses, fire alarms, sprinklers, safety plugs on boilers etc.

3.11 ELEMENTS OF GROUP-16

In continuation of group-15 elements, within this unit you will learn about general properties, structure and uses of 16-group elements. There are five elements in this group, of which the first four are non-metals. All the elements of this group are solid except oxygen. Oxygen, sulphur and selenium are non-metals, tellurium metalloid while polonium is metallic in nature. These are also called as chalcogens. Chalcogens means ore-forming elements, as a large number of metal ores are oxides or sulphides.

Several reagents of this group element are commercially important. Sulphuric acid (H_2SO_4), sodium sulphite (Na_2SO_3) and hydrogen peroxide (H_2O_2) are some of them. The elements can be divided into metal (polonium, Po) and non-metals (oxygen, sulphur, selenium and tellurium; O, S, Se and Te).

Oxygen shows different properties from the other members of this family because oxygen has strong tendency to form π bond while sulfur has greater tendency to form chains and rings. Selenium, tellurium and polonium form toxic compounds which should be handled with great care.

3.12 GENERAL CHARACTERISTICS AND USES

Atomic radius, density and metallic character increase from oxygen to polonium while ionization potential decreases from oxygen to polonium. Oxygen is a diatomic gas while sulphur, selenium and tellurium are octa-atomic S_8, Se_8 and Te_8. Electronic configurations of each element of this group are given below. All elements except oxygen exhibit –2, +2, +4 and +6 oxidation states. All the elements of 16th group exhibits allotropy. Se, S, Te, Po and oxygen have 6, 4, 2, 2 and 2 allotropes, respectively. Out of 6 allotropes of Se, three are red nonmetallic, one amorphous red and two grey metallic forms. Allotropes of sulphur are α–(rhombic or octahedral sulphur), β-(monoclinic or prismatic sulphur), γ-(monoclinic sulphur) and λ– (plastic) sulphur. Te has one metallic and one non-metallic allotrope while Po has 2 allotropes; one α–cubic and the other β–rhombohedral. The two allotropes of oxygen are O_2 (oxygen) and O_3 (ozone). Elements of group 16 form a number of binary and ternary compounds. Among binary compounds; hydrides, halides and oxides are the main compounds.

Sixteenth group elements (VIA group) form H_2M type hydrides. All hydrides are covalent in nature. All hydrides are poisonous gases with unpleasant and foul smell. Group 16 elements form monohalides (M_2X_2 type), dihalides (MX_2 type), tetrahalides (MX_4 type) and hexahalides (MX_6 type) where M is an element of 16th group and X may be F, Cl, Br or I. The oxides formed by group 16 elements are dioxides (MO_2 type) and trioxides (MO_3 type). Other important ternary complexes formed by elements of 16th group are oxoacids (-ous and -ic acids) such as sulphurous (H_2SO_3) and sulphuric (H_2SO_4) acids, sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) etc.

3.12.1 Electronic configuration of 16 group elements

Oxygen (O) – $1s^2\ 2s^2\ 2p^4$

Sulphur (S) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Selenium (Se) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

Tellurium (Te) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^4$

Polonium (Po) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^4$

We know that dioxygen (O_2) is used in respiration by both plants and animals. Besides this, it is also used in steel plants. Along with air, dioxygen is used in blast furnaces for the reduction of iron-oxides to impure pig iron by coke. Dioxygen is also used in oxy-acetylene welding, metal cutting, manufacture of HNO_3 from NH_3 and ethylene oxide from ethane. Titanium dioxide is used as a white pigment in paint and paper and as filler in plastics. Dioxygen is also used as oxidant in rockets. Sulphur is the minor constituent of certain amino acids such as cystine, cysteine and methionine. Sulphuric acid (H_2SO_4) is used for making fertilizers while sulphite (SO_3^{2-}), hydrogen sulphites (HSO_3^-) and sulphur dioxide (SO_2) are used in bleaching. Sulphur is also used in the manufacture of carbon disulphide (CS_2), rubber, fungicides, insecticides and an explosive–gunpowder. Both sulphur and selenium dehydrogenate saturated hydrocarbons. Selenium metal (Se) is used to decolorize glass. Photoreceptors of photocopiers are made up of selenium. Selenium is an essential trace element and a component of many enzymes such as glutathione and peroxidase. When taken in larger quantity, it becomes toxic to the human beings. Tellurium (Te) is used in the manufacture of steel and non-ferrous alloys. Selenium and tellurium when absorbed in human body, excreted as foul-smelling organic compounds along with breath and sweat. Polonium (Po) is a radioactive element.

3.13 OXIDES OF SULPHUR

Sulphur mainly forms dioxides (SO_2), trioxide (SO_3) and sesquioxide (S_2O_3).

3.13.1 Sulphur dioxide (SO_2)

3.13.1.1 Preparation:

Sulphur dioxide can be prepared by

(i) Burning sulphur (S) or sulphide ores in excess of air. This is the **commercial process** of SO_2 production.

$$S + O_2 \rightarrow SO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

(ii) Reaction of concentrated H_2SO_4 with Cu turnings, S, charcoal, Ag and Hg (**Laboratory method**)

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 \; 2H_2O$$

(iii) Large amount of SO_2 is produced as a waste product during coal and/or other fossil fuel burning. This SO_2 is harmful for environment.

3.13.2 Properties

3.13.2.1 Physical properties

Sulphur dioxide is a colourless gas with suffocating smell. It solidified at –76ºC and liquefied to a colorless liquid at –10ºC.

3.13.2.2 Chemical properties

The different chemical properties of SO_2 are given below:

(i) At 1200ºC, it decomposes into SO_3 and S.

$$3S + O_2 \rightarrow 2SO_3 + S \text{ (at } 1200^0\text{C)}$$

(ii) SO_2 is an **acidic oxide**. In aqueous solution, it shows acidic properties.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (Sulphurous acid)}$$

Due to its acidic nature, it also reacts with basic oxides to form sulphides.

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

$$SO_2 + CaO \longrightarrow CaSO_3$$

(iii) Formation of addition compounds. As maximum covalency of sulphur atom is six, SO_2 (with four covalency), can form addition compound with O_2, Cl_2, PbO_2 and BaO_2 to attain maximum covalency of six.

$$SO_2 + O_2 \xrightleftharpoons{\text{Pt or } V_2O_5} 2SO_3$$

$$SO_2 + Cl_2 \xrightleftharpoons[\text{or camphor}]{\text{Sunlight}} SO_2Cl_2$$

$$SO_2 + PbO_2 \xrightleftharpoons{\Delta} PbSO_4$$

(iv)Oxidizing properties:SO_2 (S = +4) acts as a good oxidizing agent with strong reducing agents and reduces itself to S (S = 0).

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

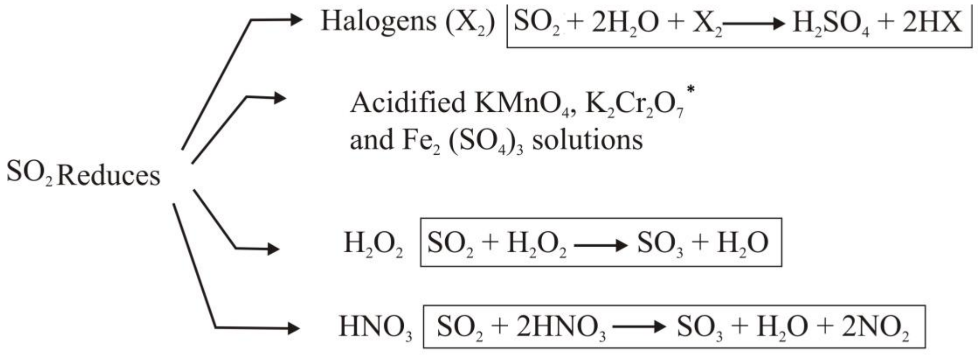
$$SO_2 + 2CO \longrightarrow 2CO + S$$

$$SO_2 + 4HCl + 2SnCl_2 \longrightarrow 2SnCl_4 + 2H_2O + S$$

(v) Reducing properties:In presence of moisture, SO_2 can act as reducing agent as it liberates nascent hydrogen on reaction with moisture (The nascent hydrogen acts as a reducing agent).

$$SO_2 + \underset{\text{(moisture)}}{H_2O} \longrightarrow SO_3 + 2H$$

During reduction process, SO_2 get oxidized to SO_3 or H_2SO_4.



$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$3SO_2 + K_2CrO_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO4)_3 + H_2O$$

$$SO_2 + 2H_2O + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 \quad 2H_2SO_4$$

3.13.3 Uses

(i) SO_2 is used for the production of other chemicals such as $NaHSO_3$, Na_2CO_3 and $Na_2S_2O_3$

$$2SO_2 + Na_2CO_3 + H_2O \longrightarrow \underset{\substack{\text{Sodium bisulphite} \\ \text{(sodium hydrogen sulphite)}}}{2NaHSO_3} + CO_2$$

$$2NaHSO_3 + Na_2CO_3 \longrightarrow \underset{\text{Sodium sulphite}}{2Na_2SO_3} + H_2O + CO_2$$

$$Na_2SO_3 + S \xrightarrow{\text{heat}} \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

(ii) SO_2 is also used as a non-aqueous solvent. Liquid SO_2 is a useful solvent as a number of inorganic and organic compounds are soluble in this solvent.

3.14. ELEMENTS OF GROUP-17

Halogens belong to VIIA/17th group of the periodic table. It consists of five elements *viz.* flourine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are non-metallic elements and also called halogens. The term halogen is derived from the Greek halo (=salt) and gens (=born) meaning salt producers because most of the elements exist in sea water, such as chlorides. Halogens contain 7 (seven) electrons in their valence shell. Astatine is radioactive. Flourine is the most electronegative, highly reactive and is called as super halogen. Halogens are not found in free state because they are highly reactive. They are found in sea water in the form of halides.

Astatine is a radioactive element and formed artificially. General electronic configuration of VIIthgroup elements is ns^2 np^5. They are very reactive and found in diatomic form like F_2, Cl_2, Br_2, I_2 (**Table 3.1**).

Elements	**Atomic no.**	**Electronic Configuration**	**Noble gas with configuration**
Fluorine (F)	9	$1s^2 2s^2 2p^5$	(He) $2s^2 2p^5$
Chlorine (Cl)	17	$1s^2 2s^2 2p^8 3s^3 3p^5$	(Ne) $3s^2 3p^5$
Bromine (Br)	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	(Ar) $3d^{10} 4s^2 4p^5$
Iodine (I)	53	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$	(Kr) $4d^{10} 5s^2 5p^5$
Astatine (At)	85	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 6p^5$	(Xe) $4f^{14} 5d^{10} 6s^2 6p^5$

Table 3.1 Electronic configuration of halogen family

3.15 GENERAL CHARACTERISTICS AND USES

3.15.1 Physical properties of halogens (Table 13.2 and Table 13.3)

Properties	**F**	**Cl**	**Br**	**I**	**At**
Atomic number	9	17	35	53	85
Atomic mass	19	35.45	79.90	126.90	210
Covalent radii (Å)	0.64	0.99	1.14	1.33	–
Ionic radii (Å)	1.33	1.84	1.96	2.20	–
Ionic enthalpy (KJmole^{-1})	1680	1256	1142	1008	–
Electronegativity	4	3.2	3	2.7	2.2
Electron affinity (KJmole^{-1})	–333	–349	–325	–296	–270

Table 3.2 Atomic halogens

Properties	**F_2 gas**	**Cl_2 gas**	**Br_2 liquid**	**I_2 solid**
Colour	Yellow	Green Yellow	Red Brown	Deep Violet
Density g/cm^3 (Liquid form)	1.51	1.66	3.19	4.94
Melting point (^{0}C)	-219	-101	–7	114
Boiling Point (^{0}C)	-188	-35	60	185
Bond length(Å)	1.43	1.99	2.28	2.66
Bond Dissociation Enthalpy (KJmole^{-1})	158.5	242.6	192.8	151.1

Table 3.3 Molecular halogens

3.15.2 Physical state

All halogen are non-polar solvent and diatomic molecules and their physical state are

F_2	Cl_2	Br_2	I_2
Gas	Gas	Liquid	Solid

Difference in the physical state depends upon their van der Waals force which further depends on their atomic size and molecular weight. Size and atomic weight of chlorine and fluorine are less and thus, the van der Waals forces are weak. Hence, Cl_2 and F_2 are in gases phase. Size of Br_2 is more than Cl_2 and F_2 which is liquid and I_2 is much higher in size and it forms in solid phase.

3.15.3 Melting and boiling points

As size of the elements in group increases, van der Waals force also increases and thus, m.p. and b.p. of molecules also increases. The order of m.p. and b.p. of the halogens follow the order:

$$F_2 < Cl_2 < Br_2 < I_2$$

3.15.4 Ionization enthalpy or ionization potential

Due to the small atomic size, halogens have higher ionization energy and less power to remove electron to form X^+ ion. Ionization enthalpy increases down words in a group because their size increase.

$$F > Cl > Br > I \text{ (I.P.)}$$

3.15.5 Electronegativity

Group 16 elements have higher electronegativity because of small size of the atoms and fluorine is most electronegative element in the periodic table.

$$F > Cl > Br > I \text{ (see table 3.2)}$$

3.15.6 Electron affinity

Electron affinity of halogens upto chlorine increases and after chlorine decreases. Flourine has lower electron affinity because of the small size of fluorine. The outer most shell has higher electron density and due to electron-electron repulsion, it cannot gain electron easily.

3.15.7Odour

All the halogens have very pungent odours. If inhaled, even in very small quantities, they cause inflammation of the mucous membrane of the throat and nose. Thus, responsible for irritation of respiratory duct. Large quantities may have fatal effect.

3.15.8 Nonmetallic character

All halogens are non-metallic. Downward in a group, their nonmetallic character decreases and metallic character increases and iodine shows some metallic properties such as:

(i) Iodine is solid (ii) Iodine has metallic luster (iii) Iodine can form cation.

3.15.9 Bond energy and reactivity

Halogens are diatomic molecules and iodine has the least bond energy because as the size increases, nucleus will be far apart from outermost shell. Thus, the subshell has weaker over lapping tendency. Bond energy of fluorine is less than chlorine and bromine due to the size of fluorine and non-bonding electron-electron repulsion in fluorine molecule.

$$Cl_2 > Br_2 > F_2 > I_2 \text{ (Order of bond energy)}$$

3.15. 10 Oxidation state

Electronic configuration of halogen family is ns^2np^5. It can gain $1e^-$ to attain noble gas configuration. Except fluorine, other elements of the group have d orbitals. Hence, fluorine shows (–1) oxidation state only. Other elements show –1, +1, +3, +5, +7 oxidation states.

3.15.11 Solubility of halogens

Halogens are nonpolar in nature, hence, are slightly soluble in water. Their solubility decreases from Cl to I. Flourine is not soluble as it decomposes with water librating O_2 and O_3.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$

The halogens are more soluble in organic solvents like CCl_4, $CHCl_3$, CS_2 and hydrocarbons. In organic solvents like $CHCl_3$ and CCl_4, Cl_2 gives yellow, Br_2 gives brown colour and I_2

gives violet colour. In the presence of sun light, they are decomposed. Cl_2 is more reactive than Br_2.

Sun light

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$Br_2 + H_2O \rightarrow HBr + HBrO$$

3.15.12 Chemical properties of halogens

Halogens are chemically more reactive due to high electronegativity, high electron affinity and low dissociation energy. Among halogens, F is the most reactive element and reactivity decreases as: F > Cl > Br > I.

3.16 HALIDES AND HALOGEN OXIDES

3.16.1Characteristics of hydrogen halides

Halides are mainly of three types: (i) Ionic halides like LiF, CaF_2, SrF_2, BaF_2 (ii) Molecular or covalent halides ($OsCl_4$, $OsBr_4$, BCl_3, PCl_3, PCl_5, CCl_4 etc.) and (iii) Bridging halides ($AlCl_3$, BeF_2, $BeCl_2$, HbF_5, TaF_5etc).

Hydrogen halides have general formula HX, where X is halogen (Cl, Br, I, F). Their aqueous solutions are called as hydrohalic acids or halogen acids. All the halogens react with hydrogen to form hydrides (HX). Reactivity of halogens toward hydrogen decreases down a group. Fluorine violently reacts with hydrogen. Hydrogen reacts with chlorine very slowly in the dark, faster in day light and explosively in sunlight. Reaction of hydrogen with iodine is very slow at room temperature.

The other characteristics of hydrogen halides are discussed in following section.

(a) Physical state: Except HF which is liquid at room temperature, other halogen halides are found in gas state. In liquid state of HF, due to the intermolecular hydrogen bonding, the HF molecules associate with each other to form liquid. The other halogens do not form hydrogen bond and hence, they are gases at room temperature.

Hydrogen bonding in HF molecule

(b) Thermal stability: Stability of halides decrease from HF to HI. HF is highly stable and HI is the least. From HF to HI, thermal stability decreases.

$$HF > HCl > HBr > HI$$

This trend is observed due to the hydrogen bonding in HF.

(c) Acidic behaviour: Downwards in the group, the acidic nature increases because size increases and release of hydrogen become easier.

$$HF < HCl < HBr < HI$$

(d) Reducing properties: Downwards in a group, reducing properties increase because bond energy decreases.

$$HF < HCl < H Br < HI$$

Order of reducing property

3.16. 2 Oxides of halogens

The electronegativity difference between the halogens and oxygen is very small; hence, the bonds in halogen oxides are covalent. Most of the oxides of halogens are unstable and explosive in nature (when exposed to light or shock). The oxides of iodine are the more stable than the chlorine oxides. While the oxides of bromine are very unstable as they decompose below room temperature. Oxides with higher oxidation states are more stable as compared to lower states.

The different oxides formed by halogens are OF_2, O_2F_2, F_2O_4, Cl_2O, ClO_2, Cl_2O_7, Cl_2O_6, ClO_3, Br_2O, BrO_2, I_2O_5, I_4O_9 and I_2O_4. Among these, ClO_2, Cl_2O, I_2O_5 and OF_2 are the most useful. ClO_2 is used in paper industry, bleaching clothes and purification of water. OF_2 and $Cl_2O_7$are strong oxidizing agents. In this section, you will read detailed chemistry of some halogen oxides.

(i) Oxygen difluoride (OF_2)

It is a pale-yellow gas used as an oxidizing agent and rocket fuel. It vigorously reacts with metals, S, P and halogens to give fluorides and oxides. It has V-shaped geometry as in case of H_2O molecule.

(ii) Dioxygen difluoride (O_2F_2)

It is an unstable orange yellow solid with oxidizing and fluorinating properties. Structurally, it is similar to H_2O_2.

(iii) Dichlorine monoxide (Cl_2O)

It is a yellow brown gas used in the preparation of hypochlorites such as NaOCl, $Ca(OCl)_2$, chlorinated solvents and as bleaching agent. It is also V-shaped but the bond angles of the three oxides (F_2O, Cl_2O, Br_2O) increases in following order:

$$F_2O < Cl_2O < Br_2O$$

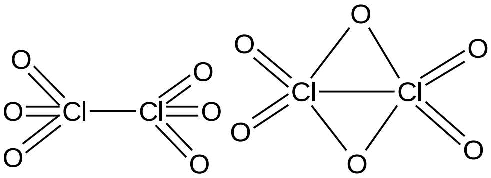
The different bond angles are due to the steric crowding of the larger halogen atoms.

(iv) Chlorine dioxide (ClO_2)

It is a yellow gas and used for bleaching purpose, purifying drinking water and manufacturing $NaClO_2$. It is paramagnetic due to the presence of an odd electron. It does not dimerize because, the odd electron is delocalized.

(v) Dichlorinehexaoxide (Cl_2O_6)

It is a dark red liquid and solidifies at –180ºC. It is a strong oxidizing agent and explodes when comes in contact with grease. The probable structure of Cl_2O_6 is–

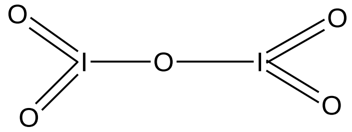


(vi) Dichlorine heptoxide (Cl_2O_7)

It is a colourless liquid and shock sensitive and less reactive than lower oxides.

Oxides of bromine are less important as those of chlorine. Br_2O is a dark brown liquid while BrO_2 is a pale-yellow solid.

Oxides of iodine are more stable as compared the other halogen oxides. Iodine pentaoxide (I_2O_5) is useful in analyzing gases. I_2O_5 is having a three-dimensional network.



The other iodine oxides are moderately or less stable.

3.17 INTERHALOGEN COMPOUNDS

Interhalogen compounds are the compounds of more than one halogen. General formula is AB_n, where A and B are halogens, A is heavier than B (n = 1, 3, 5, 7). Most of the interhalogen compounds are fluorides. They can be classified as:

i. Neutral – They are binary compounds such as BrF_3 or IF_7.
ii. Cations – They may be homonuclear I_2^+ or Cl_3^+ or heteronuclear $I_3Cl_2^+$.
iii. Anions – Polyhalide anion such as I_3^- or $IBrCl^-$.
iv. Covalent organic derivatives – $ArAF_n$ (Where Ar = arene; A = I or Br and n = 2 or 4).

3.17.1 General Properties

(i) The interhalogen compounds are covalent diamagnetic molecules.
(ii) They are generally volatile solids or liquids except ClF which is a gas at 25ºC.
(iii) These are more reactive than parent halogens. All of them show halogenation reactions: (BrF_3, IF_5, ICl are good halogenating agents).
(iv) Interhalogens can be hydrolysed by water or alkali to produce halide ion of the lighter halogen.

$$AB + H_2O \rightarrow HB + HOA \text{ (AB type)}$$

(v) Interhalogens can add to alkenes (addition reaction)

$$H_2C = CH_2 + ICl \rightarrow ICH_2 - CH_2Cl$$

(vi) They are strong oxidants and can be used to halogenate metals and metal oxides.

(vii) They act as useful fluorinating agents. There reactivity order is as follows:

$$ClF_3 > BrF > BrF_5 > IF_7 > ClF > IF_5 > BrF$$

(viii) Thermal stability order of reactivity [(IF (1.5) >BrF (1.2) >ClF (1.0) >ICl (0.5) >IBr (0.3) >BrCl (0.2)].

(ix) These are used as non-aqueous solvents.

(x) They are polar in nature.

(xi) Reactions with non-metallic and metallic oxides: when react with oxide, form corresponding fluorides.

$$4BrF_3 + 3SiO_2 \rightarrow 3SiF_4 + 2Br_2 + 3O_2$$

(xii) Self-ionization (halide ion transfer) – Show donor acceptor property (generally liquid interhalogens have this quality).

$$ICl, IBr, BrF_3, IF_5$$

3.17.2 Preparation

(A) (AB type interhalogen) – (ClF, BrF, BrCl, ICl, IBr)

(i) Direct reaction of halogens

$$Cl_2 + F_2 \xrightarrow{225^0C} 2ClF$$

$$Br_2 + F_2 \xrightarrow{300^0C} 3BrF$$

$$I_2 + F_2 \xrightarrow{\text{Room Temp.}} 2IF$$

$$Cl_2 + ClF_3 \xrightarrow{300^0C} ClF$$

(ii) By direct reaction of halogens with interhalogen compounds

$$Br_2 + BrF_3 \longrightarrow 3BrF$$

(B) AB$_3$ type interhalogens

$$Cl_2 + 3F_2 \xrightarrow[\text{Cu or Ni}]{200\text{-}300^0C} 2ClF_3$$

$$ClF + F_2 \xrightarrow[\text{Cu or Ni}]{200\text{-}300^0C} ClF_3$$

$$Br_2 + 3F_2 \xrightarrow{\text{Room Temp}} 2BrF_3$$

$$BrF + F_2 \xrightarrow{\text{Room Temp}} BrF_3$$

$$F_2 + I_2 \xrightarrow{CCl_3F} 2IF_3$$

$$I_2 + 3XeF_2 \longrightarrow 2IF_3 + 3Xe$$

(C) AB$_5$ and AB$_7$ type interhalogens

$$Cl_2 + 5F_2 \xrightarrow{\text{Excess F2, }350^0C\text{ or }250^0\text{ atr.}} 2ClF_5$$

$$ClF_3 + F_2 \xrightarrow{\text{hv, room temp, 1 art}} ClF_5$$

$$I_2 + 5F_2 \xrightarrow{> 150^0C} IF_5$$

$$I_2 + 5F_2 \xrightarrow{250^0\text{-}300^0C} IF_7$$

3.17.3 Chemical Properties

(A) AB type is terhalogen compounds

(i) Halogenation's reaction

ClF is a good fluorinating agent and reacts with many metals or nonmetals either at room temperature or above and convert them to fluorides and liberate chlorine.

$$W + ClF \rightarrow WF_6 + 3Cl_2$$

$$Se + 4ClF \rightarrow SeF_4 + 2Cl_2$$

It can also act as a chlorofluorinating agent by addition across a multiple bond:

$$(CF_3)_2\,CO + ClF \xrightarrow{MF} (CF_3)_2\,CFOCl$$

$$CO + ClF \longrightarrow COFCl$$

$$5F_4 + ClF \xrightarrow{CSF} 5F_5\,Cl$$

$$\text{Reaction with water} \longleftarrow H_2O + 2ClF \longrightarrow 2HF + Cl_2O$$

$$HNO_3 + ClF \longrightarrow HF + ClONO_2$$

(ii) Donor acceptor property

$$BrF_3 + 2ClF \rightarrow [Cl_2F]^+ [BrF_4]^-$$

As solvent system

Both ICl and IBr partially dissociate into ions which gives rise to an electrical conductivity.

$ICl + MCl \rightarrow M^+ [ICl_2)^-$

$$2ICl + AlCl_3 \rightarrow [I_2Cl]^+ [AlCl_4]^-$$

$$PCl_5 + ICl \rightarrow [PCl_4]^+ [ICl_2]^-$$

$$SbCl_5 + 2ICl \rightarrow [I_2Cl]^+ [SbCl_6]^-$$

(B) AB$_3$ type interhalogen compounds

Properties:

ClF$_3$ and BrF$_3$ are volatile liquid whereas IF$_3$ and ICl$_3$ are solids. ClF$_3$ is the most reactive chemical compound. It reacts explosively with water and with most organic substances. BrF$_3$ is used for preparative work.

(i) Fluorinating agent

$$2AgCl + ClF_3 \rightarrow 2AgF + Cl_2 + ClF$$

$$Co_3O_4 + 3ClF_3 \rightarrow 3CoF_3 + 3/2Cl_2 + 2O_2$$

$$NH_3 + 2ClF_3 \rightarrow 6HF + N_2 + Cl_2$$

$$U + 3\ ClF_3\ (l) \xrightarrow{50\text{-}90^0C} UF_6 + 3ClF$$

$$2ClF_3 \rightarrow (ClF_4)^- [Cl_2F]^+$$

(ii) Donor acceptor property

$$MF_5 + ClF_3 \rightarrow [ClF_2]^+ [MF_6]^- \qquad M = As, Sb \text{ or } Pt$$

$$MF + ClF_3 \rightarrow [ClF_4]^- [M]^+ \qquad M = K, Rb \text{ or } Cs$$

$$BF_3 + ClF_3 \rightarrow (BF_4)^- [ClF_2]^+$$

(iii) Self ionization

$2\ ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$ (has high electrical conductivity). BrF_3 is decomposed bigorously by water. It is very reactive and displaces oxygen from oxides such as B_2O_3, SiO_2, As_2O_3, CuO etc.

$$4BrF_3 + 3SiO_2 \rightarrow 3SiF_4 + 2Br_2 + 3O_2$$

(C) AB_5 and AB_7 type interhalogen compounds (ClF_5, BrF_5, IF_5 and IF_7)

Properties

All are colorless volatile liquids or gases at room temperature.

(i) Fluorinating agent

IF_7 is a stronger fluorinating agent than IF_5.

$$IF_7 + H_2O \rightarrow IOF_5 + 2HF \text{ (Partial fluorination)}$$

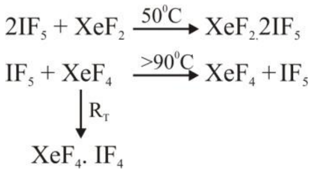
$$IF_7 + 4H_2O \rightarrow HIO_4 + 7HF$$

$$2IF_7 + SiO_2 \rightarrow 2IOF_5 + SiF_4$$

(ii) Donor acceptor property

$$ClF_5 + A_5F_5 \rightarrow [ClF_4]^+ [AsF_6]^-$$

$$BrF_5 + 2SbF_5 \rightarrow [BrF_4]^+ [Sb_2F_{11}]^-$$



$$IF_7 + A_5F_5 \rightarrow (IF_6)^+ [A_5F_6]^-$$

(iii) As solvent

$$IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

$$KF + IF_5 \rightarrow KIF_6$$

$$NOF + IF_5 \rightarrow [NO]^+ [IF_6]^-$$

$$SbF_5 + IF_5 \rightarrow [IF_4]^+ [SbF_6]^-$$

(iv) Reaction with water

Interhalogen compounds of this type react with water to from HF and corresponding halo acids.

$$ClF_5 + 2H_2O \rightarrow FClO_2 + 4HF$$

$$BrF_5 + 3H_2O \rightarrow HBrO_3 + 5HF$$

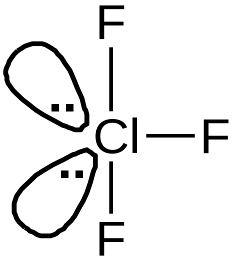
$$IF_5 + 3H_2O \rightarrow HIO_3 + 5HF$$

$$IF_7 + 4H_2O \rightarrow HIO_4 + 7HF$$

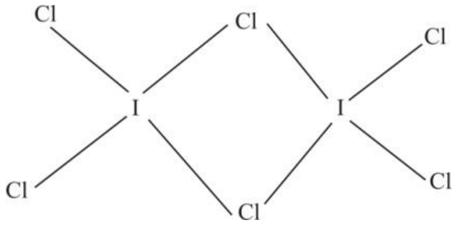
3.17.4Structure of interhalogen compounds:

i. AB type: Linear geometry due to the presence of three lone pair of electrons on central atom.

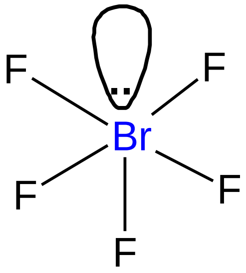
ii. AB$_3$ type: ClF_3 and BrF_3 are T-shaped due to the presence of two lone pair of electrons and the central atom is sp^{3}d hybridized.



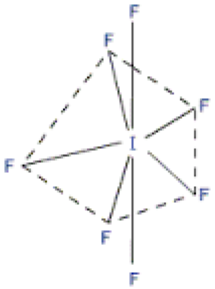
Structure of ICl_3 is entirely different, being comprised of planar I_2Cl_6 separated by normal van der Waals distances between Cl atoms. The terminal ICl distances are similar to those in ICl but bridging I-Cl distances are longer.



iii. AB_5 type: Square pyramidal geometry due to the presence of one lone pair electron with central atom. The central atom undergoes sp^3d^2 hybridization.



iv. AB_7 type: Example is IF_7, whereiodine undergoes sp^3d^3hybridization. The geometry of the molecule is pentagonal bipyramidal with bond angles 72^0 and 90^0.



3.17. 5 Applications of interhalogen compounds

i. ICl (Iodine monochloride) is used in the estimation of iodine number which is a measure of the unsaturation in acids and fats.
ii. Liquid BrF_3 and ClF_3 are used as fluorinating agents.
iii. BrF_5 is used as oxidizer for propellants.

3.18 ELEMENTS OF THE GROUP-18

Noble gases belong to the 18th group (VIIIA) in the periodic table. The noble gases are also called as ‘inert gases’ or ‘rare gasses. Because, these gases are non-reactive/unreactive, they are also called as inert or noble gases. Their shells and subshells are completely filled and thus, they have very stable configurations which can be related to their chemical inactivity. The noble gases are also considered as rare gases because they represent not more than 1% of air (<1%). Their electronic configurations are:

Element’s symbol	**Atomic Number**	**Name of element**	**Electronic configuration**
He	2	Helium	IS^2
Ne	10	Neon	$[He]\ 2s^2 2p^6$
Ar	18	Argon	$[Ne]\ 3s^2 3p^6$
Kr	36	Krypton	$[Ar]\ 3d^{10} 4s^2 4p^6$
Xe	54	Xenon	$[Kr] 4d^{10} 5s^2 5p^6$
Rn	86	Radon	$[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^6$

Among these gases, except radon (Rn), all exists in the atmosphere. Rn is an element generated through radioactive process and can be produced by the radioactive decay of radium and thorium minerals.

$${}^{226}_{88}\mathrm{Ra} \longrightarrow {}^{222}_{88}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

${}^{222}_{88}\mathrm{Rn}$ is an α ray emitter.

Cavendish in 1784, for the first time separated a mixture of noble gases. Rayleigh in 1894 discovered argon and it was the first among the noble gases to be discovered. Neon, krypton and xenon were discovered in 1898 by fractional evaporation of argon under varying reduced pressure conditions. Radon was discovered by Dorn in 1902 as a radioactive disintegration product of radium. The name of noble gases derived from Greek words and\their meaning is:

He: Helios; Neon: New; Argon: Lazy or inert; Krypton: Hidden and Xenon: Stranger

Helium is present in the atmosphere at a concentration of 5ppm, and can be obtained from natural gas deposits. The most abundant noble gas is argon (Ar) (0.9% by volume in air). Argon is produced by electron capture (β decay) of potassium.

$${}^{140}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{140}_{18}\mathrm{Ar}$$

3.18.1 Uses of noble gases/inert elements

As helium has the lowest boiling point (–269ºC) among noble gases, it is used as cooling gas in nuclear reactor and also as a carrier gas in gas-liquid chromatography. It is also used in cryoscopy. Helium is also preferable over hydrogen in airship due to inflammable nature of hydrogen. Helium is also preferably used to dilute oxygen in gas cylinders in place of nitrogen for divers. This is because helium is slightly soluble in blood while nitrogen gas is more soluble in blood at high pressure and causes painful condition in patients (nitrogen narcosis). Noble gases including neon are used in discharge tubes to give different colours (Ne gives orange colour in discharge tubes). Argon (Ar) is used in welding stainless steel, metallurgical processes of aluminum, magnesium and titanium. Argon is also used in electric bulbs, fluorescent lamps etc. Radon is used in the cancer treatment due to its radioactive nature.

3.19 GENERAL CHARACTERISTICS AND USES

At ordinary temperature and pressure, all noble gas elements are monoatomic gases except Radon. They are chemically inert but under certain conditions, they can form complexes.

These gases are cololurless, odourless and tasteless. The other general properties are explained below:

3.19.1 Atomic Radü

Their atomic radii are very large because the radii are van der Waal or non-bonded radii. Atomic radii of elements increase from top to bottom in a group.

3.19.2 Melting point (M.P.) and boiling point (B.P.)

Melting and boiling points of noble gases are very low because inter atomic forces are very weak in these gases.

3.19.3 Electron affinity

Due to completely filled electronic configuration, the electron affinity of these gases is zero.

3.19.4 Enthalpy of vaporization

Enthalpy of vaporization is very low because the forces between the atoms are very weak forces i.e. van der Waals forces.

3.19.5 Ionisation energy

Their ionisation energy is very high because they have very little tendency to accept or loose electrons.

3.19.6 Physical Properties

3.19.6.1 Adsorption

All noble gases can be adsorbed on charcoal (wood) at low temperature and the order of their adsorption is:

$$He < Ne < Ar < Kr < Xe$$

3.19.6.2 Diffusion

All noble gases have a tendency to diffuse through glass, plastic and rubber materials. Therefore, it became difficult to work with them in the laboratory. The order of diffusion depends upon their size (gas with small size diffuse easily) which is as follows:

He > Ne >Ar> Kr > Xe

3.19.6.3 Electrical conductivity

All noble gases have high electrical conductivity at low pressure and thus, can produce characteristic coloured light during electric discharge at low pressure.

3.19.6.4 Liquification

Due to the van der Waal forces (weak forces), they can be easily liquefied. The liquefaction depends upon their atomic size (larger the size, more easily liquefiable gas). The order of ease of liquefaction of noble gases is

He < Ne <Ar< Kr < Xe

3.19.6.5 Solubility behavior

All noble gases are less or sparingly soluble in water. The solubility is due to dipole-induced dipole interaction and increases from top to bottom with increase of the size of the atom. Therefore, the increasing order of their solubility is:

He < Ne <Ar< Kr < Xe

3.19.6.56Abnormal behaviour of helium

Among noble gases, helium shows abnormal behaviour. It has some different properties from other group members. Helium gas on cooling below (-)269^{0}C changes to liquid (He-I). He-I on further cooling at (-)271^{0}C and at 1 atmospheric pressure changes to a liquid (He-II) which has high thermal conductivity. Helium can be obtained in solid form under high pressure (about 25 atmospheric). While all the other noble gases solidify on cooling. He-II has a tendency to flow upwards. It acts as super-fluid.

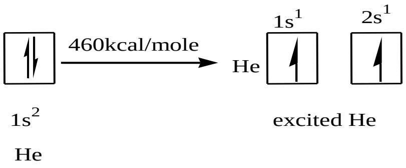
3.19.7 Chemical properties

The atoms of inert gases have completely filled shells and, therefore, they are chemically inert. Under certain specified conditions, they combine and form some rare compounds.

3.20 COMPOUNDS OF NOBLE GASES

3.20.1 Compounds formation under excited state conditions (Helides)

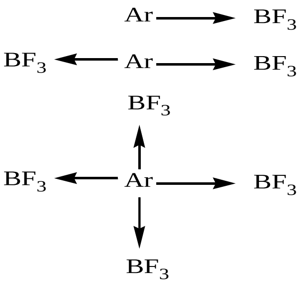
These types of compounds are formed by helium. At low pressure, in the presence of mercury, tungsten etc., helium forms $HgHe_2$, $HgHe_{10}$ and WHe_2. One electron from1s orbital of He excite and go to 2s orbital. This excitation costs about 460 kcal/mole energy.



These compounds are called helides which can survive only for a moment and can be detected spectroscopically.

3.20.2Compounds formation through coordination

Noble gases have electron pairs in their valence orbitals. In the presence of strong electron deficient groups, noble gas compounds can be prepared through coordination (electron pairs of noble gases donated to empty orbitals of electron deficient groups). Among noble gases, argon (Ar) forms a number of unstable compounds of the type Ar. xBF_3 (X = 1, 2, 3, 4, 6, 8, 16), which can be easily dissociated at their M.P.



3.20.3 Compounds formation through dipole induced dipole interactions (Formation of hydrates)

The inert gases such as Ar, Kr and Xe can form compounds with water through dipole induced dipole interactions at low temperature and high pressure. These compounds are known as hydrates.

$Ar.6H_2O$.; $Kr.6H_2O$; $Xe.6H_2O$

3.20.4 Compounds formation through physical trapping (Clathrate compound)

The inert gases such as Ar, Kr and Xe can form solid compounds with certain organic molecules such as phenol and hydroquinone under a pressure of 10-40 atmosphere. In these compounds, the noble gases (Ar/Kr/Xe) are trapped into the crystal lattices or cavities formed by the organic molecules (Figure 3.2). The organic substances that form the cavities are called the host while the atom of noble gases entrapped or enclosed in it, is called the guest. Thus, it is also called as a guest host interaction.

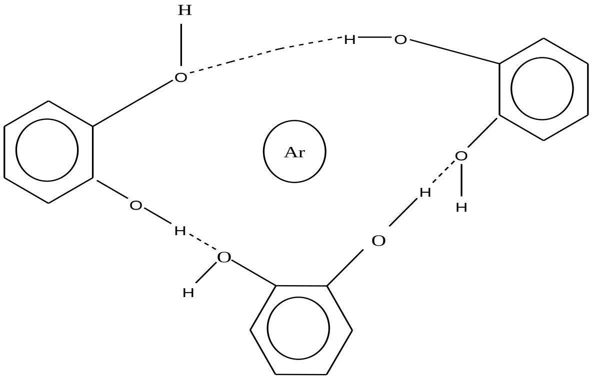


Figure 3.2 Clathrate compound of 1, 2 dihydroxy benzene and argon

In these compounds, the guest components are held together by van der Waals forces. Hence, there is no chemical bonding (only weak interactions) involved in these compounds. This is a kind of physical interaction. It is not necessary that all the cavities in the host lattice are filled. Thus, the clathrates are also called as non-stoichiometric compounds. These weak interactions can easily be broken and guest inert gas atom can escape from the host by simple heating the crystal or by dissolving them in a suitable solvent such as alcohol.

For example, clathrates can be prepared by crystallization of an aqueous solution of quinol (1,4-dihydroxybenzene) with Ar, Kr or Xe under a pressure of 10-40 atmosphere (quinol forms cavities with a diameter of about 4Å in which the inert gas atoms trapped).

The smaller noble gases like He and Ne do not have tendency to form clathrate compounds because they are too small to fit in the cavities and can easily escape from the cavities. Synthetic zeolites can also form cavities in which heavier noble gas elements can fit easily. Clathrates are very useful category of compounds because they can store radioactive Kr and Xe produced in nuclear reactors.

3.21 COMPOUNDS OF XENON

3.21.1 Preparation

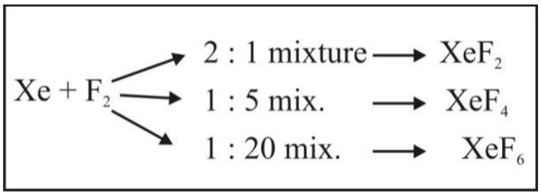
The first noble gas compound; $Xe[PtF_6]$ was prepared in 1962 by the reaction of PtF_6 with Xe in equal ratio at room temperature.

$$\underset{\text{(deep red)}}{PtF_6 + Xe} \longrightarrow Xe[PtF_6]$$

$$Xe[PtF_6] + PtF_6 \xrightarrow{25^\circ C} [XeF]^+ [PtF_6]^-$$

$$[[XeF]^+ [PtF_6]^- + PtF_6 \xrightarrow{60^\circ C} [XeF]^+ [Pt_2F_{11}]^-$$

Xenon reacts directly only with F_2 to form xenon complexes. However, oxygen compounds can be prepared from the xenon fluorides. Xenon reacts directly with fluorine at 400ºC in a sealed nickel vessel, and the final products depend on the Xe/F ratio.



3.21.2 Properties

The compounds XeF_2, XeF_4 and XeF_6 are all white solids. They sublime at room temperature, and can be stored in nickel containers for a long time. The higher fluorides can be prepared from lower fluorides by heating with F_2 under pressure.

(i) All the xenon fluorides are strong oxidizing agents. On reaction with hydrogen, they reduce themselves to Xe.

$$XeF_2 + H_2 \rightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \rightarrow 4HF + Xe$$

$$XeF_6 + 3H_2 \rightarrow 6HF + Xe$$

In similar manner, they oxidize I^- to I_2, Cl^- to Cl_2 and Ce^{3+} to Ce^{4+} and reduce themselves to Xe.

$$XeF_2 + 2HCl \rightarrow 2HF + Xe + Cl_2$$

$$XeF_4 + 4\,KI \rightarrow 4KF + Xe + 2I_2$$

$$SO_4^{2-} + XeF_2 + Ce_2^{III}(SO_4)_3 \rightarrow 2Ce^{IV}(SO_4)_2 + Xe + F_2$$

(ii) All the xenon fluorides are strong fluorinating agents. They fluorinate the other elements.

$$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_6$$

$$XeF_4 + Pt \rightarrow Xe + PtF_4$$

In the above reactions, XeF_4 is fluorinating sulphur and platinum.

(iii) In organic synthesis

XeF_2 is commercially used in synthetic organic chemistry. It does not react with alkyl or aryl groups of organometallic compounds but attack / oxidize /fluorinate only the hetero atom in the organometallic compound.

$$CH_3I + XeF_2 \rightarrow CH_3IF_2 + Xe$$

$$C_5H_5I + XeF_2 \rightarrow C_6H_5IF_2 + Xe$$

$$(C_6H_5)_2S + XeF_2 \rightarrow (C_6H_5)_2SF_2 + Xe$$

In the presence of anhydrous HF, its reactivity increased and it may be due to the formation of XeF^+.

$$Pt + 3XeF_2 \xrightarrow{HF} PtF_6 + 3Xe$$

$$Mo\ (CO)_6 + 3XeF_2 \xrightarrow{HF} MoF_6 + 3Xe + 6CO$$

(iv) Reaction with water

All the fluorides have different reactivity with water. XeF_2 reacts slowly with water and reduce itself to Xe.

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

While XeF_4 violently reacts with water and form XeO_3.

$$3XeF_4 + 6H_2O \rightarrow 2Xe + 12HF + XeO_3 + 3/2O_2$$

XeF_6 also reacts with water violently. On reaction with atmospheric moisture, XeF_6 form highly explosive solid XeO_3.

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

XeF_6 on partial hydrolysis form colourless liquid $XeOF_4$.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

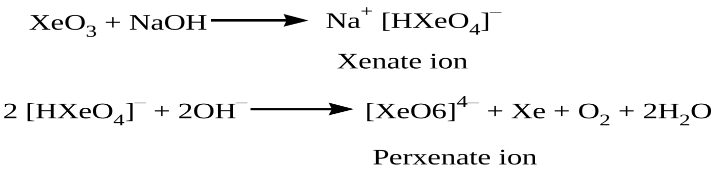
(v) Preparation of other Xenon compounds

Xenon trioxide (XeO_3) is an explosive white hydroscopic solid soluble in water. It reacts with XeF_6 and $XeOF_4$ to form $XeOF_4$ and XeO_2F_2, respectively.

$$XeO_3 + 2XeF_6 \rightarrow 3XeOF_4$$

$$XeO_3 + XeOF_4 \rightarrow 2XeO_2F_2$$

XeO_3 forms xenate $[HXeO_4]^-$ and perxenate ions $[XeO_6]^{4-}$ in alkaline solution (pH > 10.5).



$$XeO_3 + NaOH \longrightarrow \underset{\text{Xenate ion}}{Na^+ [HXeO_4]^-}$$

$$2\,[HXeO_4]^- + 2OH^- \longrightarrow \underset{\text{Perxenate ion}}{[XeO6]^{4-}} + Xe + O_2 + 2H_2O$$

Perxenate ions also act as strong oxidizing agents and oxidize HCl to Cl_2, H_2O to O_2 and Mn^{2+} to MnO_4^-. Perxenate ions; $[XeO_6]^{4-}$ form volatile and explosive compound XeO_4 (xenon telraoxide) on reaction with concentrated H_2SO_4.

$$[XeO_6]^{4-} + H_2SO_4 \rightarrow XeO_4$$

(vi) Complex formation

XeF_2, XeF_4 and XeF_6 have tendency to form complexes with BF_3, GeF_4, SnF_4, PF_5, AsF_5, SbF_5, NbF_5, RuF_5, OsF_5, IrF_5 and PtF_5. In these complexes, fluorides act as fluoride donor.

The complexes of XeF_2, XeF_4 and XeF_6 are as follows:

$$XeF_2.\ MF_5 \rightarrow [XeF)\ ^+[MF_6]^-$$

$$XeF_2.\ 2MF_5 \rightarrow [XeF]^+ [M_2F_{11}]^-$$

$$2XeF_2.\ MF_5 \rightarrow [Xe_2F_3]^+ [MF_6]^-$$

$$XeF_4.\ PF_5 \rightarrow [XeF_3]\ ^+[PF_5]^-$$

Similar complexes are formed with AsF_5, SbF_5, BF_3 etc.

3.22 COMPOUNDS OF XENON

Xenon forms a large number of compounds as compared to the other noble gas elements because ionization potential decreases from He to Rn, among these, He, Ne and Ar are inert (due to high ionization potential) and Kr, Xe and Rn are noble. The structure and bonding in different xenon compounds is discussed in this section.

3.22.1 Structure and bonding in Xenon Compounds.

(A) XeF_2

XeF_2 is linear in shape having three lone pairs of electrons. In the atom of xenon, one pair of electrons of p orbital gets unpaired and one electron is promoted to d orbital. Then, central xenon atom undergoes sp^3d hybridization with trigonal bipyramidal orientation of five sp^3d hybrid orbitals. The hybrid orbitals with lone pair of electrons takes equatorial position. The remaining two orbitals with single electron in each take axial position and overlap with p orbitals of fluorine atom. Due to the presence of lone pairs on a plane, its geometry appears and is linear. (Figure 3.3).

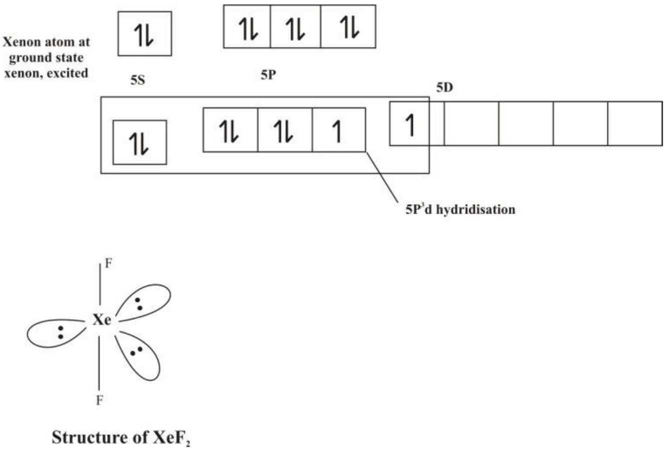


Figure 3.3Structure of XeF_2

(B) XeF_4

In XeF_4, the central Xe atom is sp^3d^2 hybridized and the six sp^3d^2 orbitals should be present on the 6 corners of octahedral geometry. But due to the presence of two lone pairs of electrons at axial position, its actual geometry becomes square planar (Figure 3.4).

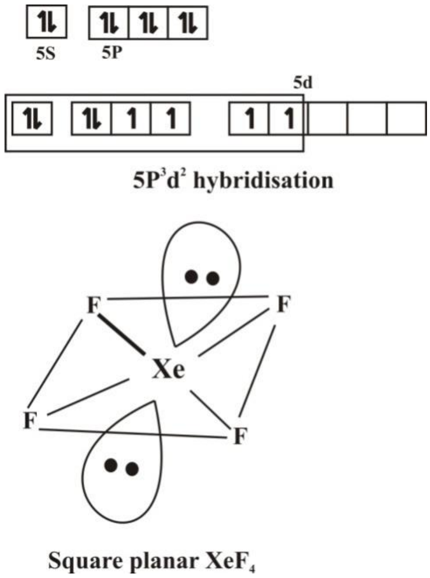


Figure 3.4 Geometry of XeF$_4$

(C) XeF$_6$

The central atom (Xe) in XeF$_6$ is sp^{3}d^3 hybridized and the geometry should be pentagonal bipyramidal. But due to the presence of one lone pair of electrons, its geometry become distorted pentagonal bipyramidal in which the lone pair of electrons pointing through one of the faces of the octahedron (Figure 3.5).

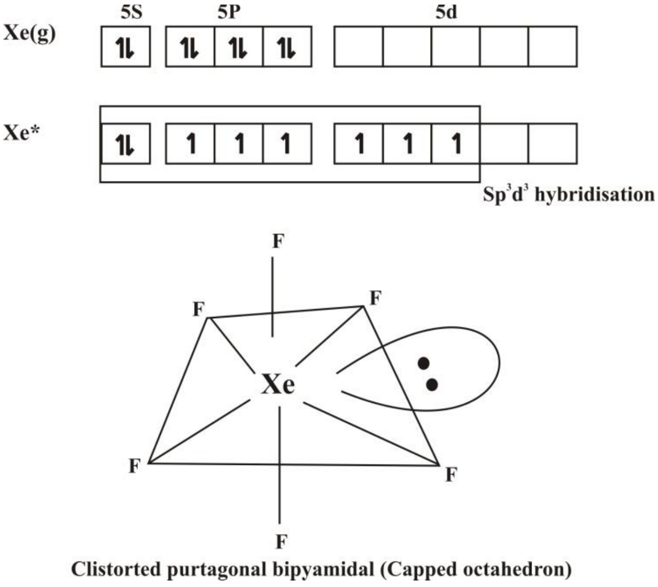


Figure 3.5 Geometry of XeF$_6$ Distorted pentagonal bipyramidal (Capped octahedron)

(D) XeO_3

In XeO_3, the central atom (Xe) is sp^3 hybridized and due to the presence of one lone pair of electrons, its geometry becomes pyramidal instead of tetrahedral. The thre unpaired electron promoted to d orbitals, form three pπ–dπ bond with three oxygen atoms (Figure 3.6).

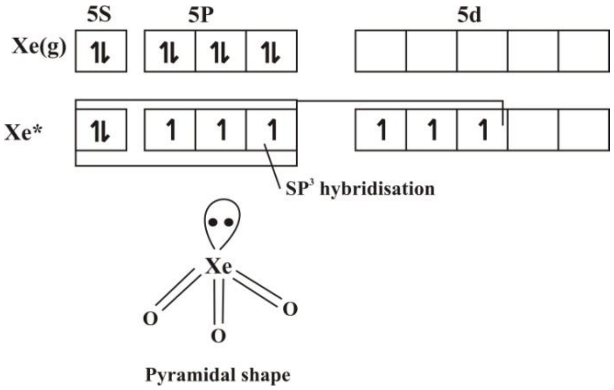


Figure 3.6 Geometry of XeO_3

(E) XeO_4

In XeO_4, the Xe atom is sp^3 hybridized and the geometry is regular tetrahedron. There are only bonded pairs of electrons and no lone pair of electrons present in the structure. All the Xe-O bonds are double bonds (pπ–dπ bonds) in XeO_4 molecule (Figure 3.7).

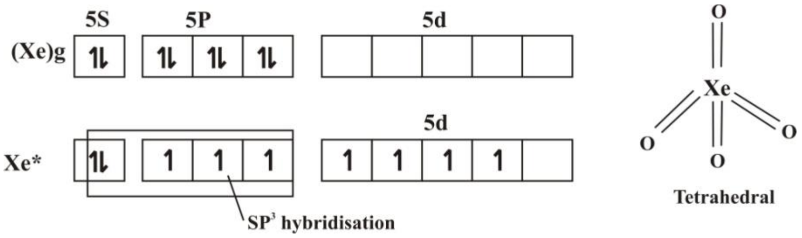


Figure 3.7 Geometry of XeO_4

(F) $XeOF_4$

In $XeOF_4$, Xe atom is sp^3d^2 hybridized and geometry of the molecule should be octahedral. But due to the presence of one lone pair of electrons, its geometry becomes square pyramidal. One Xe–O double bond is pπ–dπ type (Figure 3.8).

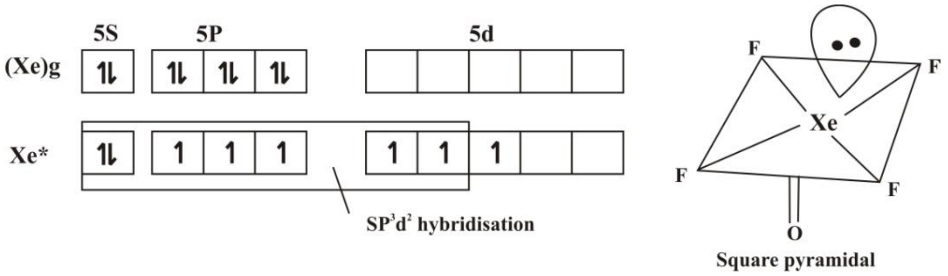


Figure 3.8 Geometry of $XeOF_4$

3.22 SUMMERY

Summery of the present unit is the:

- In this unit we described the general characters of the p-block elements viz., electronic configuration, oxidation state, atomic and ionic radii, electron affinity, electronegativity and electro positivity of the p-block elements, oxidizing and reducing properties, oxides and oxyacids, halides and hydrides.
- In this unit focus on the variations in the ionization potential electronegativity, electron affinity and size of the p-block elements across the periods and along with the groups.
- In the middle of the unit discuss the general characteristics of the elements of group 13, 14, 15, 16, 17 and group 18.
- And end of this unit discusses the compounds of the xenon and their structure.

3.23EFERENCES

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3.24 TERMINAL QUESTIONS

A. MCQs

1. Which element has the highest ionisation energy?

(a) Boron (b) Aluminium

(c) Galium (d) Thaleum

2. Boron shows diagonal relationship with

(a) Aluminium (b) Beryllium

(c) Silicon (d) Lithium

3. Graphite is a form of

(a) Carbon (b) Silicon

(c) Tin (d) Lead

4. The metallic character of the elements of Group 14

(a) Increases down the group(b) Decreases down the group

(c) Remain the same in the group(d) First decreases and the increases

B. Short and long answer types:

1. Write a note on general characteristics and uses of 16th group elements.

2. Define p-block elements. What are the chief characteristics of these elements?

3. Write electronic configuration and names of elements having ns^2p^1 configuration in outermost shell. Discuss the general characteristics.

4. Discuss the properties of elements of halogen group with reference to their electronic configuration, ionization potential, electronegativity and atomic radii.

5. Discuss the physical propr0rties of the elements of the group-17.

ANSWER KEY

1 a 2 c 3 a 4 a

UNIT-4 ARENES AND AROMATICITY

CONTENTS:

4.1 INTRODUCTION

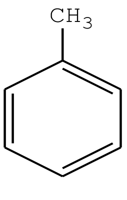
Arene is generally used for aromatic hydrocarbons. Benzene and its alkyl derivatives are important parts of arenes. The general formula of arenes is C_nH_{2n-6y} (where y =Number of rings) so the percentage of carbon in arenes is more than that of aliphatic hydrocarbons.

In 1834, Eilhardt Mitscherlich correctly determined benzene's molecular formula and decided to call it benzin because of its relationship to benzoic acid, a known substituted form of the compound. Further its name was changed to benzene. Compounds like benzene, which have relatively few types of hydrogen in relation to the number of carbons, are typically found in oils produced by trees and other Natural Plants. Early chemists called such compounds aromatic compounds because of their pleasing smell. In this way, they were differentiating from aliphatic compounds, with higher hydrogen-to-carbon ratios, that were obtained from the chemical degradation of fats. The chemical meaning of the word "aromatic" now signifies certain kinds of chemical structures. We will now examine the criteria that a compound must satisfy to be classified as aromatic. Aromatic compounds are now regarded as a class of compound which contains at least one benzene ring. They are also known as benzenoids. In other cases compound which do not contain benzene ring but they still behave as aromatic compounds. Such compounds are known as non-benzenoids.

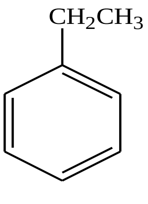
In this series benzene is first and most important member. These are called benzenoid compounds.

Example:

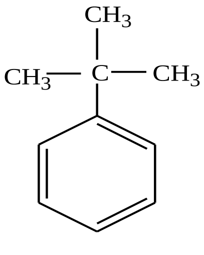
1. Alkyl benzenes:



Toluene

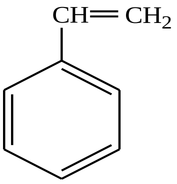


Ethyl benzene

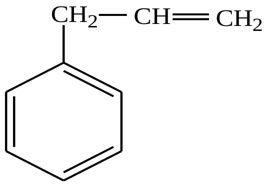


tert-Butyl benzene

2. Alkenyl benzenes:



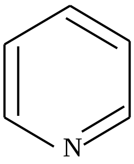
Styrene



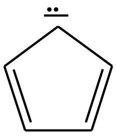
3-Phenyl propene-1

Aromatic hydrocarbons which have different those chemical properties then benzene are called non benzenoid aromatic compound.

Example:



Pyridene



Cyclopenta dienyl anion

4.2 OBJECTIVE

In this chapter we have to study about Arenes.

Arenes: Nomenclature of Benzene derivatives, The aryl group, Aromatic nucleus and side chain Structure of benzene, molecular formula & Kekule’s structure Resonance and MO pictures, Aromaticity: the Huckel’s Rule, Aromatic ions.

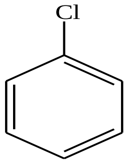
Chemical reactions of benzene : Aromatic electrophilic substitution ,General pattern of nitration, halogenations & sulphonation & Friedel-Crafts reactions, Activating and deactivating substituent, Orientation and ortho / Para ratio, Reduction of benzene (Birch reduction),Summary & Terminal questions & Answers.

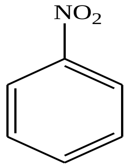
4.3 NOMENCLATURE OF BENZENE DERIVATIVE

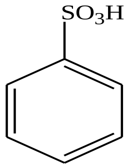
Nomenclature of benzene derivatives depends on IUPAC system and some derivatives have common names.

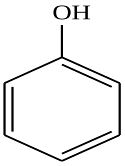
1. Monosubstituted benzene: These are named by prefixing the name of the substituent to 'benzene'

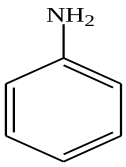
Example:

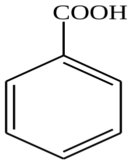

Chloro benzene

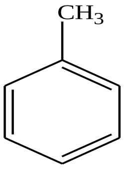

Nitrobenzene


Benzene sulphonic acid


Phenol

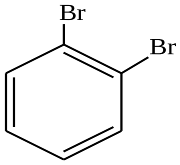

Anelene

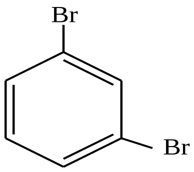

Benzoic Acid

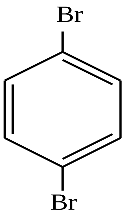

Toluene

Disubstituted benzene: When there are two substitutents on the ring, three positional isomers are possible and their positions are indicated by ortho, meta and para or by numbers.

Example:

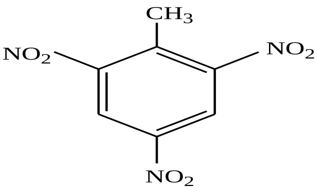

1,2-dibromo benzene
ortho benzene


1,3-dibromo benzene
mete benzene


1,4-dibromo benzene
para benzene

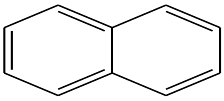
3. Polysubstituted benzene: When three or more substituent are placed on benzene then numbers are used to indicate the position.

Example:

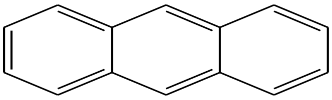

2,4,6-trinitro toluene

4. Fused polycyclic arenes: There are many polycyclic arenes having one or more benzene rings fused in ortho positions.

Example:



Naphthalene

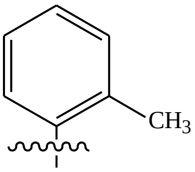


Anthracene

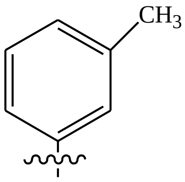
4.4 THE ARYL GROUP

The univalent group which is derived by any other aromatic hydrocarbon is known as aryl group (Ar-)

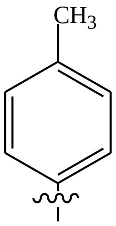
Example:



o-tolyl



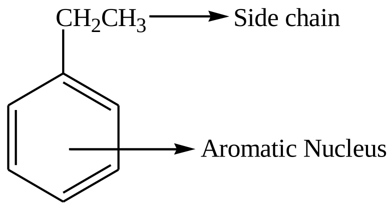
m-tolyl



p-tolyl

4.5 AROMATIC NUCLEUS AND SIDE CHAIN

The basic carbon structure of benzene is called aromatic nucleus. When alkyl group attached to thr aromatic ring is called side chain.



4.6 STRUCTURE OF BENZENE

4.6.1 Molecular Formula and Kekule structure: The structure of benzene is deduced by the following points.

A. Molecular Formula:

By the analytical measurement its empirical formula is observed as CH and its molecular mass is 78.

Empirical formula= CH

Empirical weight = 12+1 = 13

Molecular weight = 78

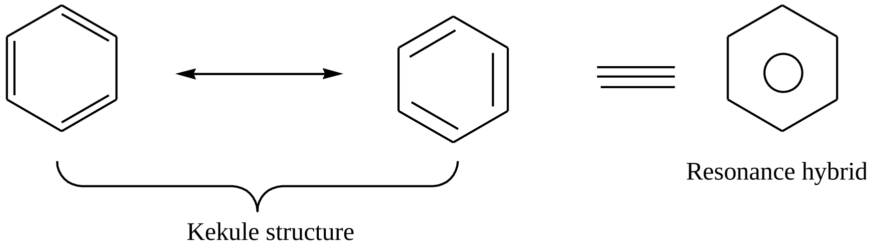
Empirical weight X n = Molecular weight

13 X n = 78

Since molecular formula = CH X 6 = C_6H_6

B. Kekule structure of benzene:

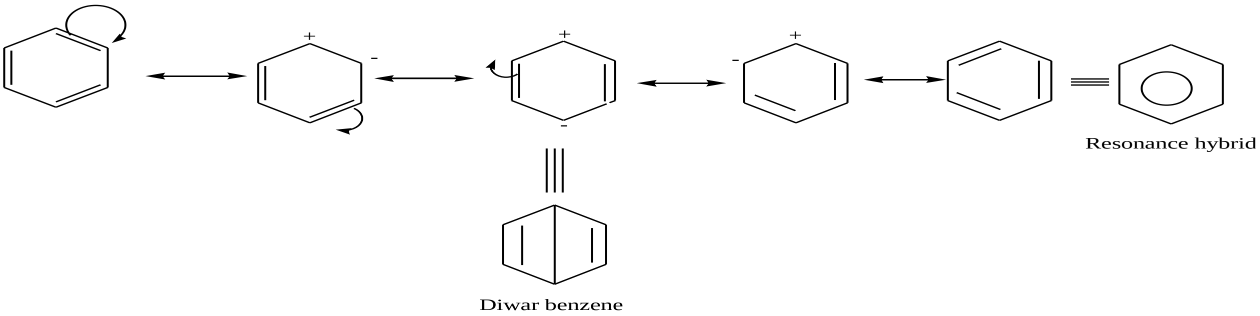
In 1865 a scientist Kekule gives the special structure of C_6H_6 and he represents that C_6H_6 shows two resonating structures which are known as Kekule structures and these structures cannot explain all properties of benzene so they have resonance hybrid and the resonating energy for it is 36 K Cal/mol.



It is cyclic planer structure of six carbons with alternate single and double bonds. Each carbon attached with one hydrogen so two structures are in a state of continuous oscillation.

4.6.2 Resonance and MO picture:

A. Resonance Structure:



According to valence bond theory, benzene is considerd as resonance hybrid of two kekule and three dewar structures, the kekule structure making major contributions. Because resonating structures are more stable so benzene should be more stable than other structure.

B. Molecular Orbital (MO) picture:

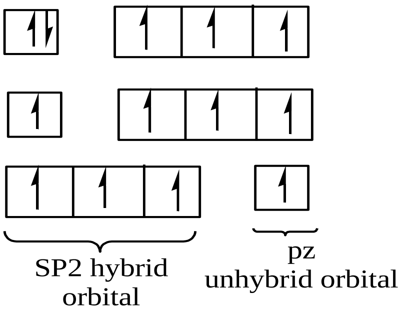
All six carbon atoms in benzene are Sp^2 hybridized. All hybrid orbitals overlap each other and with s-orbitals C-C and C-H bonds to form σ bond.

It is the modern view of structure, in benzene each carbon is SP^2 hydrides with bond angle 120^0. So it is cyclic and planner. Each carbon contains one unhybrid p orbital (pz) which is perpendicular to the σ plane and π-e^- undergoes delocalization, each carbon is overlap with two carbon atoms to form Sp^2-Sp^2 σ bond and with H-atom to form Sp^2- S σ bond.

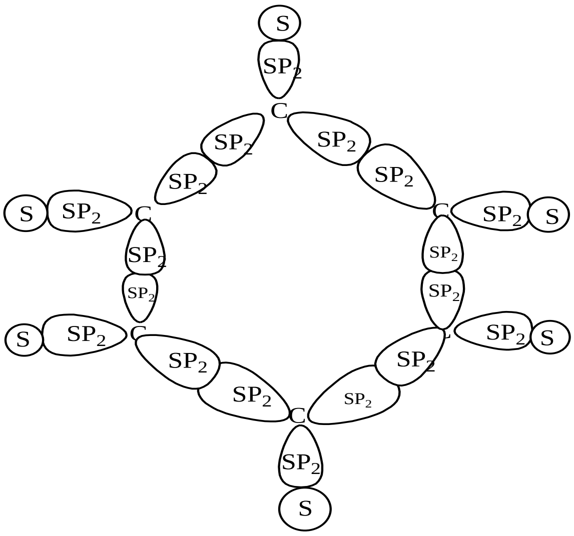
C in ground state = $1S^2, 2S^2, 2p^2$ =

C in excited state =

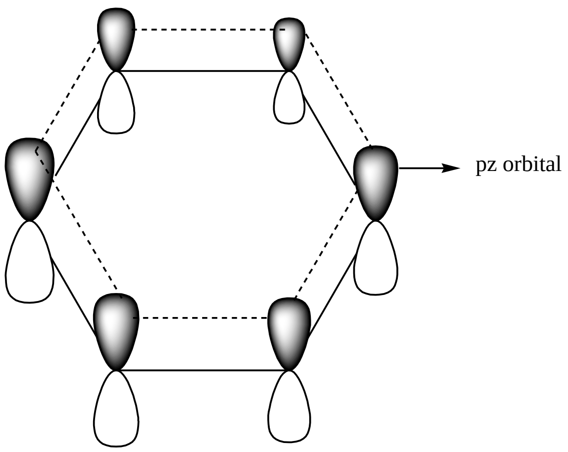
C in hybridization state =



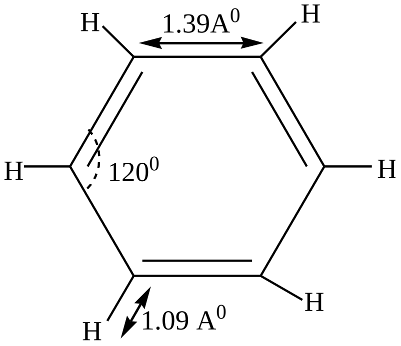
σ Frame work of benzene



π-Frame work of benzene:



Complete structure of benzene:



4.7 AROMATICITY: THE HUCKEL'S RULE

An aromatic compound is more stable than an analogous cyclic compound with localized electrons. In contrast, an antiaromatic compound is less stable than an analogous cyclic compound with localized electrons. Aromaticity is characterized by stability, whereas antiaromaticity is characterized by instability.

Aromatic compound > cyclic compound with localized electrons > antiaromatic compound

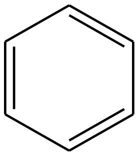
The aromatic compounds have alternate single and double bond due to this those compounds have special stability, which is known as Aromaticity. These are the following rules for compound to be aromatic.

1. An aromatic compound is cyclic and planer.

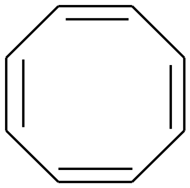
2. There is a p-orbital on every atom of an aromatic ring.

3. The cyclic arrangement of p-orbitals in an aromatic compound , must contain (4n+2) π electrons. This is known as Huckel rule. If such systems contain 4nπ electron then it will be anti aromatic.

Example:



Benzene



Cyclooctatetraene

These all compounds follows Huckel rule.

4.8. METHODS OF PREPARATION

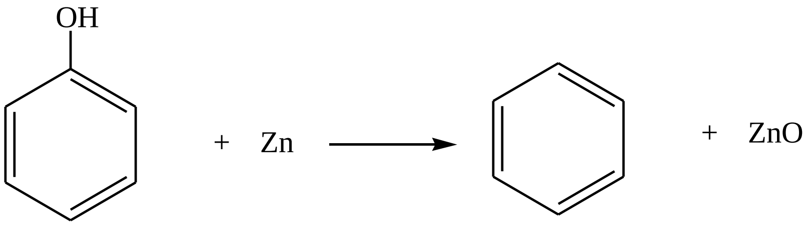
1. From sodium benzoate:

From sodium benzoate C_6H_5COONa on react with sodalime (NaOH and CaO) to give benzene.

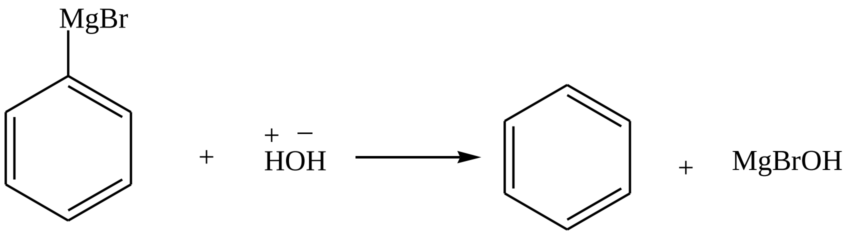
$$C_6H_5COONa + NaOH \xrightarrow{CaO} C_6H_6 + Na_2CO_3$$

2. From Phenol:

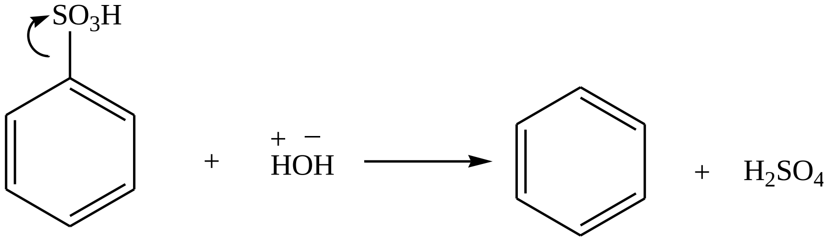
Phenol on react with Zn power gives benzene by removing ZnO.



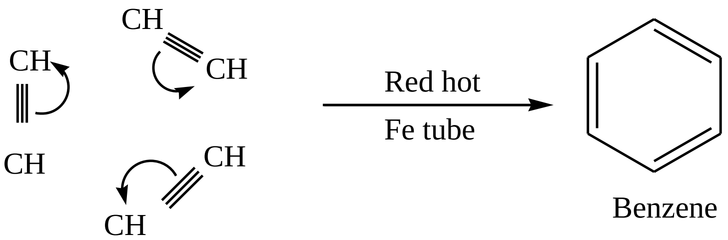
3. From Grignard Reagent: Grignard Reagent (C_6H_5X) on hydrolysis gives benzene.



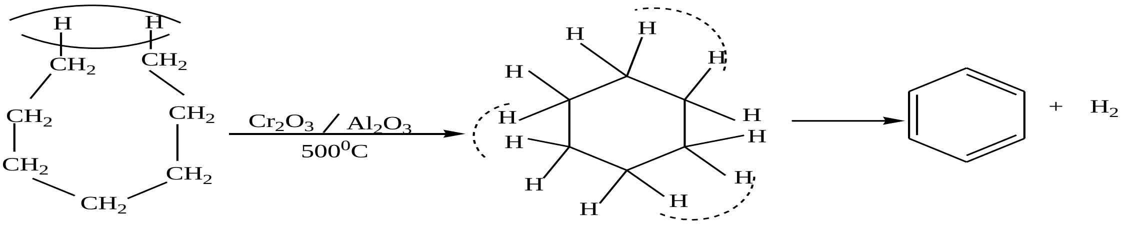
4. From Benzene sulphonic acid: Benzene sulphonic acid on hydrolysis gives benzene.



5. from acetylene (By polymerization reaction): Acetylene (Ethyne) on polymerization gives benzene.



6. Industrial Preparation of benzene: n-hexane on heating at 500^0C temperature in the presence of Cr_2O_3 supplied by Al_2O_3 gives cyclohexane, which on again dehydrogenation gives C_6H_6.



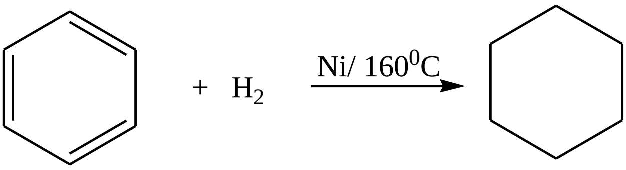
4.9. *PROPERTIES (PHYSICAL AND CHEMICAL)*

A. Physical properties:

1. Benzene is a colorless liquid
2. It is insoluble in liquid but soluble in Organic solvent.
3. Benzene itself is a good solvent.
4. Its vapour is poisonous.

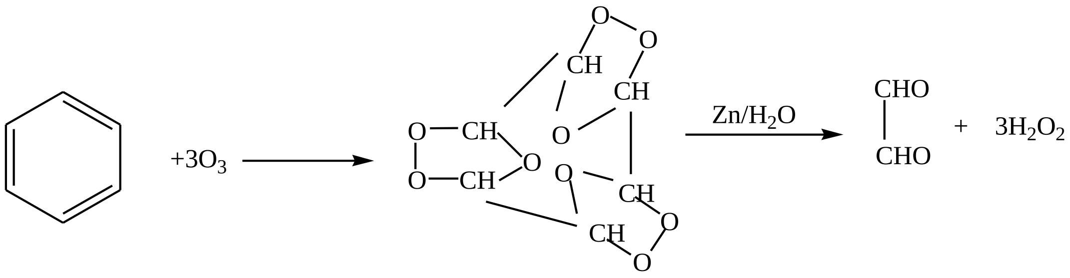
B. Chemical properties of benzene:

1. Hydrogenation: In the presence of Ni catalyst at 160^0C temperature benzene on react with H_2 gives an additional product cyclohexane.



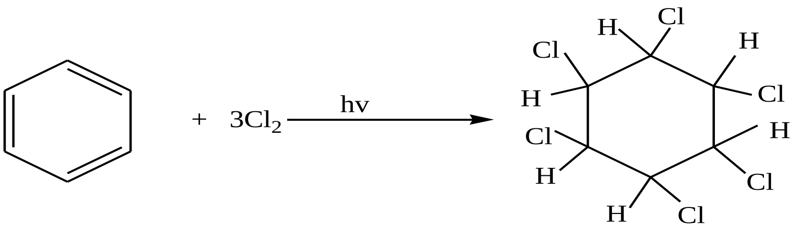
Cyclohexane

2. Ozonolysis: In the presence of CCl_4 benzene on react with O3 gives benzene tri ozonoid. This on hydrolysis in the presence of Zn gives glyoxal.



benzene tri ozonoid

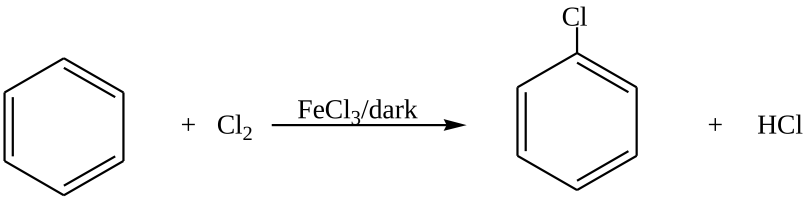
3. Chlorination: In the presence of sun light benzene on react with Cl2 gives an additional product benzene hexa chloride ($C_6H_6Cl_6$, BHC). It is also known as Gamaxine, lindane or 666. It is used as apestiside



Benzene hexa chloride

4. Electrophilic Substitution reaction:

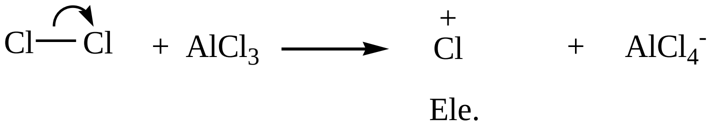
i. Chlorination: In the absence of sun light and in the presence of FeCl3 or AlCl3, benzene on react with Cl_2 gives C_6H_5Cl. This reaction known as electrophilic substitution reaction of benzene.



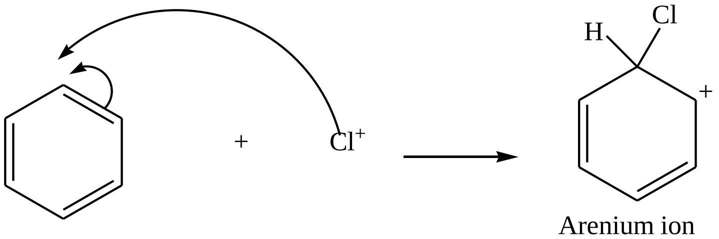
Chloro benzene

Mechanism:

Step I: Formation of electrophile:

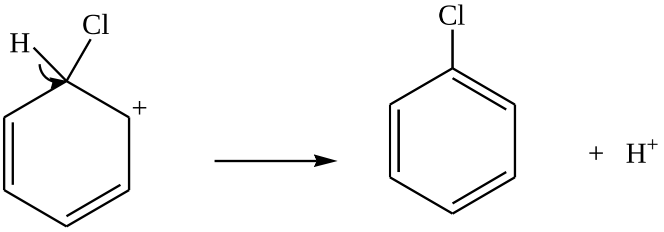


Step II: Attack of electrophile (formation of arinium ion):



Arenium ion

Step III: Formation of product:

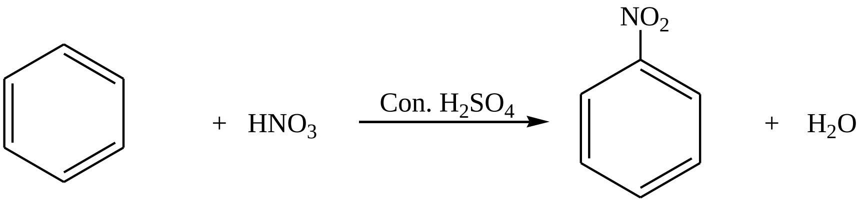


Arenium ion

Step IV: Formation of catalyst:

$$H^+ \quad + \quad AlCl4^- \longrightarrow AlCl_3 \quad + HCl$$

ii. Nitration: In the presence of H_2SO_4 benzene on react with HNO_3 gives nitrobenzene. This reaction is known as nitration.



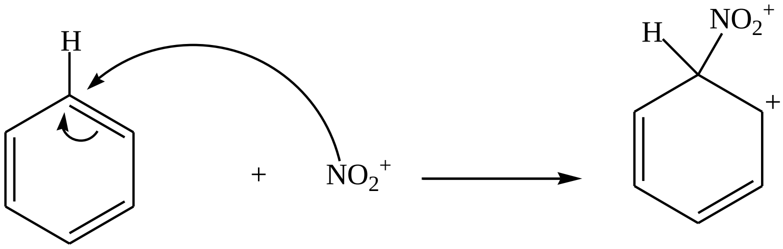
Nitro benzene

Mechanism:

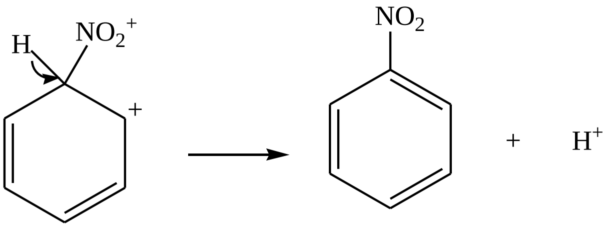
Step I: Formation of electrophile:

$$OH-NO_2 + H^+ + HSO_4^- \longrightarrow \underset{\text{Electrophile}}{\overset{+}{NO_2}} + + HSO_4^- + H_2O$$

Step II: Attack of Electrophile (NO_2^+)



Step III: Formation of product:

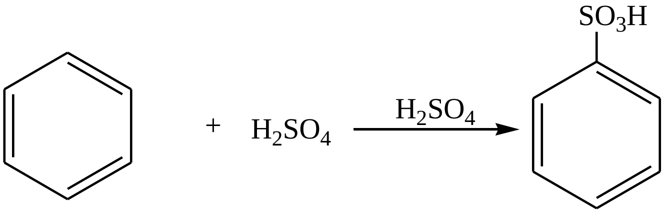


Nitro benzene

Step IV: Formation of catalyst:

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

iii. Nitration: In the presence of H_2SO_4, benzene on react with H_2SO_4 gives benzene sulphonic acid. This reaction is known as sulphonation reaction.



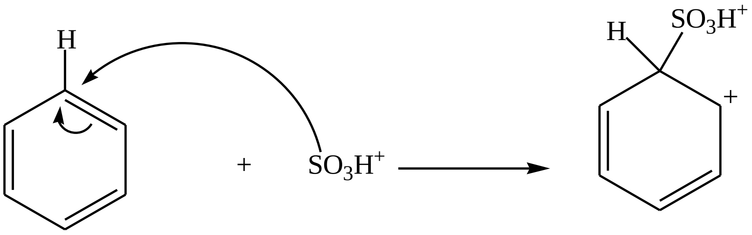
Benzene sulphonic acid

Mechanism:

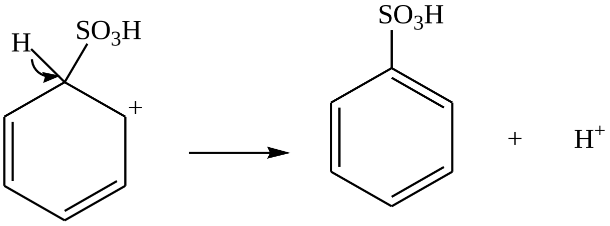
Step I: Formation of electrophile:

$$OH-SO_3H + H_2SO_4 \longrightarrow SO_3H^+$$

Step II: Attack of electrophile:



Step III: Formation of product:



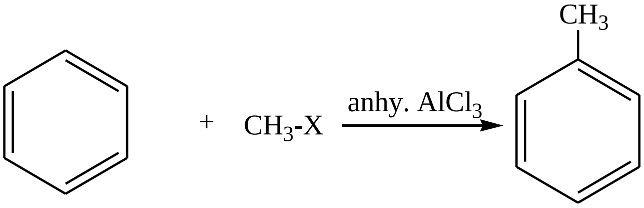
benzene sulphonic acid

Step IV: Formation of catalyst:

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

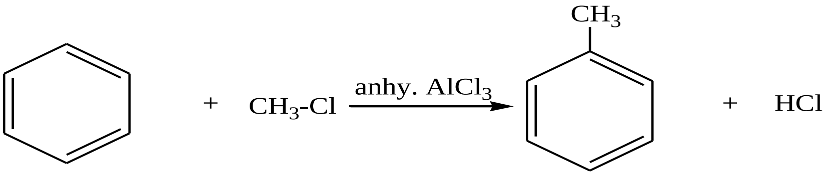
iv. Friedel Craft reaction:

a. Friedel craft alkylation: In the presence of anhydrous $AlCl_3$, benzene reacts with R-X to give alkyl benzene. This reaction is known as Friedel Craft acylation.



Tolueane

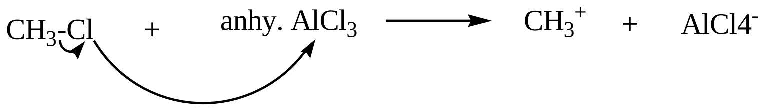
Eg.



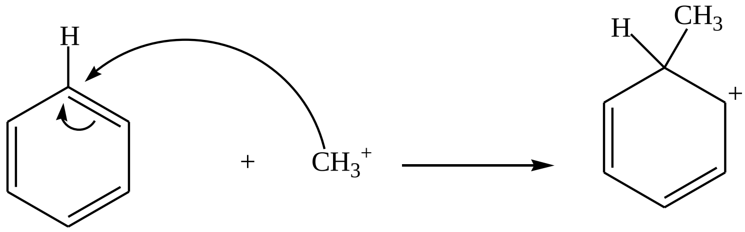
Tolueane

Mechanism:

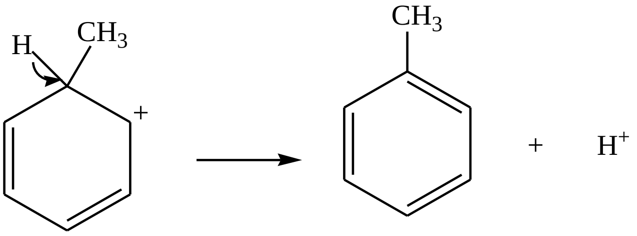
Step I: Formation of electrophile:



Step II: Attack of electrophile:



Step III: Formation of product:

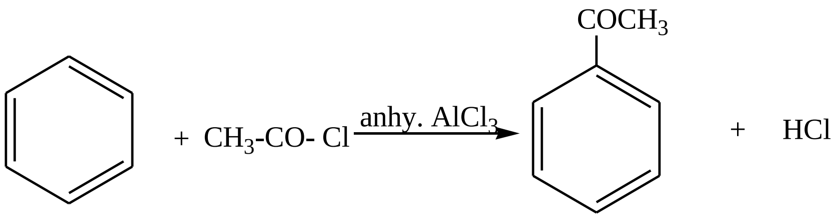


benzene sulphonic acid

Step IV: Formation of catalyst:

$$H^+ + AlCl4^- \longrightarrow AlCl_3 \; ++ \; HCl$$

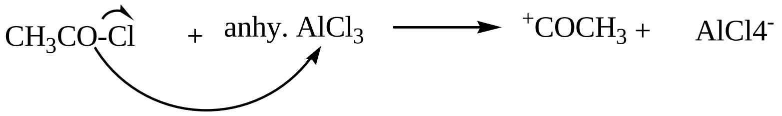
b. Friedel craft acylation: In the presence of anhydrous $AlCl_3$, benzene reacts with R-CO-X to give aceto phenone. This reaction is known as Friedel Craft acylation.



Acetophenone

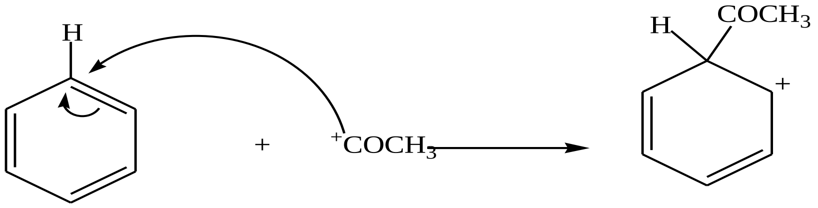
Mechanism:

Step I: Formation of electrophile:

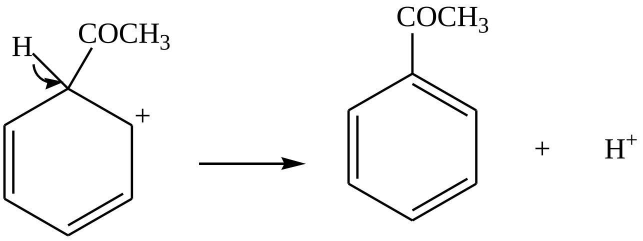


$$CH_3CO\text{-}Cl + \text{anhy. } AlCl_3 \longrightarrow {}^+COCH_3 + AlCl4^-$$

. **Step II: Attack of electrophile:**



Step III: Formation of product:



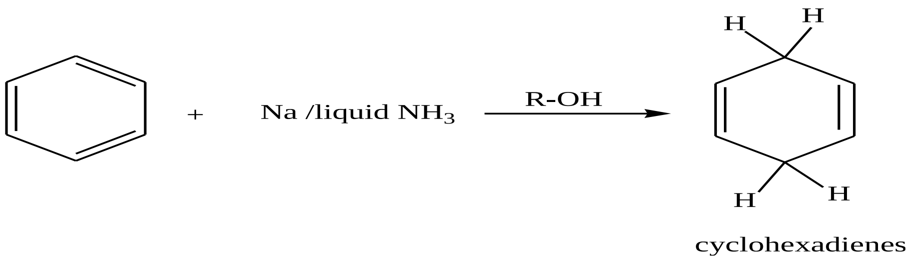
Acetophenone

Step IV: Formation of catalyst:

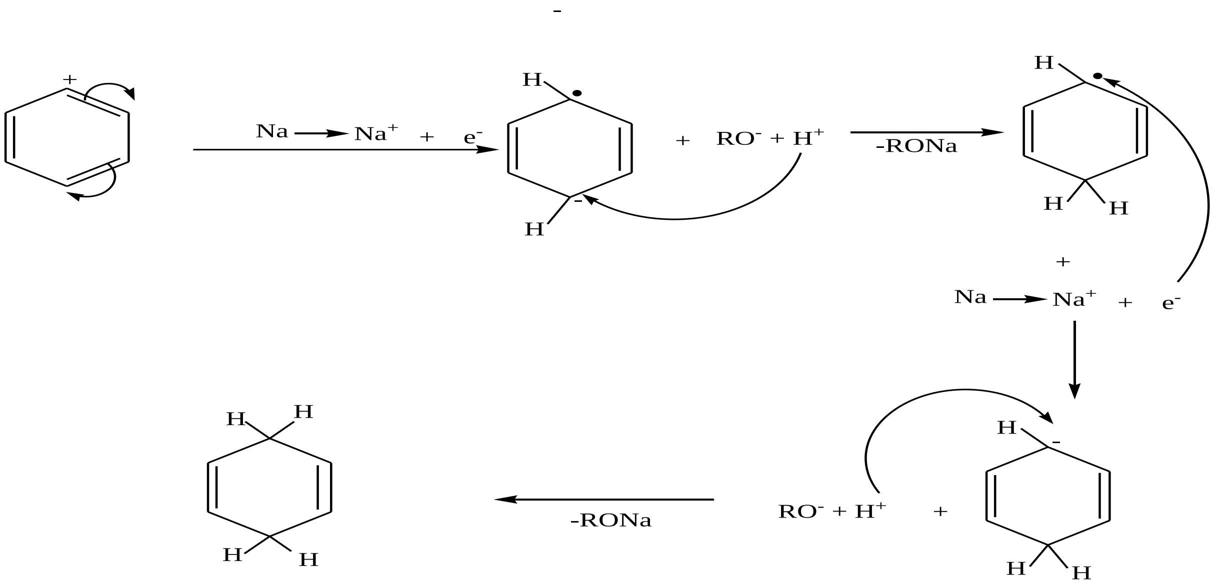
$$H^+ + AlCl4^- \longrightarrow AlCl_3 ++ HCl$$

4.10. REDUCTION OF BENZENE (BIRCH REDUCTION)

The Birch reduction is an organic reaction where aromatic rings undergo a 1,4-reduction to provide unconjugated cyclohexadienes. The reduction is conducted by sodium or lithium metal in liquid ammonia and in the presence of an alcohol.



Mechanism:



4.11. ORIENTATION AND ORTHO/PARA RATIO.

As we know that all six hydrogen atom in are identical. So they form only monosubstituate derivative. The next incoming electrophile will forward to the other condition by the I substituent group. Hence, *"The tendency of I substituent group for farwarding the II incoming substituent group on ortho, pera or meta positions is known as directive influence."* Directive influence is depends upon the nature of I substituent group.

Classification of groups according to directive influence:

According to directive influence the groups are classify into two classes-

(1) Ortho pera director.

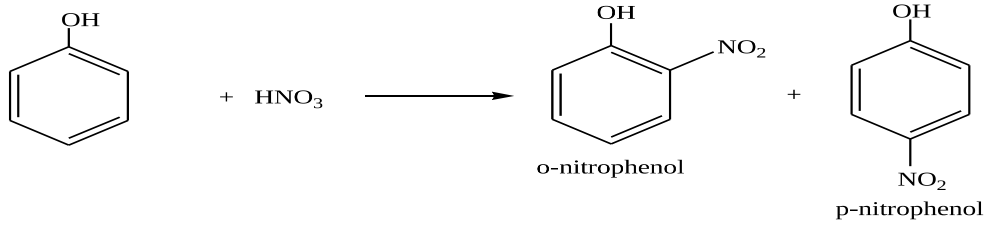
(2) Meta director.

In a C_6H_6 ring the position 2, 6 are equivalent and form ortho product.

The position 3, 5 are equivalent and gives meta product. The position 4 is unique and gives pera product.

1. Ortho/para directing: If the first substituent group forward to the incoming second substituent group primarily to ortho and pera position then it is known as *o*, *p* director.

Example: *When C_6H_5OH undergoes nitration then it form 57% o-nitro phenol and 43% p-nitro phenol.*



Condition for o-p director:

1. o, p-directors are saturated in nature.
2. They are electron rich, hence they consist loan pair of electrons (except –R groups).
3. These are ring activator (except, halogen family due to –I effect.

Examples of o,p-directors-

Strongly activator-

$-\ddot{\underset{\cdot\cdot}{O}}H, -\ddot{N}H_2, -R_2\ddot{N}, -\ddot{O}R$

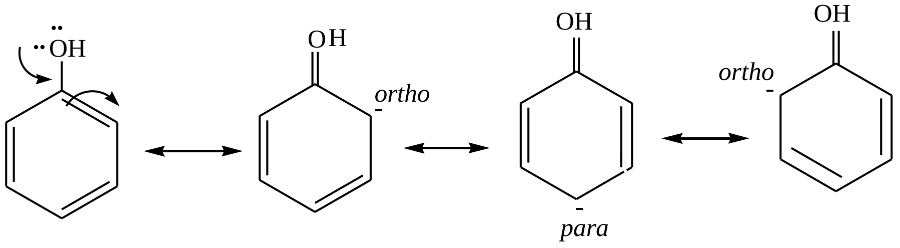
Weak activator-

-CH3, -C2H5, -R

Ring deactivator-

-F, -Cl, -Br, -I

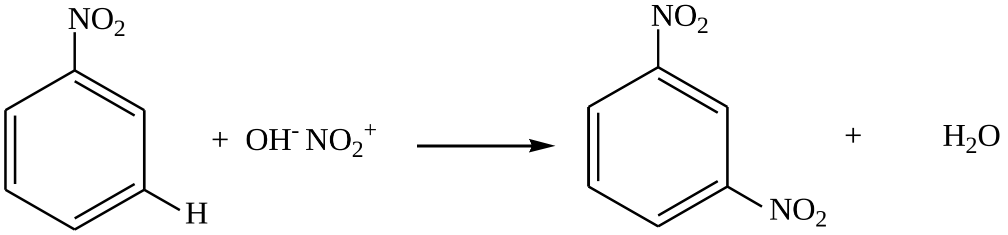
Mechanism of o, p-director: The mechanism of o, p-director group increases the density of e^- at *o*, and *p*-position due to which the incoming electrophile will easily attack at those positions. Hence these are ring activator.



Thus it is clear from above mechanism that the-OH group increases the density of e^- at o & p-position so the incoming electrophile will easily attack at o and p-positions so, o, p-directors are ring activator. But halogen (-F,-Cl,-Br,-I) are o,p directors but ring deactivator due to –I effect (inductive effect).

Meta-directors- If the first substituent groups forward to the incoming substituent group at meta position then it is referred as meta director.

Example: When undergoes nitration then it form 1, 3 dinitro benzene.



Condition for meta directors-

(1) They have multi bonded (except $-NR_3^+$).

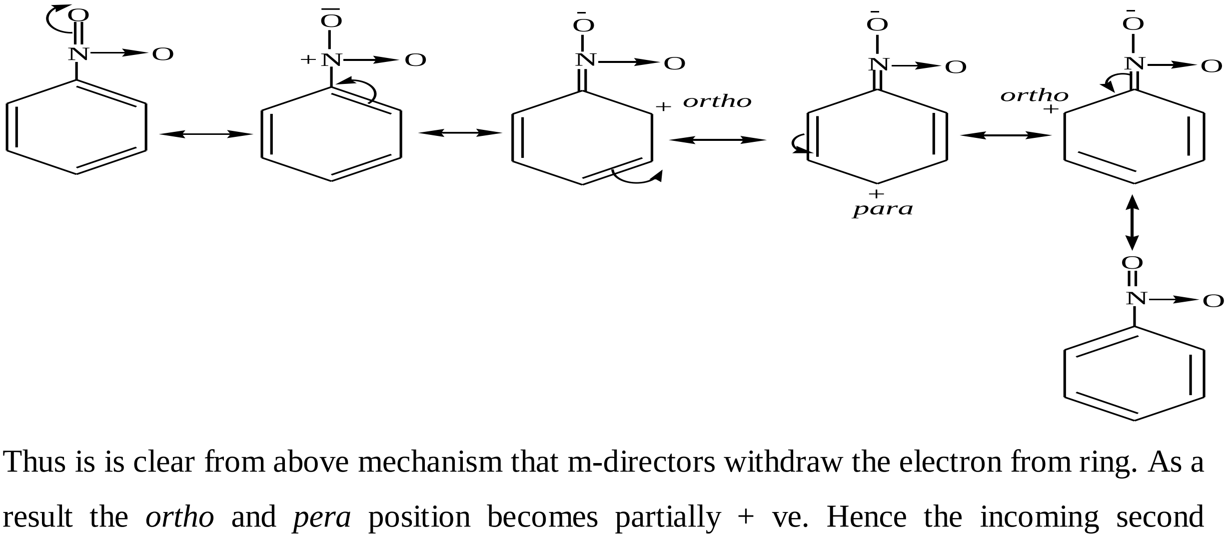
(2) These are electron deficient.

(3) These are ring deactivators because they withdraw the electron from the ring towards itself.

Examples of Meta directors:

$-NO^2$, - COOH, - CHO, $-SO_3H$, $CONH_2$, -CN, $-NR_3^+$ etc.

Mechanism of meta directors:



Thus is is clear from above mechanism that m-directors withdraw the electron from ring. As a result the *ortho* and *pera* position becomes partially + ve. Hence the incoming second electrophille will attack at neutral meta position. So these are meta directors and also ring deactivator.

4.12. SUMMARY

- Aromatic hydrocarbons are known as arenes. In arenes, Benzene is most important compound.
- Nomenclature of benzene derivatives is depending on the substituent which added with benzene. By substituent, benzene derivative have several names as Toluene or Methylbenzene.
- Benzene aromaticity causes it to undergo electrophilic aromatic substitution reactions. The electrophilic addition reactions characteristic of alkenes and dienes would lead to much less stable nonaromatic addition products. The most common electrophilic aromatic substitution reactions are halogenation, nitration, sulfonation, and Friedel–Crafts acylation and alkylation.
- Some monosubstituted benzenes are named as substituted benzenes (e.g., bromobenzene, nitrobenzene)
- Bromination or chlorination requires a Lewis acid catalyst; iodination requires an oxidizing agent.
- Nitration with nitric acid requires sulfuric acid as a catalyst. Either an acyl halide or an acid anhydride can be used for Friedel–Crafts acylation, a reaction that places an acyl group on a benzene ring. If the carbocation formed from the alkyl halide used in a Friedel–Crafts alkylation reaction can rearrange, the major product will be the product with the rearranged alkyl group.
- Stability of benzene depends on the resonating structures. By resonance we can easily define the stability of benzene.
- Aromaticity of benzene and some other stable compounds can easily be given by Huckel Rule.

4.13 TERMINAL QUESTIONS

A. Short answer type question:

1. Discuss the orbital structure of benzene,

2. State Huckel rule. Give the suitable example.

3. Give the mechanism of Friedel Crafts acylation reaction.

4. Explain meta directing nature of nitro group.

Methyl group attached to benzene ring has no loan pair of electrons but is still ortho and para directing in nature. Explain why?

5. What are non benzenoid compounds?

6. What is aromaticity?

7. What is the cause of aromatic character of benzene in terms of Huckels rule?

8. Explain why methyl group in toluene is ortho and para directing in nature.

9. Give the mechanism of nitration of benzene.

10. Explain the stability of benzene on the basis of orbital structure.

11. How will you prepare the following compounds from benzene?

a. Acetophenone b. Toluene c. Chlorobenzene d. Benzene hexa chloride

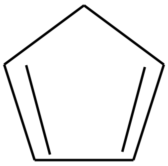
12. Discuss the orientation of electrophilic substitution in nitrobenzene.

13. What are electrophilic substitution reactions? Discuss the mechanism of sulphonation of benzene.

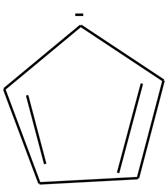
14. Explain why –NH2 group when attached to wnzene ring is ortho and para directing in nature.

15. Which of the following have aromatic and why?

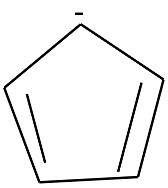
a.



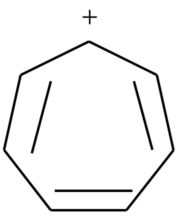
b



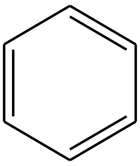
c.



d.



e



16. List the following compounds in order of decreasing reactivity toward nucleophilic aromatic substitution: chlorobenzene,1-chloro-2,4-dinitrobenzene,p-chloronitrobenzene.

17. Show how each of the following compounds could be synthesized from benzene:

a. nitrophenol b. p-nitroaniline c. p-bromoanisole.

18. Draw the structure of each of the following compounds:

a. m-chlorotoluene b. p-bromophenol c. o-nitroaniline d. m-dichlorobenzene

e. 2,5 dinitrobenzaldehyde f. m-chlorobenzonitrile g. o-xylene

B. Objective type question:

1. In nitration of benzene, the electrophile is-

a. H^+ b. SO_2 c. SO_3 d. $NO2^+$

2. Benzene reacts with chlorine in the presence of $FeCl_3$ catalyst to form.

a. Hehachlorobenzene b. Chlorobenzene

c. Hexachlorocyclohexane d. benzyl chloride

3. Gammexene is:

a. hexachloroethane b. DDT c. TNT d. Hexachlorocyclohexane

4. Ozonolysis of benzene gives:

a. formic acid b. glyoxal c. formaldehyde d. glycine

5. Which of the following compounds undergoes nitration most easily?

a. Benzene b. toluene c. Nitrobenzene d. Benzoic acid

6. Toluene reacts with bromine in the presence of UV light to give.

a. m-bromotoluene b. benzyl bromide c. o-bromotoluene d. benzoyl bromide

7. With respect to the electrophilic aromatic substitution of benzene which of the following is:

a. A non-aromatic intermediate is formed

b. Benzene acts as an electrophile

c. A proton is lost in the final step

d. Resonance forms are important

8. Which of the following statements is **incorrect**: aromatic compounds?

a. Are planar

b. Have 4n π-electrons

c. Are cyclic

d. Are generally less reactive than similarly substituted alkenes

9. When considering electrophilic aromatic substitution reactions electron withdrawing substituents (e.g. nitro) are described as:

a. Ortho/para directing and activating

b. Ortho/para directing and deactivating

c. Meta directing and activating

d. Meta directing and deactivating

10. The Friedel-Crafts alkylation.

a. Works very well for primary chlorides

b. Works very well for tertiary chlorides

c. Works very well for acyl chlorides

d. Works very well without a catalyst

11. With respect to the electrophilic aromatic substitution of benzene which of the following is not true:

a. A non-aromatic intermediate is formed

b. Benzene acts as an electrophile

c. A proton is lost in the final step

d. Resonance forms are important

12. Which of the following is not associated with electrophilic aromatic substitution?

a. The formation of nitrobenzene

b. The formation of benzyne

c. The formation of bromobenzene

d. The formation of benzene sulfonic acid

Answers

1. c**,** **2.** b, **3.** b, **4.** b. **5.** b, **6.** b, **7.** b, **8.** b, **9.** d, **10.** b. **11.** b, **12.** B

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UNIT 5: MECHANISM OF ORGANIC REACTIONS

CONTENTS:

5.1 INTRODUCTION

Organic reactions involve breaking and formation of chemical bonds that is the changes in sharing of electrons between atoms in given molecules. Movement of electrons during organic reactions is denoted by curved arrow notations. For example, movement of odd electron is represented by half headed arrow whereas movement of electron pair is represented by full curved arrows. Understanding the correct arrow notation not only helps to describe how an organic reaction is taking place but also helps to quickly understand the peculiar mechanistic steps involved. Thus, content of this chapter is essential for beginning study of organic reaction mechanisms. Later, the chapter discusses important categories of organic reagents those are useful to carry out particular organic transformations. For example, nucleophilic reagents attack on electron deficient sites in a molecule while the electrophilic reagents react with electron rich species. Thus, this chapter is a suitable package to begin learning and understanding the organic chemistry transformations.

5.2 OBJECTIVES

Objective of this chapter is to provide readers with basics of organic reaction mechanisms. Like all chemical transformations, organic reactions also involve breaking and formation of chemical bonds. Thus, understanding of electron sharing between atoms and transfer of electrons is very important to understand the organic reaction mechanisms. This chapter sheds light on bond cleavage and curved arrow notations to denote the changes involving electron sharing. Concise detail on type of reagents affecting various organic reactions is also given. The chapter is developed such that the reader inculcates fundamental terminologies and notations pertaining to organic reaction mechanism. To offer students an easy and interesting learning experience, each of the topics covered is depicted with lucid diagrams and figures. Point to point discussion progresses as per the Organic Chemistry-I COURSE-II, BCH102 syllabus.

5.3 CURVED ARROW NOTATION

Chemical reactions involve breaking and formation of chemical bonds. It means sharing of electrons between atoms in given molecules changes during reactions. This change in sharing of electron or movement of electrons is denoted by different types of curved arrows depending on the reactions. For example, movement of odd electron (or single electron) is represented by half headed arrow whereas movement of an electron pair is represented by double headed curved arrows. How a double-headed or full-headed arrow and half-headed or fish-hook arrow is drawn in organic chemistry is depicted in Figure 5.1.

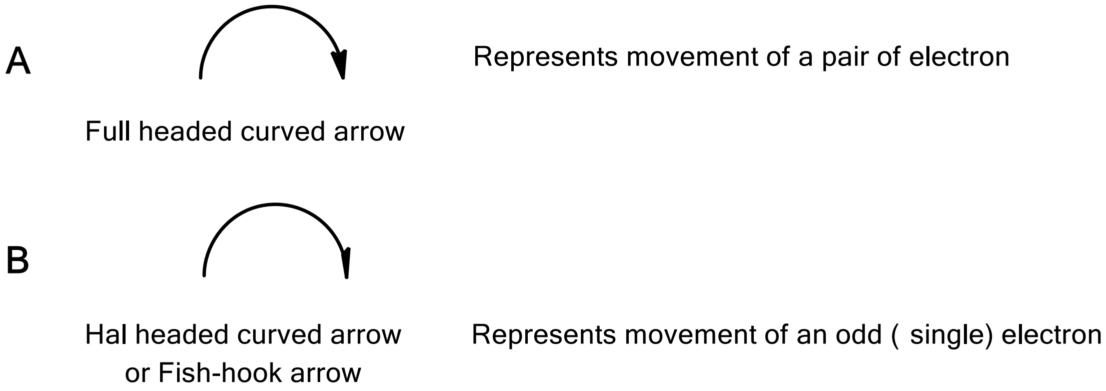


Figure 5.1 Depiction of full (A) and half (B) headed arrows

5.3.1 Drawing electron movements with arrows

Occurrence of electron movement in organic reactions or during the inter-conversion of resonating structures is obvious in organic chemistry. As the organic reactions proceed through several steps, it is important to keep track of electron movements taking place in each step to swiftly understand the mechanistic aspects. The electron movements are denoted by curved arrows as depicted in previous section. The distinct curved arrows should not be confused with other common straight arrow notations in organic chemistry. Arrow head indicates the location where electrons are moving to and the arrow tail indicates where originally electrons were located. Double headed and half headed curved arrows are discussed with some examples in the next section.

5.3.2 Half-headed and double headed arrows

Half headed arrows also referred as fish hook arrows are used to denote the movement of odd electron from one reaction site to another. Since they represent movement of single electron (odd electron) therefore, they are frequently used to depict reactions involving free radicals. Thus, mechanism of homolytic fission, reactions involving free radicals and photochemical reactions are demonstrated by half headed or fish hook arrows. Some examples are depicted in the Figure 5.2.

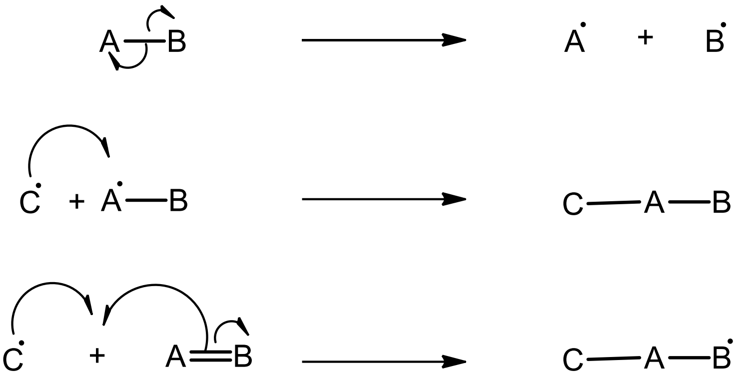


Figure 5.2 Movement of odd electrons in some processes is depicted by half headed arrows. Note the movement of electron and resulting molecular or radical species.

The first reaction indicates homolytic fission of covalent bond between atoms A and B that results in formation of free radicals $A^{\cdot}$ and $B^{\cdot}$. Tail of half headed arrows is on bond which is the original position of electrons and the arrow heads are pointing to the atoms A and B where the electrons locate on completion of the process. In the second example, equal sharing of odd electrons between free radicals, $C^{\cdot}$ and $^{\cdot}A$-B results in a molecule C-A-B. The third example illustrates hemolytic breaking of a π bond as a result of attack by radical $C^{\cdot}$. C and A equally share one electron each to form new σ bond between them, whereas one odd electron resides on atom B.

Double headed arrows are used to denote the movement of electron pair from one reaction site to another. This type of arrows frequently used to depict ionic reaction mechanisms. Arrow tail and arrow head indicate initial and final locations of electron pairs respectively. Some examples are depicted in the Figure 2.3.

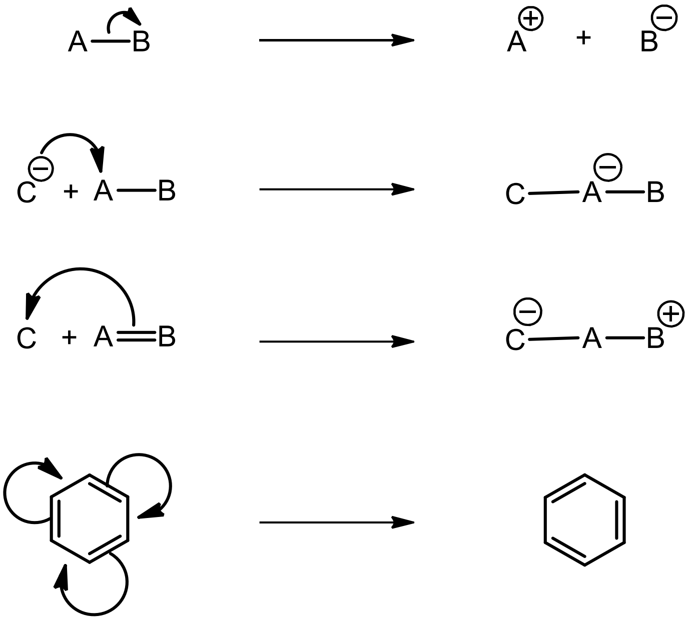
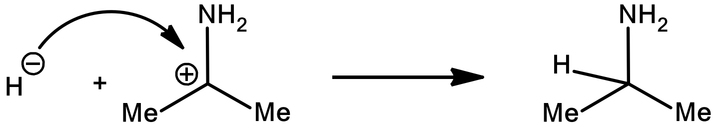
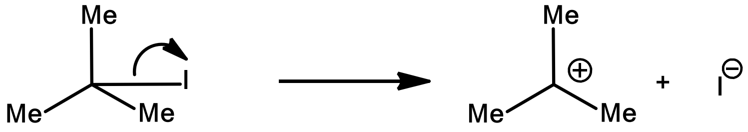


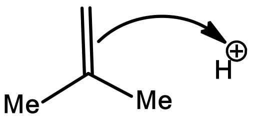
Figure 5.3 Movement of electron pairs in some processes as depicted by full headed arrows. Note the movement of electron pairs and resulting molecular or ionic species.



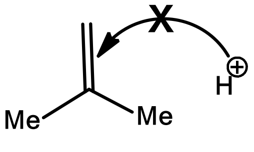
Bond Formation



Bond Cleavage



Correct arrow depiction



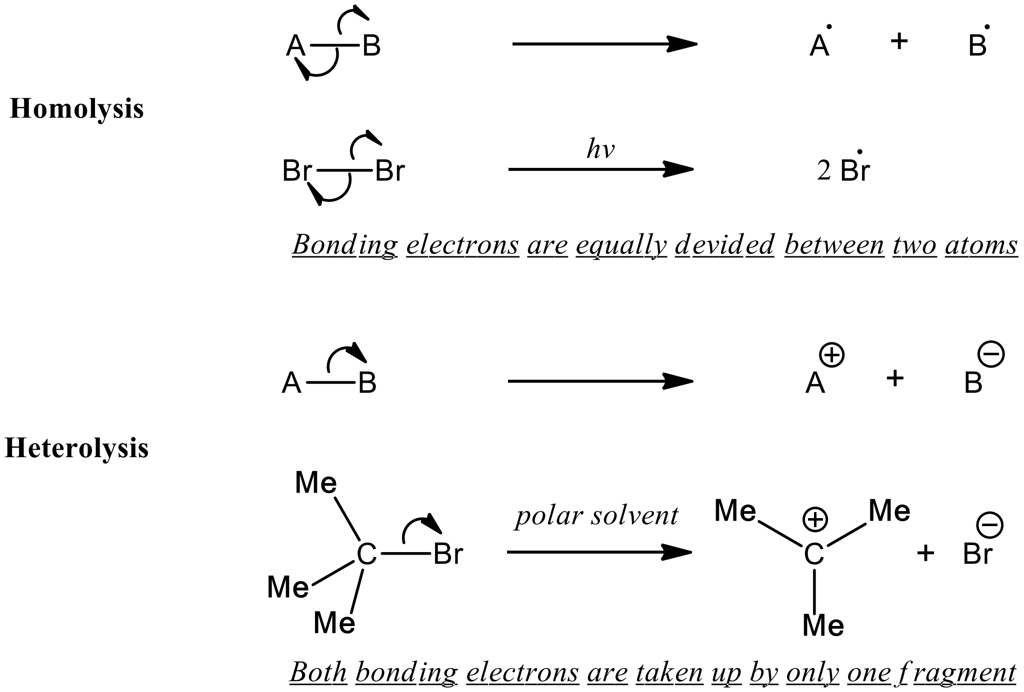
Incorrect arrow depiction

Figure 5.4 Correct depiction of curved arrow for formation and breaking of covalent bond. Inset images show correct and incorrect way to depict electron movement with curved arrows.

The first reaction indicates heterolytic fission of covalent bond that results in formation of ions A^+ and B^-. In the second example, anion C^- attacks on electron deficient site A in a molecule A-B, i.e., C^- donates electron pair to atom A in molecule A-B resulting in the anion on product side. Third example involves attack of electron deficient atom C on the electron rich site, i.e., π bond between A and B. In the resultant species atom C assumes formal negative charge because it accepts additional electron in its orbital whereas atom B loses its electron, hence the formal positive charge on B. Fourth example depicts the concerted movement of three π electron pairs in benzene ring that inter-converts two Kekulé structures into each other.

5.4 HOMOLYTIC AND HETEROLYTIC BOND CLEAVAGE

Chemical reactions involve breaking and formation of chemical bonds. How a chemical bond will break depends on factors such as temperature, reaction medium and solvent. Organic reactions usually involve breaking of covalent bonds followed by formation of new covalent bonds. The bond breaking, also termed as bond cleavage takes place in two possible ways, namely, homolytic and heterolytic bond fission.



Bonding electrons are equally devided between two atoms

Both bonding electrons are taken up by only one fragment

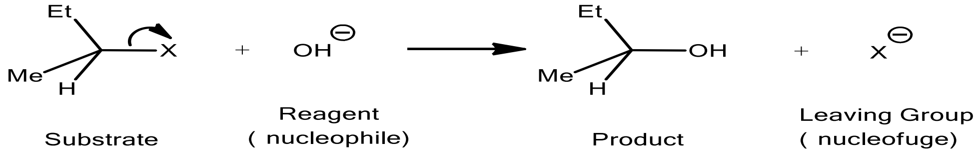
Figure 5.5 General and specific examples depicting homolysis and heterolysis of covalent bonds.

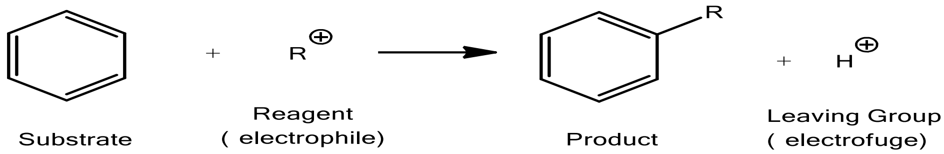
Homolytic bond cleavage is also called homolytic bond fission or homolysis. In homolysis, the two electrons in a cleaved covalent bond are divided equally between the products. On the other hand, heterolytic bond cleavage is also called heterolytic bond fission or heterolysis. In heterolysis, the two electrons in a cleaved covalent bond remain with one of the two fragments.

5.5 TYPE OF REAGENTS

Organic reactions are generally brought about by heterolysis of organic compounds. The breaking of bonds and formation of new bonds occur in presence of reagents. Thus reagents are substances or compounds that are added to bring about a reaction. In organic reactions it is convenient to call one reactant as substrate which will provide carbon to a new bond and the other is called as reagent. The attacking reagent can be (i) which provides an electron pair to the substrate, known as Nucleophile and the reaction is called a Nucleophilic reaction (ii) takes an electron pair from substrate is known as Electrophile and the reaction is called a Electrophilic reaction.

In reactions where the substrate bond is cleaved, the part that does not contain the carbon is called Leaving group. The leaving group that carries electron pair is known as Nucleofuge. If the leaving group moves out without the electron pair, it is called Electrofuge.

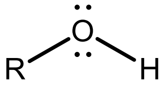




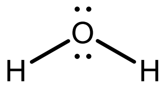
5.5.1 Nucleophilic Reagents or Nucleophiles

Nucleophile means nucleus loving. Reagents having unshared pair of electrons are known as Nucleophilic reagents or nucleophiles and they show tendency to share this lone pair of electrons with electron deficient species. They can be classified into three groups:

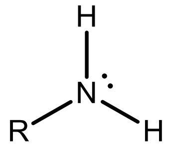
(i) Neutral Nucleophiles: These are electron rich species due to presence of non bonding pair of electrons. Central atom of such species should have a complete octet. Neutral nucleophiles are not charged and are electrically neutral.



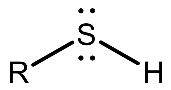
alcohol



water

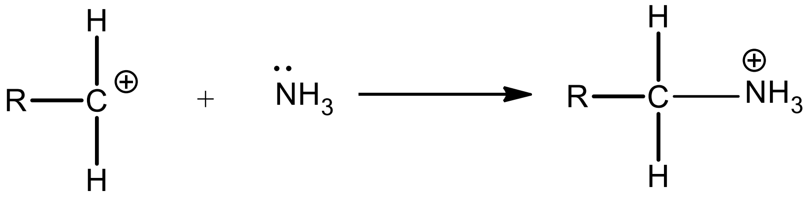


amine

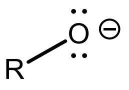


thiol

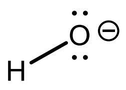
Organic compounds having C-C multiple bond/bonds also act as Neutral nucleophiles because these species have π electron cloud above and below the plane of the molecule. The addition reaction of a neutral nucleophile to a positively charged substrate gives a positively charged product.



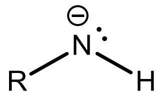
(ii) Negative Nucleophiles: These carry an electron pair and are negatively charged because of the presence of unpaired electrons.



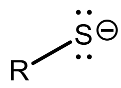
alkoxide



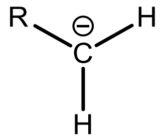
hydroxide



amide

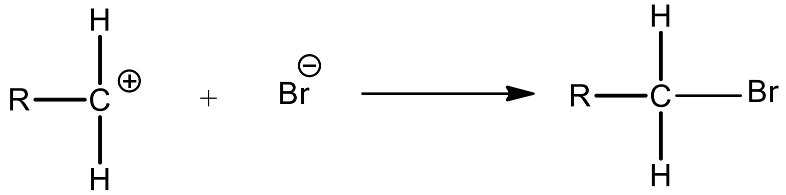


mercaptyl anion



carbanion

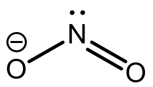
Addition reaction of a negatively charged nucleophile to a positively charged substrate results in neutral molecule.



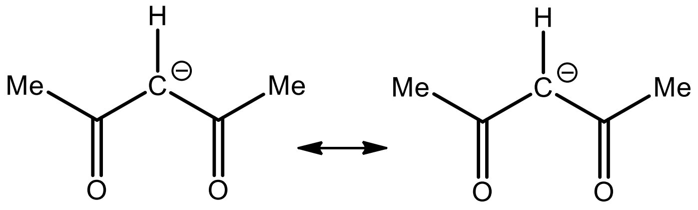
(iii) Ambident Nucleophiles: The nucleophiles which can attack through two or more atoms are called ambident nucleophiles. For Eg: CN^{-} can attack through N or C to give cyanide (RCN) or isocyanide (RNC) respectively.

$CN^{\ominus}$

cyanide/isocyanide

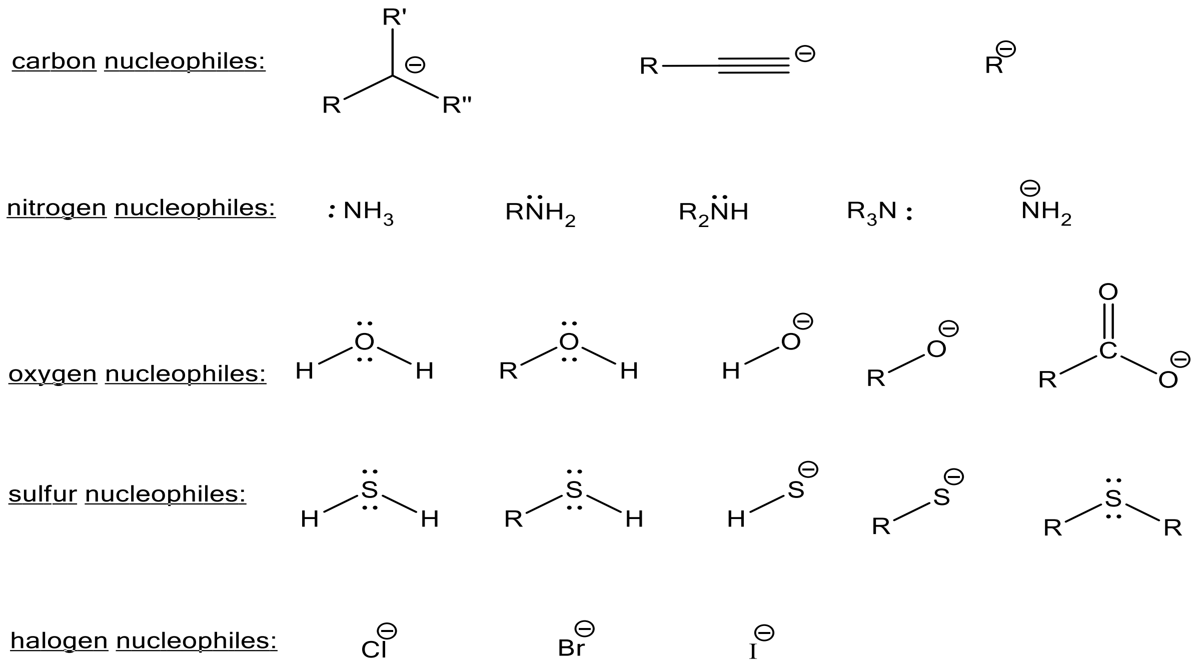


nitrite



resonance stabilized carbanion

Nucleophiles can also be classified on the basis of the kind of atom that forms a new covalent bond. The most common nucleophiles on this basis are oxygen, nitrogen, sulfur, halogen and carbon nucleophiles.

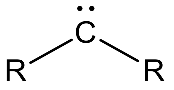


5.5.2 Electrophilic Reagents or Electrophiles

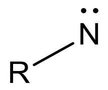
An electrophile (meaning electron loving) is a reagent that is electron deficient and due to this they show affinity for electrons. Electrophiles can also be of two types:

(i) Neutral Electrophiles: These electrophiles even though electron deficient does not carry positive charge. They have incomplete valence shells. Examples: $AlCl_3$, BF_3, carbene etc.

$AlCl_3$ $FeCl_3$ BF_3



carbene

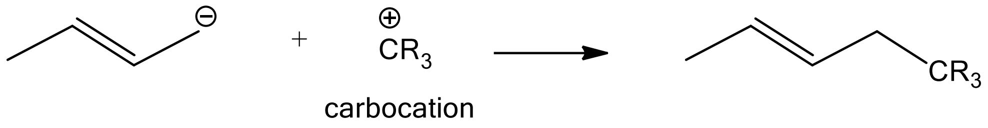


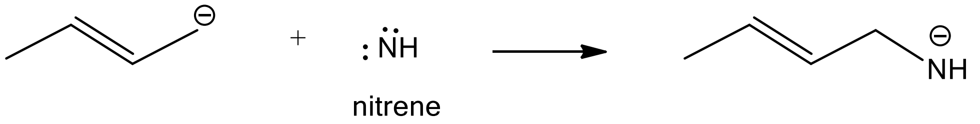
nitrene

(ii) Positive Electrophiles: These electrophiles carry positive charge on central atom and have incomplete octet.

$H^{\oplus}$ $\overset{\oplus}{S}O_3H$ $\overset{\oplus}{N}O_2$ $H_3O^{\oplus}$ $R_3C^{\oplus}$

The positive electrophile will attack the substrate (which is a negative nucleophile) and accepts an electron pair for sharing resulting in a neutral molecule. While, a neutral electrophile will attack a electron rich substrate (negative nucleophile) to form a negatively charged molecule.





5.6 RECAPITULATION OF TYPES OF REAGENTS

A nucleophile is a chemical species that donates an electron pair to an electron deficient reaction site to form a chemical bond. As the neucleophile donate electrons, they are Lewis bases. All molecules or ions with a free pair of electrons or at least one pi bond can act as nucleophiles. A neucleophile with higher affinity to the electron deficient site is said to have higher nucleophilicity. All carbanions, OH^-, Br^-, I^- and SH^- are few of the good nucleophiles in organic chemistry. Nucleophilic character of similar species comprising different elements increases top to down and decreases on moving left to right in the periodic table. Therefore, SH^- is better nucleophile that OH^- and CH_3^- is better neucleophile than NH_2^-. Neutral nucleophilic reactions with solvents such as alcohols and water are named solvolysis. Nucleophiles may take part in nucleophilic substitution, whereby a nucleophile becomes attracted to a full or partial positive charge.

On the other hand, an electrophile is a reagent that attracts towards electrons. Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre. Thus, they are Lewis acids. In chemical reactions, electrophiles accept an electron pair make bond to the electron rich reaction site. Cations such as H^+ and NO^+, polar molecules such as HCl, alkyl halide (R-X), acyl halides (R-COX), carbonyl compounds (R-CO-R or R-CHO) and polarizable molecules such as Br_2 and Cl_2 etc are commonly used electrophiles

5.7 SUMMARY

This chapter covers description of basic concepts such as curved arrow notation (arrow pushing) and bond fission, which are vital to understand and write organic reaction mechanisms. The description on topics such as full headed & half headed curved arrow, nucleophiles and electrophiles, hemolytic and heterolytic bond fission is given in the chapter with sufficient details. Other significantly important terms such as nucleofuge, electrofuge, leaving group, substrate and attacking reagents are given with guiding figures. Understanding of these topics will help us to understand and gain interest in mechanisms of organic reactions.

5.8 TERMINAL QUESTIONS

Short Answer type questions

Q.1 Briefly describe the curved arrow notation for movement of odd electrons.

Q.2 Describe the full headed curved arrow notation used in reaction mechanisms.

Q.3 What is an electrofuge? Give two examples of electrofuge.

Q.4 Write short note on heterolysis of covalent bonds.

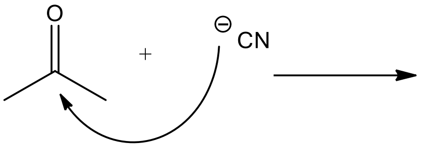
Q.5 Describe the terms substrate, reagent and leaving group.

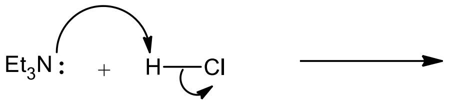
Q.6 Discuss neutral nitrogen containing neucleophiles.

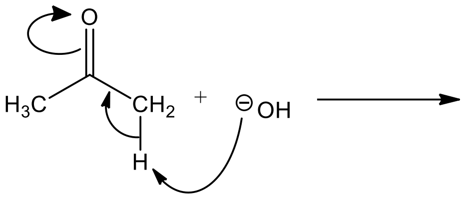
Q.7 What is the difference between neucleophile and electrophile?

Q.8 Give one example of a nucleophilic and an electrophilic substrate.

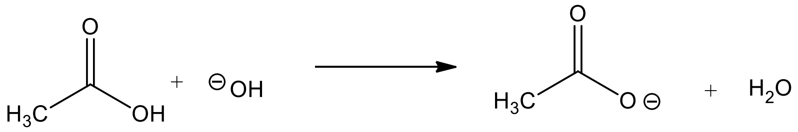
Q.9 Complete the following reactions:

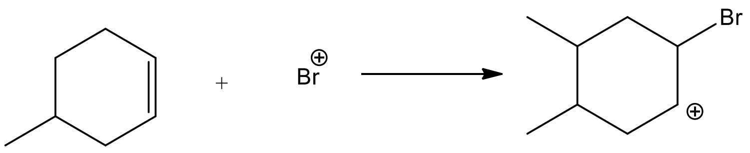






Q.10 Place the appropriate curved arrows to depict the electronic movement in following reactions.



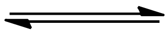


MCQ type questions

Q.1 Identify the correct arrow depicting movement of electron pair in organic reaction mechanisms:


(i)


(ii)


(iii)


(iv)

(a) iii

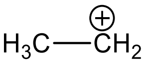
(b) i

(c) iv

(d) ii

Q.2 Select from the options given below the electrophilic species:

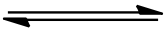
(a) SO_3

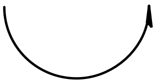
(b) 
$H_3C-\overset{\oplus}{C}H_2$

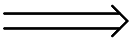
(c) BF_3

(d) both b and c

Q.3 Which one of the following represents movement of odd electron in organic reaction mechanisms:


(i)


(ii)


(iii)


(iv)

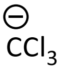
(a) iii

(b) i

(c) iv

(d) ii

Q.4 Select from the options given below the nucleophilic species:

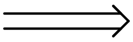
(a) 
$\overset{\ominus}{C}Cl_3$

(b) $LiAlH_4$

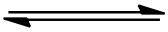
(c) $H_3C-O-CH_3$

(d) all of the above

Q.5 Find the correct depiction for fish-hook arrow:


(i)


(ii)


(iii)


(iv)

(a) ii & iii

(b) iii

(c) none

(d) i

Q.6 Identify the electrophile from the following options:

(a) CO_2

(b) SO_3

(c) $AlCl_3$

(d) Both a and b

Q.7 A leaving group is called so because:

(a) it detaches from the carbon in organic reaction

(b) it detaches from the attacking reagent

(c) it is part of incoming nucleophile

(d) it is part of incoming electrophile

Q.8 Which of the species given below behaves as ambident nucleophile:

(a) $CN^{\ominus}$

(b) $NO_2^{\ominus}$

(c) $NH_2^{\ominus}$

(d) Both a and b

Q.9 Which of the species given below is an ambident nucleophile:

(a) $Br^{\ominus}$

(b) $NO_2^{\ominus}$

(c) $NH_2^{\ominus}$

(d) All of the above

Q.10 Nucleofuge and Electrofuge are commonly called as:

(a) substrate

(b) leaving group

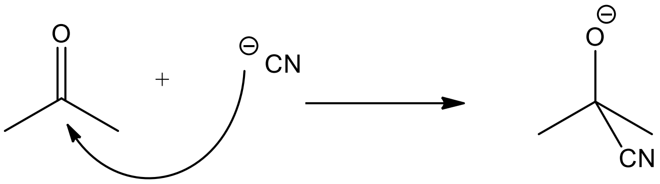
(c) incoming group

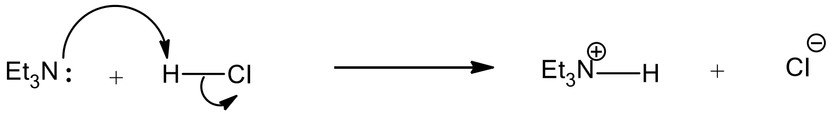
(d) attacking reagent

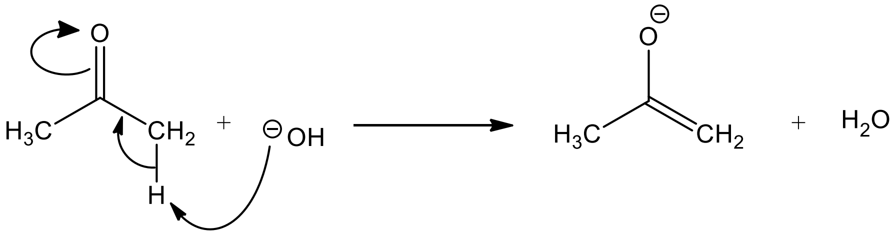
ANSWERS

Answers to the short answer type questions

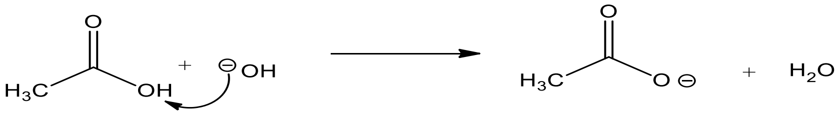
Q.9

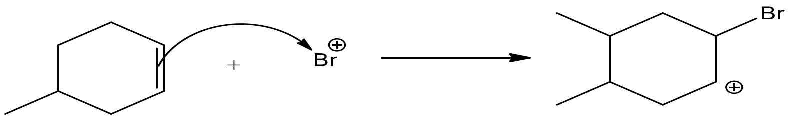






Q.10





Answers to the MCQ type questions

Q.1 (a)

Q.2 (d)

Q.3 (b)

Q.4 (d)

Q.5 (c)
Q.6 (c)
Q.7 (a)
Q.8 (d)
Q.9 (b)
Q.10 (b)

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UNIT 6: ALYL HALIDE

CONTENTS:

6.1 INTRODUCTION

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic by halogen atom(s) results in the formation of alkyl halide (haloalkane). Haloalkanes contain halogen atom(s) attached to the sp3 hybridized carbon atom of an alkyl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, chloramphenicol, produced by soil microorganisms is very effective for the treatment of typhoid fever. In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of alkyl halide.

6.2 OBJECTIVE

In this chapter we have to study about Alkyl halide: Its classification, Nomenclature. Describe the reactions involved in the preparation of alkyl halide (haloalkanes) and understand various reactions that they undergo. . Correlate the structures of alkyl halide with various types of reactions. Use stereochemistry as a tool for understanding the reaction mechanism. Nucleophilic Substitution Reaction of Alkyl Halides as S_N^1 Reaction, S_N^2 Reactions and its mechanism, Elimination Reactions as E1 and E2 reaction and its mechanism, Poly halogen compound and terminal Questions.

6.3 NOMENCLATURE AND CLASSIFICATION OF ALKYL HALIDES

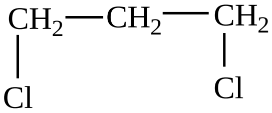
A. Classification on the basis of number of halogen atom:

Aliphatic halogen compound (alkyl halide) can be classified in to following classes:

1. Monohalogen compounds: Compound which contains one halogen in the molecule is called Monohalogen compounds.

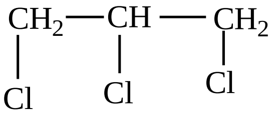
$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$

2. Dihalogen compounds: Compound which contains two halogens in the molecule is called Monohalogen compounds.



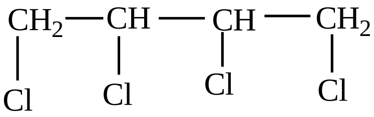
$$\underset{\displaystyle Cl}{CH_2}-CH_2-\underset{\displaystyle Cl}{CH_2}$$

3. Trihalogen compounds: Compound which contains three halogens in the molecule is called Monohalogen compounds.



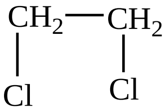
$$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH}-\underset{\displaystyle Cl}{CH_2}$$

4. Tetrahalogen compounds: Compound which contains four halogens in the molecule is called Monohalogen compounds.



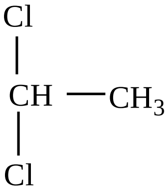
$$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH}-\underset{\displaystyle Cl}{CH}-\underset{\displaystyle Cl}{CH_2}$$

5. Vicinal dihalide: Compounds containing two halogens on adjacent carbon in the compound is called vicinal dihalide.



$$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH_2}$$

6. Geminal dihalide: Compound containing two halogen on the same carbon atom is called Geminal dihalide.

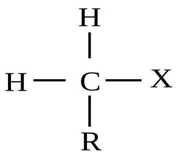


$$\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{CH}}-CH_3$$

B. Classification On the basis of the nature of the carbon attached to the halogen atom:

On the basis of the nature of the carbon attached to the halogen atom, alkyl halides are classified in three types.

1. Primary alkyl halide:

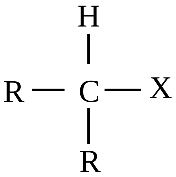


$$H-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-X$$

Primary halo alkane

1^0

2. Secondary alkyl halide:

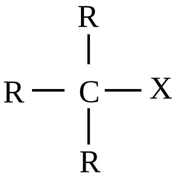


$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-X$$

secondary halolkane

2^0

3. Tertiary alkyl halide:



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-X$$

Tertary halo alkane

3^0

Here R = Alkyl group CH_3, C_2H_5, C_3H_7 etc.

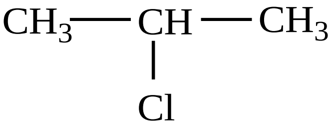
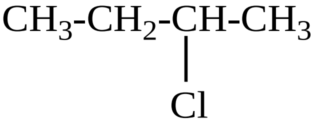
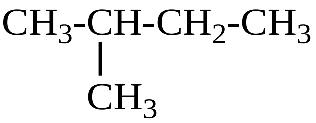
X = Halogen atom (Cl, Br, Ietc.)

Nomenclature:

Alkyl halides are named into two ways

A. Common System: In this system the alkyl group attached to the halogen atom is named first .This is then followed by an appropriate word chloride, bromide or fluoride.

Example:

1. CH_3-Cl	Methyl chloride
2. CH_3-CH_2-Cl	Ethyl chloride
3. $CH_3-CH_2-CH_2-Cl$	n-prppyl chloride
4.  $CH_3-\underset{\underset{Cl}{\mid}}{CH}-CH_3$	iso- propyl chloride
5. $CH_3-CH_2-CH_2-CH_2-Cl$	n-butyl chloride
6.  $CH_3-CH_2-\underset{\underset{Cl}{\mid}}{CH}-CH_3$	*Sec*-butyl chloride
7.  $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CH_2-CH_3$	*Iso*-butylchloride

B. IUPAC System: It has following rules-

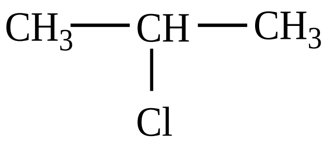
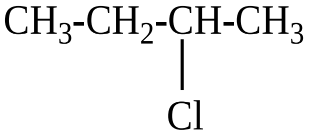
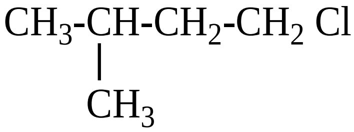
1. Select the longest carbon chain containing the halogen atom.

2. Number the chain so as to give the carbon carrying the halogen atom the lowest possible number.

3. Indicate the position of the halogen atom by a number and by the fluoro, chloro, bromo.

4. Name other substituent and indicate their position by numbers.

Example:

1. $CH_3\text{-}Cl$	1-Chloro methane
2. $CH_3\text{-}CH_2\text{-}Cl$	1-Chloro ethane
3. $CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$	1-Chloro propane
4.  $CH_3\text{—}\underset{\displaystyle Cl}{\underset{\mid}{CH}}\text{—}CH_3$	2- Chloro propane
5. $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl$	1- Chloro butane
6.  $CH_3\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\underset{\mid}{CH}}\text{-}CH_3$	2-Chloro butane
7.  $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{\mid}{CH}}\text{-}CH_2\text{-}CH_2\ Cl$	3-Methyl-1 chloro butane

6.4. METHODS OF FORMATION

Alkyl halides can be prepared by the following methods:-

1. Halogination of Alkanes: Alkanes react with Cl_2 or Br_2 in the presence of UV light or at 400^o C to give alkyl halides along with polyhalogen derivatives.

$$CH_4 + Cl_2 \xrightarrow{\text{Sul light}} CH_3\text{-}Cl$$

2. From alkene (**Addition of Halogen acids to Alkenes):** Halogen acids add to alkenes to yield alkyl halides. The mode of addition follows Markonikoff rule, except in presence of organic peroxides.

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3\text{-}CH_2\text{-}Br$$

$$CH_3\text{-}CH{=}CH_2 + HBr \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$$

3. From Alcohol:

a. Reaction with Hydrogen halide: When any alcohol react with hydrogen halide in the presence of anhydrous $ZnCl_2$, then it gives corresponding alkyl halide.

$$\text{R-OH} \quad + \quad \text{HBr} \xrightarrow{\text{Anhy. } ZnCl_2} \text{R-Br} \quad + \; H_2O$$

$$CH_3\text{-}CH_2\text{-OH} \quad + \text{HBr} \xrightarrow{\text{Anhy. } ZnCl_2} CH_3\text{-}CH_2\text{-Br} \; + \; H_2O$$

b. Reaction with phosphorus penta chloride (PCl_5):

Alcohol on react with PCl_5 gives alkyl halide by removing phosphoryl chloride ($POCl_3$).

$$\text{R-OH} \; + \; PCl_5 \longrightarrow \text{R-Cl} \; + \; POCl_3 \; + \; \text{HCl}$$

$$CH_3\text{-}CH_2\text{-OH} \longrightarrow CH_3\text{-}CH_2\text{-Cl} \; + \; POCl_3 \; + \; \text{HCl}$$

Ethyl chloride

c. Reaction with phosphorus tri chloride (PCl_3):

Alcohol on react with PCl_3 gives alkyl halide by removing of $H3PO_4$.

$$3\ \text{R-OH} \; + \; PCl_3 \longrightarrow 3\ \text{R-Cl} \; + \; H_3PO_4$$

$$3\ CH_3\text{-}CH_2\text{-OH} \longrightarrow 3\ CH_3\text{-}CH_2\text{-Cl} \; + \; H_3PO_4$$

Ethyl chloride

d. Reaction with thionyl chloride ($SOCl_2$).

Alcohol on react with $SOCl_2$ gives alkyl halide by removing of CO_2 and HCl.

$$\text{R-OH} \; + \; SOCl_2 \longrightarrow \text{R-Cl} \; + \; \text{SO2} \; + \; \text{HCl}$$

$$CH_3\text{-}CH_2\text{-OH} \longrightarrow CH_3\text{-}CH_2\text{-Cl} \; + \; \text{SO2} \; + \; \text{HCl}$$

Ethyl chloride

4. From halogen exchange reaction:

This reaction is particularly suitable for preparing alkyl iodides. The alkyl bromide or chloride is heated with a conc. sodium iodide in acetone.

$$CH_3\text{- }CH_2\text{- Br} + Na \xrightarrow{\text{Acetone}/C_2H_5I} CH_3\text{- }CH_2\text{- I} + NaBr$$

Alkyl fluorides are also prepared by treating alkyl chloride or bromide with inorganic fluorides.

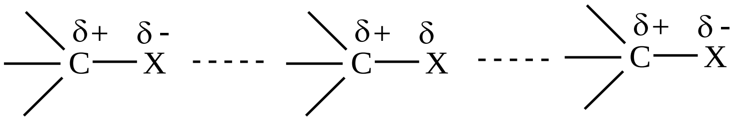
$$\underset{\text{Methyl chloride}}{2CH_3\text{- Cl}} + Hg_2F_2 \longrightarrow \underset{\text{Methyl fluoride}}{2CH_3\text{- F}} + Hg_2Cl_2$$

6.5 PHYSICAL PROPERTIES

1. The lower alkyl halides (CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl) are gases at room temperature. The other alkyl halides containing upto C18 are liquids having high boiling points.

2. Haloalkanes are moderately polar molecules. Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.

3. The melting and boiling points of haloalkanes are higher than those of their parent hydrocarbons (Table 6.1) This is due to (i) the greater molecular mass and hence greater magnitude of van-der Waals forces of attraction in halo compounds than in the parent hydrocarbons and (ii) the existence of intermolecular dipole-dipole interaction, as shown below:



For a given alkyl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 6.1 to show this variation.

Compound	**Melting point (K)**				
	X=H	X=F	X=Cl	X=Br	X=I
CH_3-X	111.5	194.6	248.8	276.6	315.4
C_2H_5-X	184.3	241	285	311.4	345
C_6H_5-X	351	358	405	429	461

Table 6.1 boiling points of halomethanes, haloethanes and halobenzene

6.6. CHEMICAL REACTIONS

1. Wurtz reaction: In this reaction R-X is treated with Na in the presence of dry ether to give alkane. This reaction is also known as coupling reaction.

$$CH_3\text{-}CH_2\text{-}\boxed{Cl \;+\; 2Na \;+\; Cl}\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{Drt ether}} CH_3\text{-}CH_2\text{--}CH_2\text{-}CH_3$$

2. Wurtz Fittig reaction: When two different alkyl halides react with Na metal in the presence of dry ether then it gives odd number containing alkanes. This reaction is known as Wurtz Fittig reaction.

$$R\text{-}X \;+\; 2Na \;+\; X\text{-}R' \xrightarrow{\text{Dry ether}} R\text{-}R' \;+\; 2Na$$

$$CH_3\text{-}CH_2\text{-}\boxed{Cl \;+\; 2Na \;+\; Cl}\text{-}CH_3 \xrightarrow{\text{Dry ether}} CH_3\text{-}CH_2\text{--}CH_3$$

3. Reaction with Magnesium (Mg): When any alyl halide reacts with Magnesium metal then it gives Organometallic compound.

$$CH_3\text{-}Br \;+\; Mg \xrightarrow{\text{THF}} CH_3\text{-}Mg\text{-}Br$$

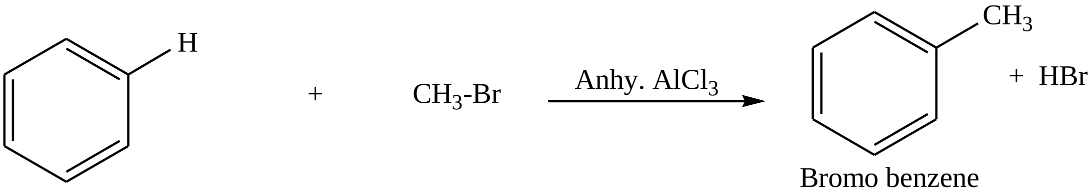
4. Frackland Reaction: In this reaction R-X is treated with Zn in the presence of dry ether to give di-alkyl-Zn compound.

$$2\,CH_3\text{-}Br \;+\; 2Zn \xrightarrow{\text{Dry ether}} (CH_3)_2Zn \;+\; ZnBr_2$$

5. Williamson synthesis: In this reaction R-X is treated with R-O-Na (sodium alkoxide) in the presence of dry ether to form ether and this reaction has great importance to form both types of ether symmetrical and unsymmetrical.

$$2\ CH_3\text{-}Br \quad + \quad CH_3\text{-}O^- Na^+ \xrightarrow{\text{Dry ether}} CH_3\text{-}O\text{-}CH_3 \ + \ NaBr$$

6. Friedal Craft reaction: In this reaction when an alkyl halide react with aromatic hydrocarbon like benzene then it gives alkyl benzene.



Bromo benzene

7. Reaction with Sodium hydro sulphide (NaSH): In this reaction when an alkyl halide reacts with Sodium hydro sulphide then it give thio alcohol.

$$R\text{-}X \quad + \quad NaSH \longrightarrow R\text{-}SH \quad + \quad NaX$$

$$CH_3\text{-}Cl \quad + \quad NaSH \longrightarrow CH_3\text{-}SH \quad + \quad NaX$$

6.7 MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES

During neocleophilic substitution reaction the C-X bond undergoes to the breaking and the C-necleophile bond to be formation. In the case of R-X this processes takes place any of the three types.

(1) The breaking of C-X bond takes place followed by the formation of C-Nu bond.

(2) The formation and the breaking takes place simultaneously.

(3) The formation of C-Nu bond takes place followed by the breaking of C-X bond.

Generally the initial two types takes place in aliphatic alkyl halides and the third types takes place in aryl halides (Ar-X).

Classification of Nucleophillic substitution reaction:

The Nucleophillic substitution Reaction is classified in to following two classes.

(1) SN1 (Unimolecular Nucleophilic Substitution reaction):

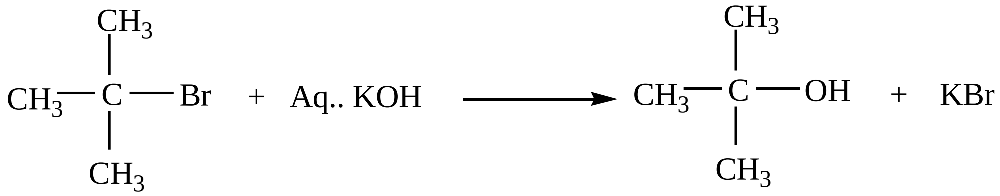
It is represents that Mononucleophillic substitution reaction. Generally such type of mechanism is carried by tert. alkyle halides and it is the two step mechanism.

Step-I

In this step the C-X bond undergoes heterolytic fission to give an intermediate carbonium ion and it is the slowest step. So it is the rate determining step.

Step-II

It is the faster one and in it the nucleophile is attack to the carbonium ion to form the required compound.



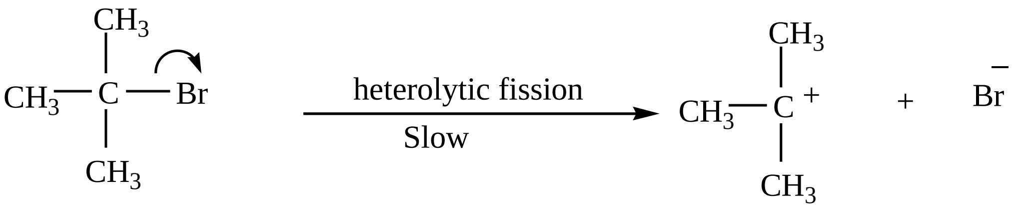
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + \text{Aq.. KOH} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + KBr$$

Mechanism:

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$

Step I- Slow step:

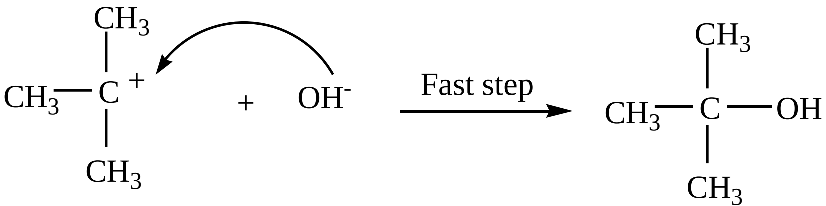


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br \xrightarrow[\text{Slow}]{\text{heterolytic fission}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + \overline{Br}$$

tert. butyl bromide

3^0 butyl carbonium ion

Step II Fast step:



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + OH^- \xrightarrow{\text{Fast step}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

3^0 butyl carbonium ion

tert. butyl alcohol

Formation of KBr:

$$K^+ + \overline{Br} \longrightarrow KBr$$

It is clear from above mechanism that in the slowest step only one reactant (ter. butyl bromide) takes placed, hence the rate of reaction is depends upon the concentration of it, so it is first order reaction. So this reaction is known as uni-molecular nucleophilic substitution (SN^1) reaction.

Mathematically:

$$\frac{dx}{dt} = K\left[\text{Alkyl halide}\right]$$

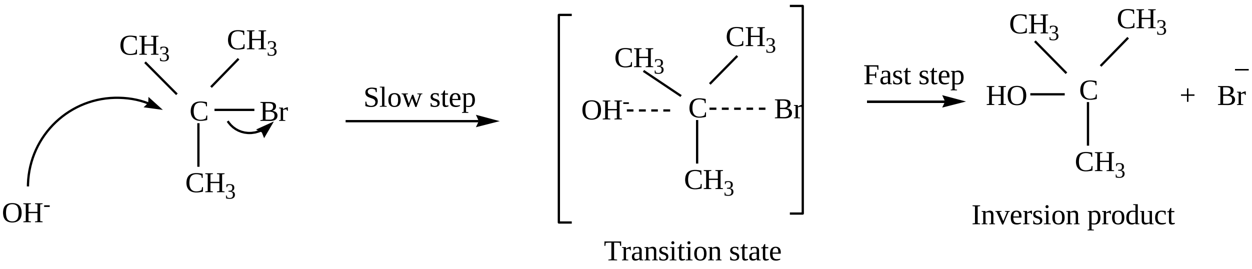
(2) SN^2 (Bi-molecular neicleophilic substitution reaction) Reaction:

This type of mechanism is generally followed by primary alkyl halides and it is the one step mechanism. In this type of mechanism Nu^- attacks to that carbon which is attached from the halogen atom, from the opposite side of the halogen carrying carbon atom because there is repulsion between nucleophilic and halogen. It is the slowest step.

Mechanism:

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$



Formation of KBr:

$$K^+ \quad \overline{Br} \longrightarrow KBr$$

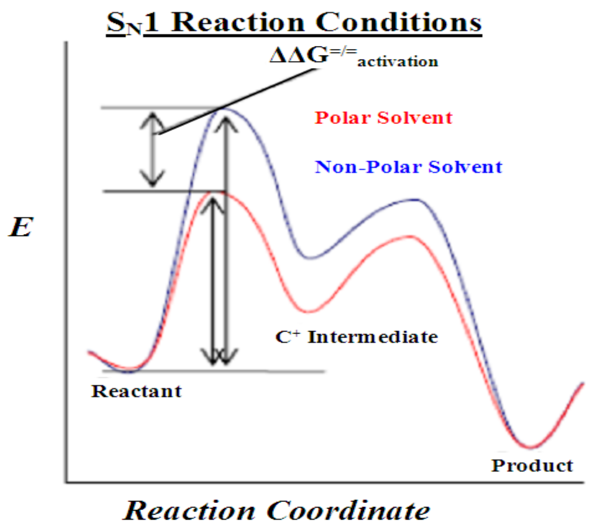
In the transition state or activated complex the C-Nu bond is partially formed and the C-Br bond is partially breaking. Hence in this stage the C-Nu bond start to form and the C-Br bond start to breaking and finally is formed. In this mechanism the C-H bond are like the spokes and are along the axel.

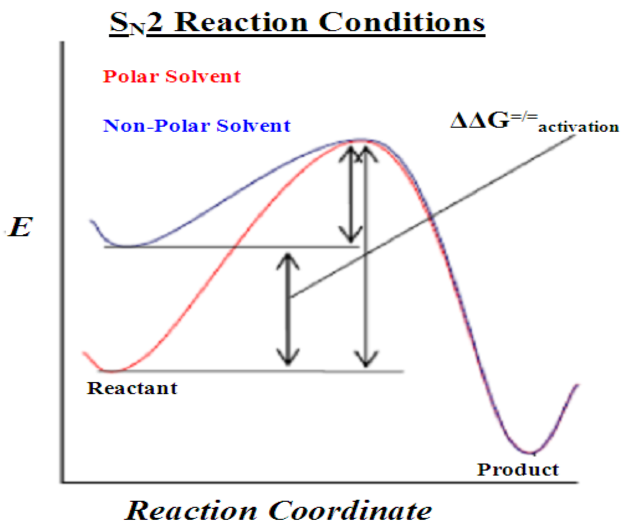
Since in the slowest step there are two reacting species one is alkali & other is R-X. So its rates depends upon the concentration of both. So its is Bi-molecular Nucleophilic Substitution reaction reaction SN^2.

Mathematically:

$$\frac{dx}{dt} = K\left[\text{Alkyl halide}\right]\left[\text{KOH}\right]$$

6.7.1. SN1 and SN2 reaction with energy profile diagrams

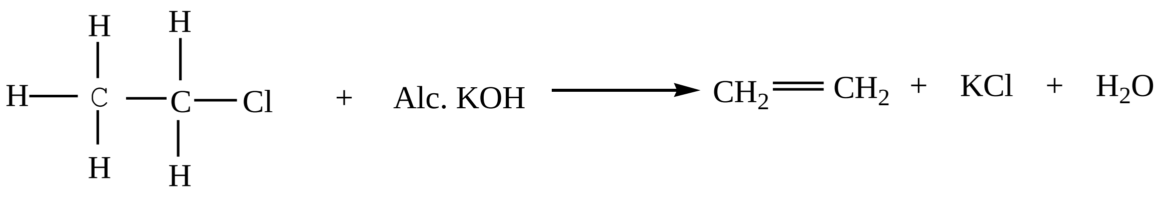




6.8. *ELIMINATION REACTIONS (TYPES OF ELIMINATION REACTIONS)*

In this type of reaction the atoms or group of atoms are eliminated from two adjacent C-atoms to give the product.

Example: R-X on react with KOH (alc.) gives alkene by undergoing dehydrohalogenation



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl + \text{Alc. KOH} \longrightarrow CH_2{=}CH_2 + KCl + H_2O$$

Types of elimination reaction:

Elimination reactions are classified into two classes. One is E^1 and other is E^2 reaction**.**

1. E^1 Elimination (Uni-molecular Elimination Reaction): Generally such type of mechanism is observed in tert. alkyl halides and it is two step mechanism.

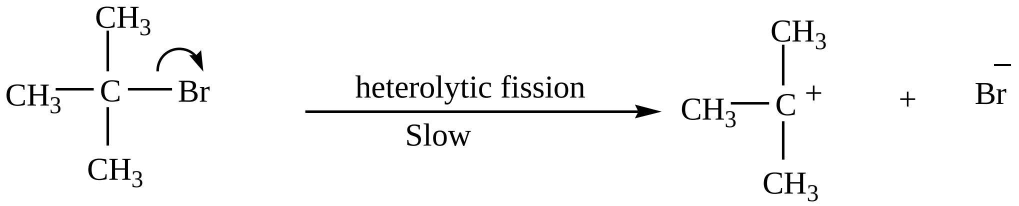
Step I: It is the slowest step. In this step the C-X bond undergoes hetrolytic fission to form an intermediate carbonium ion and this step is also known as rate determining step.

Step II: It is the faster one. In this step the Nu^- is eliminate a β- hydrogen from the carbonium ion and form alkene.

Mechanism:

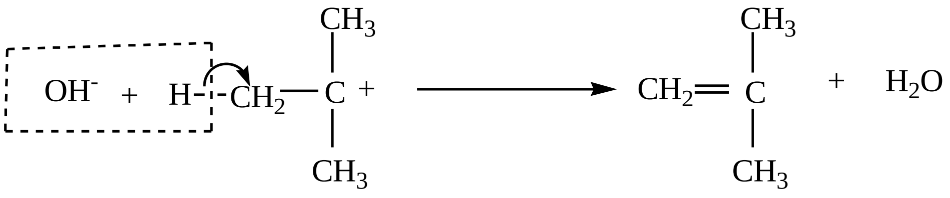
$$KOH \longrightarrow K^+ + \underset{Nu^-}{OH^-}$$

Step I:



tert. butyl bromide 3^0 butyl carbonium ion

Step II:



$$K^+ + \overset{-}{Br} \longrightarrow KBr$$

2. E^2 Elimination (Bi-molecular Elimination Reaction): E2 mechanism is concerted process and a bimolecular reaction. Because the base removes a hydrogen at the same time the C— X bond is broken to form a halide ion the rate law for the rate determining step is dependent on both the alkyl halide and the base :

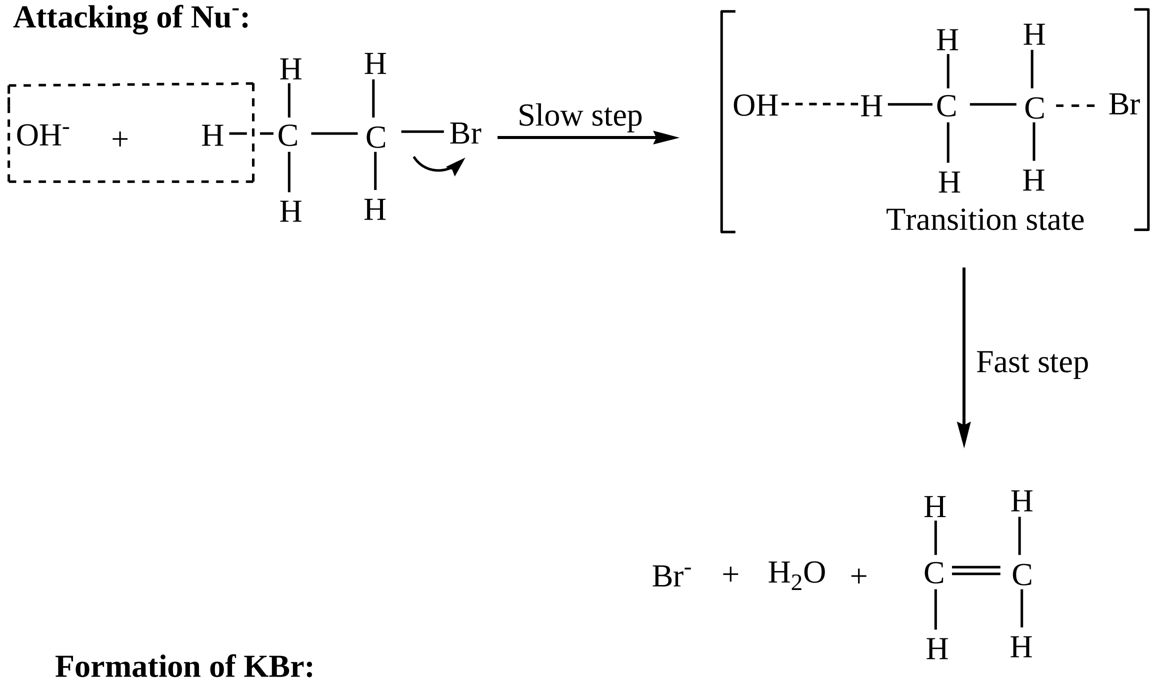
$$\text{Rate} = k\ [\text{alkyl halide}]\ [\text{base}]$$

The stronger the base the more likely it is that E2 mechanism will be in operation. E2 mechanism illustrate by reaction of 1-bromopropane with sodiumethoxide.

Formation of Nucleophile:

$$KOH \longrightarrow K^+ + OH^-$$

Attacking of Nu$^-$:



Formation of KBr:

$$K^+ + Br^- \longrightarrow KBr$$

Thus it is clear from above mechanism in the slowest step, which is rate determining step two reacting species takes palce. Hence the rate of reaction is depands upon both concentrations. So it is of two order reaction.

6.9 POLYHALOGEN COMPOUNDS- CHLOROFORM, CARBON TETRA CHLORIDE

A large number of polyhalogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform ($CHCl_3$), iodoform (CHI_3), carbon tetrachloride (CCl_4), benzene hexachloride (BHC), DDT, etc.

A. Chloroform ($CHCl_3$): Chloroform is an important trihalogen derivative of methane. In the past chloroform was extensively used as general anesthetic for surgery but it is rarely used for this purpose now because it is causes extensive liver damage. Its IUPAC name is tri chloromethane

Preparation of Chloroform:

1. From Ethanol:

Chlorofom is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali. Following is the reaction sequence in this process-

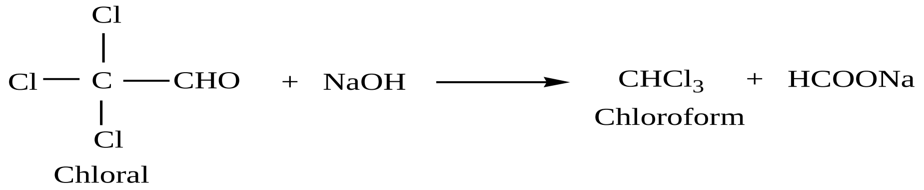
$$\underset{\text{Ethanol}}{CH_3\text{-}CH_2\text{-}OH} + Cl_2 \xrightarrow[-HCl]{} \underset{\text{Ethanal}}{CH_3\text{-}CHO} + 3Cl_2 \xrightarrow[-3HCl]{} \underset{\substack{\text{Trichloroethanal}\\ \text{(Chloral)}}}{Cl_3CCHO}$$

$$Ca(OH)_2 + 2Cl_3\text{-}C\text{-}CHO \longrightarrow \underset{\text{Calcium formate}}{(HCOO)_2Ca} + \underset{\text{Chloroform}}{2\,CHCl_3}$$

2. From Methane: Methane on chlorination gives $CHCl_3$ which is separated from the mixture.

$$CH_4 + Cl2 \xrightarrow{400^0C} CH_3Cl + CH_2Cl_2 + \underset{\text{Chloroform}}{CHCl_3} + CCl_4$$

3. From Chloral (Trichloro acetaldehyde): Chloral on react with NaOH or $Ca(OH)_2$ to give chloroform.



$$\underset{\text{Chloral}}{Cl-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CHO} + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCOONa$$

4. From trichloroacetone: Trichloro acetone on react with NaOH gives $CHCl_3$ by removing sodium acetate.

$$CCl_3\text{-}CO\text{-}CH_3 + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium acetate}}{CH_3COONa}$$

Physical Properties:

1. Chloroform is a colorless liquid with a characteristic sickly smell.
2. It is almost insoluble in water but is soluble in most organic solvents.
3. It is heavier than water.
4. Its boiling point is 334 K.
5. It is used as anesthetic in surgery.

Chemical Properties: The chemical properties of chloroform are as follows-

1. Oxidation- Chloroform undergoes oxidation in the presence of light and air to form phosgene.

$$CHCl_3 + O_2 \xrightarrow{\text{Sun light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Chloroform is used for anesthetic purposes; therefore, high level of purity is desirable. To prevent oxidation of chloroform it is stored in dark bottles.

2. Reduction- It undergoes reduction with zinc and hydrochloric acid in the presence of ethyl alcohol to form dichloro-methane.

$$CHCl_3 + 2H \xrightarrow{Zn} CH_2Cl_2 + HCl$$

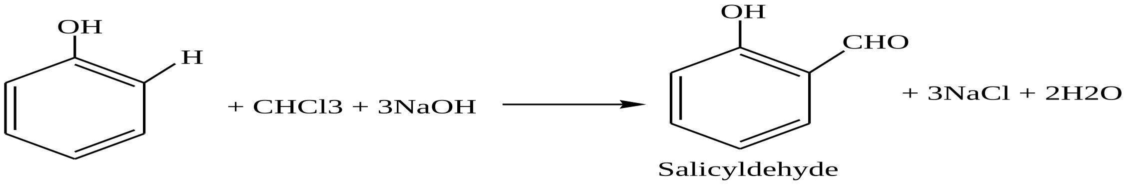
3. Reduction with HNO_3: Chloroform on react with HNO_3 form nitrochloroform which is known as tears gas.

$$CHCl_3 + HNO_3 \longrightarrow \underset{\substack{\text{Chloropicrin} \\ \text{(Tears gas)}}}{CCl_3\text{-}NO_2} + H_2O$$

4. Hydrolysis- Chloroform undergoes hydrolysis with hot aqueous sodium hydroxide to give sodium formate.

$$\underset{\text{Chloroform}}{CHCl_3} + 4NaOH \longrightarrow \underset{\text{Sodium formate}}{HCOO\text{-}Na+} + 3NaCl + 2H_2O$$

5. Rimer-Tieman Reaction- Chloroform reacts with phenol in the presence of sodium hydroxide to form salicyaldehyde.



Uses:

i. Chloroform is used as a solvent for fats, waxes and rubber.
ii. In the preparation of chloropicrin and chloretone.
iii. As a laboratory solvent
iv. As an anaesthetic.
v. In medicines such as cough syrups.

B. carbon tetra chloride:

Preparation: Carbon tetrachloride is manufactured by following process:

1. From Carbon Disulphide: By the action of chlorine on carbon disulphide. Aluminium chloride is used as catalyst

$$CS_2 + 3Cl2 \xrightarrow{AlCl_3} CCl_4 + S_2Cl_2$$

Carbon Tetra chloride

Carbon tetrachloride is removed from the mixture by fractional distillation.

2. From Chloroform:

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + HCl$$

3. From methane:

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

Physical properties:

1. Carbon tetrachloride is colourless liquid.
2. It is insoluble in water but soluble in ethanol and ether.

3. It is an excellent solvent for oils, waxes, fats and greases.

4. It is used as a fire- extinguisher under the name Pyrene because it is non-inflammable. When a spray of carbon tetrachloride is directed at fire, its dense vapours prevent the oxygen of air from reaching the burning articles.

Chemical Properties:

Carbon tetrachloride is inert to most organic reagents. It gives the following reaction-

1. Reaction with Steam: Carbon tetrachloride vapours react with steam at 500°C to give phosgene.

$$CCl_4 + H_2O(\text{Steam}) \longrightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

2. Reduction- Carbon tetrachloride can be reduced moist iron filling to give chloroform.

$$\underset{\text{Chloroform}}{CCl_4} + 3Cl_2 \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

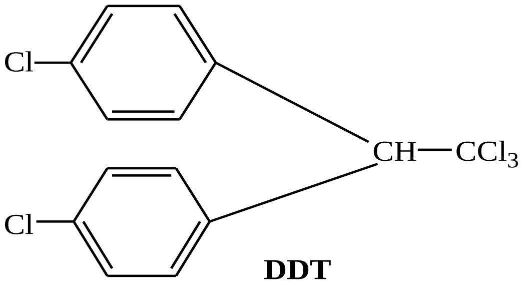
3. **Recation with HF:** Carbon tetrachloride reacts with hydrogen fluoride in the presence of antimony penta fluoride to form dichlorodifluoromethane.

$$CCl_4 + 2HF \xrightarrow{SbF_5} \underset{\text{Freon-12}}{CCl_2F_2} + 2HCl$$

Freon-12 is widely used as a refrigerant and propellant in aerosol sprays of all kinds.

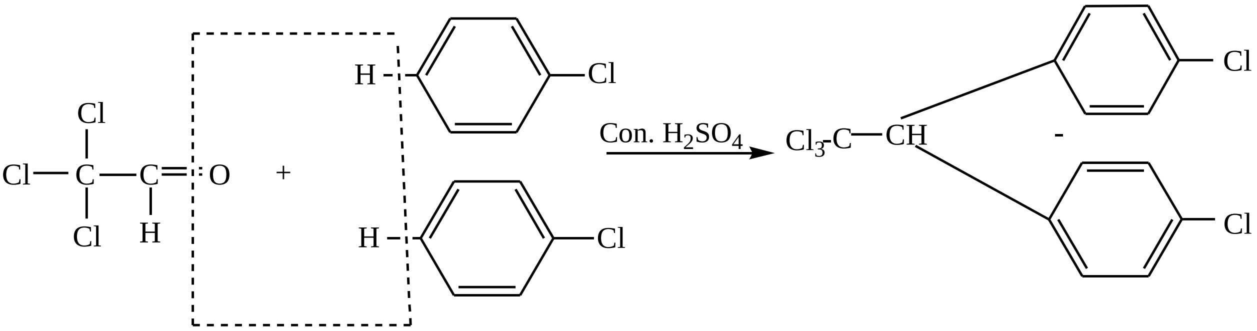
C. Dichlorodiphenyltrichloroethane (DDT):

It is available in several different forms: powder, aerosols, granules, etc.



DDT

Methods of preparation: Chloro benzene on react with CCl_3CHO (Chloral) in the presence of Con. H_2SO_4 form DDT by removing H_2O.



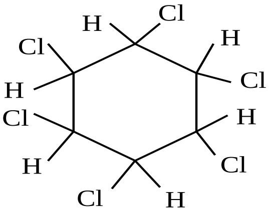
DDT

Uses:

It is used mainly to control mosquito-borne malaria. It is also used as an agricultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

D. Benzene Hexa Chloride (BHC):

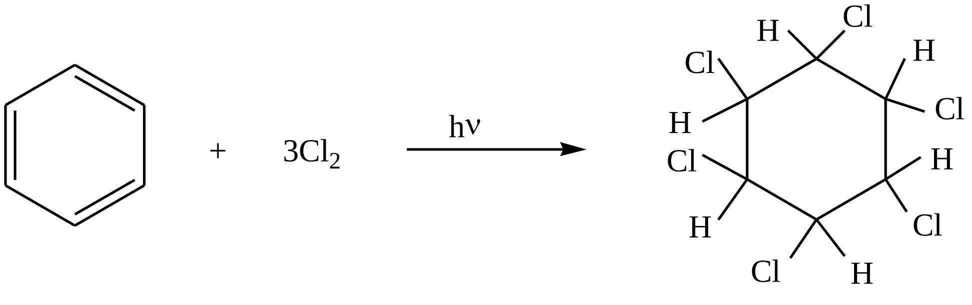
It is sold under the name gammexane, lindane or 666 and has the formula $C_6H_6Cl_6$.



BHC

Methods of the preparation:

In the presence of sun light benzene on react with Cl_2 gives an additional compound B.H.C., it is also known as 666 or Gamexene or lindane.



BHC

Uses: It is used as a pesticide in agriculture.

6.10 SUMMARY

Alkyl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures.

Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of –OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction. These are slightly soluble in water but completely soluble in organic Solvents.

In addition to undergoing nucleophilic substitution reactions, alkyl halides undergo β-elimination reaction. The halogen is removed from one carbon and a proton is removed from an adjacent carbon. A double bond is formed between the two carbons from which the atoms are eliminated. Therefore, the product of an elimination reaction is an alkene. Removal of a proton and a halide ion is called dehydrohalogenation.

A number of polyhalogen compounds e.g., dichloromethane, chloroform, iodoform, carbon tetrachloride, Freon and DDT have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving environmental hazards.

6.11 TERMINAL QUESTION

1. Draw structural formulae of the following compounds:
(i) 2-Bromo-3-methylbutane
(ii) 3-Chloro-4-methylhexane
(iii) 3-Bromochlorobenzene
(iv) 2,4-Dibromotoluene
2. Although haloalkanes are polar in nature, they are isoluble in water. Explain.
3. Why is chloroform stored in dark coloured bottles?
4. Name two commonly used polyhalogen compounds.
5. What products will obtained when ethylbromide reacts with
(i) aq. KOH and (ii) alc. KOH
6. What is the major product of elimination reactions of 2- bromobutane?
7. What is a Grignard reagent? How is it prepared?
8. What are nucleophilic substitution reactions? Explain the mechanism of S_{N1} and S_{N2} reactions in aliphatic compounds.
9. Write down the E1 and E2 mechanism of dehydrohalogenation in detail.
10. Write down the detail mechanism of reaction of halogen acid on alcohols.
11. Arrange each set of compounds in order of increasing boiling points.
(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.
12. What happens when?
(i) n-butyl chloride is treated with alcoholic KOH,
(ii) Bromobenzene is treated with Mg in the presence of dry ether,
(iii) Chlorobenzene is subjected to hydrolysis,
(iv) Ethyl chloride is treated with aqueous KOH,

Objective Type Question:

(1)Freon–12, CCl_2F_2 is used as a:

(a) Local anesthetic (b) Dry-cleaning agent

(c) Refrigerant (d) Disinfectant

(2)Which of the following reagents can be used to prepare an alkyl chloride from an alcohol?

(a) PCl_5 (b) $SOCl_2$

(c) NaCl (d) $HCl + ZnCl_2$

(3) Alkyl halides undergo-

(a) Electrophilic substitution reactions

(b) Electrophilic addition reactions

(c) Nucleophilic addition reactions

(d) Nucleophilic substitution reactions

(4)1-Bromobutane reacts with alcoholic KOH to-

(a) 1-Butene (b) 2-Butene

(c) 1-Butanol (d) 2-Butanol

(5)Which compound reacts most rapidly by an S_N^1 mechanism?

(a) Methyl chloride (b) Isopropyl chloride

(c) Ethyl chloride (d) 3°- butyl chloride

UNIT 7: ARYL HALIDES

CONTENTS:

7.1 INTRODUCTION

Alkyl halides have vast importance as it can be used for the preparation of a variety of organic functional groups. In this unit we shall discuss the halogen derivatives of benzene- Aryl halide, which are normally less reactive than alkyl halide, have their own pattern of reactivity, and these reactions are noval, useful and productive. The aryl halides produced on the largest scale are chlorobenzene and isomers of dichlorobenzene. Several aromatic chloro compounds are used extensively as insecticides, herbicides, fungicides and bactericide.

7.2 OBJECTIVES

After studying this chapter you will able to understand-

1) Name Aryl halide according to the IUPAC system of nomenclature from their given structure.
2) Describe the reactions involved in the preparation of Aryl halides.
3) Identify reactions involving aryl halides.
4) Synthesis of DDT and BHC.
5) Relative relativities of alkyl halide VS vinyl and aryl halide.

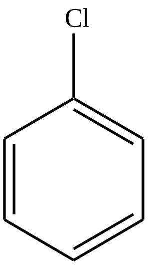
7.3 NOMENCLATURE AND CLASSIFICATION OF ARYL HALIDES

(1) Classification of Aryl halides

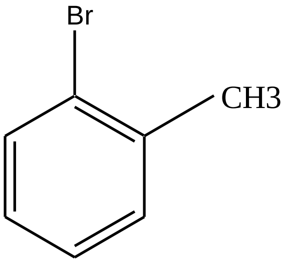
Aryl halides are those compounds which contain at least one benzene ring and one halogen atom in the molecule. They are as follows:

(i) Nuclear halogen compounds

These compounds have directly attached halogen atoms to the benzene ring. For example,



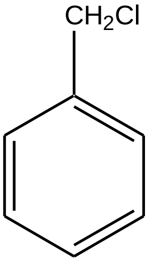
Chlorobenzene



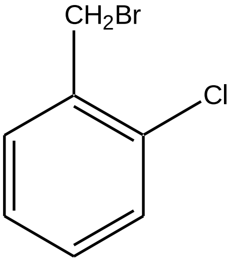
o-bromotoluene

(i) Side- Chain halogen Compound

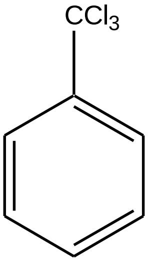
These compounds have side chain attached with halogen There may be more than one halogen in the side chain.



Benzyl chloride



o-Chloro benzyl bromide

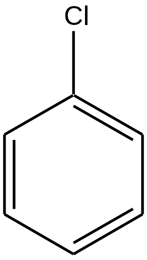


Benzotrichloride

(2) Nomenclature of aryl halide

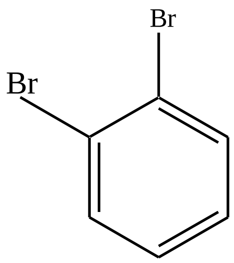
Aryl halides are also termed as haloarenes in IUPAC as well as common system. There are some rules for nomenclature of aryl halide.

(1) If there is only one halogen group bonded directly to benzene ring, it is numbered as one position and written as prefix followed with benzene as main ring. For example Chlorobenzene or aryl chloride. All six position of benzene are equivalent. Hence monohalogen compounds could be represented by attaching the halogen to any of the six positions.

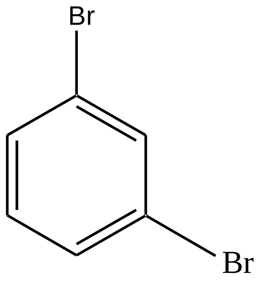


Chlorobenzene

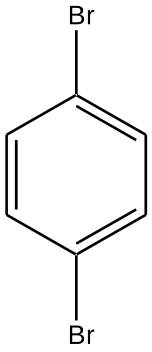
(2) For dihalogen derivatives containing same type of halogen, the prefix o-(ortho) m-(meta) and p-(para) are used in common system. If the two group are located in neighboring position the two groups are ortho to each other. If there is a gap of one position, the groups are meta to each other and if the gap is of two position the groups are para to each other. However in IUPAC nomenclature of dihalogen derivatives, numerical prefixs 1,2 , 1,3 , 1,4 are used to assigned the position of halogen.



o-(ortho)
(1,2dibromo benzene)

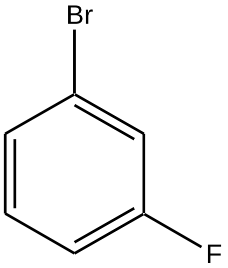


m-(meta)
(1,3dibromobenzene)



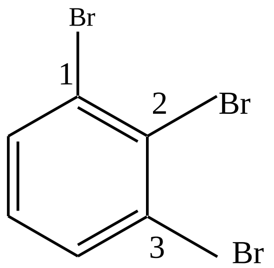
p-(para)
(1,4dibromobenzene)

(3) In the presence of two different halogen group attached to benzene ring, halogen numbered alphabetically and written in the same way. For eg. If there are two halogen groups like bromo and fluoro bonded to benzene ring bromo group will be writren first followed by fluoro group.

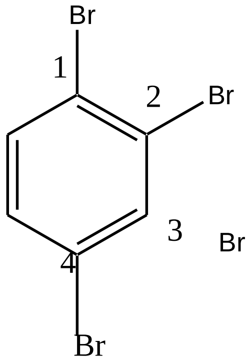


1-Bromo3- fluoro benzene

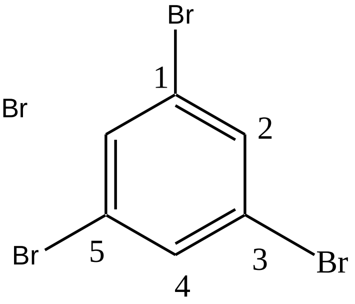
(4) For naming trihalogen compounds, we use the number system. Number 1 is given to the position of the groups and then the other groups are numbered accordingly. Clockwise direction is followed for this purpose.



1,2,3 Tribromobenzene

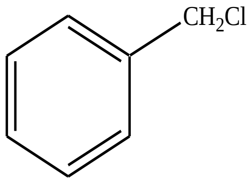


1,2,4 Tribromobenzene

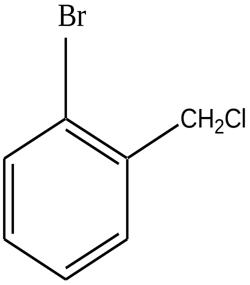


1,3,5tribromobenzene

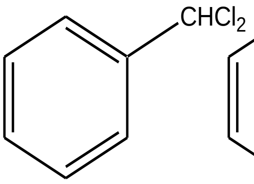
(5) Side chain halogen compounds are named as follows :



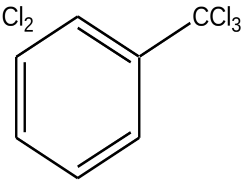
Benzyl Chloride



o-Bromo benzyl chloride



Benzal Chloride



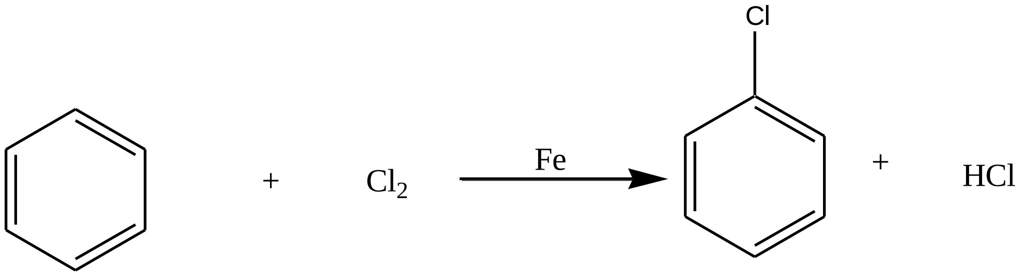
Benzo Trichloride

7.4 METHODS OF FORMATION OF ARYL HALIDES

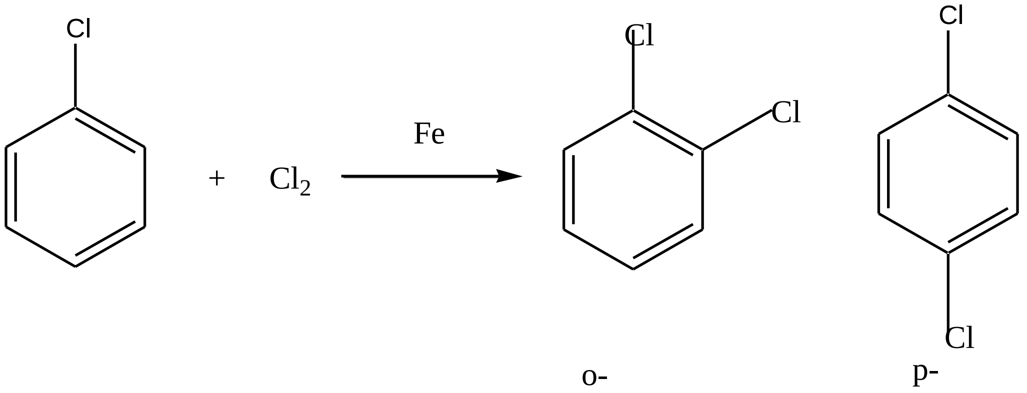
Aryl halides are prepared by following methods:

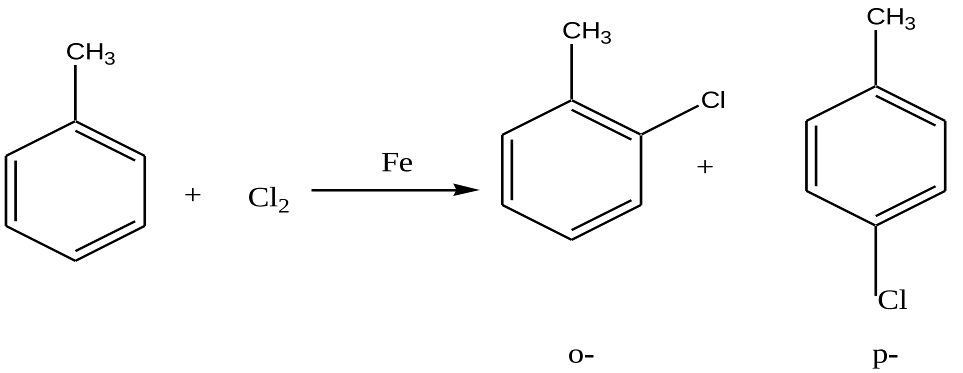
(1) Direct halogenations of benzene - Chlorination and bromination is very conveniently carried out at ordinary temperature in the absence of light and in the presence of metallic iron or lewis acids such as chlorides or bromides of Fe, Al, Sb. Fluorination and Iodination of benzene, are rarely performed because fluorine is too reactive to control the reaction and iodine is too unreactive for a favorable equilibrium constant.

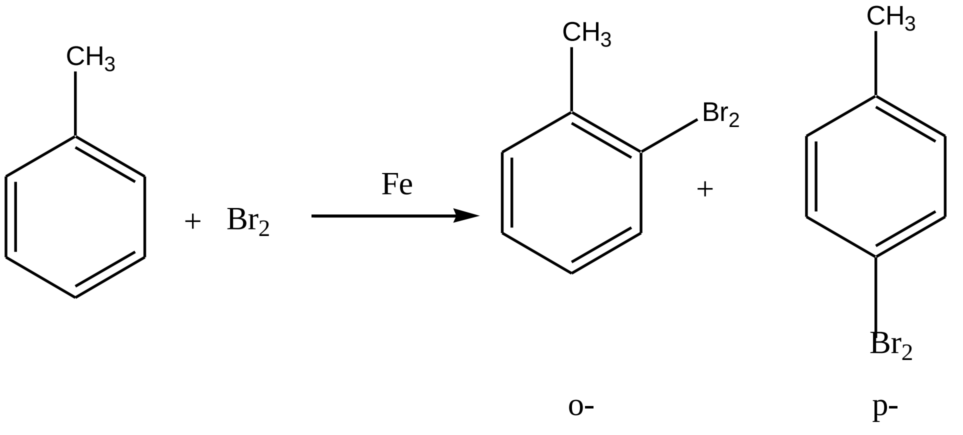
This reaction stops at the monosubstituted stage due to the deactivating influence of the halogen atom on the aromatic ring.



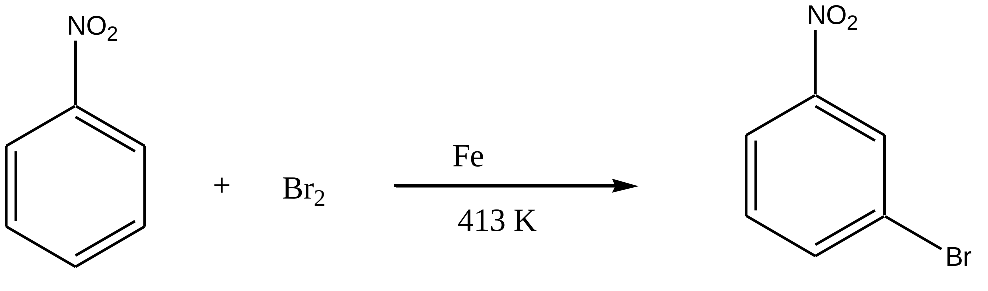
However, if chlorine is used in excess, further substitution takes place and a mixture of o- and p-dichlorobenzene is obtained.







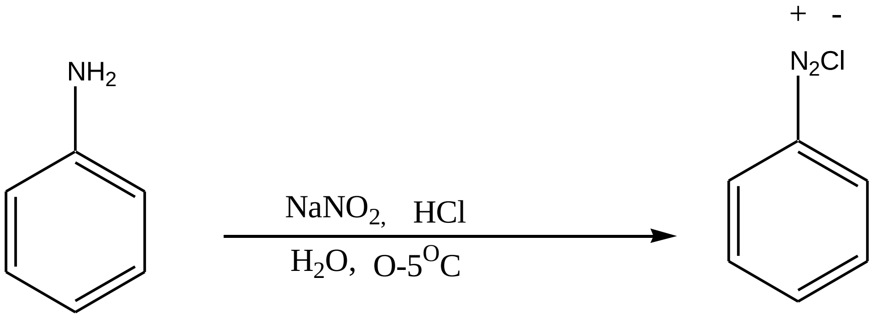
When aromatic compounds contain strongly deactivating group such as –NO2, -COOH etc., high temperature is required and the halogen enters then meta position.

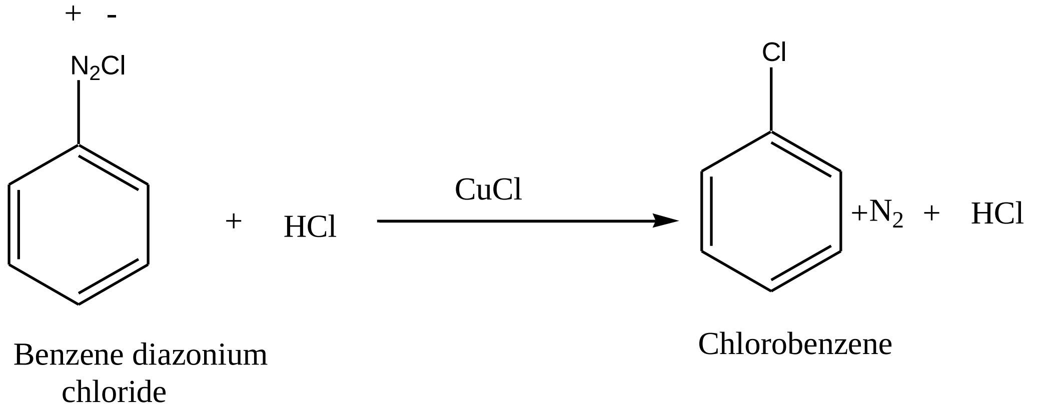


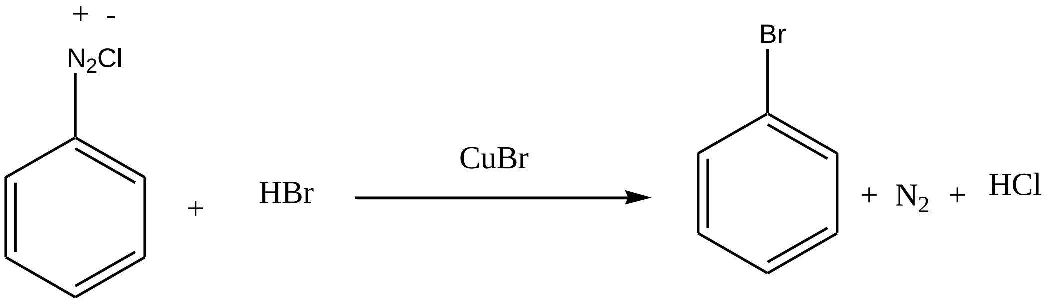
Nitrobenzene m- Bromo nitrobenzene

(2) **Decomposition of aryl Diazonium salts (Sandmeyer's reaction) -** This is an important method for the preparation of aryl halides, especially those which cannot be prepared by the direct halogenations.

Aryl amines when treated with acidified sodium nitrite at low temperature (0-5oC), result in the formation of Aryldiazonium salts.

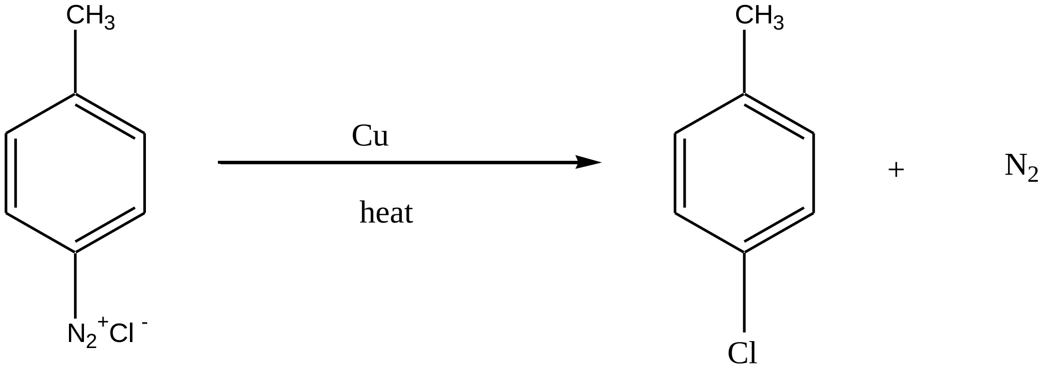






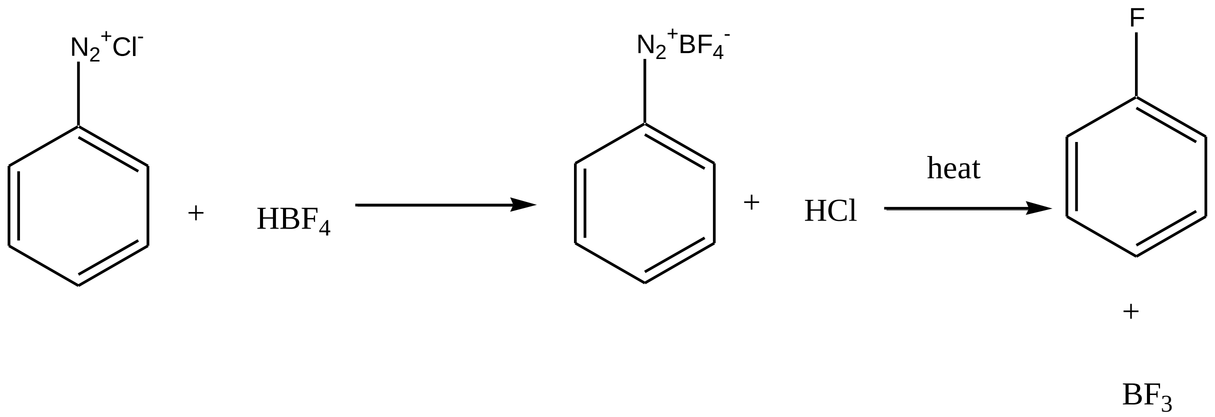
Gattermann Reaction:

Gattermann reaction is the modified form of above mentioned reactions. This reaction requires the diazonium salt to be warmed in presence of copper powder when it decomposes to give the halobenzene.



Schiemann reaction:

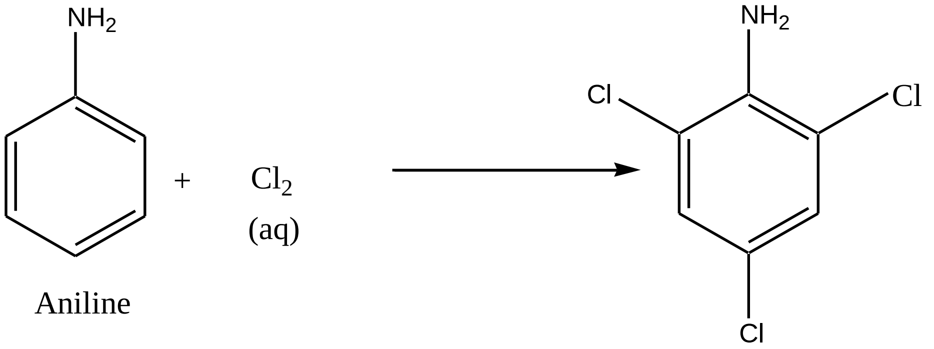
This is a good method for introducing fluorine atom in the ring. Addition of fluoroborate, to aryldiazonium salt solution gives the insoluble diazonium fluoroborate, which on gental heating gives the aryl fluoride.



Aryl iodides are obtained by warming the diazonium salt solution with potassium iodide solution

$$ArN_2{}^+Cl^- + aq\ KI \xrightarrow{Heat} ArI + HCl + N_2$$

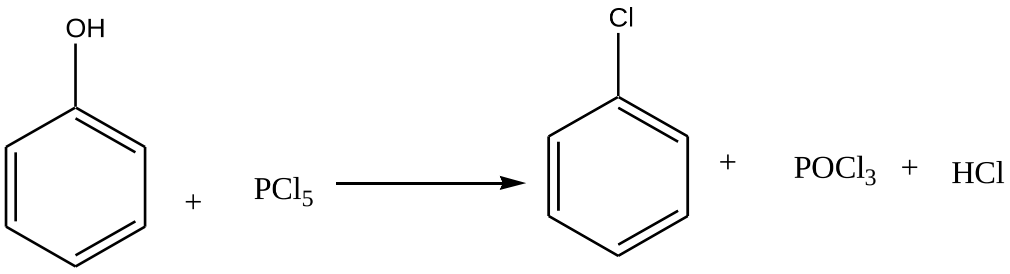
When aromatic compounds contain highly activating group such as –OH, -NH$_2$ etc. They undergo halogenation in the absence of halogen carrier and halogen enters the *ortho* and *para* position.



Aniline

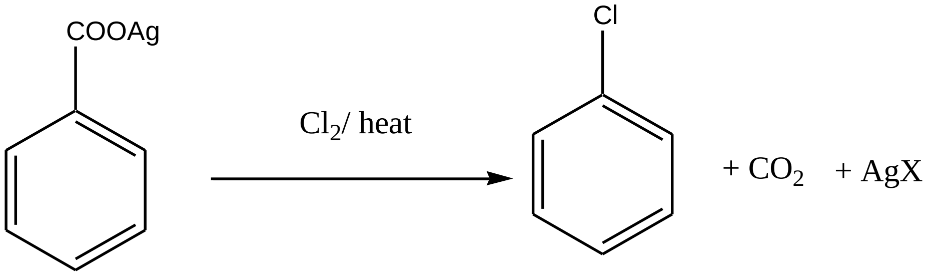
2,4,6-trichloroaniline

(3) **From phenols** – Reaction of phenol with PCl$_5$ yields aryl chloride.



Phenol

(4) From silver salt of benzoic acid (Hunsdiecker reaction) :

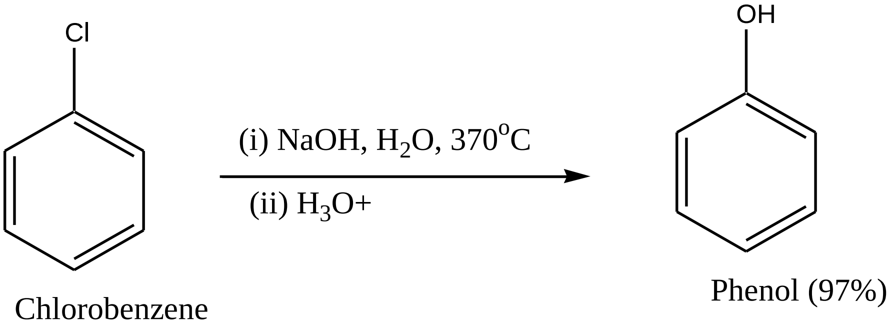


7.5 REACTIONS OF ARYL HALIDES

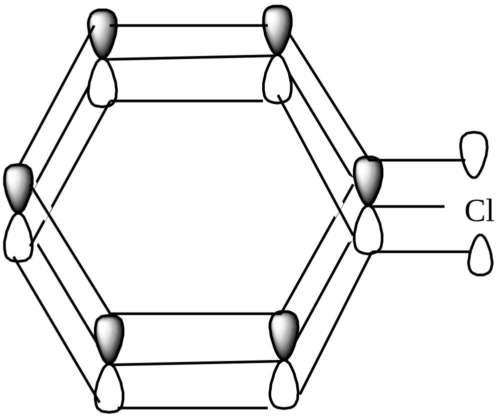
The reactions of aryl halide are due to the halogen atom (nucleophilic substitution reactions) and the aromatic ring (Electrophilic substitution reaction).

Nucleophilic substitution reactions

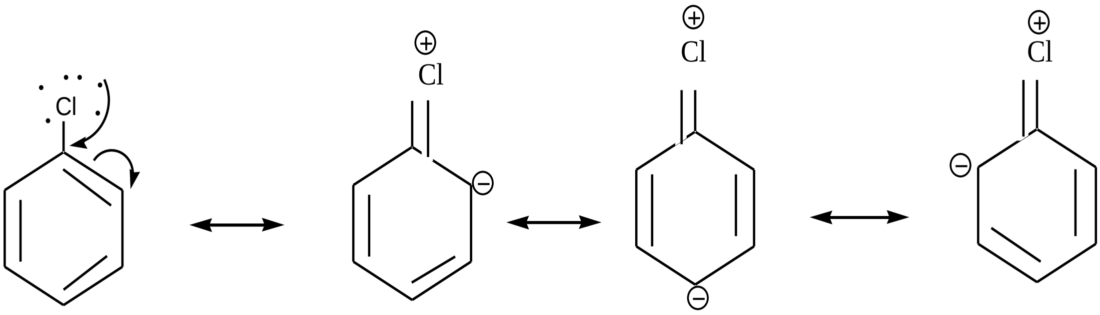
Aryl halides are relatively unreactive towards nucleophilic substitution reactions. For example Chlorobenzene is essentially inert to aqueous sodium hydroxide at room temperature. To proceed reaction at reasonable rate temperature over 300°C are required.



Aryl halides are less reactive than alkyl halide in nucleophilic substitution reaction. This lack of reactivity is due to several factors. In aryl halide the carbon chlorine bond is σ bond. However, one of the *p*-orbital of chlorine having a pair of electrons is parallel to the delocalized *p*-orbitals of the benzene nucleus. This p-orbital of chlorine can also overlap with the delocalized p-orbitals of benzene nucleus. Thus the bond between carbon and chlorine becomes strong.

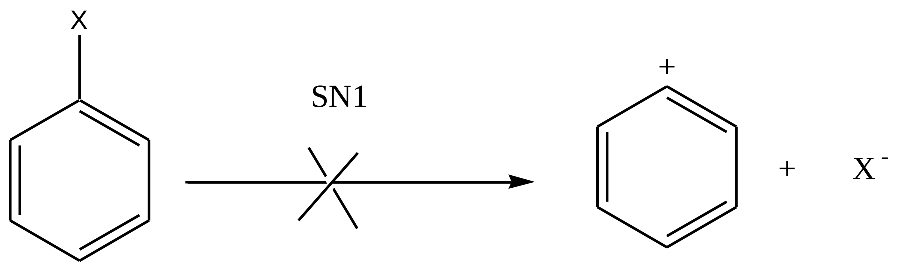


The delocalized π MO gives partial double bond character to C-Cl bond in aryl halides.



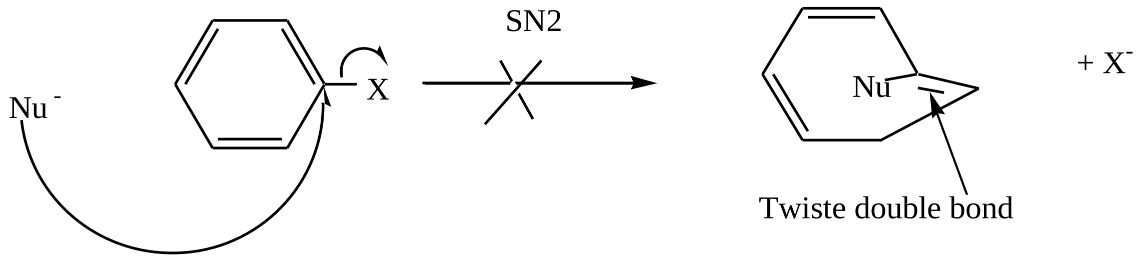
Another reason for the low reactivity of aryl halide towards nucleophilic substitution reaction is the π electron cloud in aromatic ring with which does not allow the nucleophile to attack easily on benzene ring.

Aryl halides cannot proceed through SN1-type processes because carbon- halogen bonds of aryl halides are too strong, and aryl cations formed during the reaction are highly unstable due to high in energy.



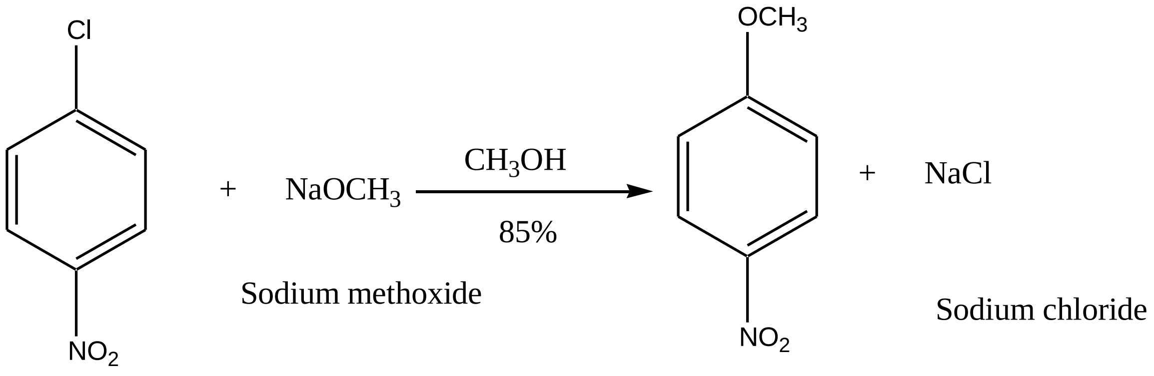
Unstable aryl cation

Aryl halides also cannot be proceeding through SN2-type process, because the aromatic ring blocks the approach of the nucleophile to carbon at the side opposite the bond to the leaving group. Inversion of configuration is impossible.



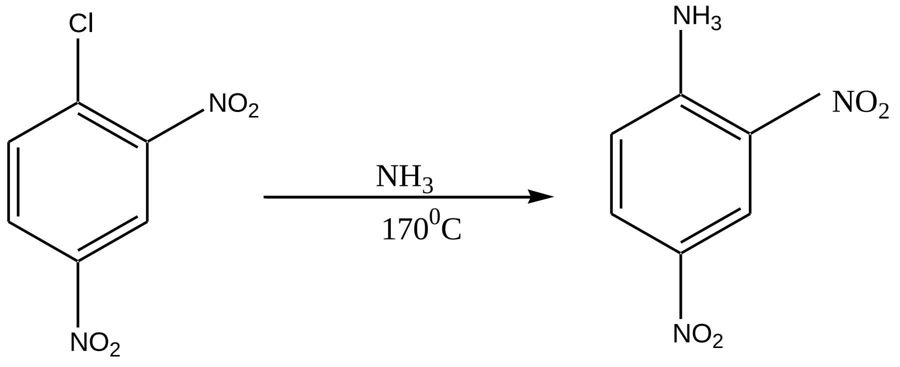
(1) Nucleophilic substitution in nitro substituted aryl halides (SNAr)

Aryl halides consists of strong electron withdrawing group such as a nitro group *ortho* or *para* to the halogen undergo nucleophilic substitution readily

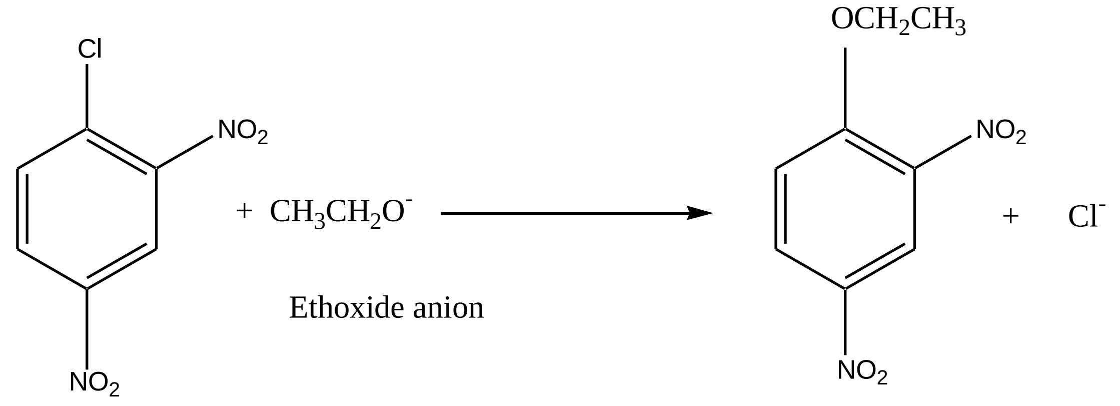


p-Chloronitrobenzene

p-Nitroanisole
92%

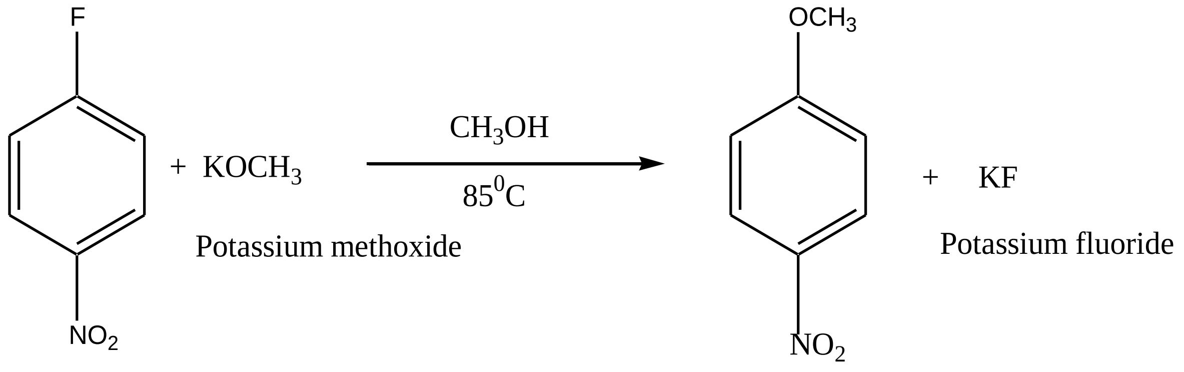


1-Chloro-2,4- dinitrobenzene 2,4- Dinitroaniline(65-75%)



1-Chloro-2,4-dinitrobenzene 1-Ethoxy-2,4-dinitrobenzene

Aryl fluorides undergo nucleophilic substitution reaction when ring bears an *o*- or a *p*-nitro group.



p-Fluronitrobenzene

p-nitroanisole (92%)

These reactions follow a second order rate law:

Rate = *k*[Aryl halide][Nucleophile]

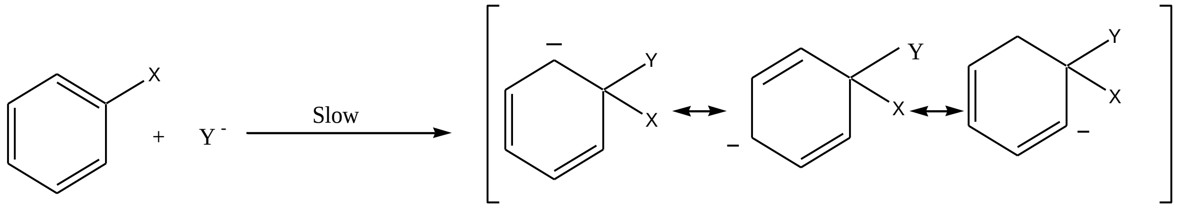
Mechanism of second order nucleophilic aromatic substitution reaction (SNAr) can be of following two types.

1) Addition/elimination mechanism
2) Elimination /addition mechanism

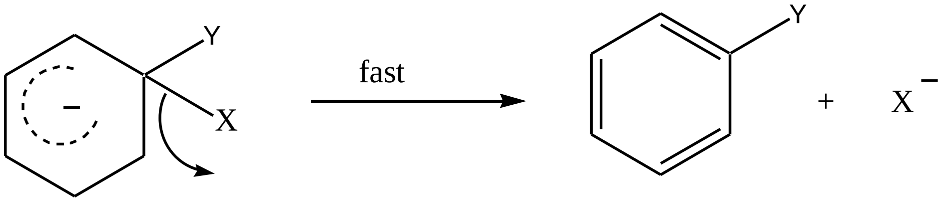
Addition /elimination mechanism

General schematic representation for addition elimination reaction: It is two step reaction.

Step I: In this step incoming nucleophile attacks at the same position where the leaving group is attached. Such attack is known as ipso attack.

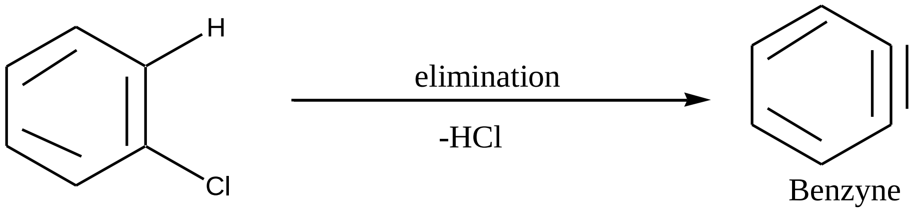


Step II: In second step the leaving group detached leading to regeneration of aromaticity in benzene ring.



Elimination/ Addition mechanism

Elimination/Addition mechanism is proceeding via benzyne mechanism. The benzyne intermediate has triple bond in benzene ring during the transition stage. Benzyne intermediate is highly reactive and they rapidly undergo nucleophilic substitution reaction. Aryl halides undergo substitution by the benzyne mechanism only in the presence of very strong bases such as alkali metal amide and organolithium reagents or somewhat weaker bases under vigorous conditions.

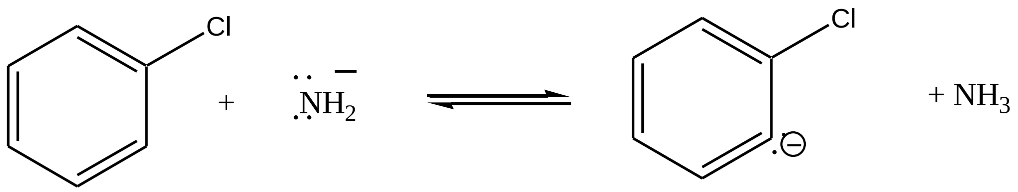


Benzyne mechanism involves two steps:

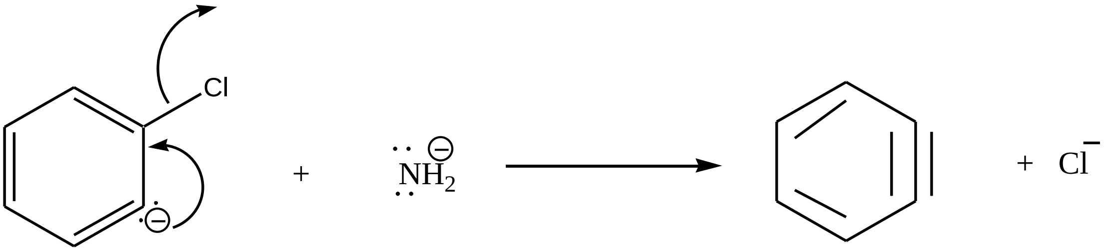
Elimination

In first step elimination of H and X (Halide) occurs to give benzyne. Elimination itself comprises of two steps.

Abstraction of a hydrogen ion by the strong base

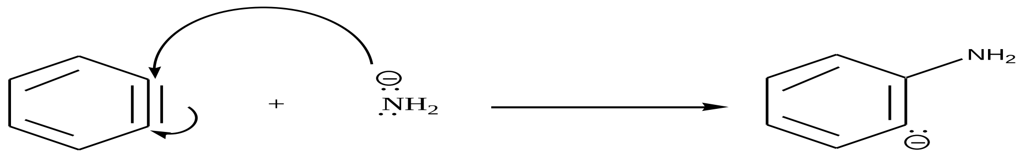


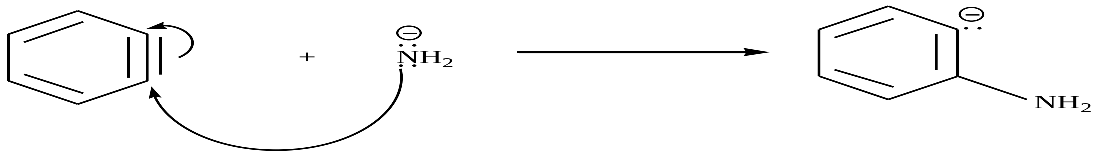
Loss of halide ion to form benzyne



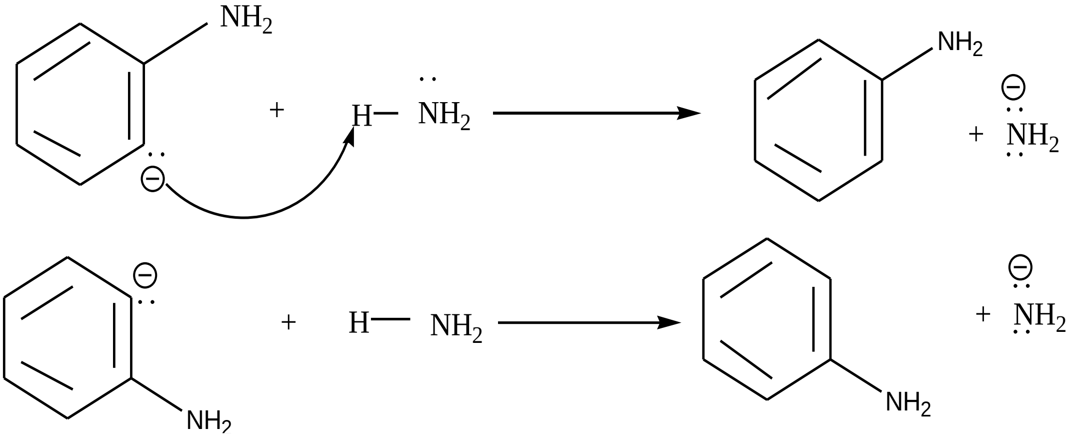
Addition

In second step addition of nucleophile and H occurs to give overall substitution product.



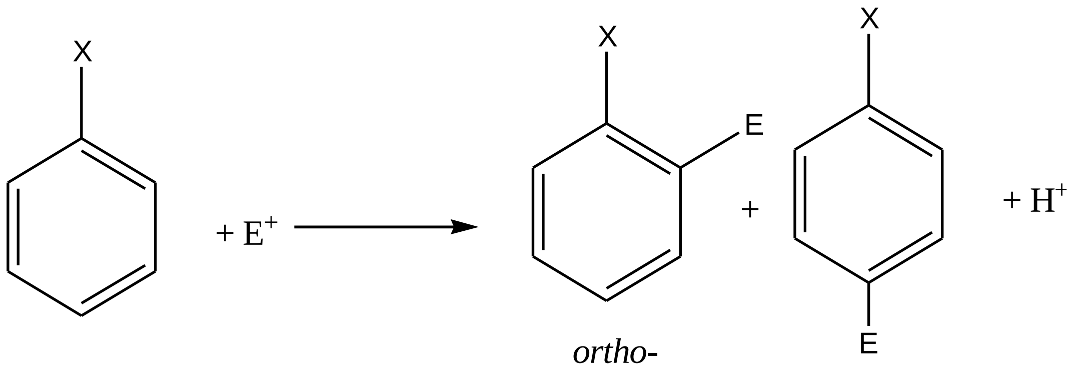


Protonation of anion by reaction with acid, ammonia etc.



(2) Electrophilic substitution reaction of Aryl halides

Aryl halides are reactive towards the electrophilic aromatic substitution but they are less reactive than benzene because halides are weak deactivators. The weak deactivation is due to the electronegativity of the halogen making the intermediate cations less stable than those produced when benzene undergoes substitution. Halides are *o*- or *p*- directing groups.



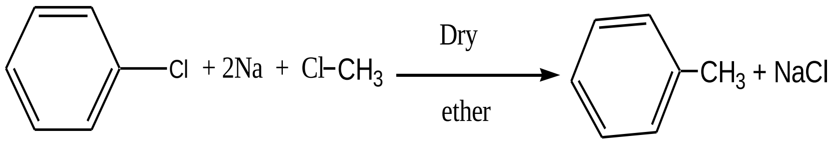
ortho-

para-

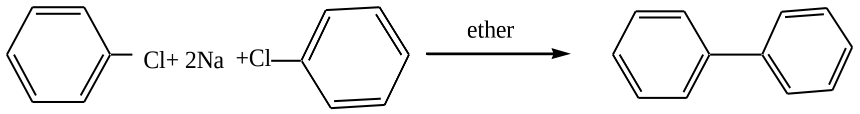
Electrophilic aromatic substitution reactions of chlorobenzene is given below.

Other reactions

Wurtz- Fittig reaction- When aryl halide is treated with ethereal solution of alkyl halide, in the presence of sodium, we obtain an alkyl benzene.

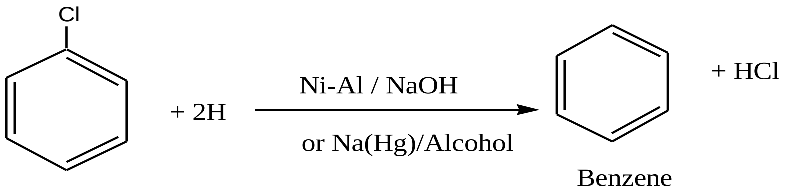


When only aryl halide is treated with sodium diaryl are produced, this reaction is called fittig reaction.



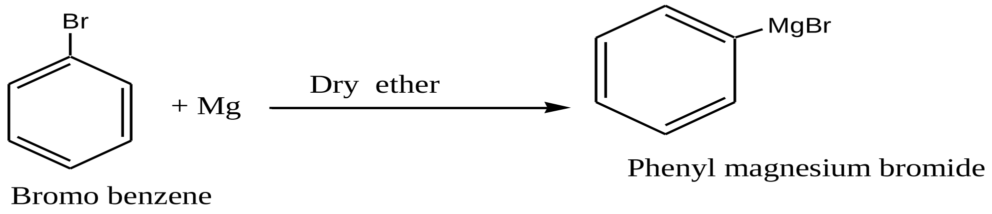
di phenyl

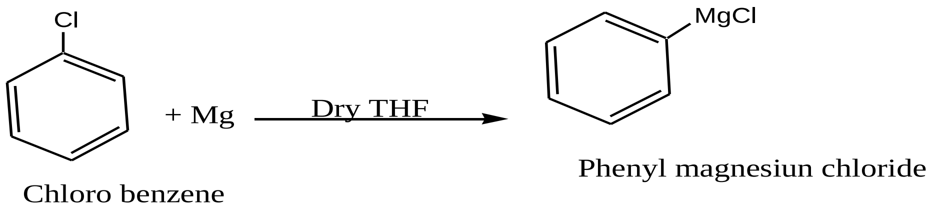
Reduction – Aryl halide are reduced by Nickel- Aluminium alloy in alkali or sodium amulgum and aqueous alcohol in the presence of alkali.



Benzene

Formation of Grignard reagent: When Aryl halides and Iodides are treated with magnesium turnings in dry ether they form Grignard reagent. Aryl chloride form Grignar reagent only when the reaction is carried out in dry tetra hydro furan (THF) as solvent.



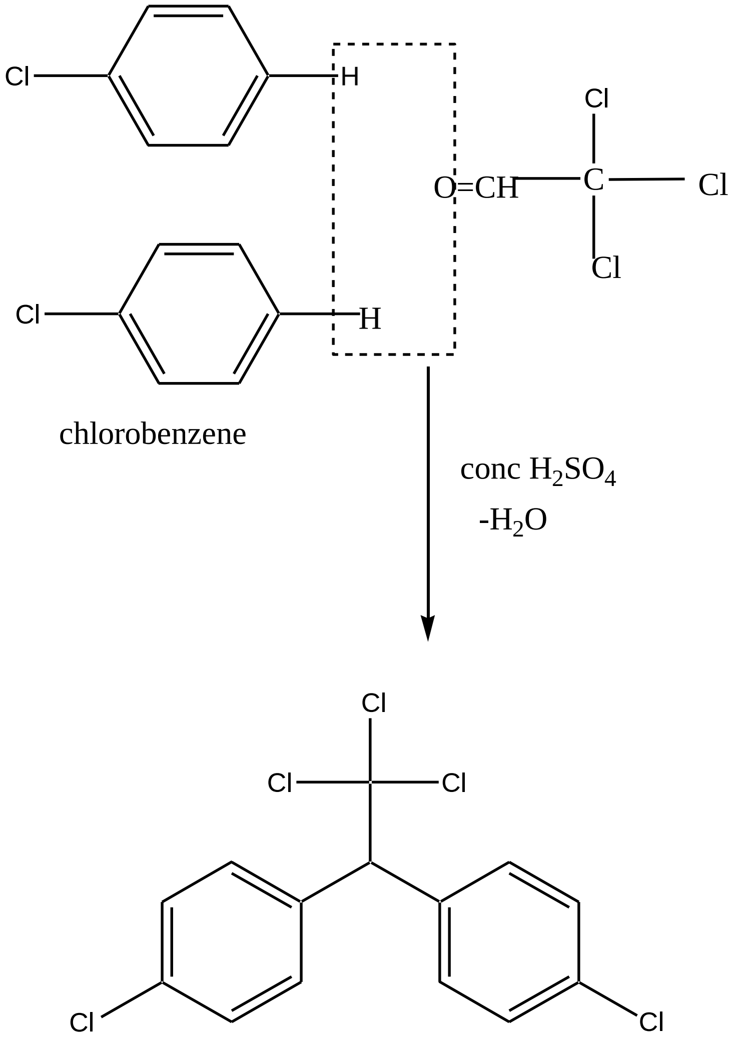


7.6 RELATIVE REACTIVITY OF ALKYL HALIDES vs ALLYL, VINYL AND ARYL HALIDES

Aryl halide for example chlorobenzene has carbon atom in ring which has p-orbital available for overlapping with p-orbital of chlorine atom and thus the p- orbital carbon atom overlap with the p-orbital of attached Cl- atom. Hence the Cl-atom is firmly attached with the C-atom of benzene ring. Moreover the bond between the C-atom in the benzene ring has partial double bond character due to delocalization of electrons in the benzene ring. All these factors make it difficult for aryl halide to undergo SN1 or SN2 reactions and thus they are least reactive in nature. In case of vinyl halide also the side wise overlapping of the p-orbitals of carbon atom occurs with Cl- atom. Thus there is sidewise overlapping in the vinyl halide which makes it difficult to undergo SN1 or SN2 reactions and they are also less reactive.. However in case of alkyl halide carbon atom attached to halide atom does not have any unhybridised p-orbital to overlap with the p-orbital of the Cl-atom and Hence it is easy for them to undergo SN1 and SN2 substitution reactions. The allyl cation has delocalization which decreases the energy of the system. This makes it easier to remove a halide.

7.7 SYNTHESIS AND USES OF DDT AND BHC

(i) Synthesis of 1, 1-Bis (4-Chlorophenyl)-2, 2, 2-Trichloroethane, (DDT)



1,1-Bis (4-Chlorophenyl)-2,2,2-Trichloroethane

DDT is used as insecticide. DDT was initially used by the military in World War II to control malaria, typhus, body lice, and bubonic plague. DDT is still used today in South America, Africa, and Asia for this purpose. Farmers used DDT on a variety of food crops in the United States and worldwide. DDT was also used in buildings for pest control. DDT was so widely used was because it is effective, relatively inexpensive to manufacture, and lasts a long time in the environment. DDT is slightly to moderately acutely toxic to mammals, including people, if eaten. DDT is poorly absorbed through mammalian skin, but it is easily absorbed through an insect's outer covering known as an exoskeleton.People exposed to DDT while working with the chemical or by accidental exposure report a prickling sensation of the mouth, nausea, dizziness, confusion, headache, lethargy, in coordination, vomiting, fatigue, and tremors .

(ii) Benzene hexa chloride:

For benzene hexa chloride eight isomers are possible but only seven are known. One of these isomers is an insecticide called lindane, or Gammexane (γ- isomer). Gama Benzene Hexachloride is used for the treatment, control, prevention, & improvement of the contagious and itchy human head infection mites skin disease and lice skin disease. There are various side effect of BHC as insomnia, paresthesia, giddiness, dizziness, headache, nausea, vomiting, restlessness, skin irritation, contact dermatitis if used in excess quantity.

7.8 SUMMARY

Aryl halide, with electron withdrawing substituents at ortho and para position react by nucleophilic aromatic substitution reactions. These reactions proceed through a resonance-stabilized anionic intermediate resulting from a nucleophilic attack of the aromatic ring. With the loss of halide ion from intermediate substituent product is formed. Elimination addition mechanism via benzyne mechanism is followed when the nucleophile is an exceptionally strong base (*e.g.* amide ion, NH_2^-) and the absence of the strong electron withdrawing groups. Aryl halides can undergo many of the same electrophilic aromatic substitution reactions that benzene can including nitration, sulfonation, further halogenation and Friedel- Crafts alkylation or acylation reactions.

7.9 TERMINAL QUESTIONS

Short answer type questions

Q1. Write the structural formula for the following.

(a) *p*- chlorotoulene

(b) 2,4- Dibromoanisole

(c) 2-Fluoro-1-chloro-4-nitrobenzene

(d) *p*- chlorostyrene

Q2 Identify the major organic product of each of the following reactions.

(a) Bromobenzene + acetyl chloride $\xrightarrow{AlCl_3}$

(b) Idobenzene + Lithium $\xrightarrow{\text{diethyl ether}}$

Q3 what are aryl halides? Give example.

Q4 Explain why aryl halides have low reactivity during nucleophilic substitution reaction.

Q5 Why aryl halide is less reactive than alkyl halide. Explain.

Q6 Describe the benzyne mechanismof nucleophilic aromatic substitution.

Multiple choice Questions

1. Aryl halides are less reactive towards nucleophilic substitution as compared to alkyl halide due to

(a) Inductive effect (c) resonance stabilization
(b) Electromeric effect (d) stereoisomerism

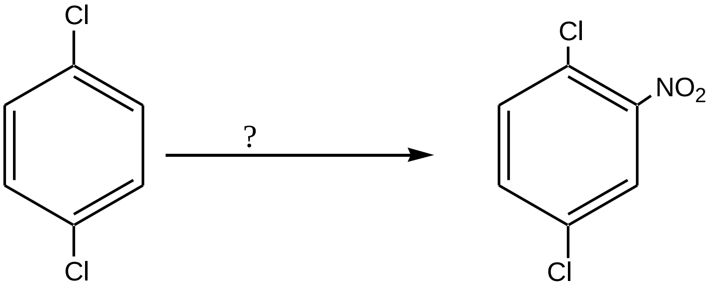
2. Which of the following reagents can be used to distinguish between chlorobenzene and allyl chloride

(a) $H2/Ni$ (c) Zn/HCl
(b) $Br2$ in CCl_4 (d) NH_2NH_2

3. Alkyl halides undergo

(a) Electrophilic substitution reaction (c) Nucleophilic substitution reaction
(b) Electrophilic addition reaction (d) Nucleophilic addition reaction

4. which reagent can be used to carry out the following conversion



(a) $HNO_3 + H_2SO_4$ (b) $NaNO_2$
(c) H_2SO_4 (d) NO_3

5. DDT is prepare by the reaction of chlorobenzene with

(a) Chloral+ H_2SO_4 (c) Chlorine + H_2SO_4
(b) Chloroform (d) Carbon tetrachloride

Answers

1 (c)
2 (b)
3 (c)
4 (a)

5 (a)

References:

1. Madan, R L (2013), Organic Chemistry, Tata Mc Graw Hill Education Private Limited, New Delhi.
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UNIT 8: CHEMICAL KINETICS

CONTENTS:

8.1 INTRODUCTION

The branch of physical chemistry which deals with the speed or rate at which a reaction occurs is called chemical kinetics. **Chemical Kinetics is the study of rate of a reaction under different conditions like different concentrations, pressures, temperatures, catalyst, pH, dielectric constant of the medium, free radical scavengers, neutral salts etc and suggesting a suitable mechanism for the reaction**.

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceding under given condition of temperature, pressure and concentration.

The study of chemical kinetics has been highly useful in determining the factors which influence rate of reaction as well as in understanding mechanism of a number of chemical reactions. The experimental data have led to the development of the modern theories of chemical reactivity of molecules.

8.2 OBJECTIVES

After study this unit you will be able to

- Know the about the chemical reactions and their classification.
- Explain the rates of reactions proceeding under given condition of temperature, pressure and concentration.
- Determine the factor which influences rates of reactions as well as in understanding mechanism of a number of chemical reactions.
- Know the rate law for zero and first order reaction and half life period of a reaction

8.3 CHEMICAL KINETICS AND ITS SCOPE

8.3.1 Scope of chemical kinetics

Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into products. When we carry out the experiment we find that the reaction proceeds so slowly that unless we are willing to wait indefinitely, practically no water results. On the other hand, experiment shows that N_2O_4 decomposes into NO_2 under atmospheric conditions almost instantaneously even though $-\Delta G^0$, which is a measure of spontaneity of a reaction, is far less for the decomposition of N_2O_4 than that for the reaction between hydrogen and oxygen to form water.

Above two examples suggest that there is essentially no correlation between thermodynamic instability and the rate of the chemical reaction. In fact, the rate of a reaction depends upon structural and energetic factors which are not uniquely specified by thermodynamic quantities such as the free energy change. Hence, chemical kinetics is a technique complementary to thermodynamics for studying a given reaction.

The first stage in studying the rate and the mechanism of a chemical reaction is the determination of overall stoichiometry of the reaction and to identify any side-reaction. The next step involves the determination of the change of the concentration of the reactant and product species with time. Since the reaction rate depends sharply on temperature, the temperature of the reacting mixture must be kept constant.

Several experimental techniques have been developed to monitor the concentration of the reactants and products and their variation with time. The selection of a typical method depends on the nature of the species involved and how rapidly their concentration change. For reactions that are relatively slow, conductometric, poteniometric, optical methods, polarimetry and spectrophotometry are used. The time taken for reactions to reach completion varies widely, from femtoseconds (1fs = 10^{-15} s) to days.

For reactions in which one or more products are gases, the reaction rate involves monitoring pressure as in the reaction :

$$N_2O_5\ (g) \longrightarrow 2NO_2\ (g) + O_2(g).$$

For optical method involves monitoring optical activitiy.

Reactions in solution involving ionic species may be studied by monitoring their conductivity. The change in EMF of an electrochemical reaction can be followed potentiometrically. Spectrophotometry, the measurement of intensity of absorbtion in a particular spectral region is widely used to monitor concentration. Reactions that involve a change in concentration of H^+ ions may be studied by monitoring pH of the solution with a glass electrode. Other methods of monitoring the composition include the detection of fluorescence and phosphorescence, mass spectrometry, gas chromatography and magnetic resonance.

In a real time analysis the composition of reaction mixture is analysed while the reaction is in progress by direct spectroscopic observation. In the quenching method, the reaction is stopped after being allowed to proceed for a certain time and the composition is analysed. The entire reaction mixture may be quenched either by sudden cooling or by adding to it a large volume of solvent. This method is applicable for reactions that are slow enough for there to be little reaction during the time it takes to quench the reaction mixture.

Femtochemistry has emersed as the most exciting field for investigating extremely fast reactions whose time-scale is of the order of femtoseconds. This method is due to A.H. Zewail, who was awarded Nobel Prize of chemistry in 1999.

Femtochemistry is extremely useful for studying biological processes such as the energy converting processes of photosynthesis and photostimulated processes of vision in which the primary energy and electron-transfer reactions occur on the femtosecond or picosecond time-scale.

8.3.2 Rate of a reaction

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction-

$$A \longrightarrow B$$

The concentration of A decreases and that that of B increases with time. The rate of a reaction is defined as the change in concentration of any

of reactant or product with time. As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression-

$r= -dC_A/dt = kC_A$ ……………………….(1)

where $-dC_A$ is very small decrease in concentration of A in a very small time interval dt, C_A gives the concentration of the reactant A at a given instant and k is constant called the rate constant or velocity of the reaction.

Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well. Thus

$r= dC_B/dt = kC_A$ ………………………….(2)

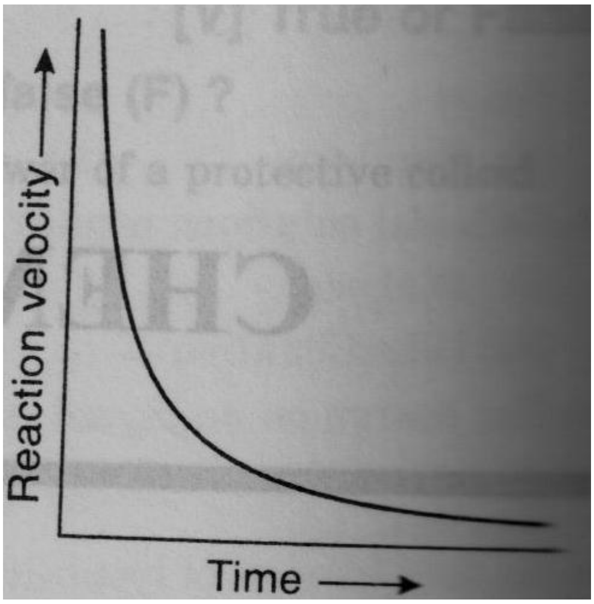
where dC_B is very small increase in the concentration of product B in a very small time interval of time dt.

Now it should be clear to you from (1) and (2)

$r= - dC_A/dt =dC_B/dt= kC_A$

and for a reaction $A+B \longrightarrow M+N$

the rate can be expressed



$r = -dC_A/dt = -dC_B/dt = dC_M/dt = dC_N/dt = kC_AC_B$ ………………(3)

Fig-8.1

As the reaction proceeds the reactants are consumed where by their molecular concentration decreases. Hence the rate of a chemical reaction will also decrease with time. The graph between reaction velocity and time will be as shown in the fig. (8.1). Now it should be clear to you that reaction velocity is maximum to start with and then falls gradually with time. The reaction velocity become so slow in the latter states that it takes a

very long time for the reaction to be completed. It can be safely assumed that in the latter stages the reaction is nearly complete.

Now let us consider a reaction-

$aA + bB \longrightarrow cC + dD$

In this reaction a moles of A reacts with b moles of B to form c moles of C and d moles of D. the rates of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole. Thus we can write as follows:

$r = -1/a\ dC_A/dt = -1/b\ dC_B/dt = 1/c\ dC_C/dt = 1/dC_D/dt = k\ C^a{}_A C^b{}_B$

8.3.3 Units of rate

Reaction rate has the units of concentration divided by time. We express concentration in moles per litre (mole/litre) but time may be given in any convenient unit second(s), minutes (min), hours (h) days (d) or possibly years. Therefore, the units of reaction rates may be

mole/litre/sec or mole $l^{-1}s^{-1}$

mole/litre/ minute mol $l^{-1}m^{-1}$ and so on

8.3.4 Factors affecting reaction velocity

There are a number of factors which affect the rate of a reaction, the most important of them are:

(a) Effect of concentration: The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules. On increasing the concentration of the reactant, the number of collisions will increase and the rate of reaction will increase and on decreasing the concentration the rate will decrease.

(b) Effect of nature of reactants: Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred takes a comparatively longer time than the reaction between ionic molecules.

You can cite the examples of neutralisation reactions or double displacement reactions which are very fast while the oxidation reduction reactions are slower.

(c) Effect of catalyst: A catalyst can increase or decrease the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is slow at ordinary temperature, while it proceeds rapidly in presence of platinum.

(d) Effect of surface area of reactant: Surface area of reactants is of importance only for heterogeneous reactions. As particle size decreases, surface area for the same mass increases.

The smaller particle thus reacts more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than large lump of coal.

(e) Effect of temperature: With the exception of few reactions, the rate of reaction is increased considerably with an increase of temperature. Generally the rate of a reaction is almost doubled or tribled by an increase of 10^0C in temperature.

$$\frac{\text{Rate of reaction at } 35^0\text{C}}{\text{Rate of reaction at } 25^0\text{C}} = \frac{K_{35}}{K_{25}} = 2 \text{ to } 3$$

8.3.5 Order of reaction and molecularity

The total number of reactant particles involved in the overall reaction, is called as molecularity of a reaction

Thus in the reaction -

$N_2O_5\ (g) \longrightarrow 2NO_2\ (g)+1/2O_2(g)$ it is unimolecular

$2HI\ (g) \longrightarrow H_2(g) + I_2(g)$ it is bimolecular

and $2NO\ (g) + O_2(g) \longrightarrow 2NO_2$ it is trimolecular

Order of reaction depends only on the reactants upon which the rate of reaction depends. It means that order is in those reactants only, by changing whose concentration, the rate of reaction changes.

If reaction rate is independent of reactant concentration, the order is zero in that reactant.

We can say that “Order is the sum of powers of concentration of reactants as given in a rate law or rate equation or rate expression for the reaction under consideration”.

A reaction is said to be first order if its rate r (or dx/dt) is given by the following rate expression -

$R = dx/dt = kC_a$

The reaction is of second order and third order if its rate expressions are given by Eqn. (i) and (ii) respectively

$dx/dt = kCa^2$ or kC_aC_b ………………(i)

$dx/dt = kCa^3$ or $kC_a{}^2C_b$ or $kC_aC_b{}^2$ ……………….(ii)

The subscripts a, b and c stand for various reactants A, B and C respectively. When the rate expression is given by

$dx/dt = kC_a{}^{n}{}_1\ C_b{}^{n}{}_2C_c{}^{n}{}_3$

The order of reaction as a whole n is given by $n= n_1+n_2+n_3$…………

The molecularity of any process can only be small position integers, while order of reaction can have zero as well as fractional values.

Difference between order of reaction and molecularity:

	Molecularity	**Order of reaction**
1	It is equal to the number of molecules of reactants which take part in a chemical reaction.	1. It is equal to some of the power of the molar concentration of the reactants in the rate expression.
2	It is theoretical concept.	2. It is an experimentally determined quantity, which is obtained from the rate for the overall reaction. It depends on rate determining step in the reaction mechanism.
3	It is always a whole number.	3. It may be negative, zero or fractional value generally not more than 3.
4	It is obtained from a single balanced chemical equation.	4. It cannot be obtained from a balanced chemical equation
5	It does not reveal anything about reaction mechanism.	5. It reveals some basic facts about a reaction mechanism.

Table 6.1

8.4. ZERO, FIRST, SECOND AND THIRD ORDER REACTIONS

(1) Zero order reaction

Reactions, in which the reaction rate does not depend upon the initial concentration of the reactant, are said to be zero order reactions. The Law of mass action fails in these reactions

$$A \longrightarrow B$$

$$\frac{d\,[A]}{dt} = kA^0 = k$$

Examples of zero order reactions:

1. Thermal decomposition of hydrogen iodide at gold surface is found to be of zero order

$$2HI \longrightarrow H_2 + I_2$$

2. The decomposition of ammonia on platinum surface at 800^{0}C in kinetically of zero order.

$$NH_3 \longrightarrow N_2 + 3H_2$$

3. The phosphine decomposition on the surface of molybdenum or tungsten at high pressure is of zero order.

$$2PH_3 \longrightarrow 2\,P + 3H_2$$

(2) First order reaction

A first order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is one.

Expression for first order reaction is given by

$A \longrightarrow$ products

A P

a 0 initially

a-x x after time t

rate expression is given as

$r = -d[A]/dt$

$= d[P]/dt$

$= dx/dt$

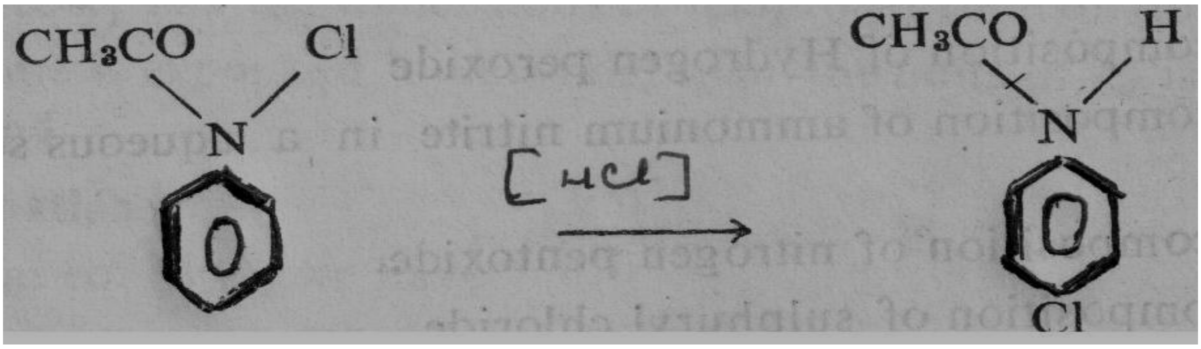
$= k[A]$

$= kC_A$

$= k.\ A$ (at zero time)

$= k\ (a-x)$ (at t time)

Example is conversion of N-chloroacetamide into parachloroacctanicide



(3) Second order reaction

A second order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is two.

$dx/dt = kC^2_A$ for reaction $2A \longrightarrow$ products

and $dx/dt = kC_AC_B$ for reaction $A+B \longrightarrow$ products

Example of second order reactions are :

Hydrolysis of an ester by an alkali (Saponification of ester)

$CH_3COOC_2H_5+NaOH \longrightarrow CH_3COONa+C_2H_5OH$

(4) Third order reaction

Definition of third order reaction:

A third order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is three.

Reactions of third and higher order are rare, but there are infact reactions which are definitely of third or sometimes higher order. This is due to the effect that the probability of three molecules coming to a single point simultaneously is must less as compared to unimolecular and bimolecular reactions.

In a reaction of the third order the number of molecules where concentration alters as a result of chemical change is three, and the change may belong to any of the following types

$A + A + A \longrightarrow$ products

$A + A + B \longrightarrow$ products

$A + B + C \longrightarrow$ products

Note: Above given examples are of elementary reactions i.e. reactions in which order and molecularity are same and there is a single step mechanism. For complex reactions (involving more than one step in mechanism and difference in molecularity and order), order may be 3 even if the number of reactants is more than 3.

Examples of third order reaction is

(i) $2\ FeCl_3 + SnCl_2 \longrightarrow 2\ FeCl_2 + SnCl_4$

(ii) $O_2 + 2NO \longrightarrow 2NO_2$

(iii) $2NO + Cl_2 \longrightarrow 2NOCl$

(5) Pseudo molecular reactions [pseudo means false]

These are the reactions in which order and molecularity are different. These reactions are named after the order and not after the molecularity. Eg. if molecularity is 2 and order is 1 than the reaction is called as pseudo first order reaction.

There are several reactions which obey first order rate equation although in reality they are bi-or tri-molecular.

For example, consider the hydrolysis of methyl acetate in presence of an acid

$$CH_3COOCH_3+H_2O(\text{Excess}) \longrightarrow CH_3COOH+CH_3OH$$

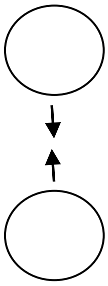
Here molecularity is 2, while order is one in ester and zero in water i.e. overall order is 1 + 0 = 1. The order becomes zero in the reactant which is taken in excess, because the overall rate of reaction does not depend upon the reactant taken in excess. If we will change the concentration of reactant taken in excess, there will not be any change in its being in excess.

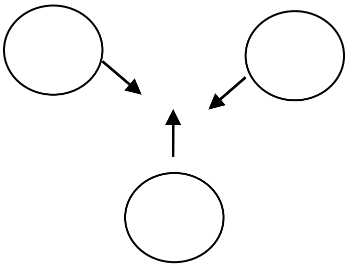
Why high molecularity reaction are rare

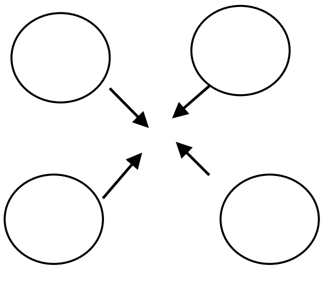
Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are rare. This can be explained on kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing will increase in number of molecules. Thus the possibility of three molecules colliding is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closer and collide will one another at the same time.

The possibility of their doing so is much less than even in the case of termolecular reactions. Hence the reactions involving many molecules proceed through a series of steps, each involving two, three or less number

of molecules. Such a reaction is called complex reaction and the slowest step determines the overall rate of reaction.







less

common **rare** **Common**

Molecularity of a complex reaction:

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert-reactants to products is called the mechanism of the reaction. In any mechanism, some of the steps will be fast other will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is rate determining step of the reaction.

The decomposition of N_2O_5

$2N_2O_5 \longrightarrow 4\,NO_2+O_2$ is an example of complex reaction.

It occurs by the following steps

Step I : $2N_2O_5 \longrightarrow 2NO_2+2NO_3$ (slow)

StepII : $NO_2+NO_3 \longrightarrow NO+NO_2+O_2$ (slow)

Step III : $NO+NO_3 \longrightarrow 2NO_2$ (fast)

Adding all the three steps

$$2N_2O_5 \longrightarrow 4NO_2+O_2$$

Each elementary reaction has its own molecularity, equal to number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each perhaps with different moelcularity. At best it could be thought of as:

"The number of molecules or atoms taking part in the rate determining step."

Thus step 2 in the above mechanism is rate determining step and has molecularity, '2' which could be considered as the molecularity of the decomposition reaction of N_2O_5. As slowest step is the rate determining step. In such complex reactions the molecularity of slowest i.e. the rate determining step, is called as order of reaction. e.g. for decomposition of n_2o_5, the molecularity is 2 but order is one.

And thermal decomposition of acetaldehyde:

$2CH_3CHO \longrightarrow 2CH_4 + 2CO$

8.5 INTEGRATED LAW FOR ZERO AND FIRST ORDER REACTION

(1) Integrated law for zero order reaction

Let us consider a reaction

$A \longrightarrow B$

a 0 initially

$a-x$ x after time t

For a zero order reaction the reaction velocity at any time t is given by -

$dx/dt = k$ (constant)

$dx = kdt$

$\int dx = \int kdt$

$x = kt + I$ (I is integration constant)

when $t=0$ $x=0$ hence $I=0$

so we have $x=kt$

this is general rate expression for zero order reaction.

Unit of zero order reaction:

The unit of zero order rate constant is that of concentration x time^{-1} (as $k=x/t$). Hence unit of k will be mole/litre time $^{-1}$ or mole lit^{-1} time^{-1}. Examples are given earlier.

8.6 RATE EXPRESSION FOR FIRST ORDER REACTION

As we know that a first order reaction is that in which the reaction rate is determined by the change of the one concentration term of reactant only.

Let us consider a first order reaction

$A \longrightarrow B$

A 0 (initially)

$a-x$ x (after time t)

Suppose the initial concentration of the reaction A be a mole/litre.

Let x mole/litre of A decompose after time t leaving behind (a-x) mole/litre of A, the amout of B formed will be x mole/litre.

The rate of first order reaction is proportional to the concentration of A at any particular time. Therefore

$dx/dt = kC_A$ ………………....(1)

where k is rate constant or velocity constant.

$dx/dt = k(a-x)$ …………..(2)

$dx/a-x = kdt$ ………………..…..(3)

$\int dx/a-x = \int kdt$ …………..(4)

integrating equation (4) we get

$-\log_e(a-x) = kt+I$ (I= constant of integration) ………(5)

When t=0 x=0 then

$-\log_e a = I$

Then equation (5) becomes

$\log_e a - \log_e(a-x) = kt$

or $kt = \log_e a/a-x$

$k = 2.303/t \log_{10} a/(a-x)$ ……………………….…(6)

It is clear from equation (6) that if we plot $\log_{10} a/a-x$ against time t a straight line passing through the origin is obtained with a slope of 2.303/k.

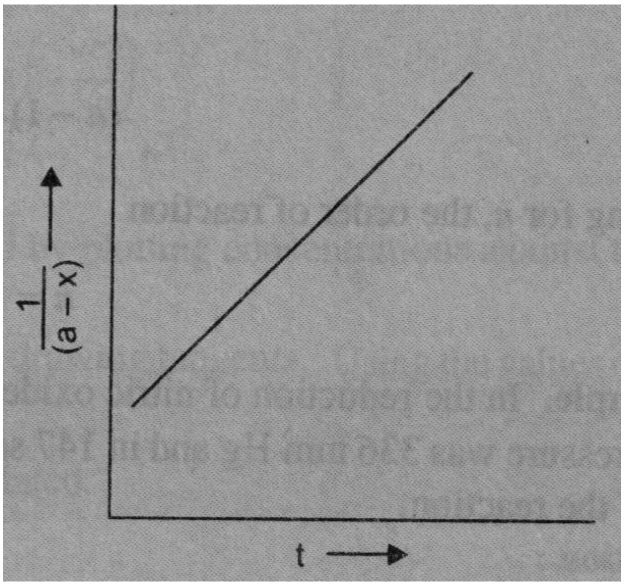


Fig 8.2

Unit of velocity constant of first order reaction:

As the rate constant for first order reaction is k=1/t ln (a/a-x), hence unit will be $\frac{1}{\text{time}} \frac{\text{concentration}}{\text{concentration}}$

i.e. 1/time

or time^{-1}

8.7 Zero order reaction

Not all chemical reaction proceeds to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react together to form A and B.

$A+B \longrightarrow C+D$ (forward reaction)
$C+D \longrightarrow A+B$ (backward reaction)

A reaction which can go in the forward and backward direction simultaneously is called reversible reaction.

Let us consider a reaction

$$A+B \rightleftarrows C+D$$

If you start with A and B in a closed vessel, the forward reaction proceed to form C and D. the concentration of A and B decreases and those of C and D increases continuously. As a result the rate of forward reaction decreases and rate of backward reaction increases. Eventually, the rate of two opposing reactions equals and the system attains equilibrium.

We assume that a chemical reaction occurs as a result of collision between the reacting molecules. Although some of these collision are ineffective, the chemical change produced is proportional to number of collision actually taking

place. Thus at a fixed temperature the rate of a reaction is determined by number of collision between the reactant molecules present in unit volume.

Now let us consider four boxes of one cubic centimeter volume; containing different number of reacting molecules A and B **(figure 8.3)**. they undergo collisions to form products C and D, the rate of reaction being governed by the number of possible collisions between them.

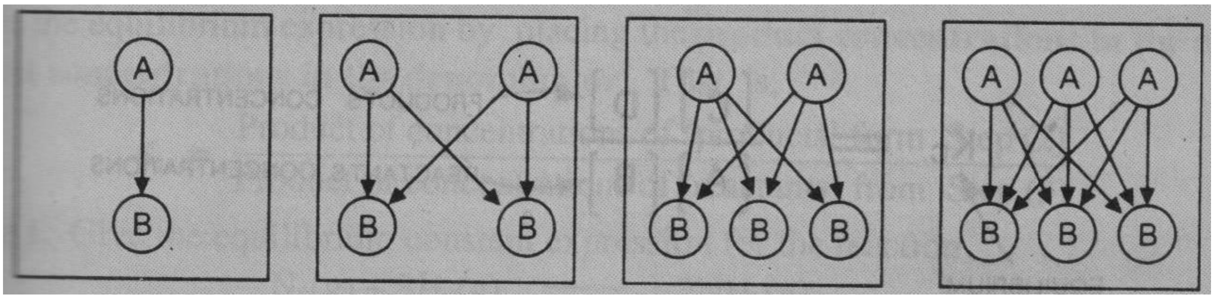


Fig-8.3

In the first box there is one molecule of A and one molecule of B and the possibilities of collision at any extent is 1x1=1. In the second box the number of molecules of A and B are two each and the possibilities of collision are 2x2=4. In the third box there are two molecules of A and three molecules of B, the number of possibilities of collisions between A and B are increased to 3x2=6. In the fourth box the possibilities of number of collision between A and B are 3x3=9.

Since the rate of reaction is determined by molecular impacts, it is proportional to moles per unit volume i.e. , molar concentration. Thus we can write

Rate of reaction ά [A][B]

$= k[A][B]$

The above concept is for equilibrium reactions. But most chemical reactions are spontaneous reactions. These reactions occur from left to right till all the reactants are converted to products. A spontaneous reaction may be slow or it may be fast.

Rate law of zero order reaction

Order of reaction:In the study of chemical kinetics, reactions are generally classified in terms of their order. The order of reaction is defined

as the number of molecules whose concentration determine the rate of chemical reaction at a given temperature. We may define order of reaction as sum of powers to which the concentration (or pressure in case of gases) terms are raised in order to determine the rate of the reaction.

Thus a reaction is said to be zero order if the rate reaction is written as $r= k_0$. If the rate expression is expressed of the type $r=k_1C_A$. if the rate is given by the expression of the type $r=k_2 C_AC_B$ and for third order rate expression is given by the expression of the type $r= k_3C_AC_BC_C$ or $r=k_3C_A^2C_B$ and so on.

8.8 RATE EXPRESSION FOR ZERO ORDER REACTION

As you have studied that rate expression:

$A \longrightarrow$ products is given by $-dC_A/dt = r = kC_A = dP_A/dt$

As the reaction progresses the concentration of reactant keeps on falling will time hence there is negative sign. Where $- dC_A$ is very small decrease in concentration of A in an infinitesimally small time interest dt, C_A gives the concentration of the reactant A at the given instant and k is constant called rate constant or velocity of the reaction.

For a reaction

$A+B \longrightarrow L+M$

$r= -dC_A/dt = -dC_B/dt = dC_l/dt = dC_M/dt = kC_AC_B$

Now consider a reaction $aA+bB \longrightarrow lL + mM$

The rate of this can be written as $r= kC_A^aC_B^b$

The rate of such as reaction is to be expressed in terms of fall of concentration of a reactant per mole or increase in concentration of product per mole. According you can express

$r= -1/a\ dC_A/dt = -1/b\ dC_B/dt = 1/l\ dC_L/dt =1/m\ dC_M/dt.$

There are reactions in which reaction rate is not affected by charges in concentration of one or more reactant. These are called zero order reactions. In these reactions, the rate may be determined by some other limiting factor such as the amount of catalyst used in a catalytic reaction or the intensity of light absorbed in a photochemical reaction. Mathematically for a zero order reaction.

$A \longrightarrow P$

A 0 initially

The reaction velocity at any time t is given by

$dx/dt = k_0$ (constant)

$dx= k_0/dt$

$\int dx =\int k_0dt$

$x= k_0t + I$ (I= constant of integration)

when t=0; x=0

then I=0.

Hence we get $x=k_0t$

8.8.1 Characteristic of zero order reactions

(i) As $k_0 = x/t$; hence unit of zero order rate constant is that of concentration x $time^{-1}$. As concentration is generally expressed as mole per litre then unit of k_0 will be mole lit^{-1} $time^{-1}$.

(ii) Concentration of the product increases linearly with time so as plot of x against time t will be straight line passing through the origin.

8.8.2 Example of zero order reaction

Photochemical reaction between H_2 and Cl_2 over water (saturated with HCl) surface is of zero order.

Now let us consider a reaction $NO_2 + CO \longrightarrow NO+CO_2$ at 200^0C

Its rate = $k[NO_2]^2$

Here the rate does not depend on [CO] so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is zeroth order with respect to CO. The reaction is second order with respect to [NO_2].

8.9 RATE LAW FOR FIRST ORDER REACTION

8.9.1 First order reaction

In a reaction of first order only one molecule is necessary for the reaction to proceed.

The change may be represented in the general form

$$A \longrightarrow \text{Products}$$

Let a be the concentration of A in gm mole per litre initially. After time t suppose the concentration is (a-x) gm moles per litre. According to the law of mass action the reaction velocity at any time t is given by the expression.

$dx/dt = k (a-x)$.

To get the value of k the velocity coefficient we integrate the expression-

$\int dx/a-x = \int kdt$

$\log (a-x) = kt+I$ (I= constant of integration)

when $t=0$; $x=0$

Hence $- \log a = I$

$-\log (a-x) = kt - \log a$

$\log a – \log (a-x) = kt$

$\log_e a/a-x = kt$

$k=1/t \log_e a/a-x$

$= 2.303/t \log_{10} (a/a-x)$

This is equation for a reaction of the first order.

When experimental values of a, x and t are inserted in the equation the value of k always comes out to be constant, if the reaction under examination is first order.

Following important conclusions can be drawn out from the study of the equation

(i) The time taken for the completion for the same fraction of change independent of initial concentration.

At half change $x=a/2$

$k=2.303/t \log_{10} (a/a-a/2)$

$=2.303/t \log_{10} a/(2a-a)/2$

$=2.303/t =\log_{10}2a/a$

$=2.303/t \log_{10} 2 = 2.303/t X .3010$

or $t= 2.303X\log_{10}2$

So t is independent of a i.e initial concentration

(ii) A change in concentration unit will not alter the velocity coefficient

$k= 1/t \log_e ma/m(a-x)$

$=1/t \log_e (a/a-x)$

8.9.2 Unit of first order rate constant

$r= -d[A]/dt =k_1[A]$

$k_1 = -1/[A] d[A]/dt$

$$\text{So units of } k_1 = \frac{1}{\text{mole per litre}} \times \frac{\text{mole per litre}}{\text{time}}$$

$$= \text{time}^{-1}$$

So units of first order rate constant are time^{-1} ie per second, per minute, per hour per day etc.

8.9.3 Half life time of a reaction

The time required for the half completion of a reaction is called half life time of a reaction. Half life time of a reaction is represented by $t_{1/2}$.

Half life time for a first order reaction is represented as-

$k_1 = 1/t_{1/2} \log_e a/(a-a/2)$

$= 1/t_{1/2} \log_e 2$

$= 1/t_{1/2}\ 2.303\log_{10}2$

$= 1/t_{1/2}\ 2.303X.3010$

$= .693/t_{1/2}$

or $t_{1/2} = 0.693/ k$

It is clear from the above discussion that

(i) Half life of a first order reaction is independent of the initial concentration.

(ii) Half life is inversely proportional to k.

Now you can calculate the time for completing any fraction of the reaction by making use of first order reaction.

We know k= 2.303/t log a/a-x

Let us calculate the time in which one third of a reaction is completed.

$$
\begin{aligned}
k &= 2.303/t \log a/(a-a/3) \\
&= 2.303/t \log 3a/2a \\
&= 2.303 \log 3/2 \\
&= 2.303/t (\log 3-\log 2)
\end{aligned}
$$

If we have to calculate the time in which two third of a reaction is completed we proceed as under-

$$
\begin{aligned}
k &= 2.303/t \log a/(a-2/3a) \\
&= 2.303/t \log q/(3a-2a)/3a \\
&= 2.303/t \log 3
\end{aligned}
$$

And half life period you can studied earlier.

8.9.4 Determination of order of reaction

(i) Integration method (Substitution in the equation)

This method consists in actually carrying out the change with known quantities of the reactants and nothing the progress of the reaction by analyzing the reaction mixture from time to time. These values are substituted in the velocity constant equation. When the values are substituted in the expression for first order that is values of a, x and t are substituted and value of k always remains constant the reaction is of first order.

Example: A solution of H_2O_2 when titrated against $KMnO_4$ solution at different time intervals gave the following results.

Time (minutes)	0	10	20
Volume of $KMnO_4$ Used for 10 ml of H_2SO_4	23.8 me	14.7	me 9.1 ml

Show that the reaction if of first order

The integrated rate equation for first order reaction is

$$k = 2.303/t \log a/a-x$$

Since volume of $KMnO_4$ used in the titration is a measure of concentration of H_2O_2 in solution.

$a = 23.8$

$a-x = 14.7$ in 10 minutes

$a-x = 9.1$ in 20 minutes

Substituting these values in the rate equation above we have

$$\begin{aligned} k &= 2.303/10 \log 23.8/14.7 \\ &= 0.2303 (\log 23.8 - \log 14.7) \\ &= 0.2303 (1.3766 - 1.1673) \\ &= 0.04794 \ldots\ldots\ldots\ldots\ldots\ldots(1) \end{aligned}$$

$$\begin{aligned} k &= 2.303/20 \log 23.8/9.1 \\ &= 0.10165 (\log 23.8 - \log 9.1) \\ &= 0.10165 (1.3766 - 0.9595) \\ &= 0.04806 \ldots\ldots\ldots\ldots\ldots\ldots(2) \end{aligned}$$

Since the value of k is almost constant hence reaction is of first order.

8.9.5 Hydrolysis of ester catalysed by hydrogen ion

The hydrolysis of ester like methyl acetate catalysed by hydrogen ion proceeds according to the following equation. It is catalysed by mineral acids say HCl. The hydrolysis of an ester by pure water is very slow; hence it is catalysed by an acid.

$$CH_3COOCH_3+H_2O \quad H^+ \longrightarrow CH_3COO + CH_3OH$$

This equation is pseudo-unimolecular. Since active mass of water being in large excess remains constant and rate of reaction depends only on the concentration of ester. It's molecularity is two and the reaction is of first order.

To study this reaction freshly distilled methyl acetate and N/2 hydrochloric acid in separate bottles were kept in a thermostat for half an hour. When they had acquired the temperature of the bath, mix 5 ml of methyl acetate in 100 ml of N/2 HCl. Immediately withdraw 5 ml of the reaction mixture with the help of the pipette and add a few pieces of ice to freeze the equilibrium. Now titrate the solution by adding N/50 solution of NaOH from the burette using phenolphthalein as an indicator. Similarly again pipette out 5 ml of reaction mixture after five minutes and repeat the above procedure. Repeat the process after 10, 20, 30, 40 minutes and finally at the end of 24 hours. As after 24 hours the reaction is almost completed.

The amount of NaOH used is equivalent to the amount of HCl present originally and the amountof acetic acid produced in the reaction. The amount of HCl present originally can be determined by titrating against the same alkali before the start of the reaction. The amount of acetic acid produced after different intervals of time t can be determined.

The amount of acetic acid formed at the end of the reaction is equivalent to the initial amount (a) of methyl acetate. Suppose V_o, V_1 and V_∞ are the volume of N/50 NaOH solution used at zero, t and infinite time respectively.

The amount of acetic acid produced after time t i.e. value of x proportional to $(V_t - V_0)$. The initial concentration of methyl acetate i.e. value of a is proportional to $(V_\infty - V_0)$. Therefore, amount of ester present at time t i.e.

$a-x$ ά $(V_\infty - V_0) - (V_t - V_0)$

ά $V_\infty - V_t$

Hence from first order rate expression

$K = 2.303/t \log (V_\infty - V_0/V_\infty - V_t)$

The value of k comes out to be constant, showing that the reaction is first order. Inversion of cane sugar into glucose and fructose is also first order reaction, here again water is in large excess and its active mass practically remain constant.

8.10 RATE OF RADIOACTIVE DISINTEGRATION

The rate of disintegration of a radioactive element is found to be independent of the temperature, pressure or its state of chemical combination. Each element disintegrates at a characteristic rate independent of all external factors. Nuclear reactions are generally first order.

Since in a radioactive transformation an atom breaks down to give one or more new atoms, it may be regarded as a chemical reaction in which one molecule changes to yield one or more products (unimolecular reaction). Let us consider an atom A changing into B.

$$A \longrightarrow B$$

a 0 initially

a-x x after time t

if in a small time dt, dx is the number of atoms which change, the rate of disintegration dx/dt can be expressed as:

$dx/dt = k\,(a-x)$………………….(1)

Where k is ordinarily called velocity constant and here it may well be named as disintegration constant or transformation constant.

From equation (1) it follows

$dx/a-x = kdt$ …………………..(2)

if $dt = 1$ then $dx/a-x = k$ ………(3)

Thus the disintegration constant k may be defined as the fraction of total number of atoms dx/a-x present at any time (t) which disintegrate per second. This disintegration constant k has a definite characteristic value for a particular radioactive element.

On integrating the equation (2) we have get

$\int dx/a-x = k \int dt$

$-\log_e(a-x) = kt + I$ I= integration constant (5)

When $t=0$ $x=0$

$-\log_e a = I$ (6)

Hence $\log_e a - \log_e (a-x) = kt$

$k = 1/t \log_e (a/a-x)$

$= 2.303/t \log_{10} a/(a-x)$ (7)

at half time i.e $t_{1/2} = T$ $x=a/2$

$T = 2.303/k \log a/a-a/2$

$= 2.303/k \log 2$

$= 0.693/k$ (8)

It is clear from the above that for a particular radioactive disintegration the value of $t_{1/2}$ is independent of amount of the substance present and depends only on k. the time $t_{1/2}$ required for the disappearance of one half of the original amount of the radioactive substance is called its half life period.

The statement that half life period of say radium is 1600 years means after 1600 years any given quantity of radium will disintegrate to half of it.

8.10.1 Average life

The reciprocal of the disintegration constant k gives the average life of the disintegrating atom.

Hence $\lambda = 1/k = T/0.693$

$= 1.44T$

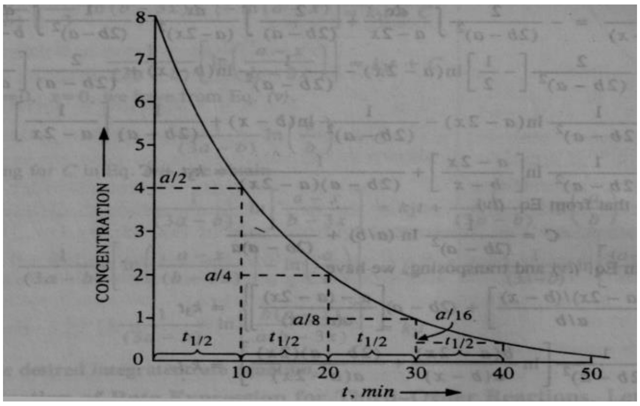


Fig-8.4

8.11 CONCEPT OF ACTIVATION ENERGY

8.11.1 Effect of temperature on reaction rate

Temperature coefficient of a reaction:

Now let us consider effect of temperature on reaction rates

It has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10^0C is known as temperature coefficient of the reaction. The temperatures usually selected for this purpose are 25^0C and 35^0C. Thus

$$\text{Temperature coefficient} = \frac{\text{Rate at } 35^0\text{C}}{\text{Rate at } 25^0\text{C}} = \frac{k_{35}}{k_{25}}$$

The value of temperature coefficient for most of the reactants is close to 2 and in some cases it approaches to 3.

$$\text{Hence temperature coefficient} = \frac{\text{Rate at } 35^0\text{C}}{\text{Rate at } 25^0\text{C}} = \frac{k_{35}}{k_{25}} = 2 \text{ to } 3$$

8.12 COLLISION THEORY OF REACTION RATE

Now let us study why such small rise of temperature speeds up a reaction to such a large extent. This can be explained on the basis of collision theory.

According to collision theory for chemical reaction to occur, there must be collisions between reacting molecules. But all collisions are not effective. Only a small fraction of collisions produce a reaction. Two main conditions for a collision between the reacting molecules to be productive are-

(i) The colliding molecules must possess sufficient kinetic energy to cause a reaction.

(ii) The reacting molecules must collide will proper orientation.

The molecules must collide with sufficient energy:

Let us consider a reaction

$$\text{A -B + B-B} \longrightarrow \text{2 A-B}$$

A chemical reaction occurs by breaking bonds between the atoms of reacting molecules and forming new bonds in the product molecules. For ***breaking the bonds energy is required and in forming the bonds energy is liberated.*** The energy for breaking the bonds comes from the kinetic energy possessed by the reacting molecules, before the collision.

The (figure 8.5) shows the energy of molecules A_2 and B_2 as the reaction $A_2+B_2 \longrightarrow 2AB$ progresses.

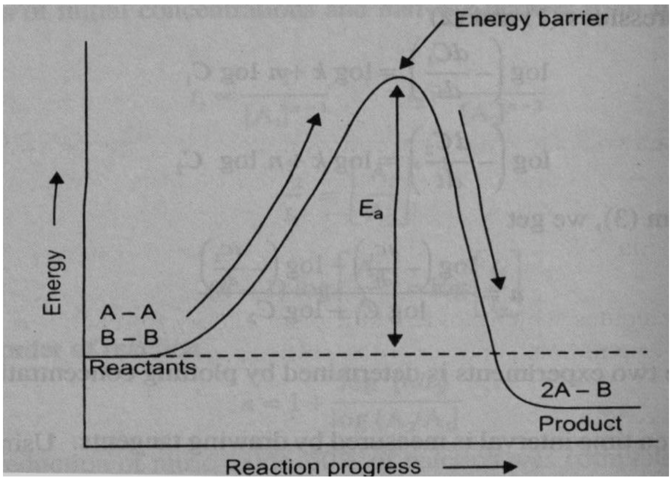
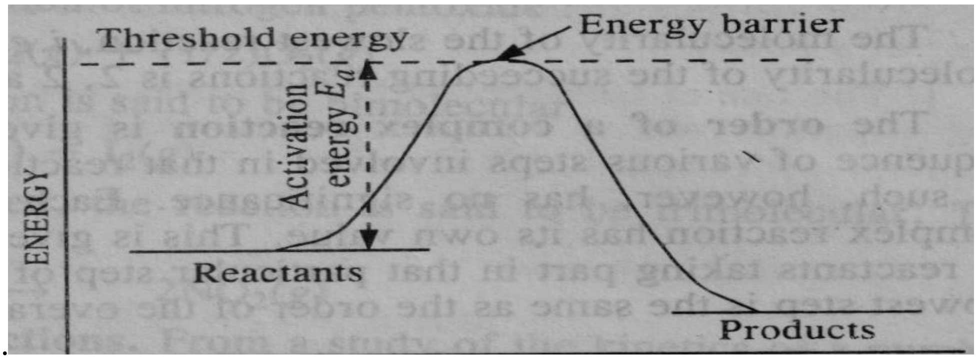


Fig 8.5

The figure 8.5 also shows the activation energy E_a, that is minimum energy required to cause a reaction between the colliding molecules. Only the molecules that collide will a kinetic energy greater than E_a are able to get over the barrier and react. The molecules colliding will kinetic energies less than E_a fail to cross the barrier.

As you have studied till now that for a reaction to occur there must be collision between molecules. And most of the collisions are ineffective. According to collision theory those collision results in chemical reaction in which the colliding molecules are associated with a certain minimum energy called threshold energy



Reaction progress ⟶

Fig- 8.6

Hence there is certain minimum energy called threshold energy which the colliding molecules must acquire before they are capable of reacting. Most of the molecules have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

That means

Activation energy = threshold energy – energy possessed by the molecules.

Now you must have followed from the above discussion that there is energy barrier placed between reactants and products (fig 8.6) The barrier has to be crossed before reactants can yield product.

8.13 EFFECT OF CATALYST

As you have studied earlier a catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction. When a catalyst is added, a new reaction path with a lower energy barrier is provided (dotted curve in the fig 8.7). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. This increases the rate of the reaction.

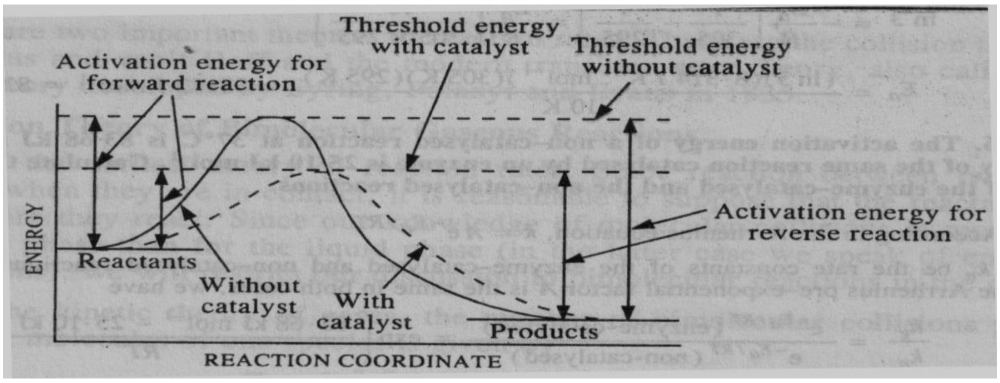


Fig- 8.7

8.14 ARRHENIUS EQUATION

For the effect of temperature Arrhenius proposed and empirical equation which is useful in calculating energy of activation of a reaction

$k = Ae^{-Ea/RT}$ ……………………….(9)

Where E_a is called Arrhenius activation energy at temperature T, k is rate constant and A is called the Arrhenius pre exponential factor, a has the same units as the rate constant k. the units of k for a first order reaction are S^{-1} which is units of frequency. Hence A is also called the frequency factor, Ea and A are called Arrhenius parameters.

Taking logs of equation (9) we have

$\ln k = \ln A - E_a/RT$ ……………….(10)

A plot of lnk against reciprocal of absolute temperature (1/T) gives a straight line with slope = $-E_a/R$ and intercept = lnA, and hence energy of activation E_a be obtained.

Differentiating equation (10) with respect to temperature, we get

$d\ln k/dT = E_a/RT^2$ …………………(11)

Integrating equation (11) between temperature T_1 and T_2 when the corresponding rate constants are k_1 and k_2 respectively assuming that Ea is constant over the entire range we get-

$\ln k_2/k_1 = E_a/R[T_2-T_1/T_1 T_2]$ ………………(12)

or $\log_{10} k_2/k_1 = E_a/2.303R \ [T_2-T_1/T_1 T_2]$

This is the integrated Arrhenius equation. Thus knowing the rate constants at two temperature the energy of activation Ea can be calculated.

It must be clear to you that different reactions require different amount of energy activation energy. A reaction which has lower activation energy will proceed at a faster rate at a given temperature. A reaction which has higher activation energy will proceed at a slower rate.

The differences in activation energy are mainly responsible for observed difference in rate of reaction.

If the reactants posses higher total energy than the products there will be a release of energy. The reaction is said to be exothermic reaction. If the reactants possess lower total energy than the products energy will be absorbed and the reaction is said to be endothermic.

8.15 SUMMARY

- In this chapter you have studied different definitions associated with chemical kinetics, rate laws for zero, first, second and third order reaction and will examples also rate laws for zero order and first order reaction.
- The difference between order of reaction and molecularity has been discussed. The factors affecting rate of a reaction have also been studied namely the factors are temperature, pressure, concentration, catalyst and surface area.
- The rate and mechanism of a chemical reaction is the determination of the overall stoichiometry of the reaction and to identify any side reaction.
- The determination of the change of the concentration of the reactant and product species with time.
- The reaction rate depends sharply on temperature; the temperature of the reaction mixture must be kept constant.
- The energy of activation concept is useful in the study of reactions. The activation energy depends upon the nature of the chemical bonds undergoing rupture. It is independent of initial and final energy contents of the reacting particles. The feasibility of a reaction is studied under 'thermodynamics'.

8.16 TERMINAL QUESTIONS

(A) Short Answer Questions:

1. Derive mathematical expression for the rate constant of reaction products of the first order.
2. Distinguish between reaction rate and rate constant.
3. Explain why the rate of reaction cannot be measured by dividing the total amount of a substance reacted by the total time taken.
4. What do you understand by energy of activation?
5. What is temperature co-efficient of reactions?

6. Write Arrhenius equation.

(B) Long answer/essay type questions

1. What are different factors which affect the rate of a reaction, explain.
2. What is meant by the terms rate constant and order of reaction?
3. Distinguish between molecularity and order of reaction.
4. Integrate the rate expression for a first order reaction. What is meant by half life time of a reaction?
5. What is meant by reaction being of first order, second order or zero order? What are pseudo-unimolicular reactions?
6. Bring out clearly the main features of the collision theory of reaction rate? What do you mean by effective collisions?

(C) Solved questions:

1. The rate constant of a first order reaction is $1.54 \times 10^{-3}\ s^{-1}$
   Calculate its half life time.

   $t_{1/2} = 0.693/k_1$

   $= 0.693/(1.54 \times 10^{-3}\ s^{-1})$
   $= 450\ s$

2. The half life of a reaction $A \longrightarrow B+C$ which obey's first order kineties, is 8:0 minutes. How long it will take for the concentration of A to reduced to 1% of it initial value

   $k_1 = 0.693/t_{1/2}$

   $= 0.693/8.0m$

   $= 0.087 min^{-1}$

   Now $k_1 = 2.303/t \log (a/a-x)$

   $t = 2.303/0.087 \log(100/1)$

= 52.93m

3. 50% 0f a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

$t_{1/2} = 0.693/k$

$k = 0.693/23$ m

$= 0.03013$ m^{-1}

For 90% completion time required can be calculated as follows:

$0.03010 = 2.303/t \log(100/10)$

As $a-x= 100-90 =10$

$t = 2.303/0.0310 \ \log10$

= 76.4 min.

UNIT 9: COLLOIDAL STATE

CONTENTS:

9.1 INTRODUCTION

During his research work Thomas Graham in 1861 found that while some substances diffused readily through parchment membrane, others diffuse at slow rate. The substance which diffuse at slow rate were given the name colloids (from Greek Kolla means glue like). These observations led to the development of a new branch of knowledge known as colloidal science.

Latter many investigators including Thomas Graham realised that distinction between crystalloids and colloids was not rigid, since many crystalline substances like sulphur, carbon and salt can be converted into colloidal form by suitable means. At the same time the so called colloidal like gum and gelatin, were shown to have a crystalline structure by X-ray examination. In fact, it is now well known that one and the same substance may show colloidal behaviour at one time and crystalloidal behaviour at another time depending upon the prevailing conditions for example, sodium salt of long chain fatty acids (the soaps) show colloidal character in water in which they are sparingly soluble but crystalloidal character in alcohol in which they are freely soluble. The term ‘colloidal substances’ has, therefore been discarded in favour of ‘colloidal state’ into which almost every substances can be brought by suitable means.

Hence colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions.

9.2 OBJECTIVES

After study this unit you will be able to

- Know about the matter and its different states i.e. solid, liquid and gaseous state.
- Discuss the characterisation of solids by incompressibility, rigidity and mechanical strength.
- Know the forces involved in the solid molecules due to these atoms or ions that make up the solid are closely packed.
- Define the colloids and its different tpes.
- Explain the different properties of colloidal solution. .

9.3 COLLOIDAL SYSTEMS

When the diameter of the particles of substance dispersed in a solvent ranges from about $10A^0$ to $2000A^0$, the system is said a colloidal solution, colloidal dispersion or simply a colloid, the material will particle size in the colloidal range is said to be in the colloidal state. A colloidal system is thus a two phase system consisting of a continuous phase or dispersion medium in which extremely minute particles, lying within the colloidal range of second substance termed as discontinuous phase or dispersed phase, are suspended.

Difference between suspensions, colloidal solutions and true solution

Property	Suspensions	Colloidal solutions	True solution
1.Nature	Hetrogeneous	Heterogeneous	Homogeneous
2. Size range	Greater than $2000A^0$ or 200 mµ	Between $10A^0$ to 2000 a^0 or 1 mµ to 200 mµ	Less than $10a^0$ or 1 mµ
3. Visibility	Particles are visible under microscope even with a naked eye	Particles are visible under ultramicroscope	Particles are not visible even under ultramicroscope
4. Diffusibiltiy	Do not diffuse	Diffuse slowly	Diffuse rapidly
5. Tyndall effect and Brownian movement	Do not exhibit	Exhibit	Do not exhibit
6. Molecular weight	Low	High	Low

Table -9.1

9.3.1 Types of Colloidal Systems

As we have seen in the above article, a colloidal system is made of two phases, the substance distributed as the colloidal particle is called the dispersed phase, the second continuous phase in which the colloidal particles are dispersed is called the dispersion medium. If we take colloidal solution of copper in water, copper particles constitute the dispersed phase and water dispersion medium (fig 9.1).

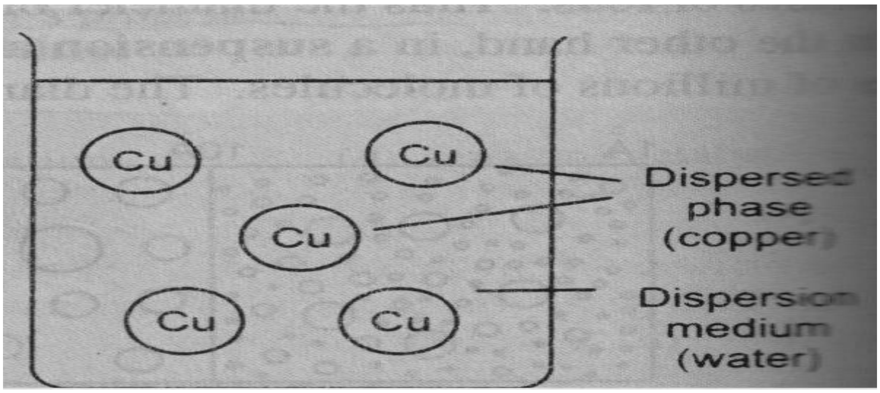


Fig 9.1

Now we see that either the dispersed phase or the dispersion medium can be gas liquid or solid, these are eight types of colloidal system possible.

A colloidal dispersion of one gas in another is not possible, since the two gases would give a homogeneous molecular mixture.

The various types of colloidal systems are given in table 9.2.

Dispersion medium	Name of the dispersion phase	Name of the colloidal system	Examples
1. Gas	Liquid	Liquid aerosol	Clouds, mist, fog
2. Gas	Solid	Aerosol	Smoke, dust
3. Liquid	Gas	Foam	Shaving cream, foam
4. Liquid	Liquid	Emulsions	Milk, hair cream, cod-lever oil
5. Liquid	Solid	Colloidal solutions	Colloidal gold
6. Solid	Gas	Solid foam	Foam rubber, occluded

			gases
7. Solid	Liquid	Gel or jelly	Butter, cheese, gels
8. Solid	Solid	Solid sol	Alloys, ruby glass (gold dispersed in glass)

Table-9.2

9.3.2 Classification of Colloids

Substance like metal, metal sulphides cannot be brought into the colloidal state simply by bringing them in contact with solvent, these are known as lyophobic colloids (or hydrophobic colloid if water is solvent).

Substances like proteins, starch and rubber whose molecules are large enough to be close to the lower limit of colloidal range, pass readily into colloidal state when mixed with a suitable solvent are called lyophilic colloids (or hydrophilic colloids if water is solvent).

9.3.3 Distinction between Lyophilic and Lyophobic Colloids

Property	Lyophobic sols	Lyophilic sols
Preparation	Formed by special method	Formed easily
Nature	Particles are true molecules	Particle consists of aggregate molecules
Viscosity	Viscosity is almost the same as that of the medium	Viscosity is much higher than that of the medium
Visibility	Particle can be readily detected under ultra microscope	Particles cannot be readily detected even under ultramicroscope
Tyndall effect	More distinct	Less distinct
Reversibility	Lyophobic salts are	These are reversible

	irreversible	
Surface tension	Surface tension is usually the same at that of the medium	Surface tension is generally lower than that of the medium
Migration in electric field	Particles migrate to anode or cathode	Medium particles migrate to anode or cathode, or not at all

Table -9.3

9.4 PREPARATION OF COLLOIDAL PARTICLES

The primary consideration in the preparation in the colloidal solution is that the dispersed particle should be 10A^0 to 2000 A^0 (1 m μ to 200 mμ) the lyophilic sols can readily prepared since colloidal materials such as starch, gelatin when added to water swell up and spontaneously break into particulates of matter of colloidal range.

Lyophobic sols cannot be prepared by simple contact or slight shaking of the substance with the solvent. Svedberg (1908-1912) suggested that there are two ways for obtaining lyophobic sols.

(i) Dispersion methods

In these methods, larger lumps of the insoluble substance are pulverized by mechanical or by other means till particles of colloidal dimensions are obtained.

(ii) Condensation methods:

In these methods, a molecular on ionic distribution is first prepared then by suitable coarsening gives rise to particles of colloidal dimensions.

Dispersion methods

(i) Mechanical dispersion:

The most obvious method of dispersion consists in breaking down the courser solid particles by one chemical grinding. This is done in the so called ‘colloidal mill’ which generally consists of two metal discs held at a very small distance apart from one another which are capable of revolving at very high speed in opposite direction. The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.

(ii) Bredig’s are method (1898)

This method is used for preparing hydrosols of metals like gold, silver and platinum. This method consists in striking an arc between two electrodes of the metal immersed in water as shown in (fig-9.2.)

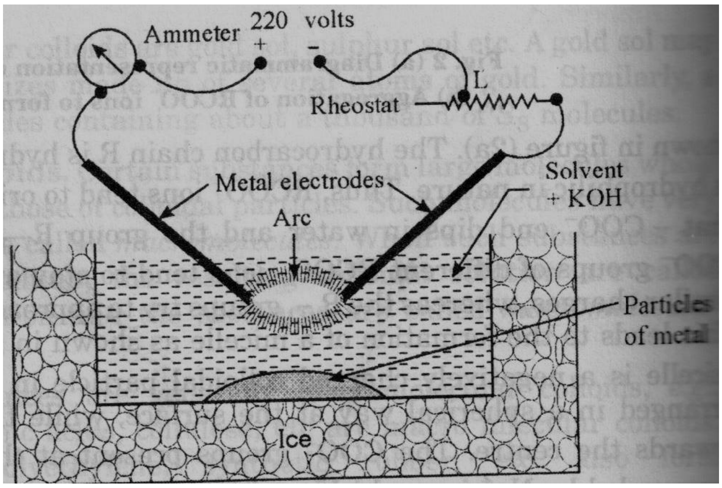


Fig-9.2

A current of one ampere and voltage of 100 volts is used. The vessel in which water is kept is surrounded by ice. On striking an arc, the vapours of metal are formed which then immediately condense to form particles of colloidal size. Sometimes it is necessary to add traces of electrolyte, say alkali hydroxide is added in water, to obtain best results.

Svedberg devised a method to obtain organo sols of metal and nonmetals. In this method electrodes are usually of iron or aluminium and an alternating current is employed. The material to be dispersed in taken in the form of granules and pasted on the electrodes (immersed in the organic medium) through which the electric current is passed.

Alternative current is used which greatly diminishes the decomposition of the liquid. Practically any metal can be obtained in the colloidal state in a liquid with which it does not react chemically.

Peptization

Peptization is a process by means of which a suitable colloidal solution can be produced from suitable substances originally present in massive forms, when the particle of colloidal size pre-exist in the substance to be dispersed.

The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is known as peptizing agent. An electrolyte having an ion in common with the material to be dispersed is required for sol formation.

Peptization action is due to the preferential adsorption of one of the ions of the electrolyte by particles of the material. As a result of the preferential adsorption of the ion which is more closely related chemically to the precipitate, the particles acquire positive or negative charge depending upon the change on the ion adsorbed.

Because of the presence of the same type of charge, the particles of the precipitate are pushed apart. The precipitate thus gets dispersed resulting in the formation of stable sol.

Thus you can see ferric hydroxide sol is obtained when a small quantity of ferric chloride solution is added. The peptization action is due to the preferential adsorption of F_e^{3+} ion. Similary silver chloride can be converted into a sol by adding hydrochloric acid (Cl^- being common ion).

9.5 CONDENSATION METHODS

Colloidal system can be obtained by various reactions such as double decomposition, oxidation, reduction, hydrolysis etc. the conditions (temperature concentration etc.) used are such as permit the formation of sol particles but prevent the particles becoming too large and forming precipitate the unwanted ions present in the sol are removed by dialysis as these ions may eventually coagulate the sol.There are four condensation methods:-

9.5.1 (i) Double decomposition- An arsenic sulphide sol is prepared by passing a slow stream of H_2S gas through a dilute solution of arsenious oxide. This is continued till the yellow colour of the sol attains maximum intensity. Excess H_2S is removed either by passing in a stream of hydrogen or by boiling.

(ii) Reduction:

Sols of metals such as copper, silver, gold and platinum are obtained by reducing the aqueous solutions of their salts by non-electrolytes such as formaldehyde, tannin, phenyl hydrazine. carbon mono oxide and phosphorus.

Thus

$AgNO_3$+tannic acid $\longrightarrow$ Ag sol

$Aucl_3$+tannic acid $\longrightarrow$ Au sol

(iii) Oxidation:

A sol of sulphur can be obtained by passing hydrogen sulphide into a solution of sulpher dioxide.

$$2H_2S+SO_2 \longrightarrow 2H_2O+S\downarrow$$

(iv) Hydrolysis:

Colloidal sols of heavy metals are obtained by the hydrolysis of the solutions of their salts.

Thus when a small amount of ferric chloride is added to boiling water, a red-brown sol of ferric hydroxide obtained.

$$FeCl_3+3H_2O \longrightarrow Fe(OH)_3+3HCl.$$

9.6 PURIFICATION OF SOLS

The presence of impurities, particularly the electrolytes, renders the sols unstable. We will discuss the cause of instability latter on. These impurities must be eliminated by suitable means. The purification of sols can be accomplished by following methods.

(i) Dialysis

The purification of colloidal solution by dialysis is based on the inability of the sol particles to pass through an animal membrane or a parchment paper which allows only the molecules or ions to pass through. The vessel in which dialysis is carried out is known as a dialyser.

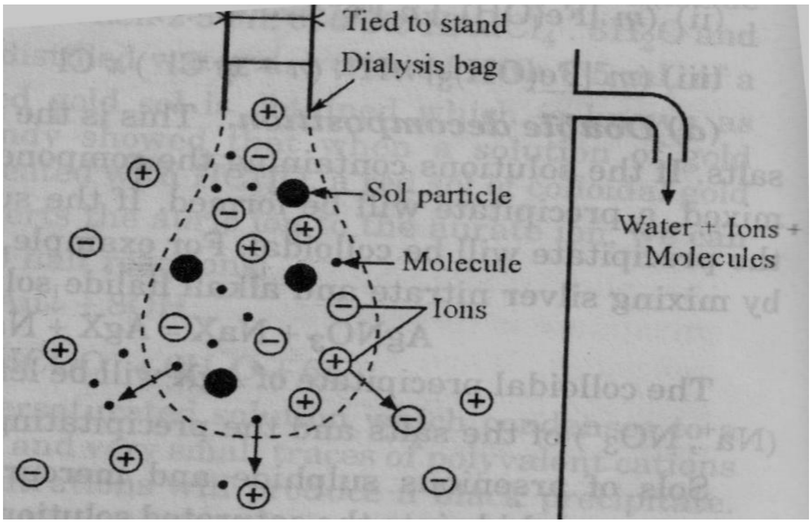


Fig-9.3

The animal membranes have very fine pours. These pores permit ions or small molecules to pass through but not the large colloidal particles when a sol containing dissolved ions (electrolyte) or molecules is placed in a bag of permeable membrane dipping in pure water, the ions diffuse through the membrane. By using continuous flow of fresh water, the concentration of electrolyte outside the membrane tends to zero. Thus diffusion of the ions into pure water remains brisk all the time and practically all the electrolyte present in the sol can be removed easily.

Ordinarily, the process of dialysis is quite slow, but it can be quickened by applying an electric field if the solution in true solution is an electrolyte. The process is then called electrodialysis.

(ii) Ultrafiltration

Ultrafiltration is a process of separating colloidal particles from the solvent and the solutes present by specially prepared filters which allows all other particles except the colloidal particles to pass through it.

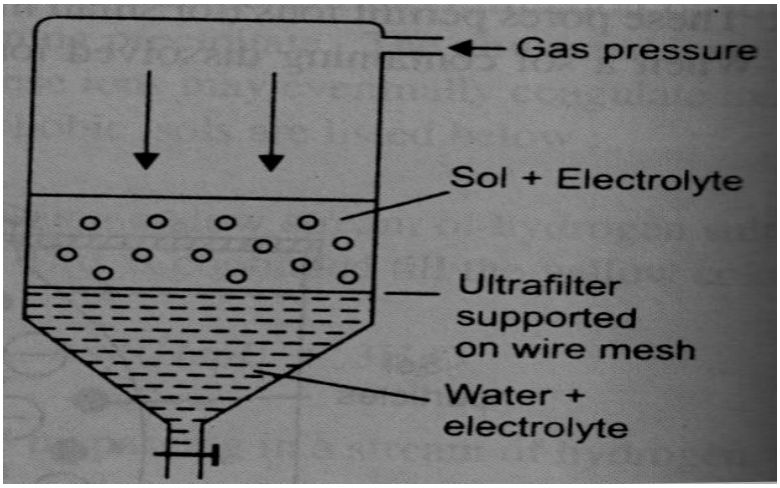


Fig-9.4

Ordinary filter papers have pours larger than 1000 mμ, so that the colloidal particles having a smaller size can easily pass through them. But if the pour's are made smaller, then the colloidal particles may be retained on the filter paper.

Ultrafiltration is a method not only for purification of the sol but also for concentrating the sol.

9.7 GENERAL PROPERTIES OF COLLOIDAL SYSTEMS

9.7.1 Heterogeneous character

As you have seen from the above discussion every colloidal system is a heterogeneous system. It consists of two phases, the dispersed phase and dispersion medium.

9.7.2 Visibility

Most of the sols appear to be true solutions with naked eye, but the colloidal particles can be seen through an ultramicroscope.

9.7.3 Colligative properties

The property which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles, is known as a colligative property.

As you know that colloidal particles are aggregate of molecules, therefore all the colligative properties would be reduced. Hence colloidal systems have very low osmotic pressure, and freeze and boil at about the same temperature as the pure dispersion medium.

9.7.4 Diffusibility

The colloidal particles do not readily diffuse through a parchment paper or any other membrane.

9.8 COLOUR OF THE SOLS

The colour of the hydrophobic sol depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and nature of the particle. This will be clear to you with following example:

Colour of Ag sol	**Particle diameter**
Orange yellow	6×10^{-5} nm
Orange red	9×10^{-5} nm
Purple	13×10^{-5} nm
Violet	15×10^{-5} nm

This can be seen in other cases also.

9.9 OPTICAL PROPERTIES

9.9.1 Tyndall effect

In 1867 Tyndall found that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in the path. But when the same light beam is passed through a colloidal dispersion it is visible as a bright beam. The phenomenon of the scattering of light by the sol particles is called Tyndall effect. The illumination of beam or cone formed by the scattering of light by the sol particles if often called as Tyndall beam or Tyndall cone.

This phenomenon is due to the scattering of light from the surface of colloidal particles. In true solutions the particle size is very small to scatter the light and hence the beam is invisible.

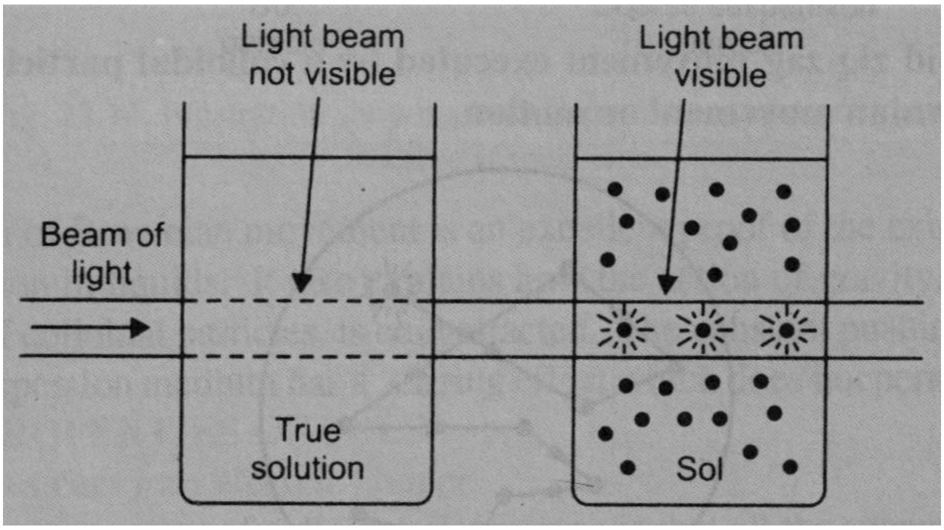


Fig 9.5

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and dispersion medium. In lyophobic sols, the difference is appreciable and hence the Tyndall effect is quite well-defined. In lyophilic sols the difference is small hence the Tyndall effect is much weaker.

Sol particles cannot be seen with microscope. Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus called ultramicroscope. The intense beam of light is focused on a sol contained in a glass vessel. The focus of light is then observed with a microscope at right angle to the beam individual sol particles appear as bright specks of light against a dark background. It may be noted that under the ultra microscope, the actual particles are not visible. It is the larger halos of scattered light around the particles that are visible. Thus the ultra microscope does not give any information regarding the shape and size of sol particles.

9.9.2 Kinetic properties of sols

Robert Brown an English botanist in 1827, observed that pollen grains in aqueous suspensions were in constant motion. Later when ultramicroscope was invented, it was found that particles of lyophobic sols were also in a state of ceaseless random motion similar to pollen grains. This

Kinetic activity of particles suspended in a liquid is called Brownian movement.

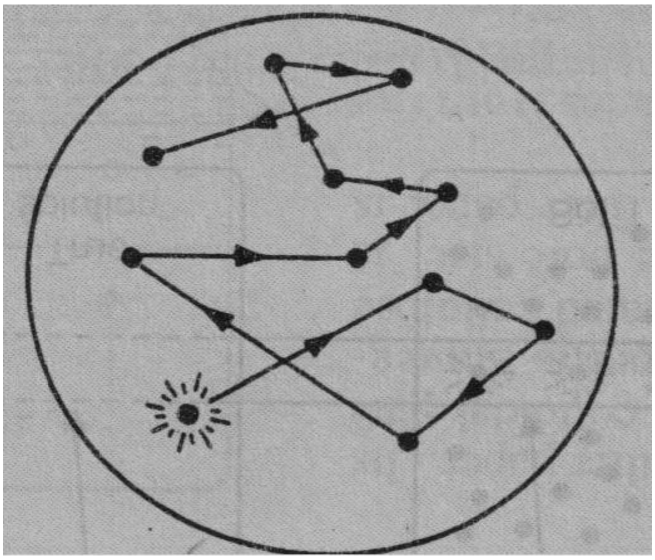


Fig-9.6 Brownian movement

The Brownian movement is independent of the nature of the colloidal particles, but was more rapid the smaller the particles and less viscous the solution. The Brownian movement is due to the bombardment of colloidal particles by molecules of dispersion medium which are in constant motion like molecules in a gas**.(fig 9.6).**

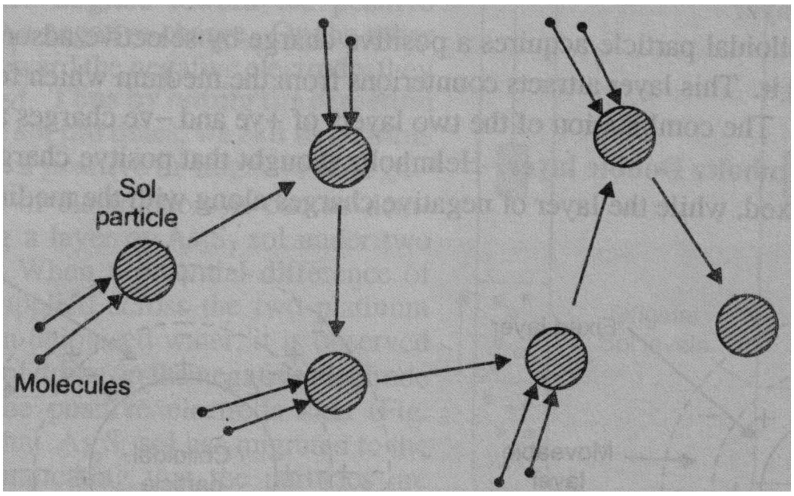


Fig- 9.7

As a result of bombardment the colloidal particle acquire almost the same amount of kinetic energy as possessed by the molecules of dispersion medium. But since the colloidal particles are considerably heavier than molecules of the dispersion medium, their movement is considerably slower than that of the molecules of the medium**. (fig 9.7).**

9.9.3 Charge on colloidal particles

The most important property of colloidal dispersions is that all the suspended particles posses either positive or negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol.

The origin of charge on colloidal particles:

It has been observed that sols are invariably associated will minute quantities of electrolytes and that if the latter are completely removed by persistent dialysis, the sols become unstable. It is believed therefore that charge on colloidal particles is due to preferential adsorption of either positive or negative ion on their surface.

Ferric hydroxide sol particles are positively charges because these absorbs Fe^{3+} ions from ferric chloride ($FeCl_3$) used in the preparation of the sol. Since the sol as a whole is neutral, the charge on the particle is counterbalanced by oppositely charged ions termed counterions (in this case Cl^-) furnished by the electrolyte in medium.

The negative charge on arsenic sulphide sol is due to preferential adsorption of sulphide ions on the surface of arsenic sulphide particle. Sulphide ions are furnished by ionization of hydrogen sulphide which is present in traces. Thus, in ferric hydroxide sol, ferric not chloride ions are preferred. Similarly, in arsenic sulphide sol, a sulphide ion not hydrogen ion is preferred.

9.10 ELECTRICAL DOUBLE LAYER

The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which forms a second layer of negative charges. The combination of two layers of positive and negative charges around the sol particles was called Helmholtz Double Layer**. (fig 9.8).**

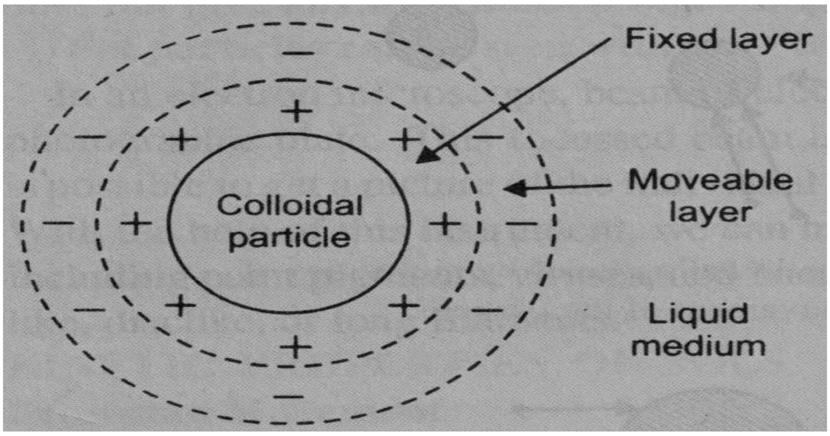


Fig-9.8

Helmholtz thought that positive charges next to the particle surface were fixed, while the layer of negative charge along with the medium were mobile. More recent considerations have shown that the double layer is made of:

(a) Compact layer of positive and negative charges which are fixed firmly on the particle surface.

(b) Diffuse layer of counter ions (negative ions) diffuse into the medium containing positive ions.

The combination of compact and diffuse layer is referred to as the Stern double layer. The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under the applied electric field. Because of the distribution of charge around the particle, there is a difference of potential between the compact layer and the bulk of solution across the diffuse layer. This is called Electro kinetic or Zeta potential.

9.11 COAGULATION

As you have already studied that stability of colloidal particle is due to the adsorption of positive or negative ion by the dispersed particles. The repulsive forces between the charged particles do not allow them to settle. If somehow, the charge is removed, there is nothing to keep the particles apart from each other. They aggregate and settle down under the action of gravity. This phenomenon of changing colloidal state to the suspended state is known as coagulation, floculation or precipitation of colloidal solution.

In case of lyophobic colloids the stability is due the electrical charge present on the colloidal particles whereas the stability of lyophilic colloid depends upon both the electrical charge and solvation. In order to cause precipitation of the dispersed particles, it is necessary that they come closer to one another and form bigger aggregates which lie outside the colloidal range.

The coagulation or precipitation of a given sol can be brought about in four ways:

(i) By addition of electrolytes

(ii) By electropholysis

(iii) By mixing oppositely charged sols

(iv) By boiling

(i) By addition of electrolytes:

When excess of an electrolyte is added to a sol the dispersed particles are precipitated. The electrolyte furnishes both positive and negative ions in the medium. The sols particles adsorb the oppositely charged ions and get discharged. The electrically neutral particles then aggregate and settle down as precipitate.

A negative ion causes the precipitation of a positively charged sol and vice versa. The effectiveness of an anion or cation to precipitate a sol will naturally depend on the magnitude of the charge or the valence of the effective ion.

From a study of the precipitating action of various electrolytes on a particular sol, Hardly and Schulz gave the following rules.

(i) Coagulation is brought about ions having opposite charge to that of the sol. Hence negative ions cause coagulation of the positively charged sol and positive ion cause coagulation of negatively charged sol. Thus $Fe(OH)_3$ sol which is positively charged is coagulated by negative ions such as Cl^-, NO_3^-, SO_4^{2-} etc. Similarly As_2S_3 sol which is negatively charged is coagulated by positive ions such as Na^+, Ba^{2+}, Mg^{2+} etc.

(ii) The higher the valency of the ion greater is its coagulating power. Thus the power of Al^{3+}, Na^+, Ba^{2+} is in the order $Al^{3+}>Ba^{2+}>Na^+$

Similarly the precipitating power of $[Fe(CN)_6]^{3-}$,Cl^- and SO_4^{2-} is in the order

$Fe(CN)_6^{3-}> SO_4^{2-}> Cl^-$

Quantitatively the efficacy varies directly as the square of the valence of the ion. Thus Mg^{2+} ion is 4 times more effective and Al^{3+} ion is 9 times more effective than Na^+ ion.

9.12 PROTECTION OF COLLOIDS

Lyophobic sols are easily precipitated by small amount of electrolyte. However these sols are often stabilized by the addition of lyophilic sols. When lyophobic and lyohilic sols are mixed and lyophilic sol is in excess then the resultant sols is avoided from being coagulated. The sol now is more stable to temperature changes and is not readily precipitated by electrolytes. The lyophilic colloids thus used for protecting the lyophobic colloids are known as protective colloids. Different protective colloids have different protective powers. Zsignondy investigated the protective action quantitatively and gave the concept of gold number.

9.12.1 Gold number

Gold number may be defined as ‘the weight in milligrams of protective colloid which will just stop the coagulation of 10 ml of a gold sol on adding 1 ml of 10% solution of sodium chloride’. Gold sol is ruby red in color and becomes blue on coagulation.

Gold number of protective colloids

Sl No.	Colloid	Gold number
1.	Gelatin	0.005-0.01
2.	Casein	0.1
3.	Gum Arabic	0.15-0.25
4.	Dextrin	6-20
5.	Starch	25.0

9.13 STABILITY OF SOLS

A true colloidal solution is stable. The stability of sols is mainly due to two factors:

9.13.1 (a) Presence of charge on colloidal particles

The dispersed particles of lyophobic sols possess a like electrical charge either positive or negative, on their surface. Since like charges repel one another, the particles push from one another and resist joining together.

However by the addition of electrolyte the lyohobic sol particles are discharged and precipitated.

(b) Presence of solvent layer around sol particle

The lyophilic sols are stable for two reasons. Their particles posses a charge and in addition have a layer of solvent bound on the surface. For example, a sol particle of gelatin has a negative charge and a water layer envelopes it. When sodium chloride is added to colloidal solution of gelatin, its particles are not precipitated. The water layer around the gelatin particle does not allow the Na^+ ions to penitrate it and discharge the particle. Thus gelatin sol is not precipitated the addition of sodium chloride solution.

Now it should be clear to you that why lyophilic sols are more stable than lyophobic sols. Generally lyohobic sols are coagulated by electrolytes at 0.001-0.1M concentrations. The coagulation is irreversible process and removal of coagulating electrolyte does not allow the coagulam to be redispersed.

Lyophilic sols on the other hand are not easily coagulated. They require much higher concentration of electrolyte **(usually of the order of 1M)** for precipitation. The coagulation of lyophilic sol by the addition of

electrolytes is not due to neutralization of charge on the particle.The electrolyte binds part of the water thereby getting hydrated. As a result, the polymer molecules in the lyophilic sol get dehydrated. The dehydration leads to coagulation.

Various ions are arranged in increasing order of their efficacy for coagulating a lyophobic sol in the form of series as shown below:

$Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^{+} > K^{+}$

$SO_4^{2-} > Cl^{-} > NO_3^{-} > ClO_3^{-} > 1^{-}$

9.13.2 Electrophoresis:

Since the solid particles and the liquid medium carry opposite charges, it is obvious that when an electrical field is applied, the particles and the liquid will migrate is opposite direction. The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis.

If the sol particles migrate toward the positive electrode, they carry negative charge. On the other hand, if they move toward the negative electrode they are positively charged. Thus by noting the direction of movement of the sol particles, we can determine whether they carry positive or negative charge.

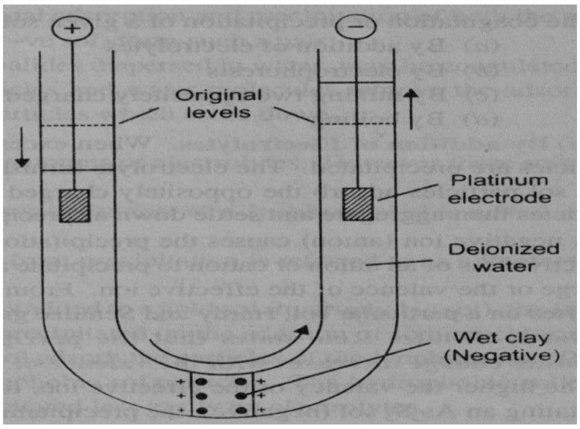


Fig-9.9

The phenomenon of electrolysis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side (fig-9.9). This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged. Similarly a sol of ferric hydroxide will move to the negative electrode showing that its particle carry positive charge.

Aplications of electrophoresis:

Some important applications of electrophoresis are: (1) Removal of smoke from chimney gases; (2) Removal of suspended impurities ; (3) Electroplating of rubber on metal surfaces from latex (a sol) ; (4) Painting of metal parts of cars from colloidal pigmants.

9.13.3 Electro-osmosis:

The movement of dispersion medium with respect to dispersed phase as a result of an electric field is known as electro-osmosis. Or when electrophoresis of dispersed particles in a colloidal system is prevented by suitable means, it is observed that the dispersion medium itself begins to move in an electric field. This phenomenon is called electro-osmosis.

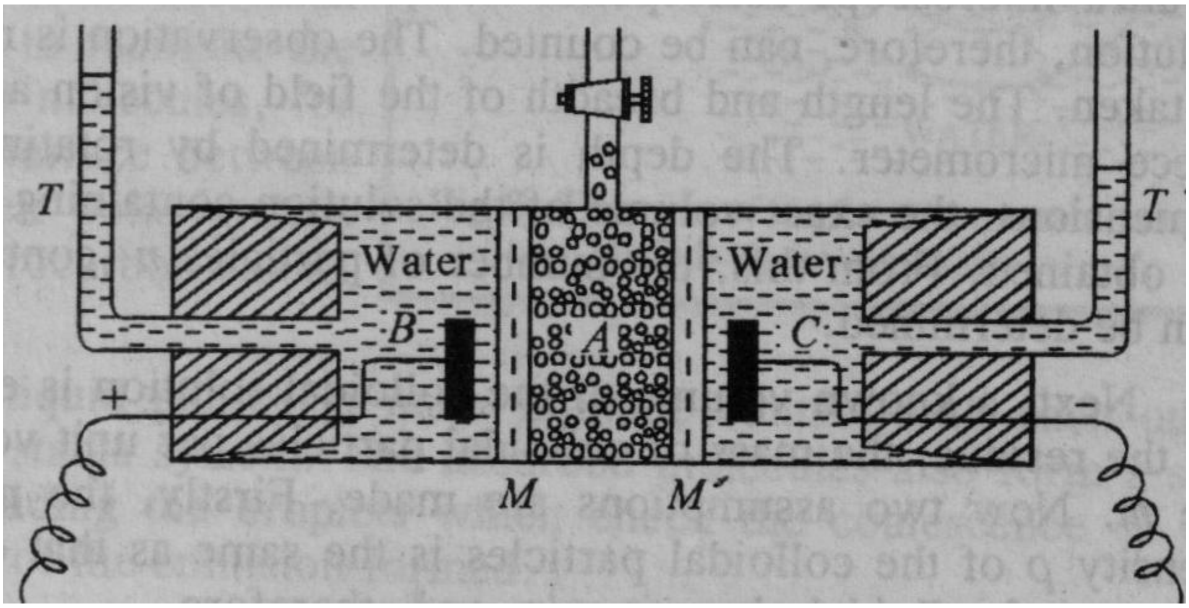


Fig-9.10

It can be observed as shown in **(fig 9.10)**

The colloidal system is put in a central chamber A which is separated from the side chambers B and C with water, by a dialysing membranes M and M^-. The water in the chamber B and C extends to the side tubes T and T^- respectively. The membrane does not allow the colloidal particles to pass through it. So when a potential difference is applied across the electrodes held close to the membranes in chambers B and C, the water starts to move. If the particles carry negative charge, the water will carry positive charge. So it would start moving towards the cathode and so the level of water in side tube ‘T^{--}’ would be observed to rise. If on the contrary the particles carry positive charge the water will carry a negative charge. The level of water will now start moving towards the anode and its level in the side tube T would start rising.

The theoretical interpretation of electro-osmosis has been given by Helmholtz, Lamb, Perrin and Smoluchowski.

Application of electro-osmosis:

(i) In the preparation of pure colloids. The case in point is the preparation of colloidal silicic acid of low molecular weight i.e. in a state of fine subdivision.

(ii) In the tanning of hides and impregnation of similar materials.

(iii) In the manufacture of gelatin for photographic emulsions. The object is to get a gelatin free from fat, mineral and reducing constituents. The phenomenon is also applied in the manufacture of high grade glue.

(iv) In the dying of peat, a process due to Schwerin.

9.14 DETERMINATION OF SIZE OF COLLOIDAL PARTICLES

There are number of methods for the determination of size of colloidal particles. Some important methods are given below-

9.14.1 Ultra-filtration method

The size of the pours of the ultrafilters can be calculated from the measurement of the pressure required to force air through the membrane saturated with water or by measuring the volume of water forced through unit area of the membrane in unit time by a known pressure. It may be repeated that in addition to the size of the particle, adsorption and electric charge will hold the particles and may simulate a lower porosity than should be present according to the size of the pours of the ultrafilters.

By finding which of the ultrafilters will just permit the particles of a sol to pass into the filtrate, while the next filter just stops the passage, the diameter of the colloidal particle can be determined, provided the particles are assumed to be spherical.

9.14.2 From Brownian movement

Colloidal particles suspended in the liquid medium exhibit Brownian motion. They tend to settle down due to gravity. Due to the influence of both these effects, the colloidal particles distribute themselves in a vertical column according to the equation:

$$\frac{2.303RT}{N} \log_{10}\left(\frac{n_1}{n_2}\right) = \frac{4}{3}\pi r^3 (h_2-h_1)(d-d^1) \ldots\ldots\ldots\ldots\ldots(a)$$

Since the number of particles n_1 and n_2 at heights h_1 and h_2 of the vertical column can be counted with the help of ultramicroscoe and densities d and d^1 of the dispersed phase and dispersion medium can be determined by

usual methods. Knowing the value of Avogadro’s number (N) r the radius of the particle can be calculated.

9.14.3 From Scattering of light

Zsigmondy used ultramicroscope for determining size of colloidal particles. Each spot of light seen in an ultramicroscope, corresponds to a particle. So the number of particles in a given volume of a solution can be counted. The observation is made a number of times and an average is taken. The length and breadth of the field of vision are measured by an eye piece micrometer. The depth is measured by rotating the slit through 90^0. From this data the exact volume of the solution containing the observed number of particles can be measured. Thus the number of particles per unit volume of the solution can be calculated.

Next, a known volume of a colloidal is evaporated to dryness. From the weight of residue the mass of colloidal particles per unit volume is calculated. Let it be m gm, Now assuming the colloidal particles to be spherical and density of (d) of the colloidal particles to be the same as that in the bulk state, the volume of the colloidal phase is

$$\frac{m}{d} = \frac{4}{3}\pi r^3 n$$

Hence r can be calculated.

9.15 ASSOCIATED COLLOIDS OR COLLOIDAL ELECTROLYTES

The molecule of substances as soap and artificial detergents are smaller than the colloidal particles. However in concentrated solutions these molecules form aggregates of colloidal size.

Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called associated or associated colloids.

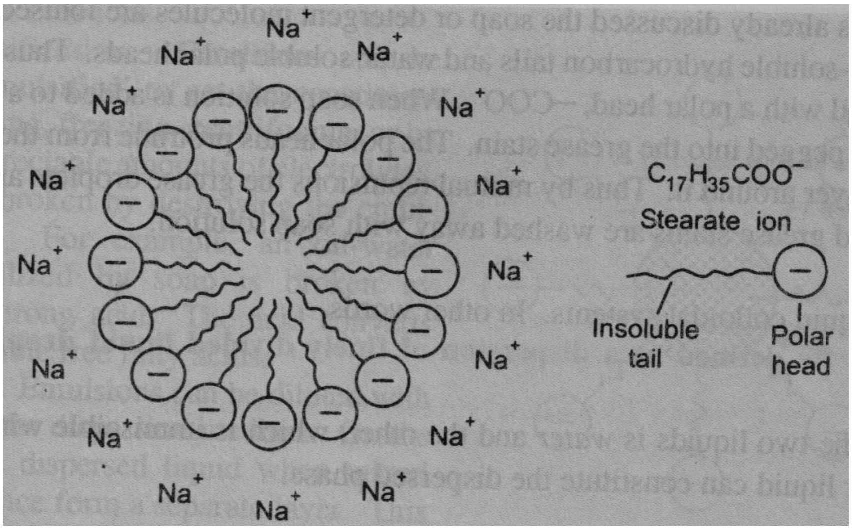


Fig-9.11

The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as micelles.

Example is sodium stearate $C_{17}H_{35}COO^-Na^+$

Explanation:

Soap or detergent molecules ionises in water to form an anion and sodium ion. Thus we get $C_{17}H_{35}COO^-$ ano Na^+ ions. As many as 70 stearate ions aggregate to form a miscelle of colloidal size. The stearate ion has a long carbon chain (17 carbons) with a polar – COO^- group at one end. The zig zag hydrocarbon tail is shown by a wavy line and the polar head by a hollow circle. In the micelle formation, the tail being insoluble in water are directed toward the centre, while soluble polar heads are on the surface in contact with water (fig-9.11). The charge on the micelle due to the polar heads accounts for the stability of the particle.

9.16 EMULSIONS

Definition

Dispersion of finely divided liquid droplets in another liquid are called emulsion. The particles of dispersed phase in emulsions are generally bigger than those is sols and are sometimes visible under microscope. In most of the cases one of the liquid phases is an oil and the other is water. Accordingly, there are two types of emulsions: oil-in-water (O/W) type in which oil is the dispersed phase and water is the dispersion medium and water-in-oil (W/O) type in which water is the dispersed phase and oil is dispersion medium.

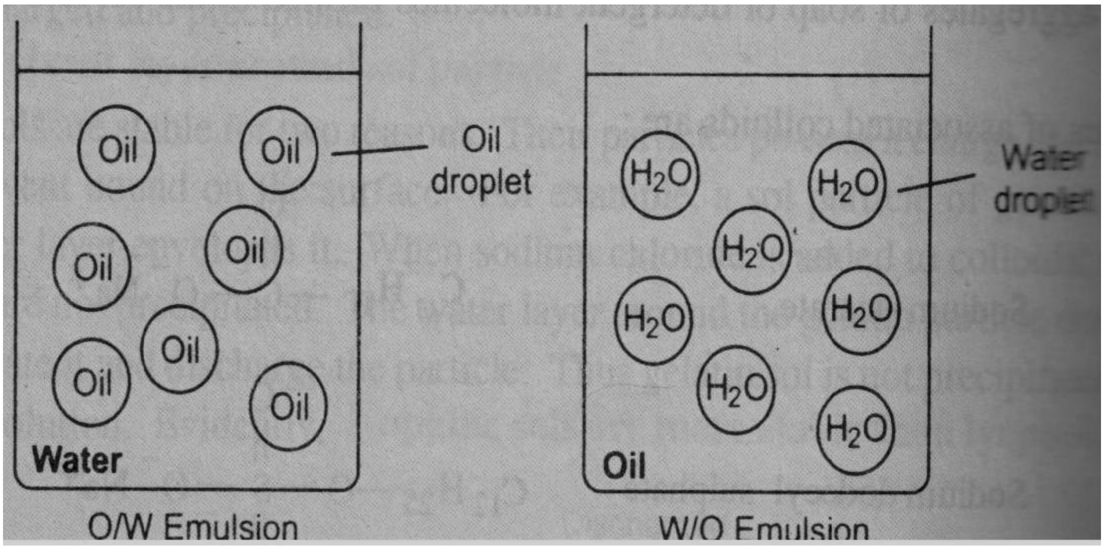


Fig-9.12

Milk is an emulsion of O/W type in which tiny droplets of fat are dispersed in water. Stiff greases are emulsions of W/O type, water being dispersed in lubricating oil.

Emulsifiers

When two imericible liquids such as a hydrocarbon oil and water are shaken together vigorously a milky looking solution result.

This is an emulsion consisting of small droplets of oil suspended in water. However the droplets remain suspended in water for a short time only. On standing the two liquids soon separate, the oil droplets rising to the top and forming a separate oil phase. This is because the cohesive forces between the molecules of each layer exceed the adhesive forces between two liquids. In

other words the emulsion formed by merely shaking the two immiscible liquids together is highly unstable. In order to get stable emulsions of fairly high concentrations it is necessary to add another substance known as emulsifier or emulsifying agent in a small quantity.

Role of emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid which rolls into droplets. Soap for example is made of a long hydrocarbon tail, which is oil soluble, with a polar head – $COONa^+$ (water soluble).

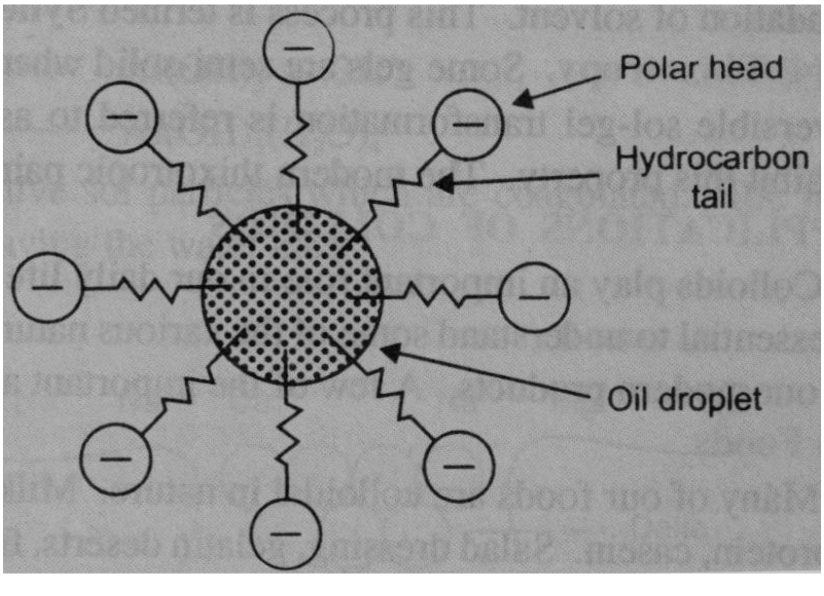


Fig 8.13

In O/W type emulsions the tail is pegged into the oil droplet which the head extends into water. Thus the soap acts as a go-between and the emulsified droplets are not allowed to coalesce.

9.17 GELS

Definition

Several lyophilic sols and a few lyophobic sols, when coagulated under certain conditions, change into a semi-rigid mass, enclosing the entire amount of the liquid with in itself. Such a product is gel. The process of transformation of a sol into a gel is known as gelation.

Gel is a colloidal solution in which a liquid is dispersed in a solid.

Elastic and non elastic gels:

There are two types of gels namely elastic gels and non-elastic gels. Elastic gels are reversible. When partially dehydrated, they change into a solid mass which however changes back into original form on simple addition of water followed by slight warming if necessary. Non-elastic gels are irreversible. When dehydrated they become glassy or change into a powder which on addition of water and followed by warming does not change back into the original gel.

Gelatin, agar-agar and starch are examples of elastic gels as they are reversible. Silica, alumina and ferric oxide gels are non-elastic as they are irreversible.

Elastic gels can imbibe water when placed in it and undergo swelling, non-elastic gels are incapable of doing so. This phenomenon is known as imbibition or swelling.

9.17.1 Sol-gel transformation

Sol transformation is a phenomenon in which a gel is formed from a sol. When a freshly prepared sol of CeO_2 containing about 10g per litre was transformed into a gel by coagulation with electrolyte. But if the sol of CeO_2 was kept for 200-300 days then it lost its power and gave a precipitate instead of a gel, by the addition of electrolytes. But in case of some lyophilic sols, such as gelatin in water, agar in water, the sol-gel transformation is well known and the transformation is reversible with in certain limits.

If gelatin sol is prepared by heating gelatin with water upto 70^0C, and it is then cooled, it is seen that the sol sets to a gel at low temperature. If the gel is again warmed, it liquefies to a sol. This process can be repeated as and when desired. This sol- gel transformation is actually reversible as long as the temperature 65^0-70^0 is not exceeded. At higher temperature the product formed are not reversible and sol-gel transformation does not take place.

9.18 APPLICATION OF COLLOIDS

Colloids play an important role in our daily life as well as in industry, agriculture, medicine and biology.

(i) Foods:

Many of our foods are colloidal in nature. Milk is an emulsion of butter fat in water protected by a protein, casein. Casein in nutrient of great value. Gelatin is added to ice cream (colloidal solution of ice in cream) as a protective agent as as to presence its smoothness.

Whipped cream, fruit jellies, salad dressings egg and a host of other materials used as food are colloidal in nature.

(ii) Medicines:

A number of medicinal and pharmaceutical preparations are emulsions. It is believed that in this form they can be more effective and are easily assimilated. Many ointments for application to skin consist of physiologically active components dissolved in oil and made into an emulsion with water.

Antibiotics such as penicillin and streptomycin are produced in colloidal form suitable for injections.

(iii) Electrical precipitation of smoke:

Smokes and dusts are a nuisance and create health problems in industrial areas. Actually those are dispersions of electrically charged colloidal particles in air.

The removal of these particles from air involves the principle of electrophoresis. The air from a furnace or industrial plant carrying these particles is passed between metal electrodes maintained at high difference of potential (about 50,000 volts). The particles are discharged and deposited as precipitates on the oppositely charged electrodes from which they can be scrapped mechanically.

(iv) Industrial goods:

Soap is a colloidal electrolyte. A series of newer detergent and wetting agents have been produced in recent years. Paints varnishes, enamals, celluloses, resins, gums, glues and other adhesives: rayon, nylon, terylene textiles, leather, paper etc. Are all colloidal in nature. Industrial processes such as tanning, dyeing, lubrication etc are all colloidal in nature.

(v) Rubber-plating:

The negatively charged particles of rubber (latex) are made to deposit on to wires or handles of various tools (in order to insulate them) by electrophoresis. The article to be rubber plated is made the anode. The rubber particles migrate in an electrical field towards the anode and get deposited on it.

(vi) Sewage disposal:

Sewage water consists of particles of dirt, rubbish, mud etc which are of colloidal dimensions and carry electrical charge and therefore do not settle down easily. On creating an electrical field in the sewage tank, these

Particles migrate to the oppositely charged electrodes, get neutralized and settle down at the bottom. This is electrophoresis property of colloids.

(vii) Detergent action of soap:

Most of the dirt and dust sticks on to grease or some oily material which somehow gathers on cloth. As grease is not easily wetted by water. It is difficult to clean the garments by water alone. The addition of soap lowers the interfacial tension between water and grease and this causes the emulsification of grease in water. The mechanical action, such as rubbing etc releases the dirt.

(viii) Artificial kidney machine:

Human kidneys purify blood by dialysis through natural membranes. The toxic waste products such as urea and uric acid pass through the membranes while colloid size particles of blood proteins are retained. Kidney failure therefore leads to death due to accumulation of poisonous waste products in blood. Now-a-days patient’s blood can be cleansed by shunting it into a artificial kidney machine. Here the impure blood is made to pass through a series of cellophane tubes surrounded by washing solution in water. The toxic waste chemicals diffuse across the tube walls into the washing solution. The purified blood is returned to the patient.

(ix) Formation of deltas:

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand contains positive ions such as Na^+, Mg^+, $Ca^{2+.}$ As the river water meets sea water these ions discharge the sand or clay particles which are precipitate as deltas.

Other uses are purification of water formation of smoke screen artificial rain and many more.

9.19 MACROMOLECULES

Definition

Colloidal solutions are formed by aggregation of atoms or molecules to give paticles of colloidal size. There are substances which are themselves composed of giant molecules and dissolve in a solvent to yield colloidal solution directly. These giant molecules are termed macromelecules or polymers.

The dimensions of the macromolecules fall in a range between $10A^0$ to $10,000A^0$. The molar mass of polymer may vary from 5000 to several millions. Proteins, synthetic polymers (plastic), synthetic rubber, cellulose and starch all posses macromolecules.

Solutions of macromoelcules behave like reversible colloids or lyophilic sols. They show a weak Tyndall effect and possess high viscosity. Macromolecules in solution do not carry an electric charge and do not show electrophoresis.

Research in synthetic polymer chemistry has grown at huge pace. Several industries in U.S.A. Japan and some Europian countries have specialized in the synthesis of high molar mass compounds from low molar mass compounds as starting materials. Some industries have specialized in the production of plastic, synthetic rubber, synthetic fibre, lacquers, paints varnishes, adhesives and insulators. In fact plastic industry covers several varities of systhetic polymers having wide range of properties. Some of them are superior to even gold and platinum in chemical resistance and retain their mechanical propertics even when cooled to -50^0C and heated to 500^0C. The strength of other polymers equals that of metals approaching even diamond in hardness. Some varieties of systhetic rubbers act as gas-impermeable and petrol and oil-resistant. Synthetic fibres are far stronger than natural fibres. These can be converted into crease proof fabrics and excellent artificial furs.

A major discovery in the late 1970’s was the preparation of conducting organic polymers such as hydrogen derivative of polyacetylene and the one-dimensional polymers $(SN)_{x.}$

9.19.1 Molecular weight of macro molecules

The molecular weight is an important property of polymeric substances such as proteins, polymers (plastics, starch) and other macro molecules. Generally; molecules of protein or a polymer may not be of the same size. Therefore all the experimental methods of molecular weight determination will give some kind of an average value. Two types of average molecular weights have been defined.

(i) Number-average molecular weight M_N

(ii) Mass-average molecular weight M_M.

For a sample consisting of N polymer molecules containing n_1 monomer molecules of molar mass M_1, n_2 monomer molecules of molar mass M_2, etc, the number-average molecular weight is defined as

$$M_N = \frac{n1M1+n_2M_2+}{n_1+n_2\ldots..} = \sum niMi/ \sum ni \ldots\ldots\ldots\ldots\ldots (1)$$

And mass-average molecular weight is

Defined as

$$M_M= \frac{n_1M_1^2+n_2M_2^2+\ldots\ldots}{N_1M_1+n_2M_2+\ldots\ldots} = \sum niMi^2 /\sum niMj \ldots\ldots.(2)$$

If c denotes the concentration of polymer solution in grams per unit volume then

$Ci=\sum niMi$

so that $M_M = \sum niMi^2/\sum ci$

The mass- average molecular weight is larger than the number-average molecular weight.

Determination of molecular weight of macro-molecules:

There are a number of methods available for the determination of molecular weight of macromolecules.

(1) Osmotic pressure measurement

(2) Diffusion method

(3) Sedimentation method

(4) Viscosity determination method

(5) Light scattering method

Viscosity method:

It is a simple method for determining molecular weight of macromolecules. The pressure of macromolecules raises the viscosity of the solvent. By measuring the viscosity of pure solvent and the solution in the laboratory we can calculate the molecular weight of the polymer.

The relative viscosity of a solution of a polymer, denoted by $ή_r$ is given by the expression

$ή_r = ή/ ή_0$ ....(1)

Where ή is viscosity of the solution and $ή_0$ is viscosity of pure solvent at same temperature.

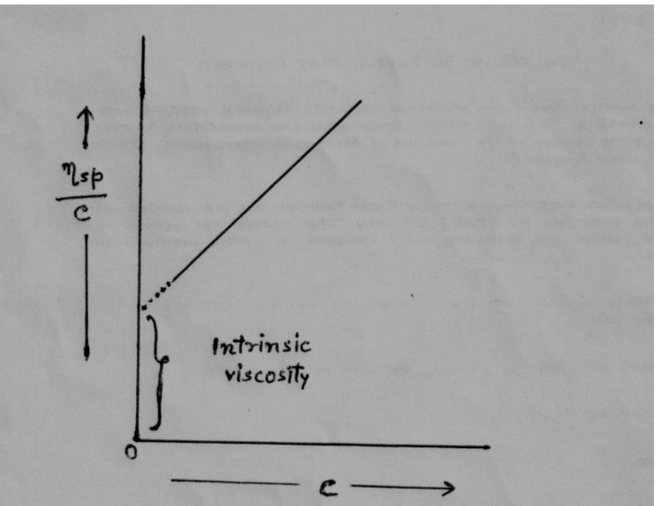


fig 8.14 Plot of η_{sp}/c versus c.

The specific viscosity, $ή_{sp}$ is given by

$ή_{sp} = ή_r - 1$ …….(2)

in terms of eqn.(1) and eqn.(2) intrinsic viscosity is defined as

$[ή] = \lim (ή_{sp}/c)$

$c \rightarrow 0$

where c is concentration of solute. The plot of $ή_{sp}/c$ against c gives a straight line. Extrapolation to c=0 yields the intrinsic viscosity.

Fig(8.4)

It was shown by Staudinger that the empirical relationship exist between intrinsic viscosity [ή] and molecular weight [M] of high polymer

$[ή] = kM^x$

Where k and x are constant for a specific polymer in a specific solvent. Once k and x are known for a polymer solvent combination, M may be calculated.

9.20 SUMMARY

- In this chapter you have studied that colloidal system is a two phase heterogeneous system in which one phase is dispersed in a fine state of subdivision in another medium termed as dispersion medium. In actual instances the size limit is not rigid and may vary on either side but most systems conform to the above description.
- The wide variety of proteins obtained from the living world form the most important group of naturally occuring macromolecules. These are produced from repetitive linking of various amino acids. As a result the proteins are amphoteric in nature.
- The sub-topics studied in this chapter include definition, type of colloidal systems, properties of sols. Preparation of sols, purification of sols, zeta potential, electrophoresis, electro-osmosis, coagulation of colloids, origin of charge on colloidal particles.
- Emulsions and gels and their properties have also been studied in this chapter. Most important above all is wide range of uses of colloids in different areas in our daily life and industry.

9.21 TERMINAL QUESTIONS

(A) Short answer questions:

1. How are colloidal solutions classified.What is meant by colloidal state of matter.
2. Explain why-

(a) Deltas are formed at a place where the rivers pour their water into the sea.

(b) Define number average and weight average molecular weight.

(B) Long answer questions:

1. What is a molecular colloid? How does a lyophilic colloid stabilise a lyophobic one? Give an account of gold number in this respect.
2. Discuss the origin of charge on colloidal particles. What is meant by electrical double layer?
3. What are lyophilic and lyophobic sols? Discuss the main differences between lyophilic and lyophobic colloids.
4. Explain the following:
   (a) stability of colloids
   (b) Difference between gels and emulsions.
   (c) The Schulze-Hardy rule of coagulation.
5. What are various methods for determining size of the colloidal particles? Describe one method in detail.
6. Write a note on Brownian movement.

UNIT 10: THERMODYNAMICS-I

CONTENTS:

10.11 Internal energy and first law of thermodynamics

10.12 Mathematical statement of the first law of thermodynamics

10.13 Enthalpy of a system

10.14 Relation between ∆H and ∆E

10.15 Heat capacity

- 10.15.1 Heat capacity at constant volume
- 10.15.2 Heat capacity at constant pressure
- 10.15.3 Internal energy change with volume and pressure:
- 10.15.4 Relation between C_P and C_V

10.16 Joule-Thomson effect

- 10.16.1 Joule-Thomson experiment
- 10.16.2 Explanation
- 10.16.3 Joule-Thomson coefficient
- 10.16.4 InversionTemperature

10.17 Reversible work: isothermal expansion, isothermal compression and adiabatic

- 10.17.1 Isothermal reversible expansion
- 10.17.2 Work done in isothermal reversible compression
- 10.17.3 Maximum work
- 10.17.4 Work done in isothermal irreversible expansion
- 10.17.5 Adiabatic expansion
- 10.17.6 Calculation of dE, and dH

10.18 Summary

10.19 Terminal questions

10.1 OBJECTIVES

After study this unit you will be able to

- Know the concept of thermodynamics
- Know about the heat and work as well as form of energy and the conversion of heat into useful work.
- Explain the transformation of heat into work but also includes all types of inter-conversion of one kind of energy into another; e.g., electricity into work, chemical energy to electrical energy, etc.
- Explain the heat engines with particular reference to the conversion of heat into useful work.
- Know the laws of thermodynamics i.e. first, second and third law.

10.2 INTRODUCTION

The study of flow of heat or any other form of energy into or out of a system as the system undergoes a physical or chemical transformation is called thermodynamics. The most distinguishing feature of thermodynamics, however, is its predominant concern with temperature and temperature-dependent variables.

Thermodynamics is essentially a practical science and it has its verification extending mainly to the fields of chemistry, physics and engineering. With the assistance of thermodynamics the chemist predicts the possibility of a chemical reaction or the maximum yield in a chemical process under a given set of circumstances. Using thermodynamic laws the physicist explains the phenomena where phase changes or inter-actions with radiations or electromagnetic field are involved. To the engineers it is the most powerful weapon to solve problems of power and consumptions, in the prediction of efficiencies of heat-engines and refrigerators, in the design of engines and so on.

The thermodynamic principles correlate different observable properties of a system but cannot always give us the exact magnitude of a property of the system. These relations help us in predicting the behaviour of a system or the ultimate result that a process would lead to. Thus, from thermodynamics we can predict under a set of defined conditions the maximum yield in a chemical process, but we cannot say anything about the rate of the reaction or the mechanism of the reaction.

Thermodynamics does not make any hypothesis as to the structure of matter. Thermodynamics derives from various laws, relations between properties experimentally observed but not offer any explanation as to why these properties arise in a system. The approach in thermodynamics is thus entirely different from that in the atomic constitution of matter. For example, in kinetic theory we consider the pressure of a gas is measure of the impact of the molecules on the wall per second, while in thermodynamics, pressure is a property of the state of a system. Similarly temperature is, according to kinetic theory, a measure of the average kinetic energy of the molecules while it is a simple property of state from the view-point of thermodynamics.

10.3 DEFINITION OF THERMODYNAMIC TERMS

10.3.1 Temperature

The hotness or the coldness of an object is understood fundamentally by our senses. The hotter body will have a higher temperature than the colder body. We also have another experience in nature. Suppose there are two bodies, A and B, A being hotter than B. If A is brought in contact with B, it is found that A gradually becomes colder and B becomes warmer. During this process, other changes in pressure or volume may also occur. Ultimately, we find that both A and B are equally warm, i.e. they have attained the same temperature. A and B are now said to be in thermal equilibrium. During this process, some energy (really the heat-energy) have moved from the hotter body A to the colder body B. Temperature then determines the direction in which in which heat would flow, namely, from the hotter body to colder body. In other words “temperature is the driving forces for the flow of heat.”

Zeroth law of thermodynamics:

Let us consider three systems A, B and C. Suppose A is in thermal contact with B through a diathermic wall. A diathermic wall is that which permits the systems in contact to influence each other. And again B is also in thermal contact with C (fig 10.1). Sufficient time being allowed A will be in thermal equilibrium.

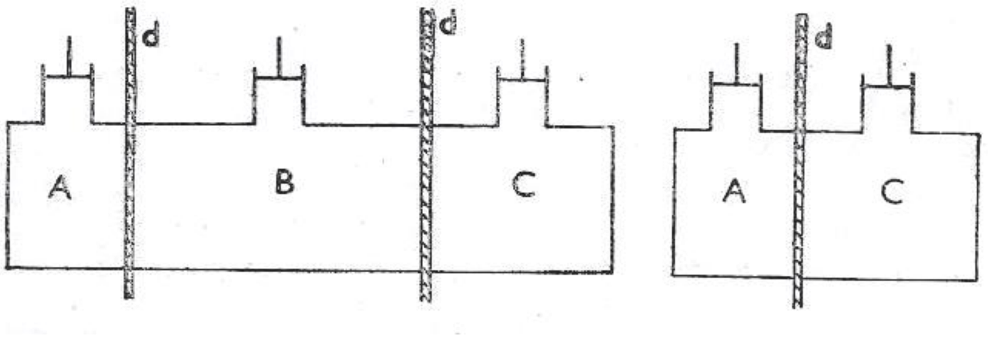


Fig 10.1 Zeroth law of thermodynamics

With B. Similarly, C will also in thermal equilibrium with B. If B is now removed and A is brought in thermal contact with C, it is found that there is no change in the coordinates of A and C. The systems A and C are in thermal equilibrium with each other. Hence

“Two systems in thermal equilibrium with a third are in thermal equilibrium with each other”. This is Zeroth law of thermodynamics.

10.3.2 System and surroundings

A system may be defined as any specified portion of matter under study which is separated from rest of the universe with a bounding surface. A system may consist of one or more substances.

The rest of the universe which might be in a position to exchange matter and energy with the system with the system is called surroundings. The real or imaginary surface separating the system from the surroundings is called the boundary. The boundary may be real or imaginary.

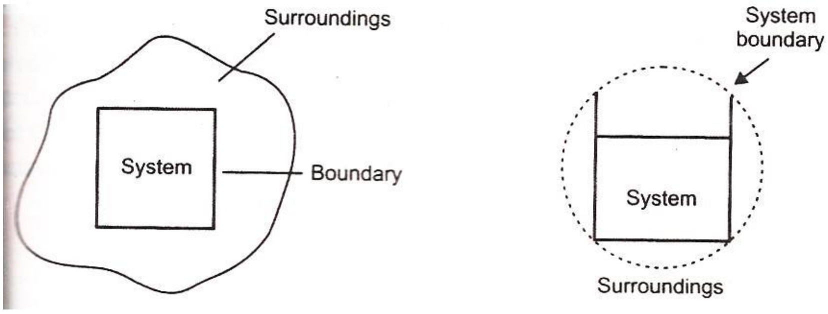


Fig 10.2 thermodynamic system and surroundings

A quantity of a gas in a closed cylinder has real and defined boundaries, but if the same gas flows through a zigzag pipe, its boundaries constantly change and have to be followed in imagination as it progresses. If say 250 ml of water contained in a beaker it will constitute a thermodynamic system. The beaker and the air in contact, are the surroundings.

If one mole of a gas confined in a cylinder fitted with a piston, is a thermodynamics system. The cylinder, the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (gas) and the surroundings (cylinder and piston) is clearly defined. A system and its surroundings constitute the universe.

System + surroundings = universe

10.3.3 Homogeneous and heterogeneous system

A system is said to be homogeneous if it is completely uniform throughout. In such a system there is only one phase. A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system. Examples of homogeneous system are pure single solid, liquid or gas, mixture of gases and true solution of solid in a liquid.

A system is said to be heterogeneous, when it is not uniform throughout. In such a system there are two or more phases. Examples of heterogeneous system are: ice in contact with water, ice in contact with vapour, etc. Here ice, water and vapour constitute separate phases.

10.3.4 Types of systems

There are three types of thermodynamics systems depending on the nature of boundary.

10.3.4.1Open system

A system which can exchange matter as well as energy with its surroundings is said to be an open system. Hot water contained in a beaker placed on laboratory table is an open system. Here the water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

10.3.4.2 Closed system A system which can exchange energy not matter with its surroundings is called a closed system. A specific quantity of hot water contained in a sealed tube in an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of tube to the surroundings.

10.3.4.3 Isolated system A system which can exchange neither matter nor energy with its surroundings is called an isolated system.

Let us consider a system 100 ml of water in contact with its vapour in a closed vessel which is insulated. Since the vessel is sealed, no water vapour (matter) can escape from it. Also as the vessel is insulated, no heat (energy) can be exchanged with its surroundings.

Isothermal and adiabatic systems:

If a system is maintained at a constant temperature it is termed as isothermal system. If a system is so insulated from its surroundings that no heat flows in or out of the system its termed as adiabatic system.

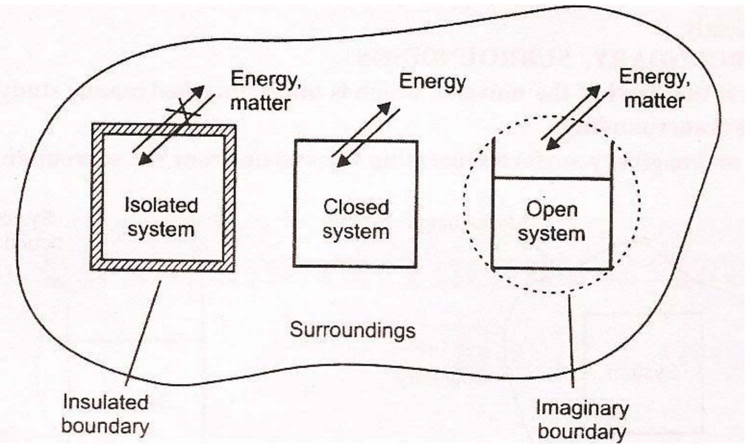


Fig 10.3 three types of thermodynamic systems

10.3.5 Intensive and extensive properties

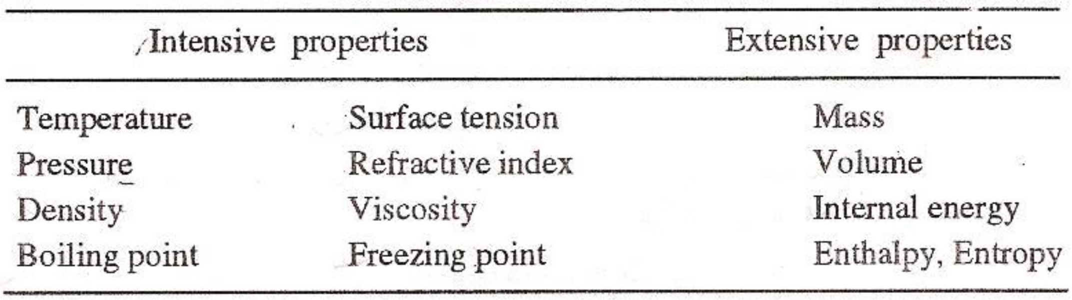
The macroscopic or bulk properties of a system (volume, pressure, mass etc.) can be devided into two classes

(a) Intensive properties

(b) Extensive properties

In intensive property of a system is that which is independent of the amount of the substance present in the system. The examples are temperature, pressure, density, concentration, viscosity. Refractive index, surface tension and specific heat.

A property that does depend on the quantity of matter present in the system is called an extensive property. Some examples of extensive properties are volume, no. of moles, enthalpy, entropy, mass and Gibbs free energy.



Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

Table 10.1 common properties of a system

10.3.6 Processes and their types

When a thermodynamic system changes from one state to another, the operation is called a process. When a system changes from one state to another it is accompanied by change in energy. In the case of open systems, there may be change of matter as well.

The following types of processes are known:

(1) Isothermal process:

A process is said to be isothermal if the temperature of the system remains constant during each state of process. For an isothermal process dT=0

(2) Adiabatic process:

A process is said be adiabatic if no heat enters or leaves the system during any step of the process. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos bottle.' High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process dq=0

(3) Isobaric process:

Those processes which take place at constant pressure are called isobaric processes. Heating of water to its boiling point and its vaporisation takes place at the same atmospheric pressure is an example of isobaric process.

For an isobaric process DP=0

(4) Isochoric process:

A process in which volume remains constant is known as isochoric process. The heating of a substance in a non-expanding chamber is an example of isochoric process.

For an isochoric process dV=0

(5) Cyclic process:

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cyclic process.

For cyclic process dE=0, dH=0.

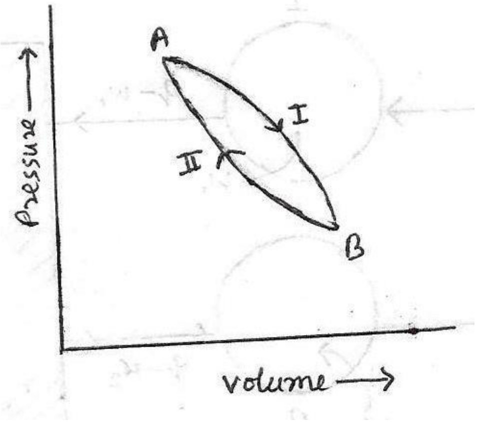


Fig 10.4 cyclic process

10.4 REVERSIBLE AND IRREVERSIBLE PROCESSES

A process carried out infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of a system is a reversible process.

In fact, reversible process is considered to proceed from initial state to final state through an infinite series of infinitesimally small stages. At the initial, final and all intermediate stages, the system is in equilibrium state, this is so because an infinitesimal change in the state of the system at each intermediate step is negligible.

When a process goes from initial state to the final state in a single step and cannot be carried in the reverse order, it is said to an irreversible process. Here the system is in equilibrium state in the beginning and at the end, but not at points in between.

A reversible process cannot be realised in practice, it would require infinite time for its completion. Hence, all those reactions which occur in nature or in laboratory are irreversible. A reversible process is thus theoretical and imaginary.

Example:

Let us consider a certain quantity of gas contained in a cylinder having a weightless and frictionless piston. The expansion of the gas is carried out by two methods illustrated in fig 10.5.

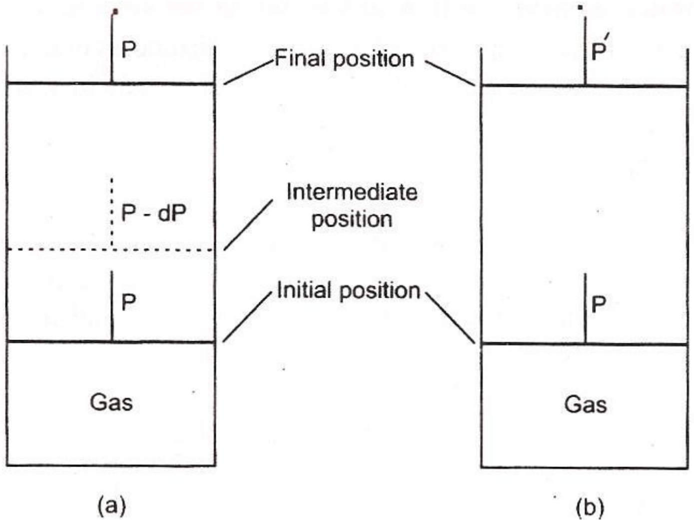


Fig 10.5 reversible expansion of a gas (a) irreversible expansion of a gas (b)

Let the pressure applied to the piston be P and this is equal to the internal pressure of the gas. Since the external and internal pressure are exactly counterbalanced, the piston remains stationary and there is no change in the volume of the gas. Now suppose the pressure on the piston is decreased by an infinitesimal amount dP. Thus the external pressure on the piston being P-dP, the piston moves up and the gas will expand by an infinitesimal small amount. The gas will, therefore, be expanded infinitely slowly i.e., by a thermodynamically reversible process. At all stages in the expansion of the gas, dP being negligibly small the gas is maintained in a state of equilibrium throughout. If at any point of the process the pressure is increased by dP, the gas would contract reversibly (Fig 10.4 a).

On the other hand, the expansion is irreversible (Fig 10.4b) if the pressure on the piston is decreased suddenly. It moves upwards rapidly in a single operation. The gas is in equilibrium state in the initial and final stages only. The expansion of the gas, in this case, takes place in an irreversible manner.

10.5 STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed. The fundamental properties which determine the states of a system are pressure (P), temperature (T), volume (V), mass and composition. Since the change in the magnitude of such properties alters the state of the system, these are referred to as state variables or state functions or thermodynamic parameters.

In actual practice, it is not necessary to specify all the variables because some of them are interdependent. In the case of a single gas composition is fixed, because it remains always 100 percent. Further, if the gas is ideal and one mole of gas is under examination, it obey's the equation PV=RT, where R is universal gas constant. Hence it is clear that if only two of the three variables (P,V and T) are known, the third can easily be calculated. The two variables, generally specified, are temperature and pressure. These are called independent variables. The third variable, generally volume, is said to be dependent variable, as its value depends on the value of P and T. Thus, the thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables, viz. temperature pressure and volume.

In a closed system, consisting of one or more components, mass is not a state variable.

10.6 THERMODYNAMIC EQUILIBRIUM

A system in which the state variables have constant values throughout the system is said to be in a state of thermodynamic equilibrium. In fact, the term thermodynamic equilibrium implies the existence of three kinds of equilibrium in the system. These are (i) thermal equilibrium (ii) mechanical equilibrium and (iii) chemical equilibrium.

10.6.1 Thermal equilibrium

A system is said to be in thermal equilibrium if there is no flow of heat from one portion of system to another. This is possible if the temperature remains the same throughout in all parts of the system.

10.6.2 Mechanical equilibrium

A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible if the pressure remains the same throughout in all parts of the system.

10.6.3 Chemical equilibrium

A system is said to be in chemical equilibrium if the composition of the system is uniform and there is not net chemical change.

Difference between reversible and irreversible processes.

	Reversible process	**Irreversible process**
1.	It takes place in infinite number of Infinitesimally small steps and it would take infinite time to occur.	It takes place in finite time.
2.	It is an imaginary process as it assumes the presence of frictionless and weightless piston.	It is real and can be performed actually.
3.	It is an equilibrium state at all stages of of the operation.	It is an equilibrium state only at the initial and final stages of equilibrium.
4.	All changes are reversed when the	After this type of process has

	process is carried out in reverse direction.	occurred all changes do not Return in the initial state by themselves.
5.	It is extremely slow.	It proceeds at measurable speed.
6.	Work done by a reversible process is greater than the corresponding irreversible process.	Work done by an irreversible process is smaller than the Corresponding reversible Process.

10.7 NATURE OF HEAT AND WORK

Whenever a system changes from one state to another, there is always a change in energy. The change in energy may appear in the form of heat, work, light etc.

We shall refer the term ‘work’ for mechanical work which is defined as

Force X work.

James Joule, in 1850, showed that there is a definite relationship between mechanical work W and heat produced H (If we rub our palms together we feel the warmth).

$$W \alpha H \qquad \text{or} \qquad W=JH$$

J is known as the joule mechanical equivalent of heat.

In CGS system the unit of energy is erg. Which is defined as the work done when a resistance of one dyne is moved through a distance of one centimetre? Since erg is small quantity, a bigger unit, called joule (=10^7 ergs) is often used.

$$1 \text{ joule} = 10^7 \text{ ergs}$$

For large quantities of work we often use kilojoule (kj)

$$1 \text{ kj}= 1000\text{J}$$

10.7.1 Unit of heat

The unit of heat, which is used for many years is calorie (cal). A calorie is defined as the quantity of heat required to raise the temperature of one gram of water by 1^0C in the vicinity of 15^0C. Since heat and work are interrelated, s1 unit of heat is the joule (J).

1 joule = 0.2390 calorie

1 calorie = 4.184 J

or 1 kcal = 4.184 kJ

10.7.2 Sign convention of heat

The symbol of heat is q. If the heat flows from the surrounding into the system to raise the energy of the system, it is taken to be positive, +q. If heat flows from the system to the surrounding, thus lowering the energy of the system, it is taken to be negative, – q.

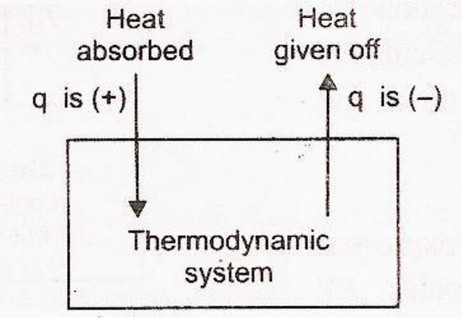


Fig 10.6 sign convention for heat flow in a thermodynamic system

10.7.3 Sign convention of work

The symbol of work is ω. If work is done on the system by the surroundings and the energy of the system is thus increased, it is taken to be positive, + ω. If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, -ω.

Thus we may summarise

Heat flows into the system, q is +ve

Heat flows out of the system, q is -ve

Heat is done on the system, ω is +ve

Heat is done by the system, ω is –ve

10.7.4 Pressure - volume work

As you know in physics mechanical work is defined as force multiplied by the distance through which the force acts. In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work or PV work or expansion work.

10.7.5 Work done in reversible isothermal expansion

Consider a gas enclosed in a cylinder fitted with a weightless frictionless piston as shown in fig 10.7. The cylinder is not insulated. It is supposed to be in thermal equilibrium with the surroundings so that the temperature of the gas remains constant.

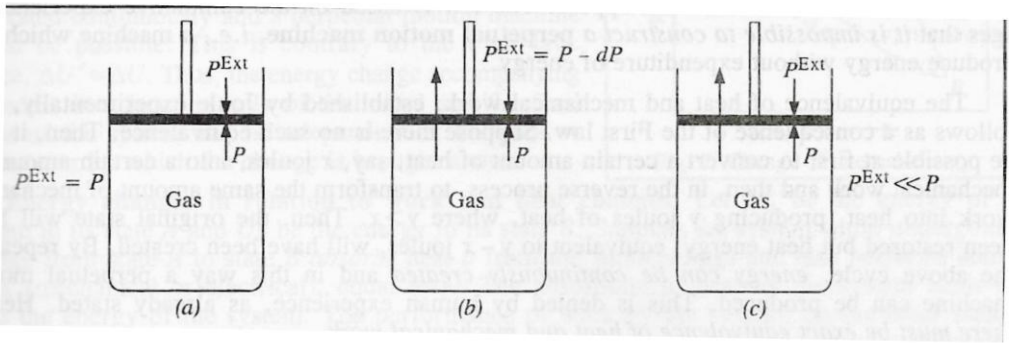


Fig 10.7 pressure volume work of a system

The external pressure on the piston is equal to the pressure of the gas within the cylinder as shown in fig 10.7 a. If the external pressure is lowered by infinitesimal amount dP that is it falls from P to P-dP fig 10.7b, the gas will expand by infinitesional volume dV, i.e., the volume changes from V to V+dV. As a result of expansion, the pressure of the gas within the cylinder falls to P-dP, i.e., it becomes again equal to external pressure. The piston then comes to rest.

If the external pressure is lowered again second time by the same infinitesimal amount dP, the gas will undergo the second infinitesimal expansion dV before the pressure again equals the new external pressure. The piston again comes to rest. The process is continued such that the external pressure is lowered by successive small amounts and, as a result, the gas undergoes a series of small successive increments of volume dV at a time.

It should be clear to you that since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step, is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.

Since during expansion, pressure decreases and volume increases these two parameters are assigned opposite signs. The work done by the gas in an infinitesimal expansion is thus given by

$$d\omega = -(P-dP)(dV)$$

$= -PdV$ ....(1)

As the product dP.dV is neglected (both dP and dV being very very small).

The total work ω done by the gas in expansion, say from original volume V_1 to final value V_2, will be sum of the series of the terms PdV in which the pressure keeps on decreasing gradually. The result may be expressed mathematically as

$$W= -\int_{V_1}^{V_2} PdV \qquad ....(2)$$

Where V_1 is the volume of the gas initial state and V_2 in the final state.

The above integral may be evaluates by substituting

P=RT/V for one mole of an ideal gas. Thus,

$$W= - RT\int_{V_1}^{V_2} \frac{dV}{V} = -RT \ln\frac{V_2}{V_1} \qquad ....(3)$$

For an ideal gas $P_1V_1 = P_2V_2$, at constant temperature, the above equation may also be written as

$$W= -RTln\,\frac{P_1}{P_2} \qquad ....(4)$$

For n moles, the above expressions may be written as

$$W=-nRTln\frac{V_2}{V_1} = -nRTln\frac{P_1}{P_2} \qquad ....(5)$$

Since during expansion, V_2 is more than V_1 and P_2 is less than P_1, hence from equation (5) the work comes out to be negative in conformity with the convention used in this regard. When work is done by system it is taken as negative.

10.7.6 Work done in reversible isothermal compression

Now let us suppose the gas undergoes isothermal reversible compression from volume V_2 to V_1. The external pressure will now be made infinitesimally hiper than P, the pressure of the gas inside the cylinder. Let the external pressure be P+dP. There will be an infinitesimal contraction in volume, say dV, of the gas. Since during compression of gas, the pressure increases and the volume decreases, hence these two parameters are assigned opposite signs as before. Thus, the work done by the surroundings on the system for this infinitesimal step is given by

$d\omega = - (P+dP)dV= -PdV$ ....(6)

Ignoring the quantity dPdV as before.

If the compression is carried out reversibly in a series of steps from initial volume V_2 to final volume V_1, the work done ($\acute{\omega}$) by the surrounding on the gas will be given by

$$\acute{\omega} = -\int_{V_2}^{V_1} P\,dV \qquad ....(7)$$

assuming the gas to be ideal, P as before, may be substituted by RT/V in the above equation so that

$$\acute{\omega} = -\int_{V_2}^{V_1} \frac{RT}{V}\,dV = -RT\int_{V_2}^{V_1}\frac{dV}{V} \qquad ....(8)$$

$$= -RT \ln V_1/V_2 \qquad ....(9)$$

$$= -RT \ln P_2/P_1 \qquad ....(10)$$

For n moles of the gas the above expression can be written as

$$\acute{\omega} = -nRT \ln V_1/V_2 = -nRT \ln P_2/P_1 \qquad ....(11)$$

Since during compression, the initial volume V_2 is greater than the final volume V1 and also since the initial P_2 is less than the final pressure P_1, hence according to equation (11), the work done $\acute{\omega}$ comes out to be positive, as was chosen as a convention in this regard.

10.7.8 Work done in irreversible isothermal expansion

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversible i.e., by instantaneously dropping the external pressure P^{ext} to the final pressure P_2. The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression

Work = pressure x change of volume

$$W_{ir} = -\int dw$$

$$= -\int P^{ext} \times dV$$

$$= -\int_{V_1}^{V_2} P^{ext}\,dV$$

$$= -P^{ext}(V_2 - V_1) \qquad ....(12)$$

Since P^{ext} is less than P_1 the work done during isothermal irreversible expansion is numerically less than the work done during reversible isothermal expansion in which P^{ext} is almost equal to P.

Now it should be clear to you that when there is free expansion that is when gas expands against zero pressure, work done will be zero.

10.8 STATE FUNCTION, EXACT AND INEXACT DIFFERENTIALS

State variables which are determined by the initial and final states of the system only and not by the path followed are called state functions. State variables which are determined or depend upon path followed are called path functions.

The state function is a property of a thermodynamic system which has a definite value for a particular state of the system. It is independent of the manner in which the state is reached. The change in the state function accompanying the change in the state of the system depends only on the initial and final states of the system and not on the path by which the change is brought about. Pressure, volume, temperature and energy are state functions. On the other hand work (ω) is not state function because the work done in a given change of state depends upon the manner in which the change is brought about. If the work is done reversibly its value is different than the value obtained irreversibly as you have seen above. And also work done would be zero if the gas expands in vacuum. First law equation ($\Delta E = q+w$), E is a definite quantity; hence if w is not a state function, q also is not a state function. Mathematically, this is expressed by saying that while the differential of energy, dE, is an exact differential, the differentials of heat and work, viz., dq and dw respectively, are inexact differentials. Exact differentials can be integrated between the appropriate limits. This cannot be done in the case of inexact differentials. Thus

$$\int_{E_1}^{E_2} dE = E_2 - E_1 \qquad \text{.....................(13)}$$

But $\int_{q_1}^{q_2} dq \neq q_2 - q_1$ and $\int_{w_1}^{w_2} dw \neq w_2 - w_1$ ....(14)

10.8.1 The Euler reciprocal relation

Let z be a state function of two independent variables x and y of the system, i.e., $z = \int(x, y)$. since z is state function, hence differential of z is an exact differential and can be written as

$$d_z = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= M(x,y)dx + N(x,y)\,dy \qquad . \qquad \text{...........(15)}$$

Where $M(x,y)= \left(\frac{\partial z}{\partial x}\right)_y$ and $N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$ ....(16)

$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y}$ and $\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \partial x}$

Taking mixed second derivatives, we get –

Since $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$

Hence $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

This equation is known as Euler's reciprocal relation. This is applicable to state functions only. Since z is a state function. The finite change, Δz as the system passes from initial state A to final state B, is given by $\Delta z = z_B - z_A$

Also $\oint dz = 0$ where cyclic integral means that the system is in the same state at the end of its path as it was at the beginning, i.e., it has traversed a close path. Thus, dz is an exact differential.

10.9 FIRST LAW OF THERMODYNAMICS

Joule in his experiment, carried out the performance of work is diverse ways. The work was done by (a) agitating paddle wheels in a mass of water or mercury, (b) rubbing iron rings in mercury, (c) passing electricity through a wire of known resistance etc. The heat so produced was measured, latter on many workers namely Rowlands, Callender and Barnes, Laby and Hercus carried on the determination of the value of J with considerable accuracy. The accepted value of J is 4.1858×10^7 ergs per calorie.

This relation between heat and work is the origin of first law of thermodynamics. The first law can be enunciated as "If or whenever, heat is obtained from work the amount of heat produced is proportional to the work spent. There are many instances to show that not only heat can be converted into work but different form of energy are also interconvertible into one another. A given quantity of electrical energy which is comparatively easily measurable, was found to be equivalent to a definite amount of heat or mechanical work. You will study in this unit that such equivalent did not only exist between heat and work but between any two forms of energy.

Hence if

X units of energy A ≡ y units of energy B

Then mx units of energy A ≡ my units of energy B

The proportionality between quantities of two given forms of energy is universally constant and the constancy of this proportionality is essence of the first law.

The first law of thermodynamics is, in fact, an application of the broad principle known as the law of conservation of energy to the thermodynamics systems.

The first law of thermodynamics states that energy can neither be created nor destroyed, although in can be transferred from one form to another. Thus, whenever energy in one form disappears, an equal amount of energy in some other form must appear.

Since the disappearance of an amount of energy causes appearance of an equivalent amount of energy of another form, neither more nor less, we are compelled to accept that energy cannot be completely destroyed nor it can be created from nothing.

Clausius, therefore, enunciated that varied changes and transformation might occur but the total energy of the universe must remain constant, hence the first law of thermodynamics is really the law of conservation of energy.

10.10 INTERNAL ENERGY

Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temperature, pressure and volume. Or by virtue of its pressure each substance is associated with certain amount of energy. This is known as internal energy of the system. This energy includes not only the translational kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies.

The total of all the possible kinds of energies of a system is called its internal energy.

The exact magnitude of this energy is not known because the chemical nature includes such factors as the translational, rotational and vibrational movements of the molecules, the manner in which the molecules are put together, the nature of the individual atoms, the arrangement and number of electrons, the energy possessed by the nucleus, etc. But, one thing is certain that the internal energy of a substance or a system is a definite quantity and it is a function only of the state (i.e., chemical nature, composition, temperature, pressure and volume) of the system at the given moment, irrespective of the manner in which that state has been brought about.

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we concerned only with the energy changes when a system changes from one state to another. The amount of internal energy depends on the thermodynamics state and hence on thermodynamics parameters of the system. It is represented by E.

The internal energy is dependent on the internal structure and composition of the system. So, in a system of constant composition, the magnitude of E will depends upon other thermodynamics variables (P,V,T), any two of which may be regarded as independent variables. Thus,

$E= f (P,T)$; or $E=f (P,V)$, or $E=f(V,T)$

An explanation of the existence of the internal energy comes from the kinetic theory, the translator motion of the molecules, the vibrations and rotations of the atoms, the electronic revolutions etc. contribute to the internal energy.

10.11 INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

Suppose, a system is subjected to change of pressure and volume. Let the initial state is represented by A and the final state by B (fig. 11.1) and let E_A and E_B represent energies associated with the system in its state A and B

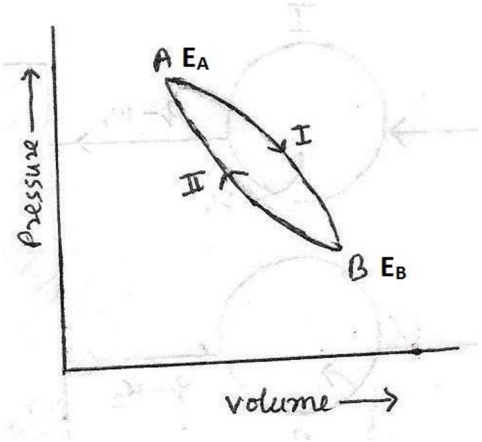


Fig 10.8 internal energy

respectively. These will be definite quantities as explained above. Then, the change in internal energy,

$$\Delta E = E_B - E_A$$

must be a definite quantity, irrespective of the path or the manner in which the change is brought about. If it were not so, it would again be possible to construct a perpetual motion machine, a machine which can produce energy without expenditure of energy. Suppose, that the system changes from state A to state B by following path I and is accompanied by change of energy equal to ΔE. Now suppose the same change of state is brought about by another path, say, path II and the change of energy is ΔE`. Suppose, ΔE >ΔE`, then coupling of these two processes:

$$A \longrightarrow B \text{ (by path I) and}$$

$$A \longrightarrow B \text{ (by path II)}$$

As shown in fig 11.1, the system would return to its initial state and at the same time a surplus of energy equal to ΔE-ΔE` would become available. By repeating the same cycle over and over again, energy would be generated continuously and a perpetual motion machine would be possible. This is contrary to the first law. Hence $\Delta E = \Delta E`$. Thus the energy change accompanying a process is a function only of the initial and the final states of the system and is independent of the path or the manner by which the change is brought about.

10.12 MATHEMATICAL STATEMENT OF THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is, in fact, an application of the broad principle known as law of conservation of energy to the thermodynamic system. It states that:

The total energy of an isolated system remains constant though it may change from one form to another.

Let us consider a system in a state A having internal energy E_A undergoing a change to a state B. During the transaction let the system absorbs a small amount of heat say q, then the net amount of energy of the system would become E_A+q. In the process of transformation, the system might have also performed some work W of any type. If E_B be the internal energy of the system at state B, then the net energy after the transformation would be E_B+W

Then from principle of conservation of energy, we clearly see

$$E_A+q = E_B + W$$

$$q = (E_B-E_A)+W = \Delta E+W$$

for infinitesimal change

$$\delta q = dE + \delta w \qquad ......(11.1)$$

that is, heat taken up by a system would be equal to internal-energy increase of the system plus the work done by the system. This is mathematical statement of first law. Here E is state function hence its change is shown as dE and q, the heat supplied and w, the work obtained depends upon the path of the change, hence shown as δq and δw respectively.

Now a few comments may be made on the above equation

(a) If the system is an isolated one, so that there is no heat exchange with the surroundings, i.e., in an adiabatic process

$\delta q=0$

hence $\Delta E+W=0$

or $W= -\Delta E$ 11.2

that means the decrease in internal energy is exactly equal to the work done on the system by the surroundings.

(b) In a cyclic process, $\oint dE=0$

Hence $\oint \delta q = \oint dE+\oint \delta w$

or $\oint \delta q =\oint \delta w$ 11.3

The total work obtained is equal to the net heat supplied and no excess work can be obtained. Thus, establishes the impossibility of perpetual motion of the first kind, which is our experience.

(c) For an adiabatic process there is no change in heat gained or lost

i.e. $q=0$

Then $\Delta E= -W$ 11.4

That means the decrease in internal energy is exactly equal to work done on the system by the surroundings or we can say work is done at the expense of internal energy and internal energy will decrease.

(d) For an isobaric process there is no change in pressure, i.e., P remains constant. Hence

$\Delta E =q-W$

$=q-P\Delta V$ 11.5

10.13 ENTHALPY OF A SYSTEM

In a process carried out at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy E, as no PV work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing PV work. Therefore, total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called enthalpy of the system and is represented by the symbol H. Thus enthalpy is defined by the equation.

$$H=E+PV \qquad ....11.6$$

Suppose the change of state of a system is brought about at constant pressure. In that case, there will be change of volume, let the volume increases from V_A to V_B at constant pressure P. Then the work done (W) by the system will be given by

$$W= -P(V_B-V_A) \qquad ....11.7$$

Substituting the value of W in equation 11.5 we have

$$\Delta E = q + [-P(V_B-V_A)]$$

$$= q - P(V_B-V_A)$$

$$= q- PV_B+PV_A \qquad ....11.8$$

If E_A be internal energy in the initial state aw E_B the internal energy at final state, then

$$\Delta E = E_B-E_A$$

So equation 11.8 becomes

$$E_B-E_A = q-PV_B+PV_A$$

$$E_B + PV_B = q+E_A + PV_A \qquad ....11.9$$

As the quantity H=E+PV is known as enthalpy of the system. It represents the total energy stored in the system.

From equation 11.6 and 11.9

$$H_B = q+H_A$$

$$\text{or} \quad q = (H_B-H_A) = \Delta H \qquad ....11.10$$

Since H_B and H_A are definite quantities, it is evident that ΔH, like ΔE, is a definite quantity depending only on the initial and final states of the system. Obviously, ΔH represents increase in the enthalpy of a system when it changes from state A to state B. Putting the value of q in equation 11.9 we get

$$E_B-E_A = \Delta H-PV_B + PV_A$$

$$\Delta E = \Delta H-P\Delta V$$

$\Delta H = \Delta E + P\Delta V$ 11.11

From equation 11.6 by definition of enthalpy

$H=E+PV$

Its differential form $dH=dE+PdV+VdP$

If a system undergoes a change at constant pressure then change in enthalpy,

$dH_P = dE_P+PdV_P$ 11.12

the suffix P used to indicate constancy of pressure.

The first law states

$\delta q=dE+\delta W$ 11.12a

The work δW may be mechanical, electrical, chemical or any type. If we consider processes in which the entire work is mechanical, i.e., expansion or compression of the system, then δW would depend on the values P and V. Further, if the change of the system be carried out at constant pressure then,

$\delta W_P = PdV_P$

Hence from the first law, for change at constant pressure

$\delta q_p = dE_P + \delta W_P = dE_P + PdV_P$ 11.13

From equation 11.12 and equation 11.13

$\delta qp = dH_P$ 11.14

That is the increase in heat content of a system during a given transformation is the heat absorbed at constant pressure during the process.

10.14 RELATION BETWEEN ΔH AND ΔE

From equation 11.11

$\Delta E= \Delta H - PdV$

or

$\Delta H = \Delta E + PdV$ 11.15

This equation means when heat supplied to a system it is used in two ways (a) to increase the internal energy of the system and (b) secondly to perform some work (PdV)

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

Suppose we have n_1 moles of gases before reaction and n_2 moles of gases after reaction. If we assume behaviour

$$PV_2 = n_2RT$$

and $$PV_1 = n_1RT$$

$$P(V_2-V_1) = (n_2-n_1)\ RT$$

$$P\Delta V = \Delta n\ RT$$ Δn is change in no. of moles.

Substituting this value in 11.11 we get

$$\Delta H = \Delta E + \Delta nRT$$

10.15 HEAT CAPACITY

If q amount of heat is given to a system of mass m, temperature is raised from T_1 to T_2. Then

$$q \alpha (T_2-T_1)m$$

or $$q = m.C(T_2-T_1) \qquad \text{..........11.16}$$

here C is known as heat capacity of the system

If $m=1$ and $T_2-T_1=1$ then $q=C$, that means heat capacity is the amount of heat required to raise the temperature of unit mass of substance by one degree.

From eqn. 11.16 we have

$$C= q/m(T_2-T_1) \qquad \text{..........11.17}$$

When one mole is considered then

$$C=\frac{q}{T_2-T_1}=\frac{q}{\Delta T}$$

Then C is molar heat capacity

Since the heat capacity varies with temperature, hence the true molar heat capacity is defined by the differential equation.

$$C=\frac{dq}{dT} \qquad \text{.......11.18}$$

Where dq is a small quantity of heat absorbed by the system producing a small temperature rise dT.

Thus heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.

From equation 11.17 it is clear that units of molar heat capacity are calorie per degree per mole (cal K^{-1} $mole^{-1}$) and in SI unit joule per degree per mole ($JK^{-1}mole^{-1}$)

It is found that amount of heat required by a system for one degree change depends upon the conditions in which the change occurs. That means heat capacity is not a state function two specific conditions are found to be very useful, whether heat is supplied at constant volume or at constant pressure.

10.15.1 Heat capacity at constant volume

As you have studied above that specific heat is amount of heat required to raise the temperature of the system by one degree. In case of solid and liquids there is very little or no change of volume when temperature is raised by an degree but in case of gases there is change of volume also. Thus if volume is kept constant heat capacity will have different value than in case pressure is kept constant.

Heat capacity at constant volume is the amount of heat required to raise the temperature of the system by one degree keeping volume constant it is denoted by c_v.

If one mole of gas is under consideration then it is molar heat capacity, defined as amount of heat required to raise the temperature of one mole of the gas by one degree at constant volume.

Molar heat at constant volume is represented as C_v.

From first law of thermodynamics

$$dq = dE + PdV$$

dividing both sides by dT we get

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT}$$

At constant volume dV=0 so

$$\left(\frac{\delta q}{\delta T}\right)v = \left(\frac{\delta E}{\delta T}\right)v = C_v \qquad ....11.19$$

10.15.2 Heat capacity at constant pressure

If temperature is raised by one degree keeping the pressure constant, the amount of heat required is called heat capacity at constant pressure, denoted by C_p. If the system contains one mole of a substance then the molar heat capacity at constant pressure is C_p.

From first law of thermodynamics

$$\Delta q = dE + \delta w$$

$$= dE + PdV$$

dividing of dT

$$\frac{\partial q}{\partial T} = \frac{dE}{dT} + \frac{PdV}{dT}$$

We know H= E+ PV

$$\left(\frac{dH}{dT}\right) = \frac{dE}{dT} + \frac{d(PV)}{dT}$$

Keeping pressure constant

$$\left(\frac{\partial H}{\partial T}\right)p = \left(\frac{\partial E}{\partial T}\right)p + P\left(\frac{\partial V}{\partial T}\right)p$$

Hence $\left(\frac{\partial q}{\partial T}\right)p = \left(\frac{\partial H}{\partial T}\right)p = C_p$

Here in our discussion some times d has been written and in some cases ∂ (del) has been adopted for changes. The difference is that if we simply see the change in some property say, enthalpy with temperature we write $\frac{dH}{dT}$ but if put some restrictions, say if volume is kept constant then change in enthalpy with temperature will be $\left(\frac{dH}{dT}\right)_V$. Then $\left(\frac{dH}{dT}\right)_p$ means change in enthalpy when pressure is constant.

It is clear from the above that two heat capacities are not equal and Cp is greater than C_v by a factor which is related to the work done. At constant pressure part of heat absorbed by the system is used up in increasing the internal energy of the system and the other for doing work by the system. While at constant volume the whole of the heat absorbed is utilised in increasing the internal energy of the system as there is no work done by the system. Thus C_p is greater than C_v.

10.15.3 Internal energy change with volume and pressure

Gay Lussac and Joule carried out experiments to find out changes in internal energy of a gas. The experiment was very simple. As shown in fig 10.9, two containers A and B connected by a stop clock at the middle were taken and kept immersed in the water of a thermostat. Initially A was filled up with the gas and B was evacuated. When thermal equilibrium was established, the stopcock was opened and the gas passed into B. The flow continued until equilibrium was again reached. Since the gas expanded against zero pressure, no work was involved. $\delta w=0$. Very careful and repeated observations showed no change in temperature of the water in the thermostat. Hence $\delta q=0$. Yet the volume of the gas has changed. From the first law of thermodynamics we can say that

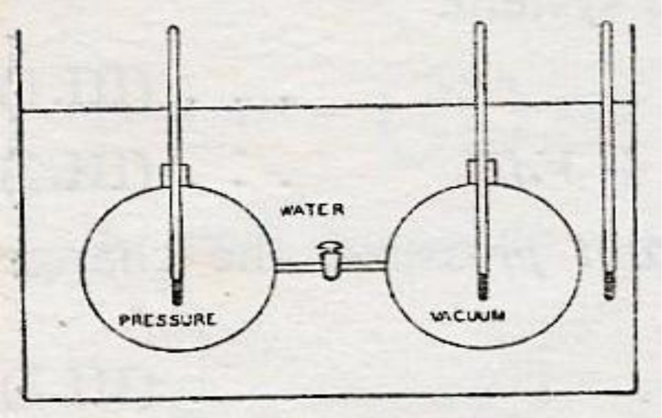


Fig 10.9 Joule's experiment

$$dE= \delta q-\delta w =0$$

again $$dE=\left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

since $dT=0$ and $dE=0$

hence $$\left(\frac{\partial E}{\partial V}\right)_T dV=0$$

but $dV \neq 0$

that means $\left(\frac{\partial E}{\partial V}\right)_T = 0$

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

Again $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$, hence $\left(\frac{\partial E}{\partial P}\right)_T = 0$

We conclude $\left(\frac{\partial E}{\partial V}\right)_T = 0,\ \left(\frac{\partial E}{\partial P}\right)_T = 0$ 11.20

This is true for an ideal gas.

10.15.4 Relation between C_P and C_V

We know E=(V,T) (E is a function of volume and temperature)

Change in E can be written as

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

dividing this equation by T and the keeping pressure constant we have

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V \qquad .....11.21$$

As $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ and $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

Now $C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$

But H=E+PV

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\partial}{\partial T}(E+PV)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_v \qquad ......11.22$$

Putting the value of $\left(\frac{\partial E}{\partial T}\right)_P$ from equation 11.21 we get

$$C_P - C_V = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left(\frac{dV}{dT}\right)_P \left\{\left(\frac{\partial E}{\partial V}\right)_T + P\right\} \qquad ......11.23$$

This equation is generally applicable for an ideal gas

$\left(\frac{\partial E}{\partial V}\right)_T = 0$

so $C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P . P$

As PV=RT

$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

So $C_P - C_V = \frac{R}{P} P = R$ 11.24

10.16 JOULE-THOMSON EFFECT

If a gas is allowed to pass from a region of high pressure to low pressure region through a porous plug or through a narrow orifice and the system is thermally insulated, its temperature was lowered.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure to a region of low pressure is known as Joule-Thomson effect or Joule-Kelvin effect.

10.16.1 Joule-Thomson experiment

The apparatus used by Joule and Thomson to measure the temperature change on expansion of a given volume of gas is shown in fig 11.3. An insulated tube is fitted with a porous plug in the middle and two frictionless pistons A and B on the sides. Let a volume V_1 of a gas at pressure P_1 be forced

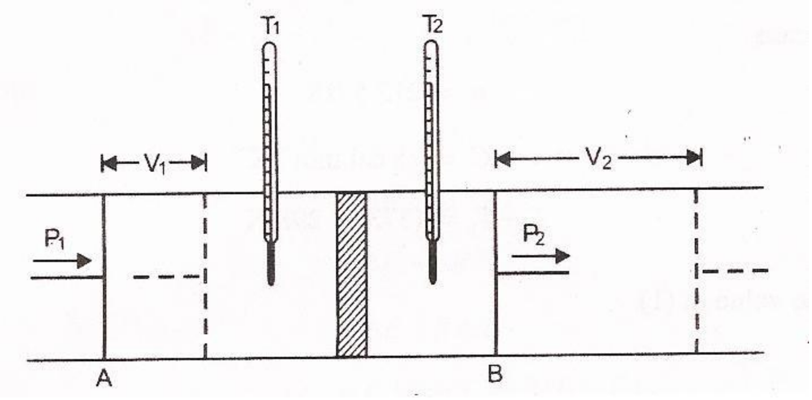


Fig 10.10 Joule Thomson experiment

through the porous plug by a slow movement of piston A. The gas in the right-hand chamber be allowed to expand to volume V_2 and pressure P_2 by moving the piston B outward. The change in temperature is found by taking readings on two thermometers.

Most gases were found to undergo cooling on expansion through the porous plug. Hydrogen and helium were exceptions as these gases showed a warming up instead of cooling.

10.16.2 Explanation

The work done on the gas (is pressure multiplied by the change in volume) at the piston A is (P_1V_1) (As initial volume on left hand side of the plug was V_1) and work done by the gas at the piston B is P_2V_2.

So,

Work done on the system at the piston A = P_1V_1 and work done by the system at piston B = P_2V_2

Net work done by the system = $P_2V_2 – P_1V_1$

$$w= P_2V_2- P_1V_1 \qquad .....11.25$$

From first law of thermodynamics

$$\Delta E = q - w$$

But the process is adiabatic and therefore $q=0$

Hence, $\Delta E = -w$ and $\Delta E = E_2 - E_1$

So $E_2 - E_1 = -w = -(P_2V_2 + P_1V_1)$

Rearranging the terms

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

As $H = E + PV$

so $H_2 = H_1$

Or, $\Delta H = 0$ 11.27

Thus, the Joule-Thomson expansion of a real gas occurs not with constant internal energy, but with constant enthalpy. This is therefore called isoenthalpic process.

10.16.3 Joule-Thomson coefficient

The rate of change in temperature with pressure when enthalpy remains constant is called Joule-Thomson's coefficient, μ.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad .....11.28$$

If μ is positive there is cooling effect and if μ is negative it means heating effect will be there. In most of the cases at ordinary temperature cooling effect is there but hydrogen and helium get warmed up under similar conditions. We will discuss the reason later (when we will discuss inversion temperature).

In Joule-Thomson effect gas runs from high pressure to low pressure hence dP is negative. Hence μ will be positive if dT is also negative, i.e., if temperature falls. Whether μ is positive (cooling) or negative (heating) we can explain this in the following way. We know, H(enthalpy) is a function of temperature and pressure, so

$$H=\int(P,T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad \text{......11.29}$$

In an isoenthalpic change as in Joule-Thomson effect, dH=0

$$\therefore \quad \left(\frac{\partial H}{\partial T}\right)_P dT = \left(\frac{\partial H}{\partial P}\right)_T dP$$

Dividing this equation by dP and keeping enthalpy (H) constant

We get

$$\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T / \left(\frac{\partial H}{\partial T}\right)_P$$

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad \text{.....11.30}$$

since $H=E+PV$

$$\mu = -\frac{1}{Cp}\frac{\partial}{\partial P}(E+PV)_T$$

$$= -\frac{1}{C_p}\left(\frac{\partial E}{\partial P}\right)_T - \frac{1}{C_p}\{(\frac{\partial}{\partial P}(PV)\}_T \qquad \text{......11.31}$$

This relation is applicable both to ideal and also to real gases. In the case of an ideal gas, both the terms on the right-hand side separately vanish. As for and ideal gas $\left(\frac{\partial E}{\partial P}\right)_T = 0$ (equation 11.20) and PV=RT hence $\frac{\partial}{\partial P}(PV)_T = 0$, hence $\mu=0$

A truly ideal gas has no J.T. coefficient.

Now let us discuss the case of a real gas. We can write equation 11.31 this way

$$\mu = -\frac{1}{C_p}\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{C_p}\left\{\frac{\partial}{\partial P}(PV)\right\}_T \qquad ....11.32$$

In this equation $(\partial E/\partial V)_T$ of a gas is usually positive, while $(\partial V/\partial P)_T$ for any gas is always negative. As a result the first term is always positive. The magnitude of second term may be negative or may be positive. At low temperature and at low pressure, $\{\partial/\partial P\ (PV)\}_T$ is negative. Under such conditions both the terms in the equation being negative, μ has a positive value and cooling will be there in Joule-Thomson's experiment.

10.16.4 Inversion temperature

The cooling effect is observed at relatively low temperatures but if the temperature be high, then instead of cooling the gas become heated, i.e., in J.T. effect μ becomes negative. For every gas there is a temperature where $\mu=0$, when neither heating nor cooing of the gas due to passage the porous plug would occur. This is called inversion temperature T_i of the gas. The value of T_i can be calculated to be equal to

$$\frac{2a}{Rb} = T_i \qquad ......11.33$$

So if a and b for a gas are known inversion temperature can be calculated. The inversion temperature for hydrogen is -80^0C and that of helium is -240^0C.

The Joule-Thomson effect support to the view that attractive forces do exist between gas molecules. As the gas expands, the molecules fall apart from one another. Therefore, work has to be done in order to overcome the cohesive or attractive forces which tend to hold the molecules together. This work is done by the system at the expense of the kinetic energy of the gaseous molecules. Consequently, the kinetic energy decreases and since this is proportional to temperature, cooling results. It may be noted that in this case no external work has been done by the gas in expansion.

10.17 REVERSIBLE WORK: ISOTHERMAL EXPANSION, ISOTHERMAL COMPRESSION AND ADIABATIC

10.17.1 Isothermal reversible expansion

From first law of thermodynamics we know energy neither be created nor destroyed, for an isolated system total energy always remains constant. Whole universe can be divided into very large number of isolated systems, for each isolated system energy remains constant, that means total energy of universe remains constant.

The mathematical representation of first law of thermodynamics

is $\delta q = dE + \delta w$, or $q = dE + w$

Which means when δq amount of heat is given to a system it is used up in two ways, first in increasing the internal energy dE of the system and secondly to perform certain amount of work δw. Here heat absorbed (or evolved) and work done (on the system or by the system) are not state functions, they depend on the path of transformation but internal energy does not depend upon path and hence it is a state function.

Let us consider a gas enclosed in a cylinder fitted with a piston (which is weightless and frictionless) as shown in fig 11.4. The cylinder is not insulated. The external pressure P on the piston is equal to the pressure of the gas within the cylinder, as shown in fig 11.4(a). If the external pressure is lowered by infinitesimal amount dP, that means pressure is now P-dP fig 11.4(b), the gas will expand by an infinitesimal

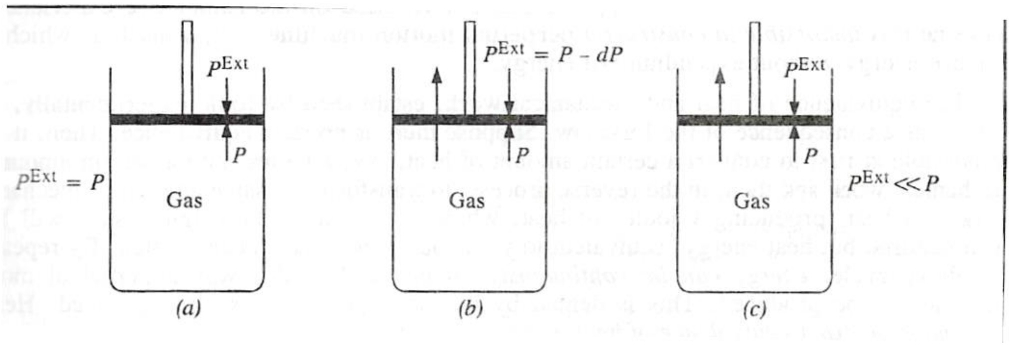


Fig 10.11 Isothermal reversible expansion work

volume dV, i.e., the volume changes (increases) from V to V+dV. As a result of expansion, the pressure of the gas within the cylinder falls from P to P-dP, i.e., it becomes again equal to external pressure. The piston then comes to rest.

If the external pressure is lowered again second time by the same infinitesimal amount dP, the gas will undergo the second very small expansion dV before the pressure again equals the new external pressure. The piston again comes to rest. The process is continued such that the external pressure is lowered by successive small amounts and, as a result, the gas undergoes a series of small successive increments of volume dV at a time.

Since the system is in thermal equilibrium with the surroundings, it is noted that the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step, is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.

Work done by the gas in driving the piston upwards

$$= -(P-dP)dV$$

$$= -PdV \qquad \text{........11.34}$$

As dPdV is negligibly small and can be neglected the total work done by the gas, w in expansion from volume V_1 to volume V_2, will be sum of the series of the terms pdV in which pressure keeps on increasing gradually. The result may be expressed mathematically as

$$W= - \int_{V_1}^{V_2} PdV \qquad ....11.35$$

Where V_1 is initial volume and V_2 is volume in the final state.

As PV=RT hence

$$W= - \int_{V_1}^{V_2} \frac{RT}{V} dV$$

$$= -RT \ lm \frac{V_2}{V_1} \qquad ....11.36$$

As we know $P_1V_1 = P_2V_2$

$$W= - RT \ln P_1/P_2 \qquad ....11.36$$

For n moles the work above expression can be written as

$$W= - nRT\ln \frac{V_2}{V_1} = - nRT\ln \frac{P_1}{P_2} \qquad ....11.37$$

Since V_2 is greater than V_1 and P_1 is greater than P_2, it is clear from the above equation that W comes out to be negative meaning thereby that work is done by the gas.

10.17.2 Work done in isothermal reversible compression

Let us suppose the gas undergoes isothermal reversible compression from V_2 to V_1. The external pressure will now be made infinitesimally higher than P, the pressure of the gas inside the cylinder. Let the external pressure be P+dP. There will be infinitesimal contraction in volume, say dV, of the gas. Since during compression of a gas, the pressure increases and volume decreases, hence these two parameters are assigned opposite signs as before. Thus, the work done by the surroundings on the system for this infinitesimal step is given by

$$dW= = - (P-dP)dV$$

$$= - PdV \qquad ......11.38$$

Ignoring the quantity dPdV, as before.

If the compression is carried out reversibly in a series of steps from initial volume V_2 to final volume V_1, the work done ω' by the surrounding on the gas will be given by

$$\omega' = -\int_{V_2}^{V_1} PdV \qquad ....11.39$$

If the gas under consideration is ideal than P can be replaced by RT/V

$$\omega' = -\int_{V_2}^{V_1} \frac{RT}{V} dV$$

$$= -RT \ln \frac{V_1}{V_2}$$

$$= -RT \ln \frac{P_2}{P_1} \qquad ....11.40$$

For n moles of the gas the above expression can be written

as $\omega' = -nRT\ ln \frac{V_1}{V_2} = -nRT \ln \frac{P_2}{P_1}$ 11.41

10.17.3 Maximum work

As we have discussed above, the work done by a gas during expansion is given by the product $P^{ext}\Delta V$ where ΔV is increase in volume. If the external pressure P^{ext} is only infinitesimally smaller than the pressure P of the gas (fig 11.4(b) then , expansion is said to place reversibly. If , however, the external pressure is much smaller than the gas pressure (fig 11.4 c), the expansion will take place rapidly, i.e., irreversibly and the work done for the same amount of expansion will be much smaller since P^{ext} is now much small than before. Taking the extreme case, if the external pressure is zero (i.e., the expand in vacuum) the work done will be zero. Hence, it follows that when a gas expands freely, i.e., when it expands against vacuum such that P^{ext} =0 no work is done by the gas.

Now it is clear from the above discussion that the magnitude of work done by a system on expansion depends upon the magnitude of opposing external pressure. The closer is the opposing pressure to the pressure of the gaseous system in the cylinder, the greater is the work performed by the system on expansion. In another words maximum work is obtained when the two opposing pressure differ only by an infinitesimal amount from each other. This condition is evidently demanded for a thermodynamically reversible process, as discussion earlier. Hence, the condition for maximum work concides with that for a thermodynamics reversibility.

10.17.4 Work done in isothermal irreversible expansion

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly i.e., by instantaneously dropping the external pressure, P^{ext}, to the final pressure P_2. The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression:

$$\omega = -P^{ext} \int_{V_1}^{V_2} dV$$

$$= -P_2 (V_2 - V_1)$$

$$= -P_2 \, dV$$

In both the process, reversible and irreversible, the same state of the system has changed from the initial to the final state. The work done is smaller in irreversible expansion than the reversible expansion. Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states, it is a path function.

10.17.5 Adiabatic expansion

In adiabatic process no heat is allowed to enter or leave the system. Hence in an adiabatic system $q=0$. From equation 11.5

$$q = dE + w$$

or $$dE = -w \qquad ....11.42$$

Since the work is done at the expense of internal energy, the internal energy of the system decreases and the temperature falls.

Let us consider one mole of an ideal gas at pressure P and volume V. For an infinitesimal increase in volume dV at pressure P the work done by the gas is –PdV. The internal energy decreases by dE, then from equation 11.42

$$dE = -PdV \qquad ....11.43$$

By definition of molar heat capacity at constant volume

$$dE = C_V dT \qquad ....11.44$$

From equation 11.43 and equation 11.44

$$C_V dT = -PdV = -\frac{RT}{V}dV \qquad \text{(gas being ideal)}$$

or $$C_V \frac{dT}{T} = -\frac{R}{V} dV$$

on integrating between limits when volume is V_1 temperature T_1 and when volume is V_2 temperature falls to T_2

$$\int_{T_1}^{T_2} Cv \frac{dT}{T} = -\int_{V_1}^{V_2} \frac{RdV}{V}$$

$$C_V \ln T_2/T_1 = -R \ln V_2/V_1$$

Since $R = C_P - C_V$ for an ideal gas we have:

$$C_V \ln T_2/T_1 = -(C_P - C_V) \ln V_2/V_1$$

$$\ln T_2/T_1 = -\frac{C_P - C_V}{C_V} \ln V_2/V_1 \qquad \text{........11.45}$$

the ratio of C_P/C_V is often written as γ (gama)

equation 11.45 then becomes

$$\ln T_2/T_1 = -(\gamma-1) \ln (V_2/V_1) = (\gamma-1) \ln \left(\frac{V_1}{V_2}\right)$$

or $T_2/T_1 = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

or $T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$

or $TV^{\gamma-1} = \text{constant}$ 11.46

we know $P_1V_1/T_1 = P_2V_2/T_2$

so $T_2/T_1 = P_2V_2/P_1V_1$

substituting the value of T_2/T_1 in equation 11.46 we get

$$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

or $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

or $PV^{\gamma} = \text{constant} = K$ 11.47

This equation is known as adiabatic expansion ratio.

10.17.6 Calculation of dE, and dH

Calculation of ΔE

As we have studied earlier the molar heat capacity at constant volume of an ideal gas is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Accordingly $dE = C_V\, dT$

And for a finite change $\Delta E = C_V\, dT$ 11.48

Calculation of ΔH

The enthalpy equation (equation 11.15) is given as

$\Delta H = \Delta E + P\Delta V$

As $PV = RT$

$P\Delta V = R\Delta T$

So $\Delta H = \Delta E + R\Delta T$

$= (C_V\Delta T + R\Delta T)$ from equation 11.48

$= (C_V + R)\,\Delta T$

or $\Delta H = C_P\,\Delta T$ 11.49

10.18 SUMMARY

- You have studied in this unit that thermodynamics is an important branch of chemistry which deals with energy transformation in all types of physical chemical process. In studying and evaluating the flow of energy into or out of a system it is useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of a system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

- In the above discussion we have studied first law of thermodynamics and its consequences in detail. The various forms of first law of thermodynamics, various definitions, namely internal energy, enthalpy, heat capacity at constant volume, heat capacity at constant pressure, work done in reversible and irreversible processes and the difference between C_P and C_V have been discussed.
- Most important of these in Joule-Thomson effect which is useful in producing low temperature or cooling. At the inversion temperature, there is no Joule-Thomson effect. If a gas under pressure passes through a porous plug and expands adiabatically into a region of very low pressure at the inversion temperature, there is neither fall nor rise of temperature. If, however the expansion takes place above the conversion temperature, there is small rise in temperature and if it takes place below the inversion temperature there is small fall of temperature.

10.19 TERMINAL QUESTIONS AND ANSWER

(A) Short answer type questions:

1. Define the terms

(a) Closed system

(b) Extensive properties

(c) Isothermal process

(d) Ideal gas

2. Define and explain the following terms

(a) Adiabatic process

(b) Open and closed systems

(c) Homogeneous and heterogeneous system

(d) Zeroth law of thermodynamics

3. Define molar heat capacity at constant volume and molar heat capacity at constant pressure.

4. State and explain first law of thermodynamics.

5. For an adiabatic process prove PV^{γ} = constant

6. Write a note on enthalpy and internal energy.

(B) Long answer type questions:

1. (a) Differentiate clearly between reversible and irreversible processes.

   (b) Calculate the work done in isothermal reversible explanation of an ideal gas.
2. Write notes on the following

   (a) Euler reciprocal relation

   (b) Sign convention of heat and work

   (c) System and surroundings.
3. Differentiate between

   (a) Exact and inexact differentials

   (b)Homogeneous and heterogeneous systems

   (c) Intensive and extensive properties

   (d) System and surroundings
4. Derive expression for the work done in isothermal reversible expansion and isothermal reversible compression of an ideal gas. What is meant by maximum work?
5. Give two definitions of first law of thermodynamics.
6. What is Joule-Thomson effect? How do you account for it? Define inversion temperature. Show that Joule-Thomson coefficient is zero for an ideal gas.

UNIT-11 CHEMICAL EQUILIBRIUM

CONTENTS:

11.1 INTRODUCTION

In a chemical reaction, chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time .Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a sate is known as dynamic equilibrium.

11.2 OBJECTIVES

After going through this unit, you will be able to know.

- Reversible and irreversible reactions.
- Chemical equilibrium.
- Law of mass action.
- Relation between free energy and equilibrium constant.
- Le Chatelier's principle and its applications.
- Clapeyron equation
- Clapeyron Clausius equation and applications.

11.3 REVERSIBLE AND IRREVERSIBLE REACTIONS

Not all chemical reactions proceed to completion .In most reactions two or more substances react to form products which themselves react to give back the original substances.Thus A and B may react to form C and D which react together to reform A and B.

$$A+B \longrightarrow C+D \quad \text{(Forward reaction)}$$

$$A+B \longleftarrow C+D \quad \text{(Reverse reaction)}$$

A reaction which can go in the forward and backward direction simultaneously is called a Reversible rection. Such a reaction is represented by writing a pair of arrows between the reactants and products.

$$A+B \rightleftharpoons C+D$$

The arrow pointing right indicates the forward reaction, while that pointing left shows the backward reaction.

Some Examples of Reversible Reactions:

A few comman examples of reversible reactions are listed below:

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

On the other hand, the reactions which proceed only in one direction are known as irreversible reactions.

Examples:

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$$

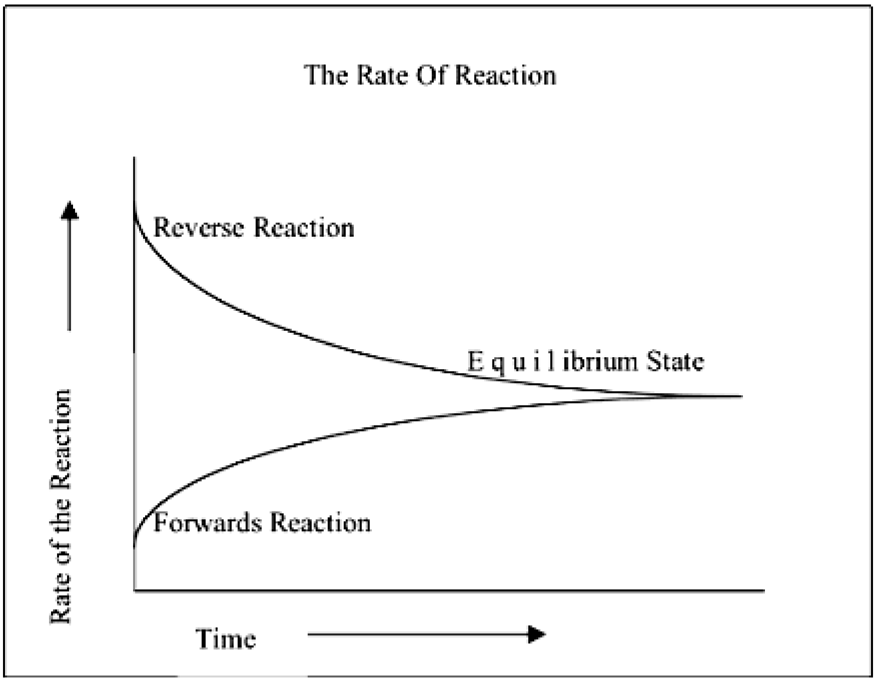
$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

11.4 CHEMICAL EQUILIBRIUM

Let us consider the rection:

$$A+B \rightleftharpoons C+D$$

If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D incease continuously. As a result the rate of forward reaction also decrease and rate of backward reaction increases. Ultimately, the rate of two opposing reactions equals and the system attains a state of equilibrium. Thus "The state of reversible reaction in which the concentrations of the reactants and products do not change is called chemical equilibrium".



At equilibrium the Forward reaction rate equals the Reverse reaction rate

Characteristics of chemical Equilibrium:

Some of the important characteristics of chemical equilibrium are follows:

(i) At equilibrium, the concentration of each of the reactants and products becomes constant.

(ii) At equilibrium, teh rate of forward reaction becomes equal to the rate of backward reaction and hence the equilibrium is dynamic in nature.

(iii) A chemical equilibrium can be established only if none of the products is allowed to escape out.

(iv) Chemical equilibrium can be attained from either direction i.e from the direction of reactants as well as from the direction of the products.

(v) A catalyst does not alter the state of equilibrium.

11.5 LAW OF MASS ACTION

Guldberg and Waage, the two Norwegian chemists, in 1864 put forward a law concerning the dependence of rate of reaction on the concentration of the reactants. This law is known as Law os Mass Action. It states as follows: **The rate of chemical reaction is proportional to the active masses of the reactants.**

The term active mass used in the above statement implies activity which, for the sake of simplicity, may be taken as equal to molar concentration.

Consider the following reversible reaction, taking place at constant temperature:

$$A+B \rightleftharpoons C+D$$

According the law of mass action, the rate (r_1) at which A and B react is given by the equation

$$r_1 \propto [A][B]$$

$$r_1 = k_1[A][B] \ldots\ldots\ldots (i)$$

Where k_1 is the proportionality constant, called rate constant of the reaction and the square brackets indicate molar concentrations. The rate of backward reaction (r_2) is given by the equation

$$r_1 = k_2[C][D] \ldots\ldots\ldots (ii)$$

Where k_2 is the rate constant of reverse reation.

Thus ultimately, a dynamic equilibrium is attained when the rate of forward reaction becomes equal to that of the reverse reaction , i.e., $r_1 = r_2$.

11.6 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Consider the following reversible reaction:

$$aB + bB \rightleftharpoons cC + dD$$

Where a, b, c and d are numerical quotients of the substance, A , B , C and D respectively.

According to law of mass action,

Rate of forward reaction, $r_1 = k_1 [A]^a[B]^b$

Rate of backward reaction, $r_2 = k_2 [C]^c [D]^d$

Since at equilibrium, $r_1 = r_2$, it follows that

$$k_1 [A]^a[B]^b = k_2 [C]^c [D]^d$$

$$or\, \frac{k_1}{k_2} = k_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \ldots\ldots\ldots (i)$$

k_c is known as equilibrium constant and has a fixed value for a certain reaction at a given temperature and pressure and is independent of the amounts of reactants and products. However, its value depends on the temperature and types of reactions.

In a general reaction reprented by the equation

$$aA + bB + cC + \ldots\ldots \rightleftharpoons lL + mM + nN + \ldots\ldots\ldots$$

The equilibrium constant is given by

$$K_c = \frac{[L]^l[M]^m[N]^n \ldots}{[A]^a[B]^b[C]^c \ldots}(ii)$$

For gaseous reactions, it is more convenient to use partial pressures instead of concentrations. The equilibrium constant in that case is represented by $K_{p.}$

Thus for a general gaseous rection

$$aA + bB + cC + \ldots\ldots \rightleftharpoons lL + mM + nN + \ldots\ldots\ldots$$

$$K_p = \frac{[P_L]^l \times [P_M]^m \ldots}{[P_A]^a \times [P_B]^b \ldots}(iii)$$

Where P_L and P_M etc stand for partial pressures of the products and and P_A, P_B, etc for the partial pressures of the reactants.

11.7 RELATIONSHIP BETWEEN K_P AND K_C

For a general reaction,

$$aB + bB \rightleftharpoons cC + dD$$

The equilibrium constant in terms of concentrations (moles/litre) is

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \ldots\ldots\ldots (i)$$

If the reactants and products are gaseous, then the concentration terms may be replaced by partial pressure. The equilibrium constant K_p written as,

$$Kp = \frac{p_C^c p_D^d}{p_A^a p_B^b} \dots\dots\dots (ii)$$

For an ideal gas, $pV = nRT or p = \frac{n}{V}RT = CRT,$

Where C is the molar concentration. For different gases A, B, C, D, we may write

$P_A = C_ART$, $p_B = C_BRT$, $p_C = C_CRT$, $p_D = C_DRT$

Putting these values in equation (ii), we get

$$K_p = \frac{(C_CRT)^c (C_DRT)^d}{(C_ART)^a (C_BRT)^b}$$

$$or K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c (RT)^{\Delta n}} \qquad \dots\dots\dots\dots\dots(iii)$$

Where $\Delta n = (c + d) - (a + b)$

= [number of moles of products]- [number of moles of reactants]

11.8 THERMODYNAMIC DERIVATION OF THE LAW OF CHEMICAL EQUILIBRIUM

Let us consider a general reaction,

$$aA + bB + \dots \rightleftharpoons cC + dD + \dots\dots$$

The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^0 + RT \ln a \dots\dots\dots\dots\dots (i)$$

Where μ^0 is the chemical potential of pure substance in standard state of unit activity, R is the gas consatant and T is the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a(\mu^0 + RT\ln a_A)$$

And similarily

$$b\mu_B = b(\mu^0 + RT\ln a_B)$$

$$c\mu_C = c(\mu^0 + RT\ln a_C)$$

$$d\mu_D = (\mu^0 + RT\ln a_D)$$

The change in free energy for the reaction is given by

$$\Delta G = G_{products} - G_{reactants}$$

On substitution we get

$$(c\mu_c\text{+d}\mu_D + \cdots) - (a\mu_A + b\mu_B = \cdots$$

$$=(c\mu_c + d\mu_D + \cdots) - (a\mu_A + b\mu_B + \cdots)$$

$$=c[\mu_C^0\text{+RT ln } a_C] + d\{\mu_D^0 + c\}\text{]-}[a(\mu_a^0 + \; RT\,ln a_A\} + \; b[\mu_B^0\text{+RT ln } a_B\}]$$

$$= [\{c\mu_C^0 + d\mu_D^0 + \cdots\} - \{a\mu_A^0 + \mu_B^0 + \cdots\}] + RT\,ln\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$$

$$\Delta G = \Delta G^0 + RT\,ln\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \dots\dots.(ii)$$

Where ΔG^0 is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

$\Delta G^0 = \{c\mu_C^0 + \ d\mu_D^0 + \cdots\} - \{\ a\mu_A^0 + \mu_B^0 + \cdots\}$

In equation (ii) the factor A is given by

$$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$$

Stands for the reaction quotient of activities of the product and reactants. It may be denoted by J.The equation (ii) becomes,

$\Delta G = \Delta G^0 + RT lnJ \dots \dots (iii)$

The equation (iii) is called van't Hoff reaction isotherm

For the reaction at equilibrium

$$\Delta G = 0$$

Therefore , $\Delta G^0 = \ -RT lnJ$

Or $\Delta G^0 = -RT ln\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$

As ΔG^0 is the free energy of the reaction in the standard state and is constant at given temperature.

Also, the gas constant R and T are constant, the factor

$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots}$is a constant i.e,

$$\frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} = aconstant\ = K$$

From equation (iii) we have

$$\Delta G^0 = \ -RT lnK \dots \dots (iv)$$

Or $c = -2.303RTlogK \ldots\ldots(v)$

The equation (iv) is also called van't Hoff Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (ΔG^0) from the equilibrium constant and vive –versa.

The sign of ΔG^0 indicates whether the forward or reverse reaction is spontaneous.Considering the equation (iv), we can have three possibilities depending on the sign of ΔG^0 for the reaction.

(1) If $\Delta G^0$is negative, log K must be positive and the reaction proceeds spontaneously in the forward reaction.

(2) If ΔG^0 is positive, log K must be negative and K is less than one. The reverse reaction is then spontaneous.

(3) If $\Delta G^0 = 0, \log K = 0\ andK = 1$. The reaction is at equilibrium.

11.9 LE- CHATELIER'S PRINCIPLE

The effect of concentration, temperature and pressure on a system in equilibrium can be predicted with the help of a generalization first proposed by by a French chemist Le Chetelier in 1884. After his name, this generalization is known as Le Chatelier's principle. It states as follows:

If a system is in equilibrium is subjected to change of concentration, temperature or pressure , the equilibrium shifts in a direction that tends to reduce the effect of the change imposed.

Let us now discuss the effect of the various factors one by one.

(1) Effect of Concentration Change on the Position of Equilibrium:

If the concentration of one of the substances present in an equilibrium reaction is changed without change in any of the other conditions, then by Le-Chatelier's principle , the position of equilibrium will move to decrease the concentration of the added substance. Thus, in the reaction

$$N_2(g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$$

At a given temperature , adding N_2 or O_2 Would shift the equilibrium from left to right, i.e, more nitric oxide (NO) will be formed.

The effect of changes in concentration of substances on the position pf equilibrium in a chemical reaction may be summarized as follows:

Change in concentration of substance	Effect on equilibrium position of reaction $A + B \rightleftharpoons C + D$
Increase in concentration of A or B	Proportion of C and D increased , i.e., Equilibrium shifts to right.
Decrease in concentration of A or B	Proportion of C and D decreased , i.e., Equilibrium shifts to left.
Increase in concentration of C or D	Proportion of A and B increased , i.e., Equilibrium shifts to left.
Decrease in concentration of C or D	Proportion of A and B decreased , i.e., Equilibrium shifts to right.

Some examples from everyday life:

(1) Clothes dry quicker when there is a breeze or we keep on shaking it. This is because water vapour of the nearby air removed and cloth loses more water vapour to re-establish equilibrium with the surrounding air.

(2) We sweat more on a humid day but it evaporates when we sit under the fan. More sweating takes place beacuase the surrounding air has large amount of water vapour and

our skin cannot lose more to it. The fan removes the humid air and evaporation starts from the skin.

(3) Transport of oxygen by haemoglobin in blood. Oxygen breathed in combines with the haemoglobin in the lungs according to the equilibrium

$$Hb\ (s) + O_2 \rightleftharpoons HbO_2\ (s)$$

When it reaches the tissues , the pressure of oxygen is low. To readjust the equilibrium, oxyhaemoglobin gives up oxygen. When it returns to lungs where the pressure of oxygen if high, more of oxyhaemoglobin if formed.

(1) Effect of Temperature Change on the Position of Equilibrium:

The change of temperature alters the state of equilibrium for only those reactions in which either heat is evolved (exothermic) or heat is absorbed (endothermic). In fact , every such reactions is made up of two opposing reactions. If the forward reaction is exothermic, the backward reaction will be endothermic and vive-versa.

(i) Consider the exothermic reaction

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)\ \Delta H = -92.4kJ$$

Or it may be written as

$$N_2 + 3H_2\ (g) \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} 2NH_3\ (g) + 92.4\ kJ$$

Obviously, the the forward reaction is exothermic while the backward reaction is endothermic. Now, if the temperature is increased i.e heat is supplied to the system, and then according to Le Chatelier’s principle, the equilibrium will shift to the side that absorbs heat i.e in the backward direction. Similarly, decrease in temperature will shift the equilibrium in the forward direction.

(ii) Again , consider the endothermic reaction

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)\ \Delta H = +180.7kJ$$

Or it may be written as

$$N_2\,(g) + O_2(g) \quad + 180.7\text{kJ} \underset{\text{exo}}{\overset{\text{endo}}{\rightleftharpoons}} 2NO\,(g)$$

Here the forward reaction is endothermic while backward reaction is exothermic .The increase of temperature will favour the forward reaction while the decrease of temperature will favour the backward reaction.Thus in general,

Exothermic reactions are favoured by low temperature whereas endothermic reactions are favoured by high temperature.

Effect of Pressure Change on the Position of Equilibrium:

This factor has significant roles to play only in case of gaseous reactions and those too which proceed with a change in number of moles.

(i) Consider the dissociation of N_2O_4 into NO_2:

$$\underset{\text{1 mole}}{N_2O_4\,(g)} \rightleftharpoons \underset{\text{2 moles}}{2NO_2\,(g)}$$

Here, the forward reaction occurs with increase in number of moles. Therefore backward reaction must proceed with decrease in number of moles. If now the pressure on the system is increased, the volume of the system will decrease correspondingly.Hence the total number of moles per unit volume will now be more than before. Therefore according to Le Chatelier's principle, the equilibrium will shift in that direction in which the total number of moles decreases. Since backward reaction takes place with decrease in number of moles so an increase in pressure will favour the formation of N_2O_4. Conversely, if the pressure on the system is decreased, the equilibrium will shift in the forward direction which is accompanied by increase in total number of moles. In other words , decrease in pressure favours the formation of NO_2.

(ii) Consider another gaseous reaction involving formation of ammonia.

$$\underset{\text{1 mole}}{N_2\,(g)} \;+\; \underset{\text{3 moles}}{3H_2\,(g)} \rightleftharpoons \underset{\text{2 moles}}{2NH_3}$$

In this equilibrium reaction, the forward reaction is accompanied by a decrease in the total number of moles. On increasing pressure number of moles per unit volume will increase as result equilibrium will shift to the product side i.e it favours the formation of ammonia. Thus, higher the pressure, the better would be the yield of ammonia. On the other hand, a decrease in pressure will favour the dissociation of NH_3 into N_2 and H_2.

(iii) Lastly, consider the following equilibrium reaction involving the formation of hydrogen iodide.

$$\underset{1\text{mole}}{H_2\,(g)} + \underset{1\text{mole}}{I_2\,(g)} \rightleftharpoons \underset{2\text{ moles}}{2HI\,(g)}$$

This reaction place in either direction without change in number of moles. So according to Le Chatelier’s princilple, pressure will have no effect on this equilibrium. In general,

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no chage in total number of moles.

Effect of addition of inert gas on the position of equilibrium:

The effect of addition of addition of inert gas can be studied under two different conditions:

(i) Addition of inert gas at constant volume: when an inert gas is added to the equilibrium state at constant volume, then the total pressure will increase. But the partial pressure of each component will remain unchanged. Under these conditions, there will no effect on the equilibrium on addition of the inert gas.

(ii) Addition of an inert gas at constant pressure: when an inert gas is added to the system at constant pressure there will be increase in the volume. As a result, the number of moles per unit volume of different components will decrease. The equilibrium will shift to the side where the number of moles is increased. For example consider the following equilibrium.

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g) \quad \text{at constant pressure}$$

The addition of inert gas at constant pressure will shift the equilibrium to backward direction.

For the equilibrium

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2(g) \quad \text{at constant pressure}$$

The addition of inert gas at constant pressure will shift the equilibrium to the forward direction.

However, addition of an inert gas to the following equilibrium

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g) \quad \text{at constant pressure}$$

Will have no effect because the number of moles of reactants and products are same.

Effect of catalyst on the position of equilibrium:

There is no effect of addition of a catalyst on the equilibrium state. This is because catalyst increases the rate of forward reaction as well as rate of backward reaction to the same extent. It simply helps to achieve the equilibrium quickly. It may be further noted that catalyst has no effect on the equilibrium concentration of a reaction mixture.

Applications of Le Chatelier’s Princilple:

(1) Physical Equilibria

(a) Melting point of ice: Ice melts with decrease in volume as well as absorption of heat, e.g.,

$$H_2O\ (s) \rightleftharpoons H_2O\ (l).$$

It is represented as:

$$\underset{\text{(More volume)}}{\text{Ice}} \overset{0^0C}{\rightleftharpoons} \underset{\text{(Less volume)}}{\text{Water} \ - \ \text{Heat}}$$

Increase of pressure or temperature will shift the equilibrium from left to right. In other words, melting point of ice is lowered by an increase of pressure or temperature.

(b) Vaporisation of water: The equilibrium between water and steam is represented as:

$$\underset{\text{(Less volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(More Volume)}}{\text{Water vapour}} \quad - \text{Heat}$$

On increasing the temperature, the equilibrium will shift in that direction in which heat is absorbed, i.e, forward reaction. So, more steam will be produced. Similarily, on increasing the pressure, the equilibrium will shift in that direction in which volume is decreased, i.e., backward reaction. So, steam will condense into liquid. In other words, formation of steam will be favoured by increase of temperature and decrease of pressure.

(c) Solubility of substances: Certain substances like sugar, NaCl etc dissolve with an absorption of heat, eg.,

$$\text{Sugar} + \text{aq} \rightleftharpoons \text{Sugar (aq)} \; - \; \text{Heat}$$

So, increase of temperature will shift equilibrium to the right. So, the solubility of such substances increases on increase the temperature.

Certain substances like $Ca(OH)_2$ etc. Dissolve with an evolution of heat, e.g.,

$$Ca(OH)_2 + \text{aq} \rightleftharpoons Ca(OH)_2 + \text{Heat}$$

So, increase of temperature will shift the equilibrium to the left, i.e., direction in which heat is absorbed. So, the solubility of such substances decreases on increasing the temperature.

(d) Solubility of gases in liquids: Consider the solution of a gas in equilibrium with the gas. The equilibrium can be represented as:

$$\underset{\text{(more volume)}}{\text{Gas} + \text{Solvent}} \rightleftharpoons \underset{\text{(less volume)}}{\text{Solution of gas}}$$

If pressure is increased, volume will reduced without affecting the pressure and some of the gas will dissolve in the solvent. Thus, the solubility of gas increases on increasing the pressure.

(2) Chemical Equilibria:

(a) Synthesis of ammonia by Haber's process: Haber's process involves the reaction.

$$\underset{\text{1 vol.}}{N_2\,(g)} + \underset{\text{3 vol}}{3H_2\,(g)} \rightleftharpoons \underset{\text{2 vol}}{2NH_3\,(g).,} \quad \Delta H = -22\ kcal$$

(i) Effect of temperature: If the temperature of the reaction is lowered, the equilibrium must shift so as to tend to raise the temperature again (Le Chatelier's principle). That is, heat must be liberated by the production of ammonia. That is low temperature favours the formation of ammonia. But lowering of temperature reduces the rate of reaction, so it is necessary to use a catalyst which will give a sufficient reaction rate inspite of a relatively low temperature.

(ii) Effect of pressure. Ammonia is produced from its elements with reduction of volume. Therefore, if the system is in equilibrium and the pressure is then raised, the equilibrium must shift so as to tend to lower the pressure (Le Chatelier's principle). To do this, the volume must be reducrd by the production of more ammonia. That is, high pressure favours the formation of ammonia.

(iii) Effect of concentration. If the system is in equilibrium and more N_2 is added to increase its concentration, then according to Le Chatelier's principle, the equilibrium will shift so as to tend to reduce N_2 concentration. That is, more ammonia will be produced to use up N_2. This increase the yield of ammonia relative to H_2, and vive versa if the H_2 concentration is increased.

The formation of ammonia is favoured by:

(i) Low temperature
(ii) High pressure, and
(iii)High concentration of the reactants.

(b) Formation of sulphuric acid by the contact process: The first step in the production of sulphuric acid is the conversion of sulphur dioxide into sulphur trioxide according the reaction

$$\underset{2\ \text{vol}}{2SO_2\,(g)} + \underset{1\ \text{vol}}{O_2\,(g)} \rightleftharpoons \underset{2\ \text{vol}}{2SO_3\,(g)} \qquad \Delta H = -47\ kcal$$

This reaction is just similar to the synthesis of ammonia described above. So, the effect of pressure, temperature and concentration will be the same as mentioned in the synthesis of ammonia. Low temperature, high pressure and increased concentrations of SO_2 and O_2 will favour the formation of sulphur trioxide.

The SO_3 is removed from the equilibrium mixture by dissolving it in fairly concentrated sulphuric acid, forming oleum which is then diluted to get the acid of the required concentration.

(c) Formation of nitric oxide: The reaction is represented as,

$$\underset{1\ \text{vol}}{N_2\,(g)} + \underset{1\ \text{vol}}{O_2\,(g)} \rightleftharpoons \underset{2\ \text{vol}}{2NO\,(g)} \qquad \Delta H = +43.2\ kcal$$

(i) Effect of pressure: As no change of volume occurs during the formation of nitric oxide, there will be no effect of pressure on the equilibrium.

(ii) Effect of temperature: if the temperature is increased then the equilibrium will shift in that direction in which heat is absorbed, i.e., in the forward direction. So , high temperature favours the formation of nitric oxide.

(iii) Effect of concentration: If to the system in equilibrium N_2 is added, the equilibrium will shift in that direction so as to reduce the concentration of N_2.So, more nitric oxide will be formed. Similar is the effect of adding oxygen.

So, the formation of nitric oxide is favoured by

(i) High temperature and

(ii) High concentrations of N_2 or O_2.

11.10 VAN'T HOFF ISOTHERM OR MAXIMUM WORK OBTAINED FROM GASEOUS REACTIONS

Consider the following reaction

$$\text{aA} + \text{bB} + \dots\dots \rightleftharpoons \text{lL} + \text{mM} + \dots\dots$$

Taking palce under any conditions of temperature, pressure and composition. The free energy change of the reaction is given by the expression

$$\Delta G = (G)_{products} - (G)_{reactants} \dots \dots \dots (i)$$

$$= (l\mu_L + m\mu_M + \cdots) - \ (a\mu_A + b\mu_B + \cdots$$

Where μ_A, μ_B,μ_L, μ_M, etc represents chemical potentials of the species concerned.

Let us suppose the various reactants and products are in gaseous state. Chemical potential of a gaseous substance in any state is given by the equation

$$\mu_{i(p)} = \mu^0_{i(p)} + \ RT\, lnp_i \dots \dots \dots (ii)$$

Where $\mu^0_{i(p)}$ is the chemical potential of gaseous component i, in the standard state (partial pressure = 1 atm) and $\mu_{i(p)}$is the chemical potential of the gaseous component i in any state of partial pressure p_i.

Substituting the values of chemical potentials of various species at their partial pressures from eq (ii) in eq(i)

$$\Delta G = \{l(\mu^0_{L(p)} + RT\, inp_L + m(\mu^0_{M(p)} + RT\, inp_M) + \cdots\} \\ - \{a(\mu^0_{A(p)} + RT\, inp_A + b(\mu^0_{B(p)} + RT\, inp_B) + \cdots\} \dots \dots \dots (iii)$$

Re arranging we have

$$\Delta G = \{l\mu^0_{L(p)} + m\mu^0_{M(p)} + \cdots) - \ (a\mu^0_{A(p)} + b\mu^0_{B(p)} + \cdots)\} \\ + RT\, ln \frac{(P_L)^l (P_M)^m \dots}{(P_A)^a (P_B)^b \dots} \dots \dots \dots . (iv)$$

The first expression on thr right hand side, evidently, is the free energy change of the reaction when the products and the reactants are all in their respective standard states. This exression may be substituted by ΔG^0.Hence,

$$\Delta G = \Delta G^0 + RT\ln Q_p \qquad ....(v)$$

Where Q_p stands for the reaction quotient of partial pressures of the products and reactants , viz, $\frac{(P_L)^l(P_M)^m...}{(P_A)^a(P_B)^b...}$

Eq (v) is known as van't Hoff reaction isotherm.This gives the free energy change of a reaction at any given temperature, pressure and composition of the reacting system,

Q_p is different from K_p. Here the values p_L, p_M, p_A,p_B....etc are not the partial pressures at equilibrium, but for any state. If the partial pressure values correspond to equilibrium state, then Q_p will become equql to K_p. As we have

$\Delta G^o = -RT lnK_p$

Substituting for ΔG^o in eq (v), we have

$$\Delta G = -RT inK_p + RT lnQ_p \ldots \ldots \ldots (vi)$$

Eq(v) and eq (vi) are two forms of van't Hoff reaction isotherm.

Example. At 25^0, the ΔG^o for the reaction

$$H_2(g) + I_2(g) \longrightarrow 2HI(g),$$

is -3.1 kcal. Calculate ΔG when hydrogen gas at 0.1 atm and iodine vapour at 0.1 atm react to form hydrogen iodide at 10 atm, and 25^0.

Solution. For the given reaction,

$$K = \frac{p^2(HI)}{p(H_2)p(I_2)}$$

Where p terms represent partial pressures of the various species in the reaction mixture.

$$\Delta G = \Delta G^o + RT \ln K = \Delta G^o + 2.303\ RT log \frac{p^2(HI)}{p(H_2)p(I_2)}$$

$$= -3100\ cal + 2.303\ (1.987 calK^{-1}mol^{-1})(298K) log \frac{(10)^2}{(0.1)(0.1)}$$

$$= \ -3100\ cal + 1363.7 \log(10^4)\ cal = -3100\ cal + 4\ (1363.7\ )cal$$
$$= +2354.8\ cal = 2.355\ kcal.$$

11.11 VAN'T HOFF EQUATION FOR THE TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VAN'T HOFF REACTION ISOCHORE)

The equation for reaction isotherm when the reactants as well as the products are gaseous and are also in their standard states, is represented as

$$\Delta G^0 = \ -RT lnK\_(p \qquad \ldots\ldots\ldots(i)$$

Differentiating with respect to temperature at constant pressure, we have

$$\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}_{\mathrm{p}} = \ -RlnK_p - RT\frac{d(\ln K_p)}{dt}$$

Multiplying throughout by T, we get

$$T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p = -RTlnK_p - RT^2\frac{d(lnK_p)}{dT} \ldots\ldots\ldots(ii)$$

Substituting ΔG^o for $-RTlnK_p$, we have

$$T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p = \Delta G^o - RT^2 lnK_p - RT^2\frac{d(lnK_p)}{dT} \ldots\ldots\ldots(iii)$$

The well known Gibbs-Helmholtz equation for substances in standard states may be written as

$$\Delta G^o = \Delta H^o + T\left\{\frac{\partial(\Delta G^0)}{\partial T}\right\}p \qquad \ldots\ldots\ldots(iv)$$

Comparing equations (iii) and (iv), we get

$$RT^2\frac{d(lnK_p)}{dT} = \Delta H^o$$

$$or \qquad \frac{d(lnK_p)}{dT} = \frac{\Delta H^o}{RT^2}\ldots\ldots\ldots(v)$$

Equation (v) is known as the van't Hoff's equation. ΔH^o is the enthalpy change for the reaction at constant pressure when the reactants as well as products are in their standard states.

It is well known from experiments that the enthalpy change, ΔH, accompanying a chemical reaction does not vary appreciably with change in partial pressures of the reactants and products . Therefore, we may take $= \Delta H^o$ as equal to ΔH , where ΔH is the enthalpy change of the reaction whatever may be the partial pressures of the reactants or products . Hence, the van't Hoff equation may be written as

$$\frac{d(\ln(K_p)}{dT} = \frac{\Delta H}{RT^2}\ldots\ldots\ldots(vi)$$

Integrating equation (vii) between temperatures T_1 and T_2 at which the equilibrium constants are $K_p{}'$and $K_p{}''$ respectively and assuming that ΔH remains constant over this range of temperature,we get

$$\int_{K_p'}^{K_p''} d(lnK_p = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$lnK_p'' - lnK_p' = \frac{-\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_{1T_2}}\right] \ldots\ldots\ldots (vii)$$

$$logK_p'' - logK_p' = log\frac{K_p''}{K_p'} = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \ldots\ldots.(viii)$$

Knowing the equilibrium constant at a temperature it is possible to calculate the equilibrium constant at another temperature provided the heat of reaction (ΔH) is known.

Alternatively, knowing the equilibrium constants of a reaction at two temperatures, the heat of reaction ((ΔH) can be calculated.

Example: The equilibrium constant K_p, for the reaction

$$H_2(g) + S(g) \longrightarrow H_2S(g)$$

Is 20.2 atm at 945^{o}C and 9.21 atm at 1065^{0}C. Calculate the heat of reaction.

Solution . Applying van’t Hoff equation

$$logK_p'' - logK_p' = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

T_1 = 945+ 273 =1218 K

T_2 = 1065 + 273 =1338 K

$K_p{}'$ = 20.2 atm

$K_p{}''$ = 9.21 atm

Substituting the values, we have

$$log 9.21 - log 20.2 = \frac{\Delta H}{(2.303)(8.314\,JK^{-1}mol^{-1})}\left[\frac{1338 - 1218}{(1218K)(1338K)}\right]$$

$$\Delta H = -88126.3\,J = -88.826\,kJ$$

11.12 THE CLAPEYRON EQUATION

Clapeyron equation is an important equation applicable to the equilibrium between any two phases of the same substance. This equation can be derived from second law of thermodynamics as follows:

Suppose a single substance exists in two phases A and b in equilibrium wirh each other at constant temperature and pressure. If one mole of substance is transferred from one phase A to the other phase B without altering the temperature and pressure , then there will be no work done other than that of expansion. So from equation ($\Delta G = VdP - SdT$), we get,

$$dG = 0, as\ dP = 0\ and\ dT = 0$$

i.e., $G_B - G_A = 0\ or\ G_A = G_B$

in other words, the molar free energy of a substance is the same in the two phases which are in equilibrium.

In a phase change, ($\Delta G = VdP - SdT$, can be written as

$$dG_A = V_A dP - S_A dT \qquad \dots\dots\dots (i)$$

And

$$dG_B = V_B dP - S_B dT \qquad \dots\dots\dots (ii)$$

Subtracting equations (i) from (ii), we get,

$$dG_B - dG_A = (V_B dP - S_B dT) - (V_A dP - S_A dT)$$

Or $0 = (V_B dP - S_B dT) - (V_A dP - S_A dT)$ $(As\ G_A = G_{B})$

Or $V_B dP - S_B dT = V_A dP - S_A dT$

Or $(V_B - V_A) dP = (S_B - S_A) dT$

Or $\Delta V dP = \Delta S dT$

Or $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

Where ,ΔS and ΔV have their usual significance.

Recognising further that at equilibrium we have the change in entropy (ΔS), given by

$$\Delta S = \frac{\Delta H}{T}$$

(as $\Delta G = 0$, at equilibrium)

Therefore,

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \qquad \dots\dots\dots (iii)$$

Equation (iii) was first derived by a French engineer Clapeyron in 1834. It gives the variation of equilibrium pressure (P) with temperature for any two phases of a given substance.

Application (iii) is applicable to various equilibria such as soild-liquid equilibria , liquid-vapour equilibriaand equilibria between two solid modifications. The Clapeyron's equation for these various equilibria can be easily obtained as follows:

(1) Solid-liquid equilibrium: We know that solid and liquid forms of a substance can exist in equilibrium only at the freezing or melting point. Hence, in equation (iii), T will be the freezing point and P will be the external pressure exerted on the system. So, equation (iii) can also be written in areversed form as:

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} \qquad \ldots\ldots\ldots(iv)$$

If V_S, and V_L represents the molar volumes of the solid and the liquid phases, respectively at temperature T and pressure P, then,

$$\Delta V = V_L - V_S$$

Where, ΔV represents the increase in volume in transferring 1 mole from solid to liquid phase, ΔH the amount of heat absorbed may be replaced by ΔH_f,i.e., molar heat of fusion. So making these changes in equation (iv), we get the following Clapeyron's equation:

$$\frac{dT}{dP} = \frac{T\ (V_L - V_S)}{\Delta H_f} \qquad \ldots\ldots\ldots(v)$$

(2) Liquid-vapour equilibrium: In this equilibrium, the increase in volume (ΔV) accompanying the transfer of one mole of liquid to the vapour will be equal to $V_V - V_L$, where V_V and V_L represents the molar volumes of vapour and liquid, respectively. ΔH may then be replaced by ΔH_V,i.e., molar heat of vaporisation.

From the above considerations, equation (iv) becomes:

$$\frac{dT}{dP} = \frac{T\ (V_V - V_L)}{\Delta H_V} \ldots\ldots\ldots(vi)$$

It is a well known fact that the boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure.

So, equation (vi) represents the variation of boiling point of a liquid with pressure P. Thus, equation (vi) can also be written as:

$$\frac{dP}{dT} = \frac{\Delta H_V}{T\ (V_V - V_L)} \ldots\ldots\ldots(vii)$$

Equation (vii) reprersents the rate of change of vapour pressure (P) of the liquid with temperature.

(3) Equilibrium between two solid modifications: If α represents the stable form of solid above the transition point and β the stable form of the solid below the transition point then equation (iii) becomes:

$$\frac{dT}{dP} = \frac{T\,(V_\alpha - V_\beta)}{\Delta H_t} \ldots\ldots\ldots (viii)$$

Where, V_α and V_β represents the molar volumes of the two forms respectively and ΔH_t is the molar heat of transition determined at T.

(ii) Applications of Clapeyron Equation

The Clapeyron equation can be applied in numerous ways to several physio-chemical problems.

(i) It can be used for predicting the effect of pressure on the volumes or densities of the solid liquid phases (V_s and V_L) and of heat of fusion(ΔH_f).

if $V_L < V_s$ then $(V_L - V_S)$ will be negative and so dT/dP will be negative . In other words, increase of pressure will decrease the melting point. This is observed in the ice-water equilibrium

if $V_S < V_L$ then $(V_L - V_S)$ will be positive and so dT/dP will be positive . In other words, increase of pressure will increase the melting point.

(ii) It is also possible to calculate the enthalpy of fusion (ΔH_f) of a substance from equation (vi), is dT/dP or rather $\Delta T/\Delta P$ and specific volumes of the solid and liquid phases are known.

(iii) Clapeyron equation can also predict the effect of pressure on the transition temperature with the help of equation (viii). Similarily, we can precisely calculate the enthalpy of transition from the change in volume, i.e., $(V_\alpha - V_\beta)$ and the value of dT/dP, from equation (viii).

(iv) The enthalpy of vaporisation (ΔH_V) can also be calculated from equation and also we can easily find the rate of change of boiling point from equation (vi).

Problem 1. The orthobaric specific volumes of ice and water at 0^0C are 1.0907 c.c. and 1.0001 c.c., respectively. What will be the change in melting point of ice per atmosphere increase of pressure? The latent heat of fusion is 79.8 cal/g.

solution: Orthobaric specific volume of ice (V_S) = 1.0001 c.c.

Orthobaric specific volume of water ($V_{L)}$ = 1.0001 c.c.

So $V_L - V_S = -0.0906$ c.c.

Latent heat of fusion ΔH_f =1 atm = $76 \times 13.6 \times 981$

$= 1.013 \times 10^6$ dynes/sq.cm.

dT= ?

we know that for solid-liquid equilibrium, we have,

$$\frac{dT}{dP} = \frac{T\,(V_L - V_S)}{\Delta H_f}$$

$$dT = \frac{T\,(V_L - V_S)}{\Delta H_f}.d$$

$$= \frac{273 \times 0.0906 \times 1.013 \times 10^6}{79.8 \times 4.2 \times 10^7}$$

$$= -\ 0.007476^0\text{C}$$

The negative sign indicates that melting point of ice decreases by increase of pressure.

11.13 CLAUSIUS-CLAPEYRON EQUATION

If the temperature of the liquid is not too near the critical point then we can easily neglect the volume of the liquid (V_L), compared with that of vapour (V_V).In such a case, the equation $\frac{dP}{dT} = \frac{\Delta H_V}{T(V_V - V_L)}$ reduces to equation (1) on replacing P by p.So

$$\frac{dP}{dT} = \frac{\Delta H_V}{TV_V} \ldots\ldots\ldots (i)$$

Furthermore, under such conditions the vapour pressure is very small, so it may be assumed that the vapour behave as an ideal gas to which the equation $pV_v=RT$ is applicable.

$$\frac{dP}{dT} = p.\frac{\Delta H_V}{RT^2}$$

$$or \qquad \frac{1}{p.}\frac{dP}{dT} = \frac{\Delta H_V}{RT^2}$$

$$or \qquad \frac{d\log p}{dT} = \frac{\Delta H_V}{RT^2} \ldots\ldots\ldots (ii)$$

Equation (ii) is sometimes known as Clausius-Clapeyron equation and is generally spoken of as first latent heat equation.It was first derived by Clausius (1850) on the thermodynamics basis of Clapeyron equation.

Equation (ii) is valid for evaporation and sublimation processes but not valid for transistion between solids or for the melting of solids. Clausius-Clapeyron equation is an approximate equation because the volume of the liquid has been neglected and ideal behaviour of the vapour is also taken into account. However equation (ii) has the advantage of greater simplicity because in the calculation of the value dp/dT or dT/dp, it is necessary to know the volumes of the liquid and the vapour.

11.13.1 Integrated form of clausius-clapeyron equation

Assuming the heat of vaporisation to be independent of temperature, if we integrate equation (ii) between the limits T_1 to T_2 (for temperature) and p_1-p_2 (for vapour pressure),we get,

$$\int_{p_1}^{p_2} d\log p = \int_{T_1}^{T_2} \frac{\Delta H_V}{RT^2} dT$$

Or $$ln\frac{p_2}{p_1} = \frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

Or $$2.303\log\frac{p_2}{p_1} = \frac{\Delta H_V}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Or $$\log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \ldots\ldots\ldots(iii)$$

If ΔH_V is expressed in cal/mole and R= 1.987 cal/degree/mole, then equation (iii) becomes

$$\log\frac{p_2}{p_1} = \frac{\Delta H_V}{4.576}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \ldots\ldots\ldots(iv)$$

Equation (iv) is the integrated form of Clausius- Clapeyron equation. If the integration is carried out indefinitely (without limits) then we can write the vapour pressure equation as(ii) as

$$\log p = -\frac{\Delta H_V}{RT} + C\ (contant) \ldots\ldots\ldots(v)$$

Problem 1.The vapour pressure of water at 95 C and 100 C are 634 and 760mm,respectively.Calculate the latent heat of evaporation of water per gram between 95^{0}C and 100^{0}C.

Solution:

$$log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Where p_1 and p_2 are vapour pressure at temperature T_1 and T_2 respectively and ΔH_V is the latent heat of evaporation/mole.It is given that:

P_1=634m.m.

P_2=760m.m.

$T_1=95+273=368^0K$, $T_2=100+273=373^0K$

$$So, \quad log\frac{760}{634}=\frac{\Delta H_V}{2.303\times 1.987}\left[\frac{373-368}{368\times 373}\right]$$

$$or \quad \Delta H_V=9886\frac{cal}{mole}=\frac{9886}{18}=549.4\frac{cal}{g}.$$

Problem 2.At what height must the barometer stand in order that water may boil at 99^{0}C?Given that the latent heat of vaporisation of water per gram is 536 cal.

Solution: As known ,the integrated form of Clausius-Clapeyron equation is,

$$log\frac{p_2}{p_1}=\frac{\Delta H_V}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

P_1=76 cm.mercury p_2=?

T_1=100+273=373 K T_2=99+273=372

ΔH_V= 536cal/g =536×18 cal/mole

$$log\frac{p_2}{76}=\frac{535\times 18}{2.303\times 1.987}\left[\frac{372-373}{372\times 373}=-\frac{536\times 18\times 1}{2.303\times 1.987\times 372\times 373}\right]$$

$$log\ p_2-\log 76=-\frac{536\times 18\times 1}{2.303\times 1.987\times 372\times 373}$$

$$or \qquad log\ p_2=log76-\frac{536\times 18\times 1}{2.303\times 1.987\times 372\times 373}$$

$= 1.8806 - 0.0159 = 1.8659.$

$taking\ antilog\ we\ get \qquad p_2 = 73.43\ cm. of\ mercury.$

11.13.2 Applications of clausius-clapeyron equation

(1)Latent heat from vapour pressure data: Suppose the vapour pressures p_1 and p_2 are determined at two temperature T_1 and T_2 respectively, then it is possible to calculate the molar or specific heat of vaporisation. It is also possible to calculate the value of H_V graphically.It is clear that if log p is plotted against the reciprocal of the absolute temperature,i.e.,1/T,then a straight line will be obtained. The slope of this line will be equal to$-\Delta H/R$.So, knowing the value of R, the value of ΔH can thus be easily determined after measuring the slope.

(2)Deduction of Trouton's law: Equation (ii) can be written in the form,

$$\frac{1}{p}.\frac{pd}{dT} = \frac{\Delta H_V}{RT^2}$$

Forl iquid vapour equilibrium $\Delta H_V = L_e$, i.e., molar heat evaporation.Hence, the last expression becomes,

$$\frac{1}{p}.\frac{pd}{dT} = \frac{L_e}{RT^2}$$

$$or \qquad \frac{T}{P}.\frac{dP}{dT} = \frac{L_e}{RT} \qquad \dots\dots\dots(vi)$$

$$we\ know\ that, \qquad \frac{T}{T_c} = \theta\ and\ \frac{P}{P_c} = \pi,$$

Where P_C and T_C represent the critical pressure and critical temperature, respectively and π, θ are the educed pressure and reduced temperature, respectively.So equation (vi) becomes,

$$\frac{\theta}{\pi}.\frac{d\pi}{d\theta} = \frac{L_e}{RT} \qquad (vii)$$

Vander waals (1888) suggested the empirical relationship,

$$\log\frac{P}{P_c} = k\left[1 - \frac{T_c}{T}\right]$$

Where k is constant which is equal to 3 for many substances. Hence in reduced terms it can be put as,

$$log\pi = 2.3k\left[1 - \frac{1}{\theta}\right] \qquad (viii)$$

Differentiating equation (viii) with respect to θ, we get,

$$\frac{dlog\pi}{d\theta} = 2.3\frac{k}{\theta^2}$$

$$or \qquad \frac{1}{\pi}\frac{d\pi}{d\theta} = 2.3\frac{k}{\theta^2}$$

$$or \qquad \frac{\theta}{\pi}.\frac{d\pi}{d\theta} = 2.3\frac{k}{\theta} \qquad \dots\dots..(ix)$$

From equation (vii) and (ix),we conclude that,

$$\frac{L_e}{RT} = 2.3\frac{k}{\theta}$$

$$or \qquad \frac{L_e}{T} = 6.9\frac{R}{\theta}$$

If the temperature is taken to be the boiling point T_b, then θ which is T_b/T_c is nearly equal to 0.6 and,therefore

$$\frac{L_e}{T_b} = 23 \qquad \dots\dots\dots(x)$$

So,the molar heat of vaporisation of a liquid divided by its boiling point on absolute scale, i.e., L_e/T_b is constant and is approximately equal to 23,provided the latent heat is expressed in calories. The fact was first observed by Pictet (1876) and rediscovered by Ramsay (1877) and Trouton (1884) and is commonly known as ***Trouton's law.***Some substances which obey Trouton's law are ethyl ether,benzene,propyl acetate,mercury,zinc,potassium chloride etc.This law is an approximate law.For non-associated substances of molecular weight of about 100,the value of (*Le/Tb*) =21, provided the boiling point is not too high.The law breaks down for associated compounds such as water and alcohol and for substances having high boiling points.

At the normal boiling point the vapour pressure of liquid is equal to 1 atm., hence equation (v) becomes,

$$log l = -\frac{\Delta H_V}{4.576T_b} + C$$

According to Trounton's law, ***for many non-associated substances,*** $\Delta H_v/T_b$ ***may be taken as equal to 21.***Hence,

$$C = \frac{21.0}{4.576} = 4.589$$

The expression for the vapour pressure p (in atm) of any substaces to which Trouton's law is applicable now becomes,

$$log p(atm) = -\frac{\Delta H_V}{4.576T} + 4.589 \qquad \dots\dots\dots(xi)$$

Problem 1.The normal boiling point of benzene is 80.1^{0}C; estimate its vapour pressure at 40^{0}C.

Solution: Since T_b is 80.1+273=353.1, then by Trouton's law

H_v=21   353.1=7415.1 cal.mole^{-1}

According to equation (xi),

$$log p(atm) = -\frac{7415.1}{4.576T} + 4.589 = -\frac{7415.1}{4.576 \times 353.1} + 4.589 = -0.586$$

∴ $p = 0.259 atm. = 0.259 \times 76 = 19.6 cm.$

11.14 SUMMARY

The summery of the present unit is:

- Chemical equilibrium is defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.
- A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction.
- Chemical equilibrium is dynamic equilibrium
- Law of mass action states that the rate of chemical reaction is proportional to the active masses of the reactants.
- Realtion between $K_{p\text{ and }}K_c$

$$K_p = K_c(RT)^{\Delta n}$$

- Thermodyanamic Derivation of Law of Chemical equilibrium is given as,

ΔG^0 = -2.303 RTlog K

- Van't Hoff reaction isotherm gives the free energy of a reaction at any given temperature, pressure and composition of the reacting system.
- Van't Hoff reaction isochore gives the temperature dependence of equilibrium constant.
- Le-Chatelier's principle states that if a system at equilibrium is subjected to a change of concentration, pressure and temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.
- Clausius-Clapeyron equation is given as

$dP/dT = \Delta H/T\Delta V$

It can be applied to various physical equilibria like melting, vaporisation and sublimation.

11.15 TERMINAL QUESTIONS

A. Long Answer type questions

1. Derive law of mass action thermodanamically.

2. Derive the following on the basis of thermodyanamics:

(a) Van't Hoff isotherm (b) van't Hoff isochore (c) Clausius-Clapeyron equation.

3. State and explain Le-Chatelier's principle. Explain the effect of pressure and temperature on an equilibrium on the basis of this princilple.

4. Derive Le-Chatelier's principle thermodynamically.

B. Short Answer and Very Short Answer type Questions

1. State law of mass action.

2. Define Le-Chatelier's principle.

3. Derive Clapeyron equation.

4. Derive integrated form of van't Hoff isochore.

5. Write an equation which relates equilibrium constant with temperature.

6. Write an application of Clausius-Clapeyron equation.

7. Explain Trouton's law.

8. State and explain Le-Chatelier's principle.

9. Write a relation between K_P and $K_{C.}$

C. Numerical Problems:

1.The melting point of sulphur is 398K and its latent heat of vaporisation is 9.3 cal/gm. Find the change in melting point of sulphur per atmosphere change in pressure if the per gram volume of its α and β forms are 0.732 c.c. and 0.7070 c.c., respectively.

2. The heat of vaporisation of water is 40.82 Kj mol^{-1}.The molar volume of liquid water is 0.019 dm^3 mol^{-1} and the molar volume of steam is 30.199 dm^3 mol^{-1},all at 1000C and 1atm.Calculate the change in boiling point of water at 100^{0}C,if the atmospheric pressure is change by 1mm?(1atm.= 101325 Nm^{-2}).

3. Calculate the vapour pressure of water at 80^{0}C if its value at 100^{0}C is 76.0 cm.The mean heat of vapourisation of water in the given temperature range is 540 cal g^{-1}.

4. At what temperature will water boil under a pressure of 790mm ?The latent of vapourisation of water is 540 cal g^{-1}.R=1.987 cal K^{-1} mol^{-1}.

5. At what temperature should water boil at space station where the atmospheric pressure is 528 mm?Latent heat of vapourisation of water is 545.5540 cal g^{-1}.

6.The vapour pressure of water at 100^{0}C is 760mm.Calculate its vapour pressure at 95^{0}C.Given : latent of water =548 cal g^{-1}.

D. Multiple Choice Questions:

1. The vapour pressure of water at 100^{0}C is 760mm.The molar heat of vapourisation of water is 41.27 kJ mol^{-1}. The vapour pressure of water at 95^{0}C is :

(a) 63.43 mm (b) 760 mm (c) 740.6 mm (d) 634.3 mm

2. The maximum work done in a reaction is given by :

(a) Van't Hoff isotherm (b) van't Hoff isochore

(c) Clausius-Clapeyron equation (d) None

3. The variation of equilibrium constant with temperature is given by:

(a) Van't Hoff isotherm (b) van't Hoff isochore

(c) Law of mass action (d) Le-Chatelier's principle

4. The variation of vapour pressure with temperature is given by:

(a) Van't Hoff isotherm (b) van't Hoff isochore

(c) Law of mass action (d) Clausius-Clapeyron equation

5. The affinity of reaction can be obtained from:

(a) Clausius-Clapeyron equation (b) van’t Hoff isochore

(c) Clapeyron equation (d)) van’t Hoff isotherm

E. Fill in the blanks:

1. The law of mobile equilibrium was given by..................
2. Van’t Hoff equation gives the variation of................with temperature.
3. The equilibrium constant............. with increase of temperature.
4. dP/Dt =H/T V is known as............equation.
5. The heat of sublimation can be calculated from ....equation.
6. K_p and K_c are related by the equation.............
7. The chemical affinity of a reaction can be determined from.............

UNIT -12 IONIC EQUILIBRIUM

CONTENTS:

12.1 INTRODUCTION

There are numerous equilibria that involve ions only. In the following sections we will study the equilibrium involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (NaCl) is added to water it conducts electricity. Also, the conductance of electricity increases with increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conducts electricity in their aqueous solutions and are called electrolytes while the other do not are thus, referred to as non electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is established between ion s and unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

12.2 OBJECTIVES

After going through this unit, you will be able to know.

- Electrolytes and non electrolytes.
- Acids, bases and salts.
- Ionic product of water.
- pH scale and pH calculation.
- Common ion effect and its applications.
- Solubility and solubility product of sparingly soluble salts.

- Salt hydrolysis.
- Acid base titration curves and use of indicators.
- Buffer solution and buffer capacity.

12.3 STRONG AND WEAK ELECTROLYTES AND IONIC EQUILIBRIUM

An electrolyte is defined as a compound whose aqueous solution or melt conducts electricity. On the other hand, a compound whose aqueous solution or melt does not conduct electricity is called a non electrolyte.

The conductance by an electrolyte is due to the presence of ions produced by the dissociation of the substance. However, different electrolytes dissociate to different extents.

The fraction of the total number of molecules which dissociate into ions is called the degree of dissociation and is usually represented by α.

$$\text{i.e.} \qquad \alpha = \frac{\text{Numer of moles dissociated}}{\text{Total number of moles taken}}$$

Depending upon the degree of dissociation, the electrolytes are divided into two categories, called ‘strong electrolytes’ and ‘weak electrolytes’.

Strong Electrolytes: these are the substances which dissociate almost completely into ions in aqueous solution and hence are very good conductors of electricity. Examples are: NaOH, KOH, H_2SO_4, NaCl, KNO_3 etc.

Weak Electrolytes: These are the substances which dissoiciate to a small extent in aqueous solution and hence conduct electricity also to a small extent. Examples are : NH_4OH, CH_3COOH etc.

As strong electrolytes are completely ionised in the aqueous solution, therefore, their ionisation is represented by putting a single arrow pointing towards right e.g.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

12.4 ACIDS, BASES AND SALTS

There are three concepts of acids and bases in current use. Each has its own peculiar advantages. The student should understand all the three concepts:

(a) Arrhenius concept
(b) Bronsted-Lowry concept
(c) Lewis concept

Arrhenius concept:

Savante Arrhenius (1884) proposed his concept of acids and bases. According to this concept an acid is compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.

Examples: HCl, HNO_3, H_2SO_4, CH_3COOH, H_2CO_3, H_3PO_4.

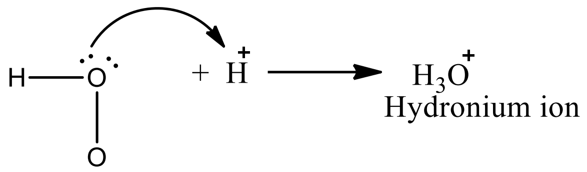
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

12.4.1 Limitations of Arrhenius Concept

Arrhenius concept of acids and bases proved to be very useful in the study of chemical reactions.However, it has the following limitations:

(1) Free H^+ and OH^- ions do not exist in water. The H^+ and OH^- ions produced by acids and bases respectively do not exist in water in the Free State. They are associated with water molecules to form complex ions through hydrogen bonding. Thus the H^+ ion forms a hydronium ion:



Similarly, OH^- ion forms the complex $H_3O_2^-$.

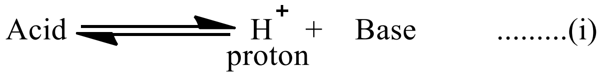
(2) Limited to water only. Arrhenius definrd acids and bases as compounds producing H^+ and OH^- ions in water only. But a truly general concept of acids and bases should be appropriate to other solvents as well.

(3) Some bases do not contain OH^- . Arrhenius base is one that produces OH^- ions in water. Yet there are compound like ammonia (NH_3) and calcium oxide (CaO) that are bases but contain no OH^- ions in their original formulation.

12.4.2 Bronsted-lowry concept of acids and bases.

Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance which has a tendency to donate a proton to any other substance and a base as a substance which has a tendency to accept a proton from any other substance. In other words, an acid is a proton-donor and a base is a proton-acceptor.

When an acid loses a proton, the residual part of it has a tendency to regain the proton. Therefore, it behaves as a base. An acid and a base, therefore, be defined by the general equation



$$\text{Acid} \rightleftharpoons \underset{\text{proton}}{H^+} + \text{Base} \qquad \text{.........(i)}$$

Conjugate Acids and Bases. Consider the dissociation of vacetic acid in water which may be represented as

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-} \qquad \text{..........(ii)}$$

It is evident that acetic acid donates a proton to water and thus acts as an acid. Water accepts a proton and, therefore, acts as a base. In the reverse reaction, hydronium ion (H_3O^+) donates a proton to the acetate ion and, therefore, acts as an acid. The acetate ion can accept a proton and, therefore, behaves as a base. Such pairs of substance which can be formed from one another by the gain or loss of proton are known as conjugate acid base pairs. Thus, acetic acid is the conjugate acid of acetate ion and acetate ion is the conjugate base of acetic acid. Similarly, water is the conjugate base of hydronium ion and hydronium ion is the conjugate acid of water.

The following points emerge out of the following discussion:

1. Firstly, it is evident that a substance is able to show acidic character only if another substance capable of accepting a proton is present. For example, acetic acid in benzene is not acidic because benzene is not in a position to take up protons .
2. Secondly, hydrogen ion in aqueous solution does not exist as H^+ ion but as hydrayted ion, H_3O^+ ion. It is calledhydronium ion because of its resemblance with ammonium ion NH_4^+.
3. Thirdly, not only molecules but even ions may act as a acids and bases.

The dissociation of acetic acid in water can be represented as

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

Acid$_1$ and Base$_1$ is a conjugate acid-base pair and so is Acid$_2$ and Base$_2$. In general, the dissociation of an acid HA in water may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Just as an acid requires a solvent that can take up a proton for its dissociation, similarly, a base requires a solvent that can give up a proton for its dissociation. Water possesses both acidic and basic properties. Therefore, acids as well as bases can dissociate in water. Thus water acts as an acid (a proton donor) towards ammonia and as a base (a proton acceptor) towards the acetic acid. Such substance are said to be amphiprotic or amphoteric.

Some common cases of equilibria between acids and bases involving proton transfer are given in following table.

Conjugate Acids and Bases.

$Acid_1$	+	$Base_2$	$\rightleftharpoons$	$Acid_2$	+	$Base_1$
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_3PO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$H_2PO_4^-$
H_2CO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HCO_3^-

Relative strengths of Acid-Base pairs. According to concept of Lowry and Bronsted, the strength of an acid depends upon the its tendency to lose protons and the strengths of a base depends upon its tendency to gain protons. If an acid, such as HCl, is a strong acid, it will have a strong tendency to donate protons. Thus, the equilibrium,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

lies very much to the right and the reverse raction, representing the gain of proton by the chloride ion leading to the reformation of HCl, will take place to a very small amount. Thus, chloride ion is a weak base.

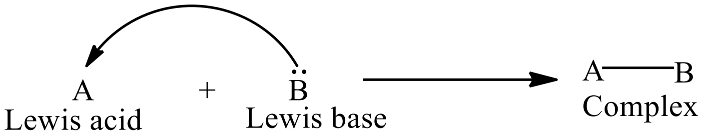
As a general rule, the stronger an acid, the weaker must be its conjugate base and vice versa. If an acid (e.g., HCl) is strong, its conjugate base (Cl^-) is weak. If a base (e.g., CH_3COO^-) is strong, its conjugate acid (CH_3COOH) is weak.

12.4.3 Lewis concept of acids and bases:

In the early 1930s, G.N.Lewis proposed even a more general model of acids and bases. According to Lewis theory,

An acid is an electron pair accepton

A base is an electron pair donor



It may be noted that: (1) all cations or neutral electron deficient molecules act as Lewis acids; and (2) all anions or molecules having electron pair act as Lewis base. A a few examples are

$$\text{(i)}\quad \underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{NH_3} \longrightarrow BF_3NH_3$$

$$\text{(ii)}\quad \underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{F^-} \longrightarrow BF_4^-$$

$$\text{(iii)}\quad \underset{\text{Acid}}{BCl_3} + \underset{\text{Base}}{(CH_3)_3N} \longrightarrow CH_3)_3NBCl_3$$

$$\text{(iv)}\quad \underset{\text{Acid}}{H^+} + \underset{\text{Base}}{\ddot{N}H_3} \longrightarrow NH_4^+$$

12.5 IONIC PRODUCT OF WATER

Pure water is poor conductor of electricity. This shows that water is weak electrolyte i.e., it is ionized to a very small extent as

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying law of chemical equilibrium, its dissociation constant K_c, is given by

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad \dots\dots\dots(i)$$

Since dissociation takes place to very small constant, the concentration of the undissociated water molecules, [H_2O], may be regarded as constant, say k.

$$\therefore \qquad K_c \times k = [\mathrm{H}^+][\mathrm{OH}^-]$$

The product of the two constants K_c and k gives another constant which is designated by K_w.

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] \qquad \dots\dots\dots \text{(ii)}$$

Where K_w is called the dissociation constant of water or, more commonly, the ionic product of water.

Hence ionic product of water may be defined as the product of the molar concentration of H^+ and OH^- ions.

The value of K_w at 298K (25^0 C) is usually taken as

$$K_w = 1.00 \times 10^{-14}.$$

Effect of temperature on K_w. The ionic product of water (K_w) increases with increase of temperature (as shown by the values given in following table). This is because of the fact that with increase of temperature , the degree of ionization of water increases.

Table.1 Values of K_w at different temperatures.

Temperature (°C)	**K_w**
0	0.1×10^{-14}
10	0.3×10^{-14}
25	1.0×10^{-14}
30	1.5×10^{-14}
40	3.0×10^{-14}
50	5.5×10^{-14}
60	

	9.6×10^{-14}

H^+ and OH^- ion concentrations in pue watert at 298K: Pure water ionizes as

$$H_2O \rightleftharpoons H^+ + OH^-$$

Obviously, for any degree of ionization, we will always have

$$[H^+] = [OH^-]$$

But at 298K, we know that

$$K_w = [H^+][OH^-] = 1.0\times 10^{-14}$$

$$\therefore \quad [H^+][H^+] = \quad 1.0\times 10^{-14}$$

$$or \qquad [\ H^+]^2 = 1.0\times 10^{-14}$$

$$\text{or} \quad [H^+] = \sqrt{1.0\times 10^{-14}} \quad = \quad 1.0\times 10^{-7}\,\text{moles/litre}$$

Thus in pure water at 25^0 C,

$$[H^+] = [OH^-] == \quad 1.0\times 10^{-7}\text{M}$$

12.6 COMMON-ION EFFECT

When a soluble salt (says A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is suppressed.

$$AB \rightleftharpoons \overset{+}{A} + \bar{B}$$

By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to Le-Chatelier's principle, the equilibrium will shift to the left, thereby the decreasing the concentration of A^+ ions. Or that, the degree of dissociation of AB will be reduced.

The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common ion effect.

Let us consider a few examples to illustrate the common-ion effect.

Example1. In a saturated solution of silver chloride, we have the equilibrium

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

When NaCl is added to the solution, the concentration of Cl^- ions will be increases. The equilibrium shown above will be shifted to the left to form more of the solid AgCl. Thus the solubility of AgCl, a

Example2. When solid NH_4Cl is added to NH_4OH solution, the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Shift to the left. Thereby the concentration of OH^- decreases.

12.7 IONIC EQUILIBRIA IN WEAK ACIDS AND BASES INCLUDING MULTISTAGE EQUILIBRIA:

Dissociation of a weak acid: Consider the dissociation of a weak monobasic acid in water, represented by the equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad ....(i)$$

Applying the law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \qquad \ldots\ldots\ldots (ii)$$

Since water is present in large excess in dilute solutions, its concentration may be taken as constant, say, k. Further, since the symbol H_3O^+ simply indicates that hydrogen ion is hyadrated, it may be replaced by H^+, for simplicity. The above equation may then be put as

$$K_c = \frac{[H^+][A^-]}{[HA] \times k} \qquad \ldots\ldots\ldots (iii)$$

Since the product of two constants K_c and k is equal to another constant, say,K_a, eq.(iii) may be written as

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots\ldots\ldots (iv)$$

The significance of eq.(iv) is that the product of the concentrations of the hydrogen ion and the anions divided by the concentrations of the undissociated acid., is equal to a constant. The constant (K_a) is characteristic of the acid concerned and is known as the dissociation constant of the acid.

Relative Strengths of Weak Acids. The above equation for the dissociation constant of a weak acid can also be expressed in terms of the degree of dissociation (α) and the total molar concentration (c) of the acid. Consider, for example, the dissociation of acetic acid, represented below:

	$CH_3COOH \rightleftharpoons$	H^+ +	$CH_3CO\bar{O}$
Original concs.	c	0	0
Equim.concs	c(1-α)	cα	cα

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad \ldots\ldots\ldots (v)$$

Since for weak acids, α is very small, $(1-\alpha)$in the denominator may be taken as 1. The above expression, therefore reduces to

$$K_a = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{c}} \qquad \ldots\ldots\ldots(vi)$$

for two weak acids of dissociation constants K_{a1} and K_{a2}, at the same concentration c, it follows from eq. (vi) that

$$\alpha_1 / \alpha_2 = \sqrt{K_{a1}} / K_{a2} \qquad \ldots\ldots\ldots(vii)$$

Where $\alpha_1$and $\alpha_2$are the respective degrees of dissociation of the two acids.

But, degree of dissociation of an acid is a measure of its capacity to furnish hydrogen ions and hence a measure of its strength.

$$\therefore \quad \frac{\text{Strength of one acid, say, HA}_1}{\text{Strength ofanother acid, say, HA}_2} = \sqrt{\frac{\text{K}_{\text{a1}}}{\text{K}_{\text{a2}}}} \qquad \ldots\ldots\ldots(\text{viii})$$

Table. Dissociation constants of some common acids at 25^0C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Acetic acid	CH_3COOH	1.75×10^{-5}		
Arsenic acid	H_3AsO_4	5.00×10^{-5}	8.30×10^{-8}	6.30×10^{-11}
Benzoic acid	$PhCOOH$	6.29×10^{-5}		
Boric acid	H_3BO_3	5.80×10^{-10}		
Carbonic acid	H_2CO_3	4.52×10^{-7}	4.69×10^{-10}	
Formic acid	$HCOOH$	1.77×10^{-4}		
Hydrocyanic acid	HCN			

Hydrogen sulphide Iodic acid Oxalic acid Phosphoric acid Sulphuric acid	H_2S HIO_3 $(COOH)_2$ H_3PO_4 H_2SO_4	7.20×10^{-10} 5.70×10^{-8} 1.67×10^{-8} 5.02×10^{-2} 7.50×10^{-3} Strong	1.20×10^{-15} 5.18×10^{-5} 6.20×10^{-8}	4.20×10^{-13}

Dissociation of a Weak Base. Representing the formula of a weak monoacid base as BOH, its dissociation, in accordance with Arrhenius concept, may be represented by the equation

$$BOH \rightleftharpoons B^{+} + \overline{O}H$$

Applying the equilibrium law equation, the dissociation constant, K_b, of the base, will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \ldots\ldots\ldots (i)$$

Assuming that the activity coefficient of the of various species involved are equal to unity each.

If the initial concentration of the base is c moles per litre and if α is the degree of dissociation, then,

$$\begin{array}{lccc} & BOH \rightleftharpoons & B^{+} + & \overline{O}H \\ \text{Original concs.} & c & 0 & 0 \\ \text{Equim.concs} & c(1-\alpha) & c\alpha & c\alpha \end{array}$$

$$\therefore \qquad K_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots\ldots\ldots (ii)$$

Since, for a weak base,α is very small as compared to 1, eq (ii) as before, is reduced to

$$K_b = c\alpha^2$$

$$or \qquad \alpha = \sqrt{K_b/c}$$

$$\therefore [OH^-] = c\alpha = c\sqrt{K_b/c} = \sqrt{cK_b} \qquad \ldots\ldots\ldots (iii)$$

The dissociation constants of some common weak bases are given in following table:

Table. Dissociation constants of some common Bases at 25^{0}C

Base	**Formula**	**K_b**
Ammonia	NH_4OH	1.81×10^{-5}
Aniline	$C_6H_5NH_2$	3.83×10^{-10}
Dimethyl amine	$(CH_3)_2NH$	5.12×10^{-4}
Ethyl amine	$C_2H_5NH_2$	5.60×10^{-4}
Hydrazine	NH_2NH_2	3.00×10^{-6}

12.8 pH SCALE EXACT TREATMENT OF CALCULATION OF H$^+$ IONS AND pH FOR HA AND BOH

Knowledge of the concentration of hydrogen ions is one of the greatest importances in chemistry. Hydrogen ion concentrations are typically quite small numbers. Therefore, chemists report the hydrogen ion concentration of solution in terms of pH. It is defined as **the negative of base-10 logarithm (log) of the H$^+$ ion concentration.** Mathematically it can be expressed as

$$pH = -\log[H^+]$$

Where $[H^+]$ is the concentration of hydrogen ions in moles per litre

Alternative and more useful forms of pH definition are:

$$pH = log\frac{1}{[H^+]}$$

For pure water or neutral solution in which

$$[\mathrm{H}^+] = 1 \times 10^{-7}\mathrm{moldm}^{-3}$$

$$pH = -\log[\mathrm{H}^+] = -\log(1 \times 10^{-7}) = 7 \text{ at } 25^0\mathrm{C}$$

Some other Logarithmic Expressions. Just as pH is used to indicatehydrogen ion concentration, pOH is used to indicate hydroxyl ion (OH^-) concentration. Thus,

$$pH = -\log[\mathrm{OH}^-] \qquad \ldots\ldots\ldots \text{(i)}$$

Ionic product of water, K_w. Is also frequently expressed ina similar manner as

$$\mathrm{pK_w} = -\log\mathrm{K_w} \qquad \ldots\ldots\ldots \text{(ii)}$$

Remembering that $[H^+][[\mathrm{OH}^-] = \mathrm{K_w}$ and taking logs and reversing signs, we have

$$-\log[\mathrm{H}^+] - \log[\mathrm{OH}^-] = -\log\mathrm{K_w}$$

$$\text{or} \quad \mathrm{pH + pOH = pK_w} \qquad \ldots\ldots\ldots \text{(iii)}$$

this relationship holds good for water as well as for any aqueous solution.

Since K_w at 25^0C is about10^{-14}, pK_w is is 14.0. Hence,

$$\mathrm{pH + pOH} = 14 \qquad \ldots\ldots\ldots \text{(iv)}$$

In other words, the sum of pH and pOH is equal to 14 in water or in any aqueous solution at 25^0C.

In pure water, as already stated, hydrogen ion concentrations are equal to hydroxyl ion concentration and each is equal to 10^{-7} moles per litre. Water is, therefore, neutral and its pH is 7. if water is made acidic, its hydrogen ion concentration will increase to a value above 10^{-7} and, therefore, pH will fall below 7. On the other hand, if water is made basic, its hydrogen ion concentration will decrease to a value less than 10^{-7} and, therefore, pH will rise above 7. Thus, if pH of solution is 7, it is neutral. If pH is less than 7, the solution is acidic and if it is more than 7, the solution is basic.

12. 9 HYDROLYSIS

The reaction of an anion or cation with water accompanied by cleavage of O-H bond is called hydrolysis.

$$A^{-} + \text{H-O-H} \rightleftharpoons \text{H-A} + \overset{-}{\text{O}}\text{-H} \quad \text{........(i)}$$

$$B^{+} + \text{H-O-H} \rightleftharpoons \text{BOH} + H^{+} \quad \text{........(ii)}$$

The term hydrolysis is derived from hydro, meaning water, and lysis, means breaking. It may be noted that in anionic hydrolysis shown in (i) the solution becomes slightly basic (pH>7) due to generation of OH^- ions. In cationic hydrolysis shown in (ii) there is excess of H^+ions which makes the solution slightly acidic (pH<7).

12.9.1 Salt Hydrolysis

Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

$$\text{Salt} + \text{Water} \longrightarrow \text{Acid} + \text{Base}$$

Or

$$\underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acid}}{HA} + \underset{\text{Base}}{BOH}$$

Depending upon the relative strengths of the acid and the base produced, the resulting solution is acidic, basic or neutral. On this basis, the salts are divided into four categories:

I. Salts of Strong acids and Strong bases:

$NaCl$, $NaNO_3$, Na_2SO_4, KCl

As an illustration, let us discuss the hydrolysis of NaCl. We may write:

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

$$\text{or} \quad Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$$

$$\text{or} \quad H_2O \longrightarrow H^+ + OH^-$$

Thus it involves only ionization and no hydrolysis. Further in the resulting solution, $[H^+]=[OH^-]$. So the solution is neutral. Hence it can be generalized that the salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.

II. Salts of Weak acids and Strong bases:

Examples are:

CH_3COONa, Na_2CO_3, NaCN, K_2CO_3 etc.

As an illustration, the hydrolysis of sodium acetate (CH3COONa) may be represented as followes:

$$CH_3COONa + H_2O \rightleftharpoons CH3COOH + NaOH$$

$$\text{Or} \quad CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$\text{Or} \quad CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

As it produces OH^- ions, the solution of such a salt is alkaline in nature.

III. Salts of Strong acids and Weak bases:

Examples are:

NH_4Cl, $CuSO_4$, NH_4NO_3, $AlCl_3$, $CaCl_2$ etc.

As an illustration, the hydrolysis of NH_4Cl may be represented as followes:

$$NH_4Cl + H_2O \rightleftharpoons NH4OH + HCl$$

$$\text{Or} \quad NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^{\cdot}$$

$$\text{Or} \quad NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

As it produces H^+ ions, the solution of such a salt is acidic in character.

IV. Salts of Weak acids and Weak bases:

Examples are:

CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$ etc.

As an illustration, the hydrolysis of CH_3COONH_4 may be represented as followes:

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$\text{Or} \quad CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$$

Thus it involves both cationic and anionic hydrolysis. Hence the resulting solution is neutral.

12.9.2 Hydrolysis Constant:

The general equation for the hydrolysis of a salt (BA) may be written as

Applying the law of chemical equilibrium, we get

$$\frac{[HA][BOH]}{[BA][H_2O]} = K, \text{ The equillibrium constant.}$$

Since water is present in very large excess in aqueous solution, its concentration $[H_2O]$ may be regarded as constant so that we have

$$\frac{[HA][BOH]}{BA} = K[H_2O] = K_h$$

Where K_h is called the hydrolysis constant.

I .Hydrolysis constant of Salts of weak acid and Strong base:

Representing the salt by BA as usual, the hydrolysis may be represented as follows:

$$\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Strong}}{BOH} + \underset{\text{Weak}}{HA}$$

$$\text{Or} \quad B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$

$$\text{Or} \quad A^- + H_2O \rightleftharpoons OH^- + HA$$

i.e it is a case of anion hydrolysis.

The hydrolysis constant K_h for the above reaction will be given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} \quad \ldots\ldots\ldots (i)$$

For the weak acid HA, the dissociation equilibrium is

$$HA \rightleftharpoons H^+ + A^-$$

∴ The dissociation constant K_a of the acid HA will be given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \ldots\ldots\ldots (ii)$$

Further the ionic product of water K_w is given by

$$K_w = [H^+][OH^-] \quad \ldots\ldots\ldots\ldots (iii)$$

Multiplying eq (i) with (ii) and dividing by (iii), we get

$$K_h = \frac{K_w}{K_a} \quad \ldots\ldots\ldots. (iv)$$

II.Hydrolysis constant of Salts of Strong acid and Weak base:

For the salt BA, the hydrolysis may be represented as

$$\underset{\text{salt}}{BA} + H_2O \rightleftharpoons \underset{\text{weak}}{BOH} + \underset{\text{strong}}{HA}$$

i.e it is case of cation hydrolysis.

The hydrolysis constant K_h for the above reaction will be given by

$$K_h = \frac{[BOH\ ]\,[H^+]}{[B^+\ ]} \qquad \ldots\ldots\ldots(i)$$

For the weak base BOH, the dissociation equilibrium is

$$BOH \rightleftharpoons B^+ + OH^-$$

∴ The dissociation constant will be given by

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH\ ]} \qquad \ldots\ldots\ldots(ii)$$

Ionic product of water,

$$K_w = [H^+][OH^-] \qquad \ldots\ldots\ldots(iii)$$

Multiplying eq (i) with (ii) and dividing by (iii), we get

$$K_h = \frac{K_w}{K_b} \qquad \ldots\ldots\ldots.(iv)$$

III. Hydrolysis constant of Salts of Weak acid and weak base:

$$K_h = \frac{K_w}{K_a K_b} \qquad \ldots\ldots\ldots.(i)$$

4.9.3 pH calculation.

I. pH of Salt of weak acid and strong base:

In this case we have

$$\begin{array}{lcccc} & A^- + H_2O & \rightleftharpoons & OH^- & + HA \\ \text{Original conc:} & c & & 0 & 0 \\ \text{Conc. at eqm:} & c(1-h) & & ch & ch \end{array}$$

i.e, $[OH^-] = ch$

$\therefore$

$$H^+ = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \cdot c}{K_w}}$$

$$or \;\; [H^+] = \sqrt{\frac{K_w \cdot K_a}{c}}$$

$\therefore$

$$pH = -log[H^+] = -log\sqrt{\frac{K_w \cdot K_a}{c}}$$

$$= log\left(\frac{K_w \cdot K_a}{c}\right)^{1/2}$$

$$or \;\; pH = -\frac{1}{2}[logK_w + logK_a - logc]$$

Thus knowing the molar concentration c of the solution and the dissociation constant K_a of the weak acid involved, the pH of the solution can be calculated.

II. pH of the Salt of weak acid and strong base:

$$pH = -\frac{1}{2}[logK_w - logK_b + logc]$$

III. pH of the Salt of weak acid and weak base:

$$pH = -\frac{1}{2}[logK_a + logK_w - logK_b]$$

12.9.4 Degree of hydrolysis:

The degree of hydrolysis of a salt is defined as the fraction (or percentage) of the total salt which is hydrolysed.

i.e

$$\mathrm{h} = \frac{\text{No. of moles of the salt hydrolysed}}{\text{Total no. of moles of the salt taken}}$$

I. Degree of Hydrolysis of the salts of weak acid and strong base.

Suppose the original concentration of the salt in the solution is c moles/litre and h is the degree of hydrolysis at this concentration. Then we have

$$\begin{array}{lccccc} & A^- & + \; H_2O & \rightleftharpoons & OH^- & + \; HA \\ \text{Original conc:} & c & & & 0 & 0 \\ \text{Conc. at eqm:} & c(1-h) & & & ch & ch \end{array}$$

The hydrolysis constant (K_h) will, therefore, be given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{ch.ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is very small as compared to 1, we can take 1-h=1 so that above expression becomes

$$ch^2 = K_h \; or \; h^2 = \frac{K_h}{c}$$

$$h = \sqrt{\frac{K_h}{c}}$$

Substituting the value of K_a, we get,

$$h = \sqrt{\frac{K_w}{K_a . c}}$$

II. Degree of Hydrolysis of the salts of strong acid and weak base:

$$h = \sqrt{\frac{K_w}{K_b . c}}$$

III. Degree of Hydrolysis of the salts of weak acid and weak base:

$$h = \sqrt{\frac{K_w}{K_a . K_b}}$$

12.10 TITRATIONS ACID BASE TITRATION CURVE

Titration is measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant. Usually the concentration of one of the solution is known (called standard solution) and it is desired to find the concentration of other by titration. The apparatus used is shown in fig. a known volume of the solution is taken in the titration flask and the other solution is taken in the burette. The point at which the required volume of one solution has been added to the other to exactly complete the reaction between the two is called **endpoint** or **equivalence point**.

The process of acid-base titrations is accompanied by a change in pH. A plot between pH of the solution during titration and the amount of acid (or base) added from burrete is called a **titration curve.**

Indicators are frequently employed in detecting end points in acid-base titrations. Since, on account of hydrolysis, the pH at the end point depends on the relative strengths of tha acid and the base being titrated and since different indicators have different pH ranges within which they can be used. The pH changes occurring in some acid-base titrations may be first considered.

I. Titrating a Strong acid with a Strong base.

Fig (a) depicts the titration curve when NaOH is added gradually to HCl. It shows that the pH of the titration solution rises extremely slowly in the beginning. In the vicinity of equivalence point, the pH rises dramatically and the curve becomes vertical. Beyond this, the curve becomes almost flat that shows a slight rise of pH when only excess base is present in the titration solution.

The vertical portion of the curve extends from pH 3 to pH 7. The pH range of methyl orange (3.1-4.4) and phenolphthalein (8.30-10.0) are fairly narrow and fall on the vertical curve. Thus both the methyl orangr and phenolphthalein are suitable indicators for strong acid/strong base titrations

II. Titrating a Weak acid with a Strong base.

Figure (b) represents the titration curve when NaOH (strong base) is added to CH_3COOH (weak acid). The pH curve rises slowly in the beginning but near the equivalence point, the pH changes abruptly from 6 to 11 and the curve becomes vertical. Beyond this the shape of the titration curve is similar to that for strong acid/strong base.

Phenolphthalein has pH range 8.3 to 10.0 that falls on the vertical part of the titration curve as marked in the figure.

III. Titrating a Strong acid with a Weak base.

The titration curve for HCl (strong acid) NH_4OH (weak base) is shown in fig. (c). As NH_4OH is added, the pH of the titration solution increases gradually. Around the equivalence point, a sharp rise in pH occurs approximately from 3 to 8, when the curve becomes vertical. The pH range of methyl orange (3.1-4.4) falls on the vertical portion of the titration curve.

IV. Titrating a Weak acid with a Weak base.

The titration curve for CH_3COOH (strong acid) NH_4OH (weak base) is shown in fig.(d). The pH of the titration solution rises gradually and there is no sharp change in pH around the equivalence point. The vertical portion is missing in the titration curve. Under these condition, all indicators change colour only gradually and no indicator is suitable.

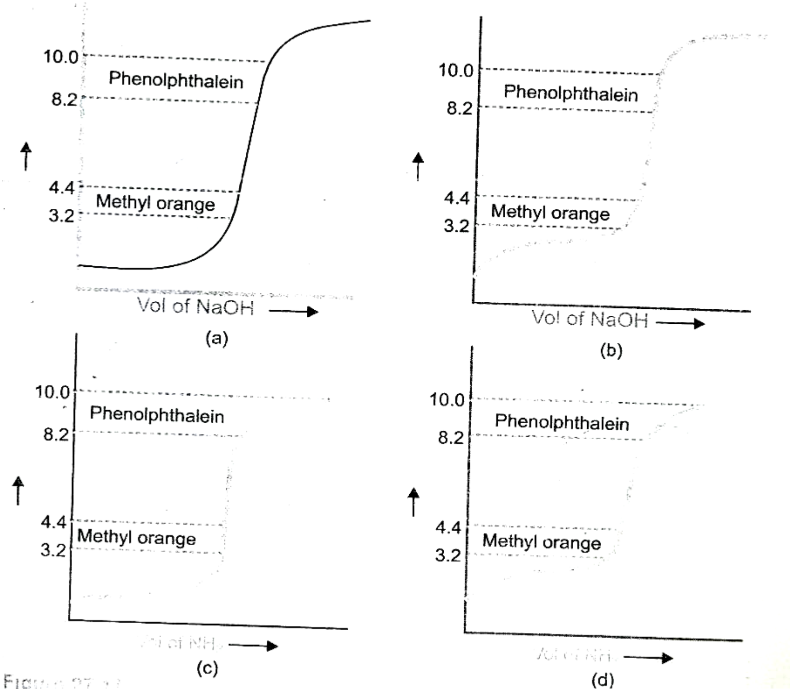


Fig. 12.10. To finds a suitable indicator from astudy of the pH curve for:

(a) A strong acid and strong base; (b) weak acid and strong base;

(c)strong acid and weak base ; (d) a weak acid and and weak base.

12. 11 BUFFER SOLUTION

For many purposes in chemistry, industry and biology, it is necessary to have solutions whose pH does not change much even on the addition of appreciable amounts of strong acids and strong alkalies. Such solutions are called buffer solutions.

A buffer solution is one which can resist change in its pH on the addition of an acid or a base.

12.11.1 Types of Buffer solutions

There are two types of buffer solutions. These are:

(i) Solutions of single substances. The solution of the salt of weak acid and a weak base e.g. ammonium acetate (CH_3COONH_4) acts as a buffer.

(ii) Solutions of Mixtures. These are further of two types:

(a) Acidic Buffer. It is the solution of a mixture of a weak acid and a salt of this weak acid with strong base (e.g. $CH_3COOH + CH_3COONa$).

(b) Basic Buffer. It is the solution of a mixture of a weak base and a salt of this weak base with strong acid (e.g. $NH_4OH + NH_4Cl$).

12.11.2 Buffer action

The property of a buffer solution to resist any changes in its pH value even when small amounts of the acid or the base are added to it is called Buffer action.

12.11.3 Buffer Action of Acidic Buffer

Let us , for example, consider the buffer action of acidic buffer containing CH_3COOH and CH_3COONa. Acetic acid dissociates to a small extent whereas sodium acetate is almost completely dissociated in the aqueous solution as follows:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

By ‘common ion effect’ the ionization of CH_3COOH is further suppressed. Thus in the solution, there are excess of acetate (CH_3COO^-) and small amount of H^+ ions.

When a few drops of an acid are added to the above mixture solution, the H^+ ions given by the acid combine with the CH_3COO^- ions to form weakly ionized molecules of CH_3COOH.

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

Thus the H^+ ion concentration and hence the pH of the solution remains almost constant.

Similarly, when few drops of a base are added, the OH^- ions given by the base combine with the H^+ ions already present to form weakly ionized molecules of H_2O.

$$H^+ \quad + \quad OH^- \longrightarrow H_2O$$

As the H^+ ions are consumed, the equilibrium shifts towards right. Thus more of CH_3COOH dissociates to make up the loss of H^+ ions. Hence the H^+ ion concentration or the pH of the solution does not change.

12.11.4 Buffer action of Basic Buffer

A mixture containing equimolar solutions of ammonium hydroxide (NH_4OH) and its almost completely dissociated salt, ammonium chloride (NH_4Cl), constitutes another good buffer. The mixture contains undissociated NH_4OH as well as NH_4^+ and Cl^- ions. The buffer action of this mixture may now be considered.

If a strong acid is added, the H^+ ions added are neutralised by the base NH_4OH:

$$H^+ + \quad NH_4OH \longrightarrow H_2O \quad + \quad NH_4^+$$

If a strong base is added, the OH^- ions added are neutralised by NH_4^+ ions forming very slightly dissociated NH_4OH.

In this case, evidently reserve acidity is due to the presence of NH_4^+ ions and reserve alkalinity is due to the presence of NH_4OH.

4.12 Buffer Capacity.

It is defined as the number of moles of an acid or a base required to be added to one litre of the buffer solution so as to change its pH by one unit. Thus

$$\text{Buffer capacity}(\beta) = \frac{\text{No. of moles of the acid or base added to 1 litre of the buffer}}{\text{Change in pH}}$$

$$= \frac{n}{\Delta pH}$$

12. 12 HENDERSON EQUATION

Consider first a buffer solution containing a weak acid HA and its highly dissociated salt NaA. The hydrogen ion concentration of such a solution is given by the equation

$$[H^+] = K_a\,[\text{salt}]/[\text{acid}]$$

Taking logs and reversing the sign, we have

$$-\log[H^+] = -logK_a + log\,[\text{salt}]/[\text{acid}]$$

$$or \qquad pH = pK_a + log\,[\text{salt}]/[\text{acid}]$$

This equation, known as Henderson’s equation, enables the calculation of pH of a buffer solution made by mixing known quantities of a weak acid and its salt.

12. 13 SOLUBILITY AND SOLUBILITY PRODUCT

When an ionic substance dissolves in water, it dissociated to give separate cations and anions. As the concentrations of the ions in solution increases, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phases. Ultimately, dyanamic equilibrium is established between the solid phase and the cations and anions in solution. For example, for a sparingly soluble salt, say AgCl, we can write the equilibrium equations as follows:

$$\underset{\text{Solid}}{AgCl} \rightleftharpoons Ag^+ + Cl^-$$

At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of solute from the solution. Now the solution is said to be saturated.

A saturated solution is a solution in which the dissolved and undissolved solute is in equilibrium. The solubility (S) of a substance in a solvent is the concentration in the saturated solution. Solubility of solute may be represented in grams per 100ml of solution. It can also be expressed in moles per litre.

Molar solubility is defined as the number of moles of substance per litre of the solution. The value of solubility of a substance depends on the solvent and temperature.

Applying Law of mass action to the above equilibrium for AgCl, we have

$$\mathrm{K} = \frac{[\mathrm{Ag}^+][\mathrm{Cl}^-]}{[\mathrm{AgCl}]}$$

The amount of AgCl in cantact with saturated solution does not change with time and the factor (AgCl) remains the same. The the equilibrium expression becomes

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

Where $[\mathrm{Ag}^+]$and $[\mathrm{Cl}^-]$ are expressed in mol/L. The equilibrium constant in the new context is called the Solubility Product Constant and is denoted by K_{sp}. The value of K_{sp} for particular solubility equilibrium is constant at a given temperature. The product $[\mathrm{Ag}^+][\mathrm{Cl}^-]$ is also called the Ionic Product or Ion product.

TABLE .SOLUBILTY PRODUCT VALUES FOR SOME SPARINGLY SOLUBLE SALTS

Substance	**K_{sp} at 25^0C**
PbS	3.4×10^{-28}
CdS	3.6×10^{-28}
$Fe(OH)_3$	1.1×10^{-38}
$Al(OH)_3$	8.5×10^{-32}
$Mg(OH)_2$	1.4×10^{-11}
$CaCO_3$	

PbI_2	4.8×10^{-9} 1.39×10^{-8}

The K_{sp} may be stated as: the product of the concentration of ions in the saturated solution at a given temperature is constant. This is sometimes called the solubility product principle.

12.14 INDICATORS

The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator.

TABLE.Common acid-base indicators and their colour changes.

Indicator	pH-range	Acidic colour	Basic colour
Methyl violet	0-2	Yellow	Violet
Methyl yellow	1.2-2.3	Red	Yellow
Methyl orange	3.1-4.4	Red	Yellow
Methyl red	4.2-6.3	Red	Yellow
Litmus	4.5-8.3	Red	Blue
Phenol red	6.4-8.2	Yellow	Red
Cresol red	7.2-8.8	Yellow	Red
Thymol blue	8.0-9.6	Yellow	Blue
Phenolphthalein	8.3-10.0	Colourless	Red
Alizarin yellow	10.1-12.0	Yellow	Violet
Trinirobenzene	12.0-14.0	Colourless	Orange

12.15 COMMON ION EFFECT AND THE SOLUBILITY OF A SPARINGLY SOLUBLE SALT

If to the solution of a sparingly soluble salt (like AgCl, PbI_2 etc.) if a soluble salt having a common ion is added, the solubility of the sparingly soluble salt further decreases.

12.16 SUMMARY

- Equilibrium involving ions in aqueous solution is called ionic equilibrium.
- An electrolyte is defined as a compound whose aqueous solution or melt conducts electricity. On the other hand, a compound whose aqueous solution or melt does not conduct electricity is called a non electrolyte
- The fraction of the total number of molecules which dissociate into ions is called the degree of dissociation and is usually represented by α.

$$i.e. \qquad \alpha = \frac{Numer\ of\ moles\ dissociated}{Total\ number\ of\ moles\ taken}$$

- **Strong Electrolytes**: these are the substances which dissociate almost completely into ions in aqueous solution and hence are very good conductors of electricity. Examples are: NaOH, KOH, H_2SO_4, NaCl, KNO_3 etc
- **Weak Electrolytes**: These are the substances which dissoiciate to a small extent in aqueous solution and hence conduct electricity also to a small extent. Examples are : NH_4OH, CH_3COOH etc.
- According to Arrhenius concept an acid is compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.
  Examples: HCl, HNO_3, H_2SO_4, KOH, NaOH etc.
- According to Bronsted and Lowery an acid is a proton-donor and a base is a proton-acceptor.
- According to Lewis theory, An acid is an electron pair acceptor while a base is electron pair donor.
- Ionic product of water may be defined as the product of the molar concentration of H^+ and OH^- ions. $K_w = [H^+][OH^-]$The value of K_w at 298K (25^0 C) is usually taken as $K_w = 1.00 \times 10^{-14}$.

- The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common ion effect.
- pH is defined as **the negative of base-10 logarithm (log) of the H^+ ion concentration. .** Mathematically it can be expressed as $pH = -\log[H^+]$.
- $pH + pOH = 14$
- The reaction of an anion or cation with water accompanied by cleavage of O-H bond is called hydrolysis
- Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.
- Titration is measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant.
- A plot between pH of the solution during titration and the amount of acid (or base) added from burrete is called a **titration curve.**
- A buffer solution is one which can resist change in its pH on the addition of an acid or a base.
- The property of a buffer solution to resist any changes in its pH value even when small amounts of the acid or the base are added to it is called Buffer action.
- Buffer capacity is defined as the number of moles of an acid or a base required to be added to one litre of the buffer solution so as to change its pH by one unit.
- Molar solubility is defined as the number of moles of substance per litre of the solution.
- The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator.

12.17 TERMINAL QUESTIONS

(1) Define the following terms

(a) Ostwald's dilution law (b) Degree of dissociation

(c) Common ion effect (d) Solubility equilibria

(e) Solubility product.

(2) What is the Henderson equation?

(3) Define and explain ionic product of water

(4) Explain any two applications of common ion effect.

(5) Define or explain the following terms

(a) Arrhenius acids (b) Arrhenius bases (c) Bronsted acids (d) Bronsted bases (e) Lewis acids

(f) Lewis bases (g) pH of solutions (h) Buffer solution

(6) What are strong and weak electrolytes?

(7) What are conjugate acid-base pairs? Give two examples

(8) What are buffers and how is their capacity measured?

(9) Define or explain the following terms

(a) Salt hydrolysis (b) Hydrolysis constant (c) Degree of hydrolysis.

(10) Derive the relation between hydrolysis constant ionic product of water and dissociation constant of a strong acid and a weak base.

(11) Deduce an expression for the degree of hydrolysis of a salt of a weak acid and a strong base.

(12) Calculate the pH of (a) 0.0001M HCl solution (b) 0.04M HNO_3 solution, assuming complete dissociation in each cases.

(13) Calculate the hydrogen ion concentration in moles per litre of a solution whose pH is 5.4

(14) Calculate the pH and pOH of a solution containing hydrogen ion concentration $3.0 \times 10^{-3} \text{moldm}^{-3}$ at 25^0C.

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 INTRODUCTION

In the laboratory it is require great care and attention in order to avoid safety hazards occures due to delicate lab instrument, open flames, hazardus chemicals etc. Negligent handling of dangerous/harmful chemicals can result in both short-term (acute) and long-term (Chronic) health issues. Burns, eye injuries, lung diseases, asphyxiation, and suffocation are some of these potential issues. Chemicals cause adverse reactions in the body through ingestion, inhalation, skin contact, and percutaneous exposure. No matter how much is being used or how it is used, a substance, operation, or activity has intrinsic hazardous characteristics or properties. Various risks to human health and physical injury can be posed by chemicals given below:

Health Hazards	Physical Hazards
Toxic	Combustible
Carcinogenic	Flammable
Mutagenic	Explosive
Reproductive toxins	Reactive or pyrophoric
Sensitizers	Oxidizers
Irritants and Corrosives	Corrosive
Asphyxiants	Compressed Gas and Liquid

The chemistry practical could involve a minor incident. Inform your teacher or the lab attendant right away, remain calm, do not panic, and use the first aid provided in the laboratory.

However, if any of these symptoms occur, you should immediately stop working, take off your personal protective equipment, wash your hands, and contact your healthcare provider.

- Unusual taste or odor,
- Respiratory irritation, coughing, choking, or shortness of breath,
- Sudden headache, dizziness, blurred vision, or loss of consciousness,
- Burning or painful sensation,
- Swelling, reddening, or itching skin.

13.2. OBJECTIVE

After completing this unit learners will be able

- To known 'What is a laboratory hazard'? The physical hazards and the chemical hazards in the laboratory.
- How to prevent chemical hazards in the laboratory.
- To know the effect of laboratory incidents on learner's health, such as heat burns, glass cuts, and the inhalation of gas.
- To assess and reduce the risks associated with chemical hazards in the laboratory.

13.3. PURPOSE OF LABORATORY & CHEMICAL SAFETY

- To promote safety awareness and encourage safe working practices in the laboratory.
- Safety guidelines should serve as a reminder of things you can do to work more safely and are applicable to all users of the laboratory.
- All learners are expected to adhere to safety guidelines and maintain safety standard strictly.

13.4. TYPES OF HAZARDS IN THE LABORATORY AND THEIR PREVENTION

Chemical and physical hazards in the laboratory fall into five major categories. Now discuss each category in details with their prevention in the laboratory.

- Chemical burns
- Heat burns
- Eyes injuries
- Injury from glassware
- Inhaling dangerous gases

13.4.1 Chemical burns

Acids, bases, etching solutions and solvents are commonly used in chemistry lab and classified as corrosive substance, and also present a serious health hazards such as chemical burns, tissue damage, organ damage, asphyxiation, corneal damage, which can lead to blindness and genetic damage if used improperly.

(Burns are a common type of hazard when dealing with harmful substances).

- Wear the gloves when working in lab.
- If the skin burn with acid , wash it with ammonium hydroxide, while in case of concentrated H_2SO_4 wash affected part with Barium chloride solution and then with cold water and apply burnol.
- If the skin burn due to the concentrated/ stong alkali (base), washed it with acetic acidand finally with cold water and apply burnol. If the injury is deep then immediately contact with the health consultant/doctor.

13.4.2 Heat burns

Burners and other heating devices are frequently used in laboratories to expedite chemical reactions and processes. As with any activity that involves fire, it is important to be aware of the potential risks associated with heat-related injuries. If exposed to temperatures higher than 70°C, it is likely that a burn will occur, even if the skin is only exposed for a split second.

It is essential to maintain a safe distance away from open flames and heating devices in order to reduce the likelihood of heat-related burn injuries in the laboratory.

- Skin clothing and protective equipment should be kept away from any other combustible materials in the vicinity. Furthermore, it is imperative to ensure that burners are not left on after use.

- If a heat-related burn occurs while in the laboratory, it is recommended to immediately put the affected area in cold running water and hold it for a few minutes before allowing the burning sensation to subside. After that apply coconut oil or burnol on the burnt part.

(The heat generated by Bunsen burners can create a range of serious physical hazards for laboratory learner who are using the equipment)

13.4.3 Eye injuries

In the laboratory at the time of working, you need to be aware of the chemicals that can be harmful to your eyes. You can be exposed to chemicals if you accidentally release liquids or gases that can damage your eyes. The severity of your injury depends on hazardus properties of chemical are and how much you have been exposed to it. For instance, if you get a mild eye injury from exposure to a chemical, it could just cause redness and irritation. But if you get a really bad eye injury, it could lead to permanent blindness. To prevent eye injuries in the lab, you need to wear the right protective eyewear.

- If the eyes injuries occur due to the some pungent vapours in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still eatvhing persists consult an eye doctor immediately.
- If chemical solution or dust particle enter into eye thenwash your eye with cold water untill you feel relief.

- If acid has been entered into eye then eye must be washed with a dilute solution of alkali sodium bicarbonate solution few timesand after that with cold water till you feel relief. an eye doctor
- If base/alkali has been entered into eye then eye must be washed with dilute boric acid solution and finally washed with cold water till irritation persists. If still problem exist immediately consult an eye doctor.

13.4.4 Injury from glassware

The use of laboratory glassware for the storage and mixing of hazardous chemicals is a common practice; however, there is a risk of laboratory glassware breaking. If the glass is broken, it can expose sharp edges, particularly if it is very thin, which can cause severe eye and skin damage. Therefore, it is important to take steps to reduce the risk of glass breaking in laboratories.

- In order to prevent cuts from glassware, it is important to handle the glassware with caution. It is recommended to hold the glassware in a secure grip and to avoid handling the glassware with wet or wet hands.
- It is important to ensure that when glassware is not in use, it is stored in a safe and secure place where there is no potential for it to fall and shatter. If glassware is not stored in an accessible cupboard with a well-maintained and even surface, it is likely to fall and break, potentially exposing to physical injury.
- If the is due to the breakage of some glassware, glass apparatus, wound washed with sprit and then aqueous alum solution because alum is antiseptic in nature and can also help in stop bleeding by coagulation.
- It is essential to take prompt action in the case of a glass cut in order to avoid the development of an infection. If a cut is sustained from glassware, the first aid officer/doctor should be contacted so that they will dress the wound.

13.4.5 Inhaling dangerous gases

A wide variety of hazardous chemicals emit toxic vapors and gases that pose a risk to human life. The health consequences associated with exposure to these hazardous vapors can be classified as acute, chronic, or both. Acute consequences are those that occur immediately after exposure to the vapors. Chronic consequences are those that do not occur immediately but occur months and even years after exposure. Heath effects of gas inhalation can include symptoms such as:

Irritation to mucous membranes in the nose, throat, respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing etc.

- If you feel any symptoms occurs due to the inhalation of gaes first go away from the working place (lab) in the open place. If still feel some problems consult with doctor immediately.

13.5. LABORATORY SAFETY

In the laboratory following safety will be taken while working in the lab.

(i) Laboratory hygiene
(ii) Fire safety
(iii) Chemical safety
(iv) Personal safety

(i) Laboratory hygiene

- Scrub hands thoroughly when finished.
- Avoid cross contamination
- Do not touch self, faucets, doorknobs, notebooks, pens etc. with gloves on.
- Keep a pen or two in your drawer for lab use only.
- Clean and disinfect your workspace

(ii) Fire safety

- Never leave flames unattended.
- Do not use flammables near ignition sources.
- Fire Extinguishers
- Fire Blanket
- Fire alarm pulls

(iii) Chemical Safety

- Wear gloves and glasses where appropriate.
- Follow instructor's directions.
- Dispose of waste properly-Do Not pour down the drain.

(iv) Personal Safety

- Lab coat to be worn all the time.
- Safety goggles must be worn all the time while working in the lab.
- Wear sensible clothing and Wear shoes.
- Appropriate gloves while handling chemicals.
- Working of alone student is not allowed

13.6. ASSESS AND MINIMIZE THE RISK OF THE HAZARDS

When you are working in a chemical lab, there is a risk associated with every chemical and glassware you use. Once you have evaluated the risks, your next step is to consider how you can reduce exposures. There are following step to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant steps you can take to reduce the risk in any laboratory environment. While incidents can occur even in the well-prepared environment, meticulous attention to detail can reduce the risk.

I. Know what you are working with. It is important to always recognize the substance that is being used and to consider how to reduce the exposure to that substance during the experiment. For example, sodium hydroxide is commonly known as lye or caustic soda. If you are unsure, look for the Chemical.

II. Ensure that the proper concentrations are prepared. In laboratory should not routinely work with basic (NaOH) or acidic (HCl) solutions at concentrations greater than 1 M.

III. Ensure that all chemical bottles are properly labeled. For example sodium hydroxide, the bottle should have the chemical name ("sodium hydroxide") spelled out, not just the formula ("NaOH"), and the concentration of the solution should also be listed.

  - The signal words "Danger", "Warning", and "Caution" are used to describe the level of the hazard.
  - Words such as "Caustic", "Corrosive", and "Flammable" are used to describe specific hazards.

IV. Write down all the chemicals you are going to use and how much you will need for the experiment.

V. Consider the physical arrangement and the facilities available in your laboratory.

13.6.2 During an experiment

It is essential that learners are monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students throughout.

I. Use the lowest concentrations and smallest volumes possible for all chemicals. Do not allow learners to handle solids that are classified as fatal or toxic if swallowed.

II. Wear appropriate eye protection that offers both impact and splash protection. This is not only for your safety but also as a precaution in the event that an accident is caused by someone else in the laboratory.

III. Wear appropriate protective clothing (laboratory apron, coat, and gloves).

IV. Long hair must be pulled back, and clothing must be tucked in.

V. After transferring a chemical (solid or liquid) from a reagent bottle into a secondary container, be certain that the reagent bottle and the container are properly closed.

VI. Students should take only the amount required of each reagent. If there is excess, it must be disposed of properly and not returned to the reagent container.

VII. No mixing of chemicals should be allowed, other than that specified in an experimental procedure.

13.6.3 What if an emergency occurs?

I. If the chemical is in the eye: Flush water using an eyewash station for at least 15 minutes. Medical attention must be summoned as soon as possible.

II. If the chemical is swallowed or ingested: Do not induce vomiting unless the SDS recommends vomiting. Medical attention must be summoned as soon as possible.

III. If the chemical comes into contact with skin: Rinse the affected area for 15 minutes with tap water. It may be necessary to use a safety shower. If the safety shower is used, all contaminated clothing should be removed while the person is under the safety shower, and medical attention must be summoned as soon as possible.

13.6.4 After an experiment

I. Return any chemicals (excess reagent, product, or waste) to the appropriate location, or dispose of them as instructed.

II. Clean any used glassware and return the items to the appropriate location.

III. Ensure that all chemicals are properly stored. Make sure that the caps on the reagent bottles are tightly secured.

IV. Ensure that benches are clean before the next class comes in. One of the major causes of accidents is carelessness on the part of someone else.

V. All gas outlets are closed; especially burners were used during the experiment.

13.7 SUMMARY

- Keep tabletops clean. Return all equipment to its original location before leaving the lab.
- Report all accidents, no matter how minor, to the instructor. If you break something made of glass, be sure to use dustpan and hand broom to sweep it up and dispose of it in the glass waste receptacle.
- In case of an emergency where we have to evacuate, proceed out the nearest exit.
- Both the door should remain open all the time while working in the lab.

- Never put anything in your mouth while in the lab (including chemicals, solutions, food and drink)
- All food and drinks should be restricted to sitting area only.

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UNIT 14: INORGANIC EXERCISE: ACID BASE TITRATION

CONTENTS

14.1 INTRODUCTION

Inorganic chemistry is the branch of chemistry that deals with the properties and behavior of inorganic compounds (non-living compounds). The experiments related to science which include chemistry, biology, physics etc. are carried out in a proper place provided with the facilities for performing the experiments is known as laboratory or colloquially lab. We have studied in lower classes that a chemistry lab consists of different types of chemicals, apparatus, equipment etc. Now moving to higher classes we must have a complete knowledge of laboratory that one have to keep in mind.

It is necessary for a science student to have a complete knowledge of laboratories because in laboratory we perform experiments, observe change and obtain result. The whole process can be easily kept in mind as we perform the experiment in spite of reading the same experiment from a book. Working in laboratory makes the topic quite interesting. Now for having a complete knowledge of a laboratory, we move forward.

A term, titrimetric analysis is also often used to describe such experiments. Thus, titrimetric analysis or titrimetry is a common laboratory method of quantitative chemical analysis. It is used to determine the unknown concentration of a known analyte by treating a certain volume of it with known concentration and volume of a reagent called titrant. You must bear in mind that volume measurement play most vital role in titrimetric or volumetric analysis, hence such measurements should be performed with utmost care.

14.2 OBJECTIVES

Laboratory exercises discussed here are designed to give you knowledge and skills to design, understand and perform volumetric analyses. You should be able to implement this knowledge to various analysis scenarios. Volumetric analysis refers to titrations, a quantitative analysis technique widely used to determine quantity of a constituent present in analyte of interest. Titrations are of several types, for instance, acid-base titrations, complexometric titrations, redox titrations and precipitation titrations.

First experiment, *i.e.*, determination of sodium carbonate and sodium hydroxide in a mixture by indicator method is an acid-base titration. You will learn that different indicators can be used depending on the pH range of indicator and the pH of reaction mixture at end point. Second and third experiments are the redox titrations utilizing oxidizing agents $K_2Cr_2O_7$ and $KMnO_4$ respectively. These experiments essentially involve oxidation reduction reactions between the analyte and titrant. Exercises second and third also put across that a suitable indicator can be used if the colour change of analyte or titrant at the end point of redox titrations is not remarkable.

After reading this unit you will be able to:

- Maintain a laboratory notebook.
- Have knowledge of commonly used apparatus in the laboratory.
- Describe the process of titration.
- Classify the titration.
- Classify the indicator.
- Determine the strength of given sodium hydroxide (NaOH) solution.
- Understand the redox titrations utilizing oxidizing agents $K_2Cr_2O_7$ and $KMnO_4$ respectively.

14.3 TITRATION

Titration is a process of mixing of two solutions in order to react in a conical flask. One solution is with known strength or standard while the other solution is unknown solution or solution whose strength is not known. The solution which is to be titrated is taken in a conical flask with the help of a pipette and other solution is taken in a burette. Indicator is added to the conical flask in order to detect the end point or equivalence point. Two solutions are mixed dropwise by opening the tap of the burette. A sharp change in color indicates the end point. At this point, the reaction between two solutions is just completed.

14.3.1 Types of titration:

There are generally four types of titration depending on the reaction taking place between the two solutions. These are as follows:

1. Neutralization titration: These titrations are also known as acid- base titration as it involves two solution, one is of acid while the other is of base. For example, mixing of sodium hydroxide (base) with oxalic acid. This titration is further classified into acidimetry and alkalimetry. In acidimetry, the strength of an acid is determined by titrating it with standard alkali solution. In alkalimetry, the strength of an alkali is determined by titrating it against standard solution of an acid.

2. Redox titration: As the name indicates, redox titration are those titration in which on mixing two solutions, one solution undergoes oxidation while the other solution undergoes reduction or in simple words we can say that redox reaction occurs on mixing. These are also known as reducation- oxidation titration. The substance which undergoes oxidation is known as reducing agent while the substance that undergoes reduction is known as oxidizing agent. In redox reaction, both oxidation and reduction takes place simultaneously. For example, mixing of ferrous ammonium sulphate (FAS) and acidified $KMnO_4$, in which FAS undergoes oxidation and and $KMnO_4$undergoes reduction. Redox titration includes iodine titration where iodine is used as an oxidizing agent. There are two types of iodine titration, one is iodimetric and another is iodometric titration. In iodimetric titration, standard iodine solution is directly titrated against some reducing agent. The reducing agent used is generally hypo solution, $Na_2S_2O_3$.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

In iodometric titration, iodine is liberated from iodine solution by using some oxidizing agent and then the liberated iodine is titrated with a standard solution of a reducing agent.

3. Precipitation titration: As the name indicates, on mixing two solutions there is a formation of precipitate. Precipitate is a solid mass which get accumulate at the bottom of the solution. For example, on mixing of sodium chloride (NaCl) with silver nitrate solution ($AgNO_3$), there is a formation of precipitate of silver chloride (AgCl). Precipitation titration is also known as Argentometric titration viz; $AgNO_3$ is used as one of the solution during titration for the estimation of chloride content in water using K_2CrO_4

4. Complexometric titration: As the name indicates, on mixing two solutions there is a formation of a complex. Complexes are formed by metals and ligands; in which ligand donate lone pair of electrons to metal mainly transition elements. For example, in the determination of hardness present in given water sample, there is a formation of a complex between Ca^{2+}/ Mg^{2+} with EDTA. EDTA is a hexadentate ligand.One of the solution is of ligand and the other is of a metal containing compound.

14.3.2 Indicators:

Indicators are those chemical substances that indicate the end point during titration by color change. There are three types of indicators:

1. Internal indicators: Indicators which are added in the conical flask containing on of the solutions are known as internal indicators. For example, phenolphthalein, methyl orange etc.

2. External indicators: Indicators which are used outside the conical flask (in a white tile) are known as external indicators. For example, potassium ferricyanide, $K_3[Fe(CN)_6]$.

3. Self-indicators: In titration, two solutions are used. When one of the solutions itself acts as an indicator, it is known as self-indicator viz;, potassium permanganate ($KMnO_4$).

14.4 SAMPLE TITRIMETRIC EXPERIMENTS

There are several experiments based on the type of titrations i.e. acid- base titration, redox titration, precipitation titration and complexometric titration. Let us discuss the determination of strength of given sodium hydroxide solution.

14.4.1 Determination of strength of given sodium hydroxide solution

As we know that NaOH is a secondary standard chemical. Exact weighing of NaOH is not done as it is hygroscopic in nature (it can absorb moisture from the atmosphere). Hence an approximate weight of NaOH is taken in 500 mL volumetric flask. Distilled water is added in a flask. First 50 mL and then allow NaOH to dissolve. After complete dissolution of NaOH, additional distilled water is added up to the mark, thereby making the solution 500 ml. We have simply dissolve NaOH without weighing. Now in order to determine its exact strength, we mix two solutions, one of the solutions is NaOH solution and the other solution is standard solution generally the primary standard solution. NaOH solution is taken in a burette and standard solution of known volume say 10 ml solution of N/10 oxalic acid is taken in a conical flask. The standard solution of oxalic acid is prepared by the method discussed in section 1.9.1. Two or three drops of indicator (phenolphthalein) are added into the conical flask. Now by opening the tap of the burette, both solution one in the burette and another in the conical flask containing the indicator are mixed drop wise in order to react until light pink color appears at the end point indicating completin of reaction. When there is change in color, close the tap of the burette and record the volume of the burette. Repeat the titration for two concordant readings and the repeating volume be V_2 mL. Using law of equivalence ($N_1V_1 = N_2V_2$), the exact normality of NaOH is calculated.

(Oxalic acid) $N_1V_1 = N_2V_2$ (NaOH)

Where N_1 is normality of oxalic acid that is 1/10, V_1 is volume of oxalic acid that is 10 ml and N_2 is normality of NaOH which is to be calculated. The N_2 is the exact normality of NaOH. In this way, the normality of NaOH is determined and is now become standard. The strength of NaOH is calculated by multiplying N_2 with the equivalent weight. For NaOH, equivalent weight is 40.

Strength(S) = Normality × equivalent weight

14.4.2 Instrumental determination of an equivalence point:

There are different instruments used for determining the end point or equivalence point like pH meter, conductivity meter. Using pH meter, we can determine the end point by measuring the pH of the solution while in conductivity meter, we can measure conductance of the solution. Let us discuss the method of determining equivalence point using conductivity meter. It is provided with a conductivity cell which is dipped in a solution for measuring the conductance. There is a display which shows conductance in Siemens or ohm^{-1}. A fixed volume of standard solution is taken in a beaker and its conductance is measured by dipping the conductivity cell. Burette is filled with the solution whose strength is to be determined. The solution is titrated and after every 2 ml addition from the burette, the conductance of the solution is recorded. In this way, we obtain a series of conductance value with similar trend in first half and with different trend in second half. Then these conductance values are plotted against the volume of solution added from the burette. The graph will show two straight lines and their point of intersection represents the equivalence point.

14.5 DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROXIDE IN A MIXTURE BY INDICATOR METHOD

14.5.1 Chemicals and equipments required:

An aqueous solution of NaOH and Na_2CO_3 (mixture solution), phenolphthalein indicator, methyl orange indicator, standard hydrochloric acid (0.1 N), burette, pipette, conical flasks etc.

14.5.2 Theory:

Determination of sodium carbonate and sodium hydroxide in a solution containing mixture of these alkalies by indicator method involves acid base titration. Thus, the solution containing both alkalies is titrated against a strong acid such as hydrochloric acid. Reaction of hydrochloric acid with sodium hydroxide is a single step neutralization reaction as presented by equation (i). At the equivalence point of reaction (i) solution turns neutral due to complete neutralization of strong alkali sodium hydroxide by the strong acid hydrochloric acid. This equivalence can be determined by indicator phenolphthalein.

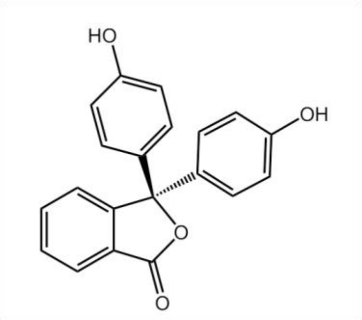


Figure 14.1. Molecular structure of phenolphthalein indicator

On the other hand neutralization of sodium carbonate with hydrochloric acid involves two steps presented by equations (ii) and (iii). At equivalence points of reactions (ii) and (iii) the reaction solutions are alkaline and acidic due to the formation of sodium bicarbonate and carbon dioxide respectively. Thus, suitable indicators for determining the equivalence points of reactions (ii) and (iii) are phenolphthalein and methyl orange respectively.

$$HCl + NaOH \longrightarrow NaCl + H_2O \quad \text{.....................} \quad (i)$$

$$HCl + Na_2CO_3 \longrightarrow NaHCO_3 + NaCl \quad \text{.....................} \quad (ii)$$

$$NaHCO_3 + HCl \longrightarrow H_2O + CO_2 + NaCl \quad \text{.....................} \quad (iii)$$

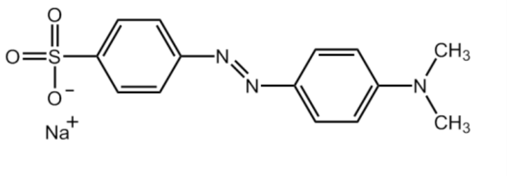


Figure 14.2Molecular structure of methyl orange indicator

14.5.3 Procedure:

Set the glassware assembly for the titration experiment. Fill the burette with supplied standard (0.1 N) hydrochloric acid. Take 10 mL mixture solution in a conical flask and add 2-3 drops of phenolphthalein. Phenolphthalein indicator gives pink colour in the alkaline mixture solution. Perform titration by incremental addition of hydrochloric acid from burette in to the conical flask very carefully and stop when the colour of phenolphthalein disappears.

At this moment sodium hydroxide is neutralized completely and sodium carbonate is converted to sodium bicarbonate. Now add few drops of methyl orange indicator to the same conical flask. The solution turns yellow in colour. Again perform titration by adding hydrochloric acid from burette. At equivalence point a sharp colour change from yellowish orange to red is observed. At this moment all of the sodium bicarbonate neutralizes as presented in equation (iii). Repeat the experiment three times and tabulate your results in observation table.1

14.5.4 Observation table:

Table 1 Titration of mixture of NaOH and Na_2CO_3 against acid

S. N.	mixture in conical flask (mL)	Burette reading for titration with phenolphthalein (mL)	Burette reading for titration continued with methyl orange (mL)	$(V_1\text{-}V_2)$

		Initial	Final	Volume (V_1)	Initial	Final	Volume (V_2)	
1	10 mL							
2	10 mL							
3	10 mL							

14.5.5 Calculations:

For calculations reactions (i), (ii) and (iii) can be interpreted as if the volume of acid consumed for titration in presence of phenolphthalein neutralizes all the sodium hydroxide and half of the sodium carbonate while the titration in presence of methyl orange neutralizes remaining amount of sodium carbonate. Therefore,

$N_{HCl} \times 2V_2 = N_{Sod.carbonate} \times 10$

$N_{Sod.carbonate} = N_{HCl} \times 2V_2/10$

Strength of sod. carbonate = $N_{Sod.carbonate} \times$ equivalent weight (g/L)

Strength of sod. carbonate = $N_{Sod.carbonate} \times 53$ (g/L)---------**(iv)**

On the other hand,

$N_{HCl} \times (V_1 - V_2) = N_{NaOH} \times 10$

$N_{NaOH} = N_{HCl} \times (V_1 - V_2)/10$

Strength of NaOH = $N_{NaOH} \times$ equivalent weight (g/L)

Strength of NaOH = $N_{NaOH} \times 40$ (g/L)---------**(v)**

Strength of sodium hydroxide and sodium bicarbonate present in the mixture can be calculated using equation (iv) and (v).

14.5.6 Results:

Supplied mixture solution contains _____ g/L sodium hydroxide and _____ g/L sodium bicarbonate.

14.5.7 Precautions:

1. Burette and other glassware must be cleaned and dried before performing experiment.
2. Lower meniscus should be read for taking observations.
3. Acid should be added carefully and dropwise in to the conical flask.
4. Least count of common laboratory burettes is 0.1 mL, hence all readings should be recorded up to first place of decimal in observation table.

14.6 DETERMINATION OF THE STRENGTH OF GIVEN FAROUS AMMONIUM SOLUTION SOLUTION BY PERMANGANATOMETRY

14.6.1 Chemicals and equipments required:

FAS solution, standard ferrous ammonium sulfate solution, KMnO4 solution, sulphuric acid, distilled water, beakers, water bath, glass rod, digital balance, burette and pipette etc.

14.6.2 Theory:

In this experiment you will use an oxidation-reduction (redox) reaction to determine the percentage of iron in a given FAS solution. This experiment consists of three parts.

1. Preparation of standard FAS solution.
2. Standardization of $KMnO_4$ solution by titrating it against standard ferrous ammonium sulfate (FAS) solution
3. Titration of unknown FAS solution against standard $KMnO_4$ solution

   The $KMnO_4$ solution in presence of H_2SO_4 converts the Fe^{2+} to Fe^{3+} as per the following reaction:-

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 3H_2O + 5O$$

$$\underset{\text{FAS}}{10[FeSO_4.(NH_4)_2.SO_4.6H_2O]} + 5O + 5H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 65H_2O$$

or

$$\left.\begin{array}{l} 2MnO_4^{\ominus} + 16H^{\oplus} + 10e^{\ominus} \longrightarrow 2Mn^{2\oplus} + 8H_2O \\ 10Fe^{2\oplus} \longrightarrow 10Fe^{3\oplus} + 10e^{\ominus} \end{array}\right] \longrightarrow \text{Redox reaction}$$

$$2MnO_4^{\ominus} + 16H^{\oplus} + 10Fe^{2\oplus} \longrightarrow 2Mn^{2\oplus} + 10Fe^{3\oplus} + 8H_2O \longrightarrow \text{Redox reaction} \quad \textbf{(i)}$$

Oxidation

Reduction

The reaction is carried out at room temperature as on heating $FeSO_4$present is FAS gets oxidised to $Fe_2(SO_4)_3$ by air or elevated temperature.

14.6.3 Procedure:

(i) Preparation of standard ferrous ammonium sulphate solution.

FAS is a primary standard chemical its standard solution can easely be prepared in present experiment this solution will be used to standardise $KMnO_4$ solution. To prepare standard FAS solution prepares N/10 solution in 100 or 250 mL volumetric flask as per your convenience. To prepare N/10 FAS solution in 100 or 250 mL weigh desired weight of FAS by using following equation:

$$w = \frac{ENV}{1000}$$

w = weight needed, E = equivalent weight, N = normality, V= desired volume

The equivalent weight of FAS is 392.

Transfer the weight quantitiy of FAS to a volumetric flask of 100 or 250 mL capacity and add half test tube of dil. H_2SO_4 in order to avoid hydrolysis of FAS. Shake the flask well till all the particls of FAS are dissolved. Add additional distilled water to make-up the volume of 100 or 250mL which represent N/10 FAS solution.

(ii) Standardization of $KMnO_4$ solution:

Rinse a clean burette with distilled water followed by supplied $KMnO_4$ solution. Mount the burette on a stand and fill up to the zero mark with supplied $KMnO_4$. Record the burette reading in observation table. Pipette out 10.0 mL of standard Mohr's salt solution into a conical flask and add 10 mL dilute sulphuric acid. Titrate the two solutions until a permanent light pink colour is obtained which indicates the endpoint of the titration. Record the final burette reading in observation table. Repeat the titrations to get at least two concordant readings and record all readings in observation table 2 (do not heat the titration mixture during the process of titration).

(iii) Determination of the strength of unknown FAS solution:

Refill the burette with same standardized $KMnO_4$ solution and take 10mL unknown FAS solution in conical flask and follow the same procedure as above in step (ii). Repeat the titrations to get two concordant readings. Record all readings in the observation table 3.

14.6.4 Observations and calculations:

Table: 2 Standard FAS solution vs potassium permanganate solution

S.N.	Volume of standard FAS taken in the conical flask (mL)	Burette readings		Volume of $KMnO_4$ used (mL)
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

Table:3 Titration of unknown FAS solution vs stanandardised $KMnO_4$

S.N.	Volume of FAS solution taken in the conical flask (mL)	Burette readings		Volume of $KMnO_4$ used, (mL)
		Initial	Final	
1	10.0			
2	10.0			

3	10.0			

14.6.5 Calculations

Standardisation of $KMnO_4$

$N_1 \times V_1 = N_2 \times V_1$

$KMnO_4 = FAS$ $$N_{KMnO_4} = \frac{N_{FAS} \text{ x } V_{FAS}}{V_{KMnO_4}}$$

Normality of unknown FAS solution

$FAS = KMnO_4$

$N_1 \times V_1 = N_2 \times V_1$

$$N_{FAS} = \frac{N_{KMnO_4} \text{ x } V_{KMnO_4}}{V_{FAS}}$$

Strength of unknown FAS solution = N_{FAS} × equivalent weight

$N_{FAS} \times 392$ = ----------------------g/L

14.6.6 Result:

The strength of given FAS solution is----------------------g/L

14.6.7 Precautions:

1. Use clean and dry glassware for titration.
2. Take $KMnO_4$ solution in burette. Since $KMnO_4$ is dark violet coloured solution, read upper meniscus.
3. Add sufficient sulphuric acid in conical flask before titration.

14.7 DETERMINATION OF THE STRENGTH OF GIVEN FERROUS AMMONIUM SULPHATE SOLUTION BY CHROMATOMETRY

14.7.1 Chemicals and equipments required:

FAS solution, standard ferrous ammonium sulfate solution, $K_2Cr_2O_7$ solution, 1% solution of diphenylamine indicator, sulphuric acid (1M), phosphoric acid (85%) distilled water, beakers, glass rod, digital balance, burette and pipette etc.

14.7.2 Theory:

In this experiment you will use redox reaction between ferrous and dichromate ions to determine the strength of given FAS solution. This experiment consists of three parts. First being preparation of standard FAS solution. Second, standardization of $K_2Cr_2O_7$ solution by titrating it against standard ferrous ammonium sulfate (FAS) solution in presence of diphenyl amine indicator and the third part of experiment involves titration of unknown FAS solution against standardized $K_2Cr_2O_7$ solution in presence of diphenyl amine indicator. Diphenyl amine, a colourless compound in its benzenoid form gets oxidized to bluish-violet coloured quinonoid form in the presence of strong oxidizing agent, $K_2Cr_2O_7$. However, Fe^{2+} are more susceptible towards oxidizing agent that the indicator. Hence, as long as $Fe^{2+}$are present in titration flask, the solution remains colourless. As soon as the Fe^{2+} are completely consumed/converted to Fe^{3+}, $K_2Cr_2O_7$ reacts with indicator diphenyl amine producing blue-violet colour marking the end point of the reaction.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$\underset{\text{FAS}}{6[FeSO_4.(NH_4)_2.SO_4.6H_2O]} + 3O + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 39H_2O$$

or

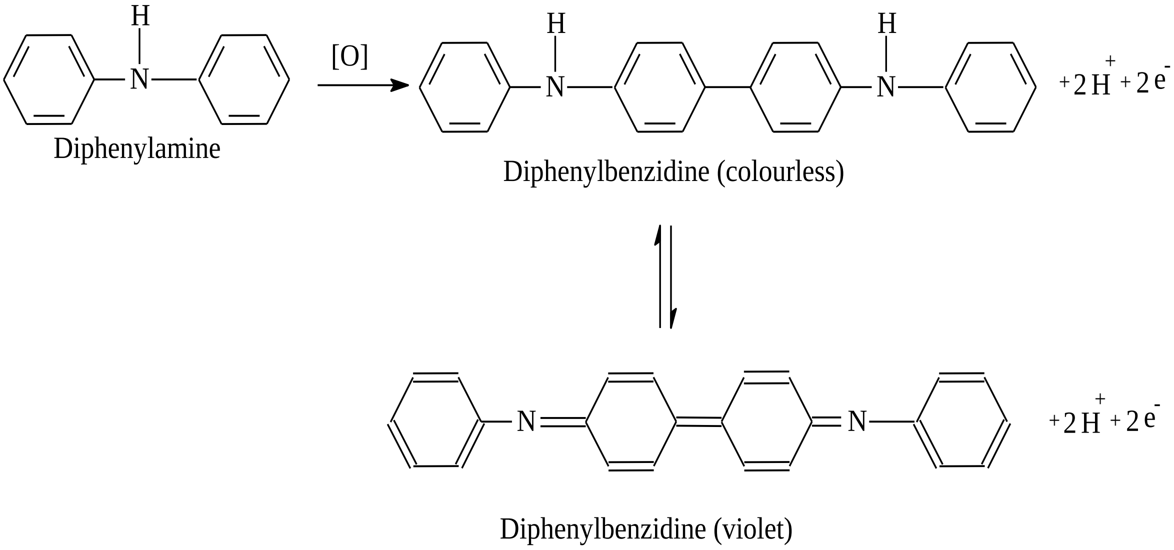
$$\left.\begin{array}{l} Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3\oplus} + 7H_2O \\ 6Fe^{2\oplus} \longrightarrow 6Fe^{3\oplus} + 6e^{\ominus} \end{array}\right] \longrightarrow \text{Redox reaction}$$

$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6Fe^{2\oplus} \longrightarrow 2Cr^{3\oplus} + 6Fe^{3\oplus} + 7H_2O \longrightarrow \text{Redox reaction} \quad \textbf{(i)}$$

Oxidation

Reduction

Reaction of $K_2Cr_2O_7$ with diphenylamine



14.7.3 Procedure:

***(i)* Preparation of standard ferrous ammonium sulphate solution**.

Transfer a known weight of Mohar's salt (say1.0g) in to a 100 mL volumetric flask. Add a test tube of dil.H_2SO_4 solution to the volumetric flask to prevent hydrolysis of the Fe^{2+} ions. Dissolve Mohar's salt in distilled water and make up the volume up to the mark with additional distilled water. Make the solution homogeneous; invert the flsk, six to ten times, to mix thoroughly.

***(ii)* Standardization of $K_2Cr_2O_7$ solution:** Rinse a clean burette with distilled water followed by supplied $K_2Cr_2O_7$ solution. Mount the burette on a stand and fill up to the zero mark with supplied $K_2Cr_2O_7$. Record the burette reading in observation table. Pipette out 10.0 mL of standard Mohr's salt solution into a conical flask and add 10 mL dilute sulphuric acid and half test tube syrupy phosphoric acid (or one test tube of 1:1 mixture of dil. H_2SO_4 – phosphoric acid). Now add 2-3 drops of indicator and titrate until the blue violet colour is obtained which indicates the endpoint of the titration. Record the final burette reading in observation table. Repeat the titrations to get at least two concordant readings and record all readings in observation table1

(iii) Determination of the Molarity of unknown FAS solution: Refill the burette with same standardized $K_2Cr_2O_7$ solution and take unknown FAS solution in conical flask. Repeat the titrations by following above method to get two concordant readings. Record all readings in the observation table. 2

14.7.4 Observations and calculations:

a. Preparation of standard FAS solution

Mass of FAS transferred into 100 mL of volumetric flask

$$\text{Molarity of ferrous ammonium sulphate solution } (M_1) = \left[\frac{\text{mass}}{\text{molar mass}} \text{ x } \frac{1000}{\text{V (in cm}^3)}\right] \text{mol dm}$$

$$= \left[\frac{\text{m}}{392{\cdot}15} \text{ x } \frac{1000}{100\,\text{cm}^3}\right] \text{mol dm}^{-3}$$

$$= \text{.............} \text{ mol dm}^{-3}$$

Table 1: Standardisation of $K_2Cr_2O_7$ solution

S.N.	**Volume of standard FAS taken in the conical flask (mL) V_1**	**Burette readings**		**Volume of $K_2Cr_2O_7$ used (mL) V_2**
		Initial	**Final**	
1	10.0			
2	10.0			
3	10.0			

b) Standardization of $K_2Cr_2O_7$ solution.

Molarity of standard Mohar's salt (FAS solution) = M_1

=...........mol dm^3

Volume of standard Mohar's salt (FAS solution) pipetted = V_1 =10·0 cm^3

Volume of $K_2Cr_2O_7$ solution used (table 1) = V_2 = ...cm^3

Molarity of $K_2Cr_2O_7$ = M_2= ?

Using molarity equation, $M_1V_1 = 6\,M_2V_2$

Molarity of dichromate solution, $M_2 = \dfrac{M_1V_1}{6\,V_2}$ = ...mol dm^{-3}

Table 2: Unknown FAS solution v_s standard $K_2Cr_2O_7$ solution

S.No.	**Volume of givin FAS solution taken in the conical flask, (mL) V_4**	**Burette readings**		**Volume of $K_2Cr_2O_7$ used, (mL) V_3**
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

a. Molarity and strength of unknown FAS solution

Molarity of $K_2Cr_2O_7$ = M_3 = M_2 = ...mol dm^{-3}

Volume of $K_2Cr_2O_7$ solution used (table 2) = V_3 = ... cm^3

Volume of given Mohar's salt(FAS solution) pipetted = V_4 = $10{\cdot}0\,cm^3$

Molarity of given Mohar's salt (FAS solution) = M_4 = ?

Using molarity equation, $M_4V_4 = 6M_3V_3$

Molarity of dichromate solution, $M_4 = \frac{6M_3V_3}{V_4}$ = ...mol dm^{-3}

Strength of given Mohar's salt(FAS solution) = Molarity x molar mass

= M_4 x $392{\cdot}15$ g dm^{-1}

= ....g dm^{-3}

14.7.5 Result:

The strength of given Mohar's salt (FAS solution) is _________ g/ dm^3

14.7.6 Precautions:

1. Use clean and dry glassware for titration.

2. Take $K_2Cr_2O_7$ solution in burette and handle carefully as it is corrosive and carcinogenic and also cxause chromium dermatitis.also handle phosphoric acid carefully it cause severe irritation and burns to the area of contact

3. Handle diphenylamine carefully as it has been dissolved in con. H_2SO_4

3. The endpoint of this experiment involves greenish to blue-violet colour change which requires special care for identification.

4. Add sufficient sulphuric acid in conical flask before titration.

14.8 SUMMARY

In this unit, we have discussed the concept of gravimetric analysis.In First experiment reveals the titration of hydroxyl and carbonate ions by titrating the mixture solution against HCl. This experiment gives us an idea about alkalinity of water and its types.basically hydroxyl and carbonate alkalinity. Experiment two and three rducate us how amount of iron in its ore and compound can be determined volumetrically basically through permagnatometry and chromatometry (redox titrations).

14.9 TERMINAL QUESTIONS

A.Fill in the blanks:

1. Standard solution is a solution of known ……….

2. Titration of oxalic acid with sodium hydroxide is ………. titration.

3. ………. are used for determining the end point during the titration.

4. Self- indicator is ………..

5. Least count of burette is………………………………...

6. Sodium hydroxide is ………. standard substance .

7. Potassium ferricyanide is an ………. Indicator.

8. ………. standard solution are prepared by direct weighing of the substance.

B.Short Answer type questions

Q.1 Discuss the procedure of titrations, in general.

Q.2 What are endpoint and equivalence point?

Q. 3 What is an indicator?

Q.4 What is equivalent weight of sodium carbonate?

Q.5 How does *pH* of the solution changes for titration of NaOH-Na_2CO_3 mixture solution with hydrochloric acid in presence of phenolphthalein and methyl orange?

Q.6 Justify your choice of phenolphthalein and methyl orange indicators for the titration of NaOH-Na_2CO_3 mixture solution with hydrochloric acid.

Q.7 Why preparation of standard solutions must be done with extreme care?

Q.8 How do you identify the endpoint of titration of FAS solution with $KMnO_4$?

14.10 ANSWERS

A. Fill in the blanks answers :

1. Strength **2.** Neutralization **3.** Indicators **4.** $KMnO_4$ **5.** 0.1mL

6. Secondary **7.** External **8.** Primary.

B.Short questions Answers :

A.1 Titration is chemical analysis by which the quantity of some constituent of a sample is determined by reacting exactly known quantities of sample and a titrant. The process usually involves gradual addition of a standard solution of titrant, from a glass burette to an Erlenmeyer flask (a conical flask with narrow neck) containing analyte solution and internal indicator, if required. The addition of titrant is stopped when the endpoint is reached as indicated by colour change of contents of Erlenmeyer flask.

A.2 At the equivalence point of a titration, an exactly equivalent amount of titrant has been added to the sample. The experimental point at which the completion of the reaction is marked by some signal is called the end point.

A.3 Indicator is a substance that changes colour in response to a chemical change. Colour change of indicator suggests that endpoint of titration has arrived. Endpoint is an approximation of equivalence point. Acid-base indicators such as phenolphthalein and methyl orange; redox indicators such as iodine and diphenyl amine and complexometric indictors such as EBT are commonly used in laboratory.

A.4 Sodium carbonate is a diacidic alkali, hence its equivalent weight is half of its molecular weight, *i.e.*, 106/2 = 53 g/mol.

A.5 First part of titration involves neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$. pH of the solution at this stage is just below 8.3. Since the pH range of phenolphthalein is 10 to 8.3, hence disappearance of colour of phenolphthalein indicates that the neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$ is completed. Further titration in presence of indicator methyl orange involves neutralization of sodium bicarbonate to result in acidic solution with pH value close to 4. This is well within the range (3.1-4.4) of methyl orange indicator.

A.6 First part of titration involves neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$. pH of the solution at this stage is just below 8.3. Since the pH range of phenolphthalein is 10 to 8.3, hence disappearance of colour of phenolphthalein indicates that the neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$ is completed. Further titration in presence of indicator methyl orange involves neutralization of sodium bicarbonate to result in acidic solution with pH value close to 4. This is well within the range (3.1-4.4) of methyl orange indicator.

A.7 Any mistake (such as incorrect weight or volume) done during the preparation of standard solutions, causes deviation from standard values. Such mistakes carry through the entire experiment and significantly affect the accuracy of the results.

A.8 Potassium permanganate is purple in aqueous solution, whereas the final products of the reaction between ferrous ion and KMnO4 are colourless. Hence the completion of reaction is indicated by the appearance of slight pink colour in the conical flask containing sample being titrated.

14.11 GLOSSARY

- **Indicators**— Substance that indicates end point by color change.
- **Titration** — Process of mixing of two solution in order to react in a beaker or conical flask.
- **End Point:** Point at which the reaction between two solutions just completes.

- **Standard Solution**: Solution of known strength.

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UNIT- 15 ORGANIC EXERCISES: CHEMICAL, PHYSICAL AND FUNCTIONAL GROUP TESTS

CONTENTS:

15.1 INTRODUCTION

In this chapter, you will identify anions in unknown substances. Instead, in this lab, you first will perform some preliminary tests using $AgNO_3$, $BaCl_2$, and H_2SO_4. In these tests, certain groups of anions will react while other groups of anions will not react. By analyzing the results of the first part of the experiment, you should be able to eliminate half - if not more- of the anions as possibilities in your unknown. The goal of this experiment is to develop techniques for identifying unknown substances. You will identify unknown solutions as containing one of the following: Cl^-, Br^-, I-, HPO_4^{2-}, or $SO_4{}^{2-}$

The salt consists of anion and cation. The basis of identification is the observed chemical behaviour of the components. The salt analysis may be systematically carried out in the following three steps:

i) Preliminary examination
ii) Detection of anions and
iii) Detection of cations

After they have been separated, identification of each cation depends on the observation of a characteristic chemical reaction. Solubility equilibria and complex-ion equilibria play crucial roles in the separations and subsequent identifications.

The cations (or the basic radicals) have been classified into seven groups, *viz.* from zero, I to VI group according to their nature to form the precipitate with various reagents. Because no single reagent is available which could form precipitate with all the cations, hence they have been classified into groups and the cations of each group give precipitate with a particular reagent called group regent.

The most common elements present in an organic compound are carbon, hydrogen, oxygen, nitrogen, halogen and sulphur. Sometimes, elements such as phosphorus and some metals may also be present. Therefore, qualitative analysis is limited to the detection of only a small number of elements usually present in organic compounds.

15.2 OBJECTIVES

The main objects of this unit are:

- To separate different cations anions and in solution using simple qualitative chemical tests.
- Plan a procedure for the analysis of an unknown solution of an anion and describe that procedure with a flow chart.
- Preliminary Investigation of the Sample
- The purpose of this experiment is to determine what anions are present in an unknown sample. We will be looking for the common anions sulfide (S_2-), sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), chloride (Cl^-), bromide (Br^-), iodide (I^-), acetate ($C_2H_3O_2^-$) and nitrate (NO_3^-).
- Analysis of the cations of Analytical Group I,II, III, IV, V VI and zero group.
- To detect nitrogen, sulphur and halogen in given mixture.
- To identify functional groups with known samples.

15.3 CLASSIFICATION OF ANIONS (ACIDIC RADICALS)

The anions are provided by the acids in the process of salt formation; hence these are generally referred to as acidic radicals. These radicals cannot be divided in the systematic groups as has been done in the case of the cations. However, for the sake of simplicity, these have roughly been divided into three groups depending upon their reactions with certain regents.

Classification of acidic radicals or anions:

Group	Name and formula of the Radical	Group Reagent	Inference of the group

Class I anions (First group)	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Acetate (CH_3COO^-) Nitrite (NO_2^-) Thiosulphate ($S_2O_3^{2-}$)	Dil. HCl or H_2SO_4 (Cold or hot.)	Gases of different colours and smells are evolved.
Class II anions (Second group)	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-) * Oxalate ($C_2O_4^{2-}$) * Borate (BO_3^{3-}) * Fluoride (F^-)	Conc.H_2SO_4 (hot.)	Gases of different colours and smells are evolved.
Class III anions (Third group)	Sulphate (SO_4^{2-}) * Phosphate (PO_4^{3-})	Barium chloride ($BaCl_2$) in presence of dill. HCl. Ammonium molybdate $(NH_4)_2MoO_4$ in presence of conc. HNO_3.	A white precipitate appears. A yellow precipitate appears.

* Interfering radicals (or anions)

15.4 PRELIMINARY TEST FOR THE ANIONS

A preliminary test for the anions is done on the basis of their class or group.

Preliminary Tests for the Anions of Class I (Group I)

The salts of these anions are decomposed by dil. H_2SO_4 or dil. HCl which serves as their group reagent. These anions with their preliminary tests are summarized below.

Take a small amount of salt or mixture in a dry test tube and add 5-6 ml of dil. H_2SO_4 or dil. HCl. Observe the reaction taking place in the test tube. If there is no reaction, heat the contents of the test tube gently and observe the sound, colour and odour of the gas evolved. From the observation, guess the presence of the anion according to the following table:

S. No.	Anion	Experiment	Observation	Inference
1.	Carbonate anion (CO_3^{2-})	On conducting the above experiment with dil. acids in cold or on heating.	*Brisk effervescence with evolution of colourless, odourless gases (CO_2).	CO_3^{2-} may be present.
2.	Sulphite anion (SO_3^{2-})	In the above experiment.	If the colorless gas with suffocating odour of burning sulphur is evolved (SO_2)	(SO_3^{2-}) may be present.
3.	Sulphide anion (S^{2-})	On conducting the above experiment.	** Evolution of colourless gas with smell of rotten eggs occurs (H_2S)	(S^{2-}) may be present.
4.	Nitrite anion (NO_2^-)	In the above experiment.	***Brown fumes with pungent odour (NO_2) are evolved.	NO_2^- may be present.
5.	Thiosulphate anion ($S_2O_3^{2-}$)	On conducting the above experiment.	If the colorless gas with suffocating odour is evolved and solution in test tube becomes yellowish white	($S_2O_3^{2-}$) is expected to be present.

			with turbidity.	
6.	Acetate anion (CH_3COO^-)	The same experiment as has been given above is conducted and thus	Small of vinegar is noticed without evolution of any gas (CH_3COOH)	(CH_3COO^-) is expected to be present.

Note:

* Basic carbonates of Pb and Bi do not evolve CO_2 with effervescence, but do so gradually.

**Many sulphides, e.g. those of Ag, Hg, As, Co and Ni do not decompose on heating with dil. HCl or dil. H_2SO_4. Therefore, the salt or mixture is heated with conc. HCl alone or with little zinc to observe the evolution of H_2S. If no H_2S smell is noticed, the above sulphides are taken as absent.

***All nitrites are soluble in water. The liberated NO_2 gas turns $FeSO_4$ solution black.

Preliminary Tests for the Anions of class II (group II).

The group reagent for the anions of this class is conc. H_2SO_4, i.e., the salts of these anions are readily decomposed by conc. $H_2SO_4^-$ After performing the preliminary tests of the anions of group I or class I, take a small amount of the salt or mixture in a separate dry test tube and add conc. H_2SO_4(2-3ml). then heat gently for some time. Observe the reactions occurring in the test tube as well as the gases evolved according to the following table.

S. No.	Anion	Experiment	Observation	Inference
1.	Chloride anion (Cl^-)	In the above experiment,	Colorless pungent gas (HCl) is evolved	(Cl^-) may be present.
2.	Bromide anion (Br^-)	In the above experiment,	Red brown gas (Br_2) is evolved and solution becomes	Br^- is expected.

			orange.	
3.	Iodide anion (I^-)	On conducting the above reaction.	Dark violet fumes (I_2) are observed	(I^-) May be present.
4.	Nitrate anion (NO_3^-)	In the above reaction.	* Pungent light brown gas (NO_2) is evolved.	(NO_3^-) may be present.
5.	Oxalate anion ($C_2 O_4^{2-}$)	On conducting the above experiment (strong heating),	**colorless, odourless gas is evolved which burns with blue flame at the mouth of the test tube on bringing a burning stick near the mouth	($C_2 O_4^{2-}$) is expected
6.	Fluoride anion (F^-)	On strong heating the contents of the test tube.	White pungent smelling gas is evolved and test tube becomes greasy	(F^-) is expected
7.	Borate anion (BO_3^{3-})	The borates are not decomposed by only conc. H_2SO_4 but in presence of ethyl alcohol or $CaCl_2$, they give compounds which can easily be detected. It will be discussed latter.		

Note: * All nitrates are soluble in water.

**Oxalates of K^+ and NH_4^+ are soluble in water. Ferrous oxalate is sparingly soluble. All other oxalates are insoluble.

15.5 PREPARATION OF SOLUTION FOR IDENTIFICATION OF THE ANIONS

For the identification of the anion(s) in the salt or the mixture, the anion (s) must be brought in solution, i.e., in free state so that the anion (s) may give suitable tests with the suitable regent (s). Many salts are soluble in water to give free anions and cations in solution, e.g. most of the ammonium salts and those of alkali metals are soluble. All nitrites, nitrates, acetates and many halides are also soluble in water. In the aqueous solution many anions can be detected. It is usually better to bring the anion (s) into the solution as soluble sodium salts by preparing soda or sodium carbonate extract which is obtained after boiling the salt or mixture with an excess of sodium carbonate solution.

Preparation of Soda Extract:

Mix one part of the solid salt or mixture with 3 parts by weight of sodium carbonate and 10-12 ml. distilled water (mineral free) and boil for about 8-10 minutes in a beaker or comical flask. Filter the contents while hot. The filtrate, known as soda extract, is used for detecting (or testing) most of the anions. The residue left on the filter paper may be dissolved in water or dil. HCl and tested for basic radicals whose salts are insoluble both in dil. and conc. HCl.

The excess sodium carbonate taken reacts with salts or mixture of the salts whereby the anions or acidic radicals are converted to their corresponding sodium salts which are water soluble and can be filtered off. Thus the anions come down in the filtrate along with the excess of sodium carbonate. The cations or the basic radicals are converted into their corresponding carbonates almost all of which are insoluble in water and therefore remain as residue on the filter paper along with unchanged salts (amm. carbonate is soluble).

Let X represents the basic radical (cation) and Y the acidic radical (anion) of any salt. When such a salt (XY) is heated with excess of sodium carbonate, the following reactions take place:

e.g.

$$XY+Na_2CO_3 \longrightarrow XCO_3+Na_2Y \text{ (X and Y are bivalent radicals)}$$

$$SnCl_2+Na_2CO_3 \longrightarrow SnCO_3+2NaCl \text{ (Soda extract)}$$

$$CaC_2O_4+ Na_2CO_3 \longrightarrow CaCO_3+Na_2C_2O_4 \text{ (Soda extract)}$$

The filtrate so obtained after neutralization with suitable acid, can be used to detect certain anions. The acid is to be added in excess till bubbles cease to evolve. This indicates the complete neutralization of the solution (soda extract). The common anions which can be identified easily using soda extract along with the acid used for its neutralization and the reagent added for the identification are given in the following table:

Anion	Experiment	observation	Inference
Cl^-, Br^-, I^-	dil. HNO_3	$AgNO_3$ soln.	AgCl: white ppt, AgBr: light yellow ppt., AgI-yellow ppt.
NO_3^-	dil. H_2SO_4	Freshly prepared $FeSO_4$ solution	Brown ring of $FeSO_4$. NO compd. results.
SO_4^{2-}	dil. HCl	$BaCl_2$ soln.	$BaSO_4$: White ppt.
$C_2O_4^{2-}$	dil. CH_3COOH	$CaCl_2$ soln.	CaC_2O_4: White ppt.
CH_3COO^-	dil. HCl	Neutral $FeCl_3$ solution.	Basic ferric acetate: brownish red ppt.
PO_4^{3-}	dil. HNO_3	Conc.HNO_3+$(NH_4)_2MoO_4$, heated and cooled.	Canary yellow ppt.

Here,

Column 1 represents the acidic radicals whose sodium salts are found in the extract.

Column 2 gives the acid to be added for neutralizing the excess of sodium carbonate.

Column 3 contains the names of the reagents added for the identification.

Column4 represents the characteristic changes which are observed during identification of the said anions.

Following are the advantages of preparing soda extract:

(i) It removes the basic radicals which may interfere in the systematic identification of the anions, by converting them into insoluble metal carbonates.

(ii) The identification of anions becomes easier in the case of compounds insoluble in water and dil. acids.

(iii) It helps in the identification of certain basic radicals (cations) of compounds insoluble in water, conc. HCl, HNO_3, etc. For example: $BaSO_4$, $SrSO_4$, etc.

Precaution: Na_2CO_3 used in the preparation of soda extract should be pure, free from chloride and sulphate which are generally present as impurities.

Note: Carbonate ion (CO_3^{2-}) is not detected by this method because it already comes from sodium carbonate. Hence it should be detected in the solid salt or mixture.

15.6 CONFIRMATORY TESTS FOR THE ANIONS

The presence of the anions in the salt or mixture is confirmed after the preliminary tests have been done. The confirmatory test for various anions is carried out as follows:

1. CO_3^{2-} anion:

It the colourless gas evolved during the preliminary test is passed into lime water*, it turns milky due to the formation of calcium carbonate, $CaCO_3$. If passing CO_2 is continued for a long time (excess), milky colour disappears, i.e., becomes soluble due to the formation of calcium bicarbonate, Ca $(HCO_3)_2$. This confirms the presence of CO_3^{2} ion.

Note. SO_3^{2-} ion also gives the same test Hence the presence CO_3^{2-} ion is confirmed after testing for SO_3^{2-} ion. It is better to test both CO_3^{2-} and SO_3^{2-} ions simultaneously.

2. SO_3^{2-} anion:

(i) If the colorless gas evolved during the preliminary test is brought in contract with the filter paper moistened with acidified potassium dichromate, solution**, the paper turns green.

(ii) Take 1ml. soda extract, add to it acetic acid in excess to make it neutral. Then add to it $BaCl_2$ solution and filter. To the filtrate, add bromine water and heat, white precipitate of $BaSO_4$ is obtained. These tests confirm the presence of SO_3^{2-} ion.

3. S^{2-} anion:

(i) If the colorless gas evolved during the preliminary test turns filter paper dipped in lead acetate solution black on bringing it at the mouth of test tube, it confirms the presence of S^{2-} ion.

(ii) Take 1 ml. soda extract and add to it few drops of sodium nitroprusside, the solution becomes violet, again confirming the presence of $S^{2—}$ion.

4. NO_2^-anion:

(i) If the brown gas evolved during the preliminary test turns paper dipped in starch + KI solution blue, presence of NO_2^- ion is confirmed.

(ii) Add 2-3 drops of KI and starch solution in the test tube during the preliminary test, deep blue or violet color if appears, it again confirms the presence of NO_2^- ion.

5. $S_2O_3^{2-}$ anion:

(i) If SO_3^{2-}, S^{2-} or SO_4^{2-} is present, shake a portion of the soda extract with $CdCO_3$ or $PbCO_3$ and then with Sr $(NO_3)_2$ solution. Filter and discard the precipitate if formed. Use filtrate for the detection of thio sulphate ion. If S^{2-}, $SO32^-$, or SO_4^{2-} is absent, use the water extract for testing $S_2O_3^{2-}$. The mixture solution+$AgNO_3$→white precipitate. This ppt. is unstable and decomposes on warming or on addition of HCl into black Ag_2S through colour change from yellow to brown and finally black.

(ii) Soda extract of the substance + iodine solution → decolorization of iodine solution confirms the presence of $S_2O_3^{2-}$ anion.

6. CH_3COO^- anion:

(i) A water extract of the substance gives blood-red colour in cold with neutral ferric chloride, solution, confirming the presence of acetate ion.

(ii) On rubbing the substance + oxalic acid (few crystals) + water (few drops) between the fingers, smell of vinegar is noticed again confirming the presence of acetate ion.

(iii) Solution of the substance + a little ethyl alcohol + a little conc. H_2SO_4 + heat gently → fruity smell is noticed (of ethyl acetate).

Note. *Method of passing CO_2 gas into water: If the delivery tube is available, insert its two ends with corks in the sample tube and line water tube (Delivery tube must be dipped in lime water) and heat the contents of sample (mix.+acid) tuble. Otherwise collect the evolved CO_2 in a test tube which just fits in the mouth of sample tube. After heating the sample tube, close the mouth of the second test tube with the thumb and add line water to it to check the presence or thumb and add line water to it to check the presence or absence of CO_2 gas.

**Preparation of acidified $K_2Cr_2O_7$ solution: Take approx. 1gm. of $K_2Cr_2O_7$ crystals and dissolve in 5ml. water, then add 2-3ml. dil. H_2SO_4. This is acidified dichromate solution.

***The shelf $FeCl_3$ contains free HCl in small amount due to hydrolysis of $FeCl_3$. Add a very dilute solution of NH_4OH drop wise to a little $FeCl_3$ solution taken in a test tube and shaking after each addition till a permanent precipitate is formed. Now boil the contents of the test tube and filter. The filtrate is known as neutral ferric chloride.

7. Cl^- anion:

(i) On bringing a glass rod dipped in NH_4OH near the mouth of the test-tube during the preliminary test, white dense fumes of NH_4Cl are formed.

(ii) On heating the given mixture with conc. H_2SO_4 and MnO_2, greenish yellow, pungent smelling gas (Cl_2) is evolved.

(iii) Soda extract+dil. HNO_3+$AgNO_3$ solution→ a white precipitate (AgCl) is formed which is soluble in NH_4OH solution.

(iv) Chromyl chloride test: Heat a small amount of the mixture, add to it soild $K_2Cr_2O_7$ (3 times of mixture) and conc. H_2SO_4. Orange-yellow vapors of chromyl chloride (CrO_2Cl_2) are evolved and are collected in a test-tube containing NaOH. This is acidified with CH_3COOH and treated with lead acetate solution. A yellow precipitate of lead chromate ($PbCrO_4$) is formed.

All these tests confirm the presence of Cl^- ion.

Note. The chromyl chloride test does not respond in case of chlorides of Ag, Hg, Pb and Sn. In such cases, it can be performed by the residue obtained on evaporating 5 ml. of soda extract.

8. Br^- anion:

(i) On heating the given salt or mixture with a little MnO_2 and conc. H_2SO_4, red-brown vapours of Br_2 are evolved.

(ii) Soda extract+dil. HNO_3+$AgNO_3$ solution→ a pale yellow precipitate is formed (Ag Br) which is partially soluble in NH_4OH.

(iii) Soda extrac+ a little dil. HNO_3 (to neutralise)+ few drops of chloroform or CCl_4+ Cl_2 water or conc. HNO_3 + Shake →chloroform or CCl_4 layer (lower) becomes yellow or orange These tests confirm the presence of Br^- ion.

9. I^- anion:

(i) Given salt or mixture+ MnO_2+conc. H_2SO_4+heat→violet vapours (I_2) in excess are evolved which turn the paper dipped in starch solution blue.

(ii) Soda extract+dil. HNO_3+$AgNO_3$ solution→yellow precipitate of AgI is formed which is insoluble in NH_4OH solution.

(iii) Soda extract+ a little HNO_3(dil.) (to neutralize)+ few drops of $CHCl_3$or CCl_4+conc. HNO_3 or Cl_2 water+ shake well→layer of organic liquid becomes pink or violet These tests confirm the presence of I^- ion.

10. NO_3^- anion:

(i) On heating the salt or mixture with copper turnings and conc. H_2SO_4, deep brown fumes (NO_2) are evolved in excess but the solution does not become yellow or pink.

(ii) Aqueous extract or solution of the salt or mixture in dil. HCl + freshly prepared solution of $FeSO_4$+shake well+add gradually conc. H_2SO_4 by the side of the test tube→a brown ring of $FeSO_4$. NO is formed at the junction of two liquids (This is called ring test)

The above tests confirm the presence of NO_3^- ion.

11. $C_2O_4^{2-}$ anion:

(i) Take soda extract of the salt or mixture in a test tube, acidify it with excess of CH_3COOH and then add $CaCl_2$ solution. A white precipitate of CaC_2O_4 is formed. Dissolve the precipitate in dil. H_2SO_4 and warm it. To the warm solution, add few drops of $KMnO_4$ solution and shake, pink colour of $KMnO_4$ solution disappears.

(ii) Take a little salt or mixture in a test-tube, add dil. H_2SO_4 and heat till effervescence ceases to appear. Add a pinch of MnO_2 and heat again. Effervescence due to evolving CO_2 reappears.

The above tests confirm the presence of $C_2O_4^{2-}$ ion.

12. F^- anion:

(i) Take a little salt or mixture with some sand in a test tube, add conc. H_2SO_4 to it and heat, bring a glass rod moistened with water at the mouth of the test tube. A waxy white deposit on the glass rod is obtained (NH_4Cl and $HgCl_2$ also leave a white deposit on the rod but this deposit is crystalline and not waxy).

After performing this test the contents of the test tube should not be thrown in the sink without cooling and diluting.

(ii) Soda extract+CH_3COOH (to neutralise) + $CaCl_2$ solution + shake → white precipitate appears after sometime. To the precipitate add dil. H_2SO_4+heat+$KMnO_4$ solution → pink color of KMnO4 is not discharged.

These tests confirm the presence of F^- ion.

13. BO_3^{3-} anion:

(i) Take a little salt or mixture in a porcelain dish, add a little conc. H_2SO_4 just to make the paste of the substance, 1/2ml. of ethyl alcohol or methylated spirit well by a glass rod and ignite →a green edged flame is developed (copper and barium salts also give the same test and interfere in the detection of BO_3^{3-} ion by this test. Hence test should be performed in a test tube instead of porcelain dish and the vapours evolved after heating should be burnt at the mouth of the test-tube).

(ii) Make a paste of little mixture + calcium fluoride (CaF_2) with a little conc. H_2SO_4. Take a portion of this paste with a thin glass rod or Pt-wire and bring it near the edge of the flame (do not introduce the paste into the flame)→green flame is obtained (Cu & Ba-salts do not interfere).

These tests confirm the presence of BO_3^{3-} ion.

14. SO_4^{2-} anion:

Take the solution of the substance in dil. HNO_3 or soda extract + dil. HCl. Add $BaCl_2$ solution. A curdy white precipitate is formed ($BaSO_4$) which is insoluble in all the conc. acids. This confirms the presence of SO_4^{2-} ion.

15. PO_4^{3-} anion:

(i) Boil a little substance with conc. HNO_3 and add ammonium molybdate solution to it, boil again and cool. A canary yellow precipitate is formed which is soluble in ammonium and alkali hydroxides.

(ii) This ion can also be tested in the soda extract as has already been given above These are the confirmatory tests for PO_4^{3-} ion.

Reactions Involved:

Carbonate :
anion (CO_3^{2-})

$$Na_2CO_3 + 2\,HCl \rightarrow 2NaCl + H_2O + CO_2 \uparrow$$

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{White (milky)}}{CaCO_3 \downarrow} + H_2O$$

$$CaCO_3 + H_2O + \underset{\text{excess}}{CO_2} \rightarrow Ca(HCO_3)_2 \text{ (Soluble)}$$

Salphite
anion (SO_3^{2-})

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 \uparrow$$

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \text{ (Milky)} + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4) \text{ (Green)} + H_2O$$

Sulphide
anion (S^{2-})

$$FeS + H_2SO_4 \rightarrow H_2S \uparrow + FeSO_4$$

$$(CH_3COO)_2Pb + H_2S \rightarrow PbS \text{ (black)} \downarrow + 2CH_3COOH$$

$$Na_2S + Na_2[Fe(NO)(CN)_5] \rightarrow \underset{\text{Sod. Nitroprusside}}{Na_4[Fe(NOS)(CN)_5]}$$

(Violet Complex)

Nitrite $2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$

anion (NO_2^-) $3HNO_2 \rightarrow HNO_3 + 2NO \uparrow + H_2O$

$2NO + O_2 \rightarrow 2NO_2 \uparrow$ (Brown)

$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$

I_2 + starch → Starch-Iodide (Blue)

Ring test:

$FeSO_4 + NO \rightarrow FeSO_4.\ NO$ (Brown ring)

Thiosulphate: $Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3 \downarrow$ (white) $+ 2NaNO_3$

anion ($S_2O_3^{2-}$) $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S \downarrow$ (Black) $+ H_2SO_4$

$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (tetrathionate)

Acetate:

$2CH_3COONa + H_2SO_4 \rightarrow 2CH_3COOH$ (vinegar smell) $+ Na_2SO_4$

Anion (CH_3COO^-)

$3CH_3COOH + FeCl_3 \rightarrow (CH_3COO)_3Fe$ (Blood red color) $+ 3NaCl$

Chloride anion (Cl-)

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (pungent gas)

$HCl + NH_4OH \rightarrow NH_4Cl \uparrow$ (white fumes) $+ H_2O$

$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow$

(greenish yellow gas)

$NaCl + AgNO_3 \rightarrow AgCl \downarrow$ (ppt) $+ NaNO_3$

$AgCl \downarrow + 2NH_4OH \rightarrow Ag(NH_3)_2Cl$ (soluble) $+ 2H_2O$

Bromide : $KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$

anion (Br^-) $2HBr + H_2SO_4 \rightarrow Br_2\uparrow$(reddish brown vapours)$+ SO_2\uparrow + 2H_2O$

$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$

$NaBr + AgNO_3 \rightarrow AgBr \downarrow$ (Light yellow ppt.)$+ NaNO_3$

$2\ NaBr + 4\ HNO_3 \rightarrow Br_2\uparrow + 2NaNO_3 + 2NO_2\uparrow + 2H_2O$

$2HBr + Cl_2 \rightarrow Br_2\uparrow + 2HCl$

$Br_2 + CHCl_3$ or $CCl_4 \rightarrow$ Orange yellow colour (Br_2 dissolves)

Iodide anion (I^-)

$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$

$2HI + H_2SO_4 \rightarrow I_2\uparrow$ (Violet vapours) $+ SO_2\uparrow + 2H_2O$

$2\ NaI + MnO_2 + 3H_2SO_4 \rightarrow I_2\uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$

I_2 + starch → starch – iodide (Blue)

$NaI + AgNO_3 \rightarrow AgI\downarrow$ (yellow ppt.) $+ NaNO_3$

$2NaI + Cl_2 \rightarrow 2\ NaCl + I_2$

$2NaI + 4HNO_3 \rightarrow I_2\uparrow + 2NaNO_3 + 2NO_2\uparrow + 2H_2O$

$I_2 + CHCl_3$ or $CCl_4 \rightarrow$ Pink or purple color (I_2 dissolves)

Nitrate: Anion (NO^-_3)

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$4\ HNO_3 \rightarrow 4\ NO_2\uparrow$ (Brown fumes)$+ O_2\uparrow + 2H_2O$

$3Cu + 8HNO_3 \rightarrow 3\ Cu\ (NO_3)_2 + 2NO\uparrow + 4\ H_2O$

$2\ NO + O_2 \rightarrow 2\ NO_2\uparrow$ (Brown)

Ring Test: $6\ FeSO_4 + 2\ HNO_3 + 2\ H_2SO_4 \rightarrow 3\ Fe_2\ (SO_4)_3 + 4\ H_2O + 2NO\uparrow$

$FeSO_4 + NO \rightarrow FeSO_4.\ NO$ (Brown ring)

Oxalate : **anion ($C_2O_4^{2-}$):**

$Na_2C_2O_4 + 2H_2SO_4 \rightarrow 2NaHSO_4 + H_2O + CO_2\uparrow + CO\uparrow$

$2CO + O_2 \rightarrow 2CO_2$

$Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4\downarrow$ (white ppt.) $+ 2NaCl$

$Ca\ C_2\ O_4 + H_2\ SO_4 \rightarrow Ca\ SO_4 + H_2\ C_2O_4$ (oxalic acid)

$2\ KMnO_4 + 3\ H_2SO_4 + 5\ H_2C_2O_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 10\ CO_2\uparrow + 8\ H_2O$

$Na_2C_2O_4 + MnO_2 + 2\ H_2SO_4 \rightarrow Na_2\ SO_4 + MnSO_4 + 2\ H_2O + 2\ CO_2\uparrow$

Fluoride: **Anion** (F-)

$2\ NaF + H_2\ SO_4 \rightarrow Na_2\ SO_4 + 2\ HF\uparrow \rightarrow$

$Si\ O_2 + 4\ HF \rightarrow Si\ F_4 + 2\ H_2O \rightarrow$

$3\ Si\ F_4 + 3\ H_2O \rightarrow 2\ H_2\ Si\ F_6 + H_2Si\ O_3$ (white deposit)

Borate: **Anion** (BO_3^{3-})	$Na_3BO_3 + 3\ H_2SO_4 \rightarrow 3\ NaHSO_4 + H_3\ BO_3$ (Boric acid) $H_3\ BO_3 + C_2H_5OH \rightarrow (C_2H_5)_3\ BO_3 \uparrow$ (ethyl borate) + $3\ H_2O$ $CaF_2 + H_2SO_4 \rightarrow Ca\ SO_4 + 2HF$ $Na_3\ BO_3 + 3\ H_2\ SO_4 \rightarrow 3\ Na\ HSO_4 + H_3\ BO_3$ $2\ H_3\ BO_3 \rightarrow B_2\ O_3 + 3\ H_2O$ $B_2\ O_3 + 6\ HF \rightarrow 2\ BF_3$ (burns with green flame)+ $3\ H_2O$
Sulphate **anion** (SO_4^{2-})	$Na_2\ SO_4 + BaCl_2 \rightarrow Ba\ SO_4$ (white ppt) $+2\ NaCl$
Phosphate **anion** (PO_4^{3-})	$Na_3\ PO_4 + 3\ HNO_3 \rightarrow H_3\ PO_4 + 3\ NaNO_3$ $H_3PO_4 + 12\ (NH_4)_2\ Mo\ O_4 + 21\ HNO_3 \rightarrow$ $(NH_4)_3\ PO_4\ 12\ Mo\ O_3 \downarrow + 12\ H_2O + 21\ NH_4\ NO_3$. (amm, phospho molybdate - canary yellow ppt.)

Special Tests for the Mixtures of Anions (Combinations).

1. **Carbonate and Oxalate:**

   If given as a combination in a mixture, decompose carbonate anion completely by dil. H_2SO_4 (oxalate remains unaffected and then add MnO_2. If effervescence appears again, it indicates the presence of oxalate which can be confirmed by decolorization of $KMnO_4$ solution.

2. **Carbonate and Sulphite:**

   Carbonates and sulphites both are decomposed by dil. H_2SO_4 to give CO_2, and SO_2 gases which give white ppt. with lime water. But sulphite only (SO_2) reacts with pot. dichromate in presence of dil. H_2SO_4 to change the colour from light yellow to green $[Cr_2\ (SO_4)_3]$.

3. **Sulphide, Sulphite and Sulphate:**

   Sulphide can be tested with sod. Nitroprusside solution. Where, sulphite and sulphate do not interfere. If all the three anions are given together, remove sulpide by $Pb\ CO_3$ or $Cd\ CO_3$ as $Pb\ S$ (black) or CdS (yellow). Filter and add dil. HCl and $BaCl_2$

solution to the filtrate to give white ppt. of $BaSO_4$, filter again and boil the filtrate with conc. HNO_3 or bromine water to oxidize sulphite to sulphate [$Na_2SO_3 + O$ (from HNO_3 or Br_2 water] which can be tested with $BaCl_2$ solution (white ppt. $BaSO_4$ appears again).

4. **Chloride, Bromide and Iodide.**

   Chloride is tested by chromyl chloride test where bromide and iodide do not interfere. Bromide and iodide given together are tested by organic layer test. Acidify one ml. soda extract with dil. HCl or dil. H_2SO_4, add few drops of $CHCl_3$ or CCl_4 followed by freshly prepared chlorine water drop by drop while shaking. If organic layer is pink or violet, iodide is confirmed. Continue adding excess of chlorine water with vigorous shaking. If organic layer becomes orange brown or yellow, bromide is also confirmed.

5. **Nitrite and Nitrate.**

   If nitrite gives positive test as given above, decompose it by urea or NH_4Cl as below:

   $NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$

   $(NH_2)_2CO + 2HNO_2 \rightarrow 2N_2\uparrow + 3H_2O + CO_2\uparrow$

   $NaNO_2 + NH_4Cl \rightarrow NaCl + N_2\uparrow + 2H_2O$

   Now reduce nitrate using zinc and dil. H_2SO_4 to nitrite and test it by KI and starch solution as given below:

   $Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$

   $NaNO_3 + 2H \rightarrow NaNO_2 + H_2O$ (rest as given above)

6. **Nitrite and Iodide.**

   If both are preset in the mixture, add conc. H_2SO_4 to it heat and then add starch solution. Blue color of starch iodide confirms the presence of both anions.

7. **Nitrate and Bromide.**

   Reduce nitrate to nitrite by zinc and dil. H_2SO_4 and test as usual.

   Confirm bromide by organic layer as usual.

8. **Nitrate and Iodide.**

Reduce nitrate to nitrite and then nitrite and iodide can be tested by starch solution (blue). Iodide can also be detected by organic layer test.

The reactions of the tests for combination of acidic readicals or mixtures of anions are the same as given above. Therefore the reactions involved in the tests can be referred to the above.

15.7 SEPARATION OF CATIONS INTO GROUPS

(i) Precipitation of group I cations. The cations of group I are precipitated as insoluble chlorides in the presence of dil. HCl.

(ii) Separation of group II cations from group IV cations. The cations of both these groups are precipitated as sulphides but in different media, group II cations are precipitated in acidic medium (HCl) and those of group IV in basic medium (NH_4OH). As has already been stated, the precipitation of sulphides can occur only when $[M^{2+}]$ $[S^{2-}]$ exceeds the solubility product of the sulphide, MS at given temperature,

i.e. $[M^{2+}] [S^{2-}] > KS$

In presence of HCl, due to common H^+ ions, the ionisation of H_2S is suppressed thereby giving less concentration of S^{2-} ions in solution. Under this condition, the ionic product of metal and sulphide ions only exceeds the solubility product of sulphides of group II cations (such metal sulphides have low values of solublility products) and as a result these sulphides are precipitated. The solubility product values for sulphides of group IV cations being high are not surpassed by ionic product and these cations remain in the filtrate. These cations are then precipitated as sulphides in presence of excess S^{2-} ions in basic medium, i.e., NH_4OH.

(iii) Precipitation of group III cations. The group III cations are precipitated as hydroxides with the help of NH_4OH in the presence of NH_4Cl. NH_4Cl suppresses the ionisation of NH_4OH thereby giving less OH^- ions in solution, just sufficient to precipitate the group III cations and keeping higher group, i.e. IV, V & VI, cations in solution. This happens because of the low values of solubility products of the hydroxides of group III cations which are surpassed by ionic products of $[OH^-]$ and $[M^{3+}]$.

(iv) Precipitation of group V cations. These cations are precipitated as carbonates using $(NH_4)_2CO_3$ in presence of NH_4OH when Mg remains in solution.

15.8 PRELIMINARY INVESTIGATION OF THE SAMPLE

Basic radicals or cations in a sample can be tested by two types of tests:

(1) Dry tests, (2) Wet tests.

(1) Dry tests: These are the preliminary tests and include the following:

(a) Dry heating test
(b) Flame test
(c) Borax bead test
(d) Cobalt nitrate test
(e) Charcoal cavity test
(f) Microcosmic bead test

Of these, flame test, borax bead test, cobalt nitrate test and charcoal cavity test are more important and impart more valuable information about the cations in the sample under investigation.

(b) Flame test. Chlorides of certain metals when heated strongly using a loop of Pt-wire cleaned by conc. HCl, are volatilized easily in non-lumious flames of bunsen burner and their vapours become incandescent in the flame. The salt or group ppt. is picked by Pt-wire loop and kept into the edge of non-luminous flame. The imparted colour by the metals can be observed by naked eye:

Na – golden yellow, K-violet, Cu-bluish green,

Ca – brick or dull red, Sr – crimson red, Ba- apple green.

(C) Borax bead test. This test is performed mainly for the coloured substances and sometimes for white substances leaving coloured residue on dry heating.

The loop at the tip of the Pt-wire is heated in the flame, then dipped into borax powder, heated again strongly till borax swells up and finally converted into a transparent glassy bead. This bead is touched with the substance or group ppt. heated strongly in non-luminous flame and then in luminous flame, and color is observed.

Cation	**Non-luminous flame (Oxidising)**	**Luminous flame (reducing)**
Copper	green or light blue	red or colorless
Iron	Yellow	bottle green
Chromium	Green	Green
Cobalt	deep blue	deep blue
Nickel	light brown	Black
Manganese	Violet	Colorless

Chemistry of borax bead test: On strongly heating borax transforms into glassy bead:

$$Na_2B_4O_7\ 10H_2O \xrightarrow{-10H2O} Na_2\ B_4O_7 \rightarrow B_2O_3 + 2NaBO_2 \text{ (glassy bead)}$$

B_2O_3 combines with basic oxides to form meta borates which have characteristic colours.

(d) Cobalt nitrate test. Cobalt nitrate on heating is decomposed to CoO which combines with certain metallic and non-metalic oxides to give colored compounds. The powdered substance or mixture is mixed with an equal amount of solid Na_2CO_3 placed in a charcoal cavity, moistened with water and heated with the help of blow pipe. It is then moistened with few drops of cobalt nitrate and heated again. The color of the residue indicates the radical.

Blue - Al^{3+}, PO_4^{3-}, BO_3^{3-}

Green - Zn^{2+}

Dirty blue-green - Sn^{2+}

Pink - Mg^{2+}

Example. $Zn\ SO_4\ Na_2CO_3 \rightarrow Zn\ CO_3 + Na_2\ SO_4$

$ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$

$2CO\ (NO_3)_2 \rightarrow 2Co\ O + 4\ NO_2 \uparrow + O_2\uparrow$

$Zn\ O + Co\ O \rightarrow Zn\ O.\ Co\ O \rightleftharpoons Co\ Zn\ O_2$

(e) Charcoal cavity test. In this test, the powdered sample is mixed with an equal amount of solid Na_2CO_3, placed in a charcoal cavity, moistened with water and strongly heated in a reducing flame by means of blow pipe. From the color of the bead or deposit round the cavity (incrustation), cation/metal is identified.

Hot residue	**Cold residue**	**Inference**
Yellow	White	Zn
Reddish brown	reddish brown	Cd
Brown	yellow	Pb
Orange	yellow	Bi
Yellow	white	Sn
White	white	As, Al, Mg, Ca, Ba
Red	Red	Cu
Black	white	Fe, Co, Ni, Mn

(2) Wet tests. These are most important tests and are performed to confirm the presence of almost all the cations. The first step for the wet tests is the preparation of the original solution.

15.9 METHODS FOR THE PREPARATION OF ORIGINAL SOLUTION

The solution that contains all the cations is known as original solution. It can be prepared as follows:

(i) A little of the mixture sample is boiled with water with shaking. If does not dissolve then,

(ii) Mixture is boiled with dil. HCl. Still if does not dissolve then,

(iii) About 1gm mixture is boiled with 5ml. conc. HCl in 100ml beaker for a while, diluted with water and boiled again. Mostly the mixture is dissolved and solution becomes transparent.

(iv) If the mixture is insoluble in conc. HCl, then solubility should be observed in least quantity of dil. HNO_3, then conc. HNO_3 and finally in aqua regia.

(v) If the solution is made in HNO_3 or aqua regia, it has to be evaporated to dryness and dry residue is dissolved in dil. HCl or water after boiling. Sulphuric acid is never used as a solvent as it precipitates Ba, Sr, Ca & Pb as sulphates which are insoluble even in aqua regia.

15.10 SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

On the basis of solubility product and reagents, the cations are divided into the following six groups:

1. First group: Pb^{2+}, Ag^{+}, Hg_2^{2+} (ous)
2. Second group A : Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+} (ic)
   B : As^{3+}, Sb^{3+}, Sn^{2+} + (ous), Sn^{4+} (ic)
3. Third group: Al^{3+}, Cr^{3+}, Fe^{3+}
4. Fourth group: Ni^{2+}, Co^{2+}, Zn^{2+} Mn^{2+}
5. Fifth group: Ba^{2+}, Sr^{2+}, Ca^{2+}
6. Sixth group: Mg^{2+}

Zero group is also there containing NH_4^+ ion.

The cations, group reagents and salts precipitated along with their colors are summarized below:

5. Fifth group: $Ba^{2+}, Sr^{2+}, Ca^{2+}$

6. Sixth group: Mg^{2+}

Zero groups are also there containing $NH_4 +$ ion.

The cations, group reagents and salts precipitated along with their colors are summarized below:

S.No.	**Group**	**Group Radiclas**	**Group Reagent**	**Salt Reprecipitated**	**Colour of the precipitate**
1.	First Group	Ag^{+}, Pb^{++}, Hg_2 (ous)	Dil. HCl	(Chlorides) AgCl, AgCl, $PbCl_2$, $HgCl_2$	White ppt.
2.	Second group	Pb^{++}, Hg^{++} (ic.) Bi^{+++}, Cu^{+++}, Cd^{++}, Sb^{+++}, Sn^{++}, Sn^{+++}, Sn^{++++}(ic), As^{+++}	Dil. HCL+H_2s	(Sulphides)	Black ppt. (Sometimes red ppt.)
3.	Third group	$Al^{+++}, Cr^{+++}, Fe^{+++}$	After ,removing H_2S boil the solution with V_2	(Hydroxides) Al(OH_3) Fe(OH_3) $Cr(OH_3)$	White ppt. Brown ppt. Green ppt.
4.	Fourth group	$Ni^{++,}$ $Co^{++}, Zn^{++,} Mn^{++}$	Iiird Group	(sulphides) Zns	White or state ppt. Chocoloate-

					pink ppt. Black ppt. White ppt.
5.	Fifth group	$Ba^{++}, Sr^{++}, Ca^{++}$	Boil off $H_2S$and then add $NH_4CL + NH_4Oh$	(Carbonates) $BaCO_3$, $CaCO_3$, $SrCO_3$	Black ppt. White ppt.
6.	Sixth Group	Mg^{++}	& (NH^4) $_2CO_3$ and shake well. Fifth Group (Phosphate) Filtrate+ Na_2HPO_4 Solution	(Phosphate) $MgNH_4PO_4$	White crystalline ppt.

Important Hints for proceeding with the tests of Basic Radicals

(i) Group reagents should be added in systematic order.

(ii) A little excess of the group reagent must be added to ensure the complete precipitation fot he group radicals.

(iii) Solution in every group, if after adding group reagent is heated, granular precipitate is obtained.

(iv) The volume of the solution should not be unnecessarily increased at any step. If the volume of solution at any stage has become too large (in spite of great precautions) do not throw any a portion. Put it in a dish, and evaporate it to a small volume.

(v) There are Na^+, K^+ and $NH_4{}^+$ radicals also, among them Na^+ and K^+ are examined by flame test and for $NH_4{}^+$ radical, special test is performed.

(vi) Group reagent is added to original solution one after another, till the ppt. in any group is obtained. The ppt. shows the presence of any radical in that group. The complete precipitation of the radical in that group should be judged by adding sufficient amount of the group reagent otherwise it will create a great disturbance in the usual analysis of the subsequent group radicals.

(vii) Hydrogen sulphide is a very important gas reagent for the precipitation of IInd and IV th group radicals. It is prepared in the Kipp's apparatus by the action of dil. H_2So_4 on ferrous sulphide. Through the kipps apparatus continuous supply of the gas is available. See fig ahead.

15.11 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

Analysis of first group (silver group)

A white ppt. is obtained after the addition of dil. HCL to the original solution. It is filtered and washed with water and then boiled with 5-10 ml water. Filter and keep the filtrate for II group.

Note: If solution is prepared in dil. HCL, 1 st group is considered to be absent.It is not necessary that there should be complete precipitation of metallic ions of a particular group by means of that group reagent before proceeding of the next group. Mercuous salts are partially oxidized to mercuric salts and so are precipitate as mercuric sulphide also.

Analysis of second group

This group is divided in two groups:

(i) II nd A group(copper Group)
(ii) IInd B group (arsenic group)

II A copper Group:

Copper Group consists of

$Pb^{++}, Hg^{++}(ic), Bi^{+++}, Cu^{++}$ and Cd^{++} while Arsenic group contain

$Sb^{+++}, As^{+++}, Sn^{++}(ous)$ and $Sn^{++++}(ic.)$

In this group H_2S is passed in a little portion of the 1st group filtrate. If precipitate does not come, then it should be diluted with water, warmed and then H_2S is passed in the rest of the solution. It is faltered and washed well with H_2S water. The filtrate is kept for III group. Different radicals give the following coloured precipitates.

Hgs	Black(sometimes red)	Cds	Yellow
Pbs	Black(or Brown)	As_2S_2	Yellow
Bi_2S_2	Brown	SnS_2	Yellow
CuS	Black(or Brown)	Sb_2S_3	Orange

Yellow ammonium sulphide contains excess of sulphur dissolved in colourles ammonium sulphide solution and is expressed as (NH_4) $_2Su$.

The washed precipitate is warmed with a little yellow ammonium sulphide solution and filtered.

Residue Filtrate

(II A Group) (II B Group)

Hg(ic), Pb, Bi, Cu, Cd As, Sb, Sn (ous), Sn(ic)

15.12 ANALYSIS OF THE CATIONS OF GROUP II

II A copper group- Residue is washed with water and then treated with 50% HNO_3 boiled cooled and filtered.

<table>
<tr>
<td rowspan="4">Black residue
It may be HgS. Dissolve it in aqua regia and evaporate it to almost dryness. Add water and divide it in two parts (i) To first part add $SnCl_2$ Soln white or grey ppt (II) To second part add Cu turnings whitish deposti on Cu Hg^{++} confirmed.</td>
<td colspan="4">Filtrate: It may contain the nitrates of Pb, Bi, Cu. Take a little part of it add dil.
H2SO$_4$. If a white ppt. appears then add alcohol and dil. H_2SO_4 to the whole filtrate and filter.</td>
</tr>
<tr>
<td rowspan="3">White residue
It may contain Dissolve this residue in conc. Solution of CH_3COONH_4 and add K_2CrO_4 yellow ppt pb (Lead) confirmed.</td>
<td colspan="3">Filtrate: It may contain Bi, Cu and Cd as nitrate. Add to it excess of NH_4OH and filter:</td>
</tr>
<tr>
<td rowspan="2">White residue: It may be $Bi(OH)_3$. Dissolve the residue in the least quantity of conc. HCl divide it in two parts: (I) To first part add excess of water white ppt. (II) To second part add. Sod stannite soln. black ppt.</td>
<td colspan="2">Filtrate: It may contain Cu and Cd. If it is bule Cu is there if it is colourless Cu is absent. First Method:
(i)To first part add ch3cooh in excess K4 Fe(CN)6 brown coloured ppt. Cu++ (copper)confirmed.
(ii) To second part add KCN soin. Till the filtrate becomes colourless. Now pass H_2S yellow ppt. Cd++ (cadrnium) confirmed.
Second method: Add. conc. HCl and pass H_2S and filter.</td>
</tr>
<tr>
<td>Black residue: Cu^{++} (Copper) confirmed.</td>
<td>Filtrate: Dilute it and pass H_2S again yellow ppt. (cadmium)confirmed.</td>
</tr>
</table>

		(Bismuth confirmed)		
			(iii) To third part add 1 c.c. of conc. HCl and $FeSO_4$ soln. and filter.	
			Residue Cu^{++} (copper) confirmed.	**Filtrate:** Dilute it with water and pas H_2S gas yellow ppt. Cd^{++} (Cadmium) confirmed.

15.13 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP III

IIB Arsenic Group

Dilute the filtrate with water obtained after treating the second group ppt. with yellow ammonium sulphide and dil. HCl (in excess). A coloured ppt. indicates the presence of arsenic group but if a white ppt. is obtained it shows the absence of arsenic group radicals and reject it. Fiter the ppt. and boil it with conc. HCI and filter.

Yellow residue:	**Filtrate :**	
It may be As_2S_3. Dissolve it in conc. $HNO_3$and add ammonium molybdate solution and heat Yellow ppt. As^{+++}(Arsenic) Confirmed.	It may contain chlorides of Sb and Sr which may be confirmed by two different methods. First Method: Make the filtrate just alkaline by adding NH_4OH soln. Add 1-2 gms. Solid oxalic acid boils and passes H_2S gas. Filter if a ppt. is obtained.	
	Orange residue:	**Filtrate:**

	It may be Sb_2S_3: Dissolve it in least quantity of conc. HCl Dilute it with water white ppt. or turbidity. Sb^{+++} (Antimony) confirmed.	It may contain Sn. To it add NH_4OH to make it alkaline and pass H_2S gas Dirty yellow ppt. Sn^{+++} (Stannic) confirmed
	Second Method: To the filtrate add iron filling and heat for five minutes and filter.	
	Black residue: Sb^{+++} (Antimony confirmed.)	**Filtrate** It may contain $SnCl_2$. To it add $HgCl_2$ Soln. White or gray ppt. Sn^{++} (Stannous) confirmed.

ANALYSIS OF THIRD GROUP

Boil off H_2S completely (test with lead acetate paper for this) from filtrate of the second group and concentrate it. Boil it again with 1 c.c. of conc. HNO_3 as to convert all ferrous salt (if present) to ferric salt; otherwise ferrous hydroxide will not be completely precipitated in this group and thus will interfere in IVth group giving a black precipitate of Fes. Then after cooling add NH_4CL and NH_4OH (in excess) till the solution distinctly smells of ammonia.

Filter and wash the precipitate with water and keep the filtrate for IVth group. Dissolve the ppt. in 2 c.c. of H_2O_2 or in excess of Br_2water + $NaOH_2$, boil* it and filter. Boiling at this stage is essential since this ensures the complete oxidation of Fe^{++} to Fe^{+++}

$Fe(OH)_3$ – Brown ppt.

$Al(OH)_3$ – White ppt.

$Cr(OH)_3$ - Green or light bluish green ppt.

Residue : Brown ppt . it may contain $Fe(OH)_3$ or MnO(OH).	**Filtrate :** It may contain $NaAlO_2$ and $NaCr_4$. if it is yellow Na_2CrO_4 will be there otherwise $NaAIO_2$ may be there. Divide it in two parts.	
Divide the precipitate in two parts: (i) ppt. +conc. HNO_3 + PbO_2 Boil and cool By adding a little water Light, pink, violet colour Mn^{++} (Manganese) confirmed. (ii) Dissolve the precipitate in dil. HNO_3 or dill. HCI and divide it in two parts: (a) To first part add $K_4[Fe(CN)_6]$ deep blue colour or ppt. (b) To second part add ammonium Sulphocyanide Blood red colour Fe^{+++}(Ferric) Confirmed.	(a) First part CH_3COOH + ($CH_3COOH)_2$ $\downarrow$ Pb Yellow ppt. (b) Second part + $AgNO_3$ Brick red ppt. Cr^{+++} (Chromium) confirmed.	To the part add NH_4CI and boil White gelatinous ppt. Al^{+++} (Alumunium) confirmed.

Notes:

(i) H_2S should be completely removed before adding conc. HNO_3; otherwise it will be oxidized into H_2SO_4; and thus will precipitate the Vth group radicals as sulphates.

(ii) Sometimes Mn also precipitates as MnO.OH (Brown ppt.) in this group so its test becomes necessary.

(iii) After boiling off H_2S addition of conc. HNO_3 is essential so as to convert all ferrous salts into ferric salts.

(iv) Addition of NH_4Cl before NH_4OH is absolutely essential otherwise the basic radicals of IV^th^ and V^th^ groups will precipitate out as hydroxide in this group.

(v) Interfering radicals should be removed before proceeding in this group.

(vi) H_2S should be passed in hot solution. At higher temperatures sulphides precipitated are granular and easy to filter.

15.14 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP IV

ANALYSIS OF FOURTH GROUP

Some of the characteristics of the basic radicals of this fourth group are tabulated as follows:

Form of the salt	**Nickel (NI^{++})**	**Cobalt (Co^{++})**	**Zinc (Zn^{++})**	**Manganese (Mn^{++})**
1- Sulphide	Black (NIS) Green- Green	Black (CoS) Pink Pink	White or Grey (ZnS) White Colourless	Light Pink(MnS) White Colouriess Light pink, pink violet.

Pass H_2S continuously in the hot ammonical filtrate of II group. Formation of the precipitate shows the presence of fourth group. Filter and wash the ppt. and keep the filtrate for fifth group.

Different radicals give the following coloured precipitates:

NIS	Black	ZnS	White or grey
CoS	Black	MnS	Light pink

Notes:

(i) H_2S must be passed in hot solution otherwise ZnS and MnS will from colloidal solution.

(ii) H_2S should not be passed for a very long time otherwise NiS and MnS will turn into colloidal solution.

Ppt. is treated with dill. HCI and filtered:

Residue: It may contain NiS and CoS. Dissolve it in aqua-regia(3HCI+ HNO_3) and evaporate to dryness+ water and divide it in number of parts.		**Filtrate:** it may contain $MnCl_2$ and $ZnCl_2$. Boil off H_2S, and add excess of NaOH and filter.	
To one part and NH_4OH (in excess) + dimethyl glyoxime Scarlet red ppt. Ni^{++} (Nickel) Confirmed	(i)To one part add NH_4OH (in excess) + CH_3COOH (in excess) + KNO_2 solution. Yellow crystalline ppt. Co^{++} (Cobalt) Confirmed. (ii) To other part in a porcelain dish + $NaHCO_3$ solid (in excess) + Br_2 water. Shake for some time Apple green colour (in cold) Co^{++} (Cobalt) confirmed. Apple green colour in cold changing to black on heating Co^{++}(Cobalt) and Ni^{++} (Nickel) both confirmed.	**Residue** White turning brown due to oxidation. (i) Dissolve the residue in conc. HNO_3 and add PbO_2. Boil for 2-3 minutes and dilute with water Pink or violet colour. Mn^{++}(manganese) confirmed. (ii) Residue + oxidizing fusion mixture (KNO_3+ Na_2CO_3). Heat strongly on a porceian piece green mass is obtained which dissolves to give pink solution Mn^{++} (Manganese) confirmed.	**Filtrate:** It may contain zinc. Pass H_2S in the filtrate. A white grey ppt. Zn^{++} (Zinc) confirmed.

15.15 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

After boiling off H_2S, concentrate the fourth group titlrate to one-third (1/3) of its original volume. Then add $NH_4OH$and $(NH_4)_2CO_3$ (never boil at this state.) Formation of white precipitate shows the presence of fifth group. Filter and was the ppt. keep the filtrate for the radicals of sixth group. Dissolve the precipitate in least quantity of acetic acid and boil for a few minutes. Take a small part of this soln. and add. K_2CrO_4 solution. If a yellow ppt appears, heat the whole solution with excess of K_2CrO_2 so as to precipitate barium completely. If no ppt. appears on adding K_2CrO_4 soln, then do not add $K2CrO_4$ solution to the whole soln. Now proceed as follows:

Residue: Yellow ppt. $BaCrO_4$. Ba^{++} (Barium) confirmed.	It may contain $(CH_3COO)_2$ and $CH_3COO)$ Ca. To it add $(NH_4)_2SO4$ solution in excess and boil it filter it.	
	Filtrate: it may contain ca. to it add $(NH_4)_2C_2O_4$ soln. white ppt. Ca^{++} (calcium) confirmed.	Residue: White ppt. $(SrSO_4)$ Sr^{++} (strontium) confirmed.

Notes:

(1) It is better to use saturated solution of $(NH4)\ _2SO_4$ to detect Sr^{++} radical. After addition of the reagent, wait for few minutes to see if a precipitate of $SrSO_4$ is obtained.

(2) Sometimes calcium does not get precipitated in its group due to the formation of $Ca(HCO_3)_2$ on addition of $(NH_4)_2\ CO_3$ to the concentrated filtrate of IVth group. As $Ca(HCO_3)_2$ is soluble and it passess into the filtrate of Vth group. Hence filtrate of Vth group must be tested for calcium before proceeding to VIth group.

(3) They are tested in the order BSC(Barium, strontium, Calcium).

(4)

15.16 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP VI

Heat the fifth groups filtrate with ammonium oxalate and discard the precipitate, if comes. Add 2-3 c.c. of NH4OH and excess of sodium phosphate (Na_2HPO_4) to the filtrate. Shake the solution with a glass rod. After a few minutes a white crystalline precipitate results. Mg^{++}(Magnesium) confirmed.

Analysis of ammonium (NH4+) Radical (zero group)

(1) Heat a little mixture with 2-3 c.c NaOH in a test tube. A characteristic smell of (NH_3) is obtained. On bringing a glass rod dippedin conc. HCl at the mouth of the test tube, enormous white fumes are produced.

(2) On adding Nessler's regent to the solution of the mixture →brown color of ppt. is obtained. This test is extremely sensitive and characteristic.

Note. Nesster's reagent is prepared by adding KI to Hg Cl_2 solution until the red ppt (HgI_2) formed, is dissolved. It is mixed with NaOH solution.

CHEMICAL REACTIONS INVOLVED IN THE TEST OF BASIC RADICALS

First Group: Lead (Pb^{++}), Silver(Ag^{+}) Mercurous (Hg_2^{++}) and lead (Pb^{++}).

$$Pb(NO_3)_2 + 2\,HCl \longrightarrow \underset{\text{White ppt}}{PbCl2\downarrow} + 2\,HNO3$$

$$PbCl_2 + 2\,KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2\downarrow} + 2HCl$$

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_2\downarrow} + 2KCl$$

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{White ppt}}{PbSO_4} + 2KCl$$

SILVER (Ag+) :

$$AgNO_3 + HCl \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + HNO_3$$

$$AgCl + 2\,NH_4OH \longrightarrow \underset{\text{Silver ammonichloride}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Ag(NH_3)_2Cl + 2\,HNO_3 \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + 2NH_4NO_3$$

Mercurous (Hg^{++}):

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow \underset{\text{White ppt}}{Hg_2Cl_2\downarrow} + 2HNO_3$$

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{HgNH_2Cl}_{\substack{\text{Ammino mercuric chloride}\\ \text{Black}}} + Hg + NH_4Cl + 2Cl$$

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl$$

$$Hg + 2\,Cl \longrightarrow HgCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White ppt}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey ppt}}{2\,Hg\downarrow} + SnCl_4$$

Second Group : Mercuric (Hg^{++}), Lead(Pb^{++}), Bismuth(Bi^{++}), Copper(Cu^{++}), Cadmium(Cd^{++}), Arsenic(As^{+++}), Antimony(Sb^{+++}), Tin (Sn^{++}, Sn^{+++})

Sometimes, in second group, white or a light yellow ppt. is observed which is due to sulphur precipitated from H_2S by excess of HNO_3 or osther oxidizing agents e.g. (NO_2^-, SO_3^{--}, Fe^{+++}). The ppt. should be rejected.

$$2HNO_3 + 3H_2S \longrightarrow 4H2O + 2NO\uparrow + 3S\downarrow$$

$$2NaNO_2 + 2HCl + H_2S \rightarrow 2NaCl + 2NO\uparrow + 2H_2O + S\downarrow$$

$$Na_2SO_3 + 2HCl + 2H_2S \rightarrow 2NaCl + 3H_2O + 3S\downarrow$$

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S\downarrow$$

Mercuric (Hg^{++}):

$$HgCl_2 + H_2S \longrightarrow HgS\downarrow + 2HCl$$

Black ppt

$$3HgS + 2HNO_3 + 6HCl \rightarrow 3HgCl_2 + 2NO\uparrow + 3S + 4H_2O$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4$$

Mercuric Chloride White ppt.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$$

Mercurous chloride Grey ppt.

Lead (Pb^{++}):

$$PbCl_2 + H_2S \longrightarrow PbS\downarrow + 2HCl$$

Black ppt.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO\uparrow + 3S + 4H_2O$$

$$Pb(NO3)2 + H2SO4 \rightarrow PbSO_4\downarrow + HNO_3$$

White ppt

$$PbSO_4 + 2CH_3COONH_4 \rightarrow (NH_4)_2Pb(SO_4)_2 + (CH_3COO)_2Pb$$

$$(CH_3COO)_2Pb + K_2CrO_4 \rightarrow PbCrO_4\downarrow + 2CH_3COOK$$

Bismuth (Bi^{+++})

$$2BiCl_3 + 3H_2S \rightarrow Bi_2S_3\downarrow + 6HCl$$

Brown ppt.

$$Bi2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO\uparrow\ 3S\downarrow\ 4H_2O$$

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

Milky

$$2BiCl_3 + 3Na_2SnO_2 + NaOH \longrightarrow 2Bi + 3Na_2SnO_3 + 6NaCl + 3H_2O$$

Copper (Cu++) :

$CuCl_2 + H_2S \longrightarrow CuS\downarrow + 2HCl$

Black ppt.

$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 3S\downarrow + 4H2O$

$Cu(NO3)2 + 4NH4OH \longrightarrow Cu(NH_3)_4(NO_3)_2 + 4H_2O$

Tetraaminecoppernitrate
Blue colour

$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_3COONH_4$

$2\,Cu(NO_3)_2 + K_4[Fe(CN)_4] \longrightarrow Cu_2[Fe(CN)_6]\downarrow + 4KNO_3$

Pott. Ferocyanide   Copper ferrocyanide
Chocolate red ppt

Cadmium (Cd++):

$CdCl_2 + H_2S \longrightarrow CdS\downarrow + HCl$

Yellow ppt

$CdS + 2HCl \longrightarrow CdCl_2 + H_2S\downarrow$

$CdCl_2 + 2NH_4OH \longrightarrow Cd(OH)_2\downarrow + 2NH_4Cl$

$Cd(OH)_2 + 2NH_4Cl + 2NH_4OH \longrightarrow [Cd(NH_3)_4]Cl_2 + 4H_2O$

Tetramine cadmium chloride
Colourless

Copper- Cadmium Separation :

$CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2\downarrow$

$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2\downarrow + (CN)_2\uparrow$

White ppt.

$Cu_2(CN)_2 + 6CN \longrightarrow 2K_3[Cu(CN)_4]$

Cuprous cyanide   Pot. Cuprocyanide

$CdSO_4 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$

$Cd(CN)_2 + 2KCN \longrightarrow K_2[Cd(CN)_4]$

Cadmium cyanide   Pot. Cadmicyanide

The complex of Cu and Cd dissociate as follows:

Primary : $K_3[Cu(CN)_4 \rightleftharpoons 3K^+ + [Cu(CN)]^{3-}$

Pot. Cuprocyanide

Secondry : $[Cu(CN)] \rightleftharpoons Cu^+ + 4\,CN^-$

(Very small dissociation
due to to greater stability
of the complex ion)

Primary : $K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)]^{2-}$

Pot. Cadmicyanide

Secondary : $[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{++} + 4CN^-$

(Considerable dissociation
due to lesser stability of the complex ion)

Thus when H_2S is passed through a solution containing these complexes, solubility product of CdS only is exceed and therefore it gets precipitated.

Arsenic (As^{+++}):

$$AsCl_3 + 3H_2S \longrightarrow \underset{\text{Yello ppt.}}{As_2S_3\downarrow} + 6HCl$$

$$As_2S_3 + 3(NH_4)2S_2 \longrightarrow \underset{\text{Ammonium thio arsenite}}{3(NH_4)3AsS_3}$$

$$\underset{\text{Ammonium thio arsenite}}{3(NH_4)3AsS_3 + 6HCl} \longrightarrow \underset{\text{Yello ppt}}{As_2S_3\downarrow} + 6NH_4Cl + 3H_2S\uparrow$$

As_2S_3 dissolves in nitric acid forming arenic acid(H_3AsO_4)

$$H_3AsO_4 + 12(NH_4)2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{Yello ppt}\\ \text{Ammonium arsenomolybdate}}}{(NH_4)_3AsO_4.12MoO_3\downarrow} + 21NH_4NO_3 + 12H_2O$$

Antimony (Sb^{+++}):

$$3SbCl_3 + 3H_2S \longrightarrow \underset{\text{Orange ppt.}}{SbS_3\downarrow} + 6HCl$$

$$SbS_3 + 3(NH_4)2S_2 \longrightarrow 2(NH_4)3SbS_3$$

$$SbS_3 + 3(NH_4)2S_2 \longrightarrow \underset{\text{Ammonium thio-antimonate}}{2(NH4)_3SbS_4 + S\downarrow}$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_5\downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$SbS_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow$$

$$SbS_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow + 2S\downarrow$$

$$SbCl_3 + H_2O \longrightarrow \underset{\substack{\text{Milky(Antomony}\\ \text{oxychloride)}}}{SbOCl} + 2HCl$$

Tin (Sn^{++},Sn^{++++}):

$$SnCl_2 + H_2S \longrightarrow \underset{\text{Brown ppt.}}{SnS\downarrow} + 2HCl$$

$$SnCl_4 + 2H_2S \longrightarrow SnS_2\downarrow + 4HCl$$

SnS- Insoluble in ordinary amm. sulphide but soluble in yello amm. sulphide.

SnS_2- Soluble in ordinary amm. sulphide

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_2$$

$$SnS_2 + (NH_4)_2S \longrightarrow \underset{\text{Amm. thio-stannate}}{(NH_4)_2SnS_2}$$

$$(NH_4)_2\,SnS_3 + 2HCl \longrightarrow SnS_2\downarrow + 2NH_4Cl + H_2S\uparrow$$

$$SnS_2 + 4HCl \longrightarrow SnCl_4 + 2H_2S\downarrow$$

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$\mathrm{Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_2}$$

Third Group

IRON, ALLMINIUM, CHROMIUM

$\mathrm{Fe^{+++}, Al^{+++}, Cr^{+++}}$

In the third group ferrous salts($\mathrm{Fe^{++}}$) areoxidized to ferric salts ($\mathrm{Fe^{+++}}$) by boiling it with few drops of con. $\mathrm{HNO_3}$.

$$\mathrm{2FeCl_2 + 8HNO_3 \longrightarrow 2Fe(NO_3)_3 + 4HCl + 2NO_2\uparrow + 2H_2O}$$

Iron ($\mathrm{Fe^{+++}}$):

$$\mathrm{FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3NH_4Cl}$$

Brown ppt.

$$\mathrm{Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O}$$

$$\mathrm{2FeCl_3 + 6NH_4CNS \longrightarrow Fe[Fe(CNS)_6]_3\downarrow + 12KCl}$$

Ammo. thiocyanate

Ferric sulphocyanide
Blood red colour

$$\mathrm{4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe[Fe(CNS)_6]_3 + 12KCl}$$

Pot. ferrocyanide

Ferric ferrocyanide
Deep blue colour

Aluminium ($\mathrm{Al^{+++}}$):

$$\mathrm{AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + NH_4Cl}$$

White ppt.

$$\mathrm{Al(OH)_3 + NaOH \longrightarrow NaAlO_3 + 2H_2O}$$

$$\mathrm{NaAlO_3 + NH_4Cl + H_2O \longrightarrow Al(OH)_3\downarrow + NH_3 + NaCl}$$

Chromium (Cr+++):

$$\mathrm{2CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3\downarrow + 3NH_4Cl}$$

Green ppt.

$$\mathrm{Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O}$$

$$\mathrm{2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O}$$

$$\mathrm{Cr(OH)_3 + 4NaOH \;\; 3H_2O_2 \longrightarrow Na_2CrO_4 \;\; 5H_2O \;\; 3NaBr}$$

$$\mathrm{Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4\downarrow + 2CH_3COONa}$$

Yello ppt.

Fourth group

ZINC, MAGNASIUM, COBALT

Zinc ($\mathrm{Zn^{++}}$)

$$\mathrm{ZnCl2 + H2S \longrightarrow ZnS\downarrow + 2HCl}$$

White grey ppt.

$$\mathrm{ZnS + 2HCl \longrightarrow ZnCl_2 \;\; 2H_2S\uparrow}$$

$$\mathrm{ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl}$$

White ppt.

$$\mathrm{Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2HCl}$$

MANGANESE (Mn^{++}) :

$$MnCl_2 + H_2S \rightarrow \underset{\text{Buff coloured ppt.}}{MnS \downarrow} + 2HCl \uparrow$$

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S \uparrow$$

$$MnCl_2 + 2NaOH \rightarrow Mn(OH)_2 \downarrow + 2NaCl$$

$$2Mn(OH)_2 + O \rightarrow \underset{\text{Brown ppt.}}{2MnO(OH) \downarrow} + H_2O$$

$$MnO(OH) + 2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + \underset{\substack{\text{Pink colour} \\ \text{(Permanganic acid)}}}{HMnO_4}$$

COBALT (Co^{++}) :

$$CoCl_2 + H_2S \rightarrow CoS \downarrow + 2HCl$$

$$3CoS + \underbrace{2HNO_3 + 6HCl}_{\text{Aqua-regia}} \rightarrow 3CoCl_2 + 2NO \uparrow + 3S \downarrow + 4H_2O$$

$$CoCl_2 + 2HNO_2 \rightarrow Co(NO_2)_2 + 2KCl$$

$$CO(NO_2)_3 + 4KNO_3 \rightarrow \underset{\text{Pot. cobaltonitrite}}{K_4[Co(NO_2)_6]}$$

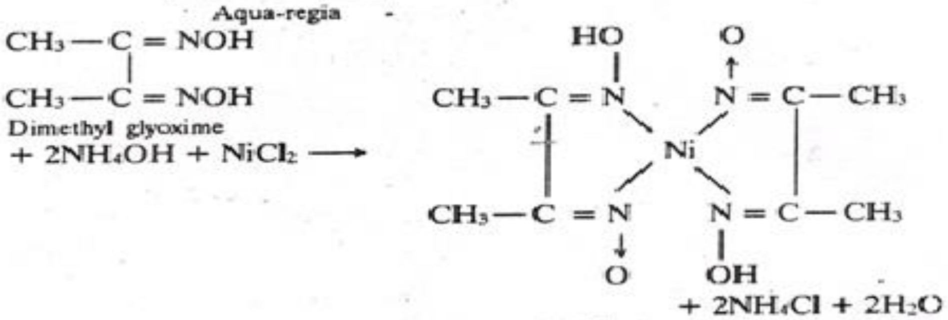
$$\underset{\text{Pot. cobaltonitrite}}{2K_4[Co(NO_2)_6]} + 2CH_3COOH + O\ (air) \rightarrow \underset{\substack{\text{Yellow ppt.} \\ \text{Pot. cobaltinitrite}}}{2K_3[Co(NO_2)_6] \downarrow} + 2CH_3COOK + H_2O$$

NICKEL (Ni^{++}) :

$$NiCl_2 + H_2S \rightarrow \underset{\text{Black ppt.}}{NiS \downarrow} + 2HCl$$

$$3NiS + \underbrace{2HNO_3 + 6HCl}_{\text{Aqua-regia}} \rightarrow 3NiCl_2 + 2NO \uparrow + H_2O + 3S \downarrow$$

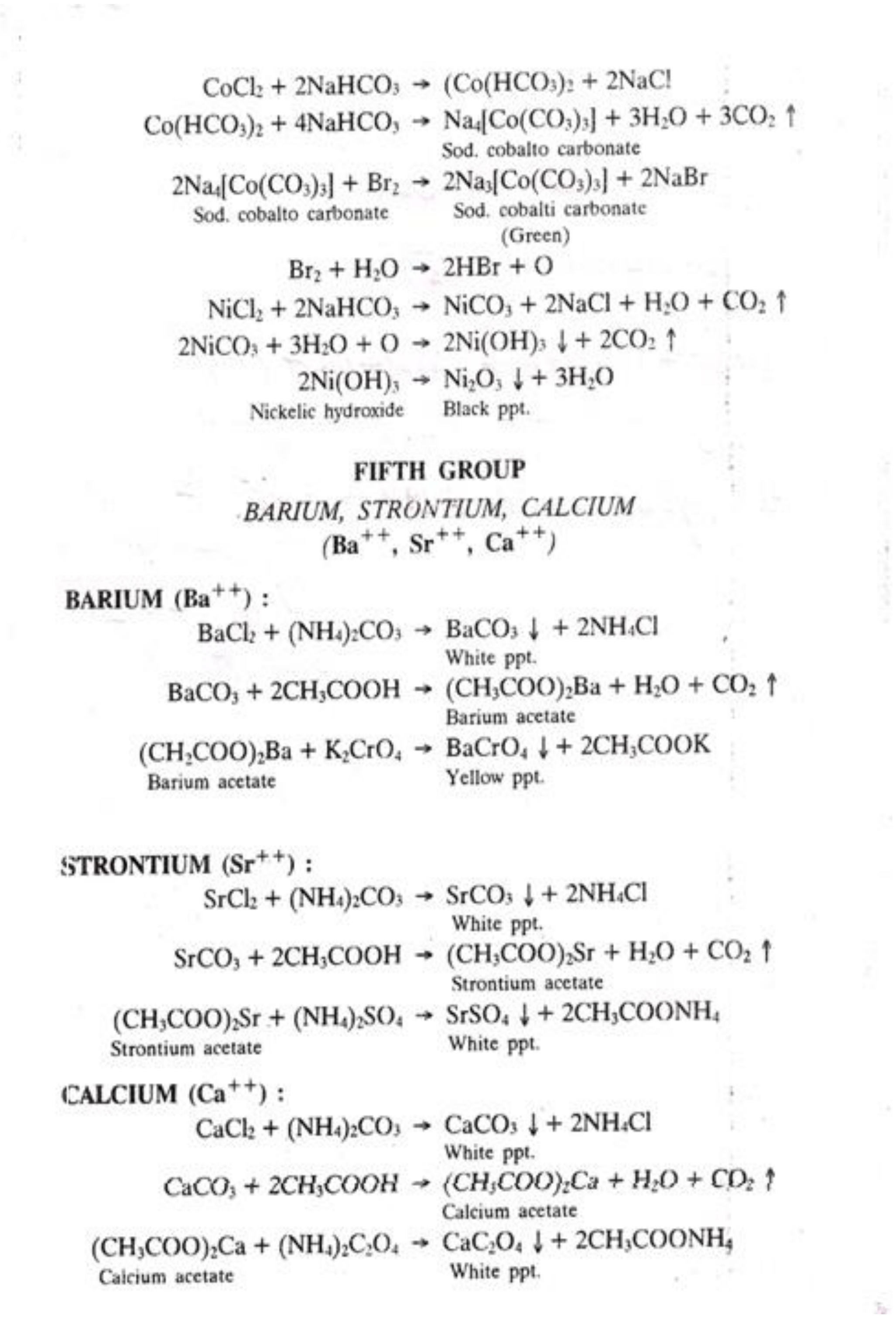
2.



Red ppt.
Nickel dimethyl glyoxime complex

Test of Co and Ni with $NaHCO_3$-Br_2 water (Palit's test):

When the solution of cobalt and nickel salt is treated with excess of sodium bicarbonate, cobalt forms a pink coloured complex sodium cobalto-carbonate. Which on treated with bromine wateris oxidised to green coloured sodium cobalti--carbonate. Nickel does not form a complex with $NaHCO3$ but on heating with bromine water, it is oxidised to black nickelic oxide.



$$CoCl_2 + 2NaHCO_3 \rightarrow (Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \rightarrow \underset{\text{Sod. cobalto carbonate}}{Na_4[Co(CO_3)_3]} + 3H_2O + 3CO_2 \uparrow$$

$$\underset{\text{Sod. cobalto carbonate}}{2Na_4[Co(CO_3)_3]} + Br_2 \rightarrow \underset{\substack{\text{Sod. cobalti carbonate}\\ \text{(Green)}}}{2Na_3[Co(CO_3)_3]} + 2NaBr$$

$$Br_2 + H_2O \rightarrow 2HBr + O$$

$$NiCl_2 + 2NaHCO_3 \rightarrow NiCO_3 + 2NaCl + H_2O + CO_2 \uparrow$$

$$2NiCO_3 + 3H_2O + O \rightarrow 2Ni(OH)_3 \downarrow + 2CO_2 \uparrow$$

$$\underset{\text{Nickelic hydroxide}}{2Ni(OH)_3} \rightarrow \underset{\text{Black ppt.}}{Ni_2O_3 \downarrow} + 3H_2O$$

FIFTH GROUP

BARIUM, STRONTIUM, CALCIUM

(Ba^{++}, Sr^{++}, Ca^{++})

BARIUM (Ba^{++}) :

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{BaCO_3 \downarrow} + 2NH_4Cl$$

$$BaCO_3 + 2CH_3COOH \rightarrow \underset{\text{Barium acetate}}{(CH_3COO)_2Ba} + H_2O + CO_2 \uparrow$$

$$\underset{\text{Barium acetate}}{(CH_3COO)_2Ba} + K_2CrO_4 \rightarrow \underset{\text{Yellow ppt.}}{BaCrO_4 \downarrow} + 2CH_3COOK$$

STRONTIUM (Sr^{++}) :

$$SrCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{SrCO_3 \downarrow} + 2NH_4Cl$$

$$SrCO_3 + 2CH_3COOH \rightarrow \underset{\text{Strontium acetate}}{(CH_3COO)_2Sr} + H_2O + CO_2 \uparrow$$

$$\underset{\text{Strontium acetate}}{(CH_3COO)_2Sr} + (NH_4)_2SO_4 \rightarrow \underset{\text{White ppt.}}{SrSO_4 \downarrow} + 2CH_3COONH_4$$

CALCIUM (Ca^{++}) :

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{CaCO_3 \downarrow} + 2NH_4Cl$$

$$CaCO_3 + 2CH_3COOH \rightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + H_2O + CO_2 \uparrow$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{White ppt.}}{CaC_2O_4 \downarrow} + 2CH_3COONH_4$$

Sixth group

Magnesium (Mg^{2+}):

$Mg(NO_3)_2$+Na_2HPO_4+NH_4OH→$Mg(NH_4)PO_4$↓+ $2NaNO_3$ (white ppt.) +H_2O

zero group:

Ammonium (NH_4^+)

NH_4Cl+ NaOH →NaCl + H_2O + NH_3 ↑

NH_3 + HCl →NH_4 Cl (white fumes

15.17 DETECTION OF N, S AND HALOGENS

In organic compounds the most commonly occurring elements are nitrogen (N), sulphur (S) and halogens along with carbon (C), hydrogen (H) and oxygen (O). In the identification of an organic compound N, S and halogens are detected before the functional groups are to be looked for. This is done by **Lassaigne's Test** in which these elements are converted into ionisable inorganic substances. This is because these elements along with the others are covalently linked in the organic compounds and do not respond to ionic reactions. This may be accomplished by fusing the substance with metallic sodium in an ignition tube. Thus N, S and halogens are converted to sodium cyanide, suphide and halides respectively. If N and S both are present in the same compound these are converted into NaCNS (thiocyanate).

In the Lassaigne's test, sodium extract is first prepared as follows: A sodium metal piece is dried by pressing between the folds of a filter paper. It is then introduced into a clean ignition tube and covered by pouring the given substance into the tube. The ignition tube is first heated very gently in the flame holding it by means of a pair of tongs, taken it away from the flame and heated again. This process is repeated three to four times till the bottom of tube becomes red hot and reaction begins. The red hot ignition tube is plunged into a beaker or porcelain dish containing about 10 to 15 ml. distilled water. The contents are stirred and allowed the remaining sodium to react with water. The mixture is boiled for five minutes and filtered. This filtrate is known as Lassaigne's solution or sodium extract which should be colourless and transparent. Otherwise the fusion is repeated with larger piece of sodium and sodium extract is prepared as above. The conversion of the elements into ionic form occurs as follows:

$Na + C + N \rightarrow NaCN \rightleftharpoons Na^+ + CN^-$

$2Na + S \rightarrow Na_2S \rightleftharpoons 2Na^+ + S^{2-}$

$2Na + X_2 \rightarrow 2NaX \rightleftharpoons 2Na^+ + 2X^-$ (X =Cl, Br, I)

(1) Detection of Nitrogen.

About 2 ml. of sodium extract is treated with 3-4 drops of fresh and saturated solution of $FeSO_4$ followed by 2-3 drops of NaOH. The contents are boiled for two minutes. Then the solution is cooled and 2 ml. of dil. H_2SO_4 are added to it to dissolve the precipitate of ferrous hydroxide if formed and make the solution acidic. Then added 2-3 drops of $FeCl_3$ solution. Formation of Prussian blue or greenish blue precipitate or colouration indicates the presence of nitrogen. The reactions involved are given below:

$Fe SO_4 + 2NaOH \rightarrow Fe(OH)_2 \downarrow + Na_2SO_4$

$Fe SO_4 + 6NaCN \rightarrow Na_4[Fe(CN)_6] + 2NaOH$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3$(Prussian blue) $+12NaCl$

In the presence of N and S both in the compound, the above test gives blood red colour as follows:

$Na + C + N + S \rightarrow Na CNS$

$3Na CNS + Fe Cl_3 \rightarrow Fe(CNS)_3$ (blood red) $+ 3NaCl$

Ferric sulphocyanide

(2) Detection of Sulphur.

(1) 2ml. of freshly prepared sodium nitropursside solution (colourless) are added to 1ml. of sodium extract. A violet or purple colour is developed confirming the presence of sulphur, $Na_2S + Na_2[Fe(CN)_5 NO] \rightarrow Na_4[Fe(CN)_5 NOS]$ (violet colour).

(2) Alternately, to 2ml. of sodium extract acidified with acetic acid is added 2ml. of lead acetate solution, a black precipitate of PbS if formed, it also indicates the presence of sulphur.

$$Na_2S + (CH_3COO)_2\ Pb \xrightarrow{a.c.} PbS(\text{Black ppt.}) + 2CH_3COO\ Na$$

Acid

(1) Detection of Halogens.

The halogens (Cl, Br, I) present in an organic compound are detected in two ways:

(i) By silver nitrate test. - This is done as follows: 2ml. of sodium extract is boiled with 1ml. conc. HNO_3 and then $AgNO_3$ is added to it:

(a) White curdy precipitate is formed; soluble in NH_4OH-Cl is present.

(b) Pale (light) yellow precipitate appears; partially soluble in NH_4OH-Br is present.

(c) Yellow precipitate is formed, insoluble in NH_4OH-I is present.

$$Na\ Cl + Ag\ NO_3 \rightarrow Ag\ Cl \downarrow (\text{White ppt.}) + NaNO_3$$

$$Ag\ Cl + 2NH_4OH \rightarrow [Ag\ (NH_3)_2]Cl\ (\text{soluble}) + 2H_2O$$

$$Na\ Br + Ag\ NO_3 \rightarrow Ag\ Br \downarrow (\text{light yellow ppt.}) + NaNO_3$$

$$Ag\ Br + 2NH_4\ OH \rightarrow [Ag\ (NH_3)_2\ Br]\ (\text{partially soluble}) + 2H_2O$$

$$NaI + Ag\ NO_3 \rightarrow Ag\ I \downarrow (\text{Yellow ppt}) + NaNO_3$$

$$AgI + NH_4\ OH \rightarrow \text{insoluble}$$

(ii) By chloroform test. - 2ml. of sodium extract are acidified with dil. HNO_3, then added 2-3 drops of chloroform or CCl_4, followed by chlorine water shaking first gently and then vigorously, if chloroform layer turns pale-brown-bromine is present but if it turns purple or violet iodine is present.

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

$$Br_2 + CHCl_3 \rightarrow \text{Pale- brown colour.}$$

$$2\ Nai + Cl_2 \rightarrow 2NaCl + I_2$$

$$I_2 + CHCl_3 \rightarrow \text{purple or violet colour.}$$

15.18 IDENTIFICATION OF FUNCTIONAL GROUPS

Organic compounds may be regarded as the derivatives of hydrocarbons having different functional groups in place of one or more hydrogen atoms. Their characteristic properties and reactions are largely due to the presence of functional groups present in them. Correct detection of functional groups in the organic compounds leads to a very reasonable and accurate identification of those compounds.

For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne’s test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds.

Type I : Compounds containing C and H with or without oxygen.

S.N.	Experiment	Observation	Inference
1.(a)	On treatment of the compound with $NaHCO_3$ solution	Brisk effervescence appears	Acids
(b)	On treating of the compound with blue litmus,	Blue litmus turns red	Acids
2.	On adding ceric ammonium nitrate solution to the compound,	Red colouration is observed	Alcohols
3.(a)	Two drops of $FeCl_3$ are added to an aqueous of alcoholic solution of the compound,	Typical colour changes are observed	Phenols
(b)	Phthalein test is performed,	Positive result is observed	Phenols
4.	The compound is heated with Fehling’s solution or Benedict’s solution,	Red precipitate is formed	Aldehydes or reducing sugars

5.	The compound is treated with Schiff's solution.	Pink colouration is observed.	Aldehydes
6.	On Shaking the compound with sodium bisulphite solution,	White precipitate is formed.	Aldehydes or Ketones
7.	The compound is treated with alkaline sodium nitroprusside solution,	Red colouration appears	Methyl Ketones
8.	Molisch's test is performed,	Result is positive	Sugars
9.	On heating the compound with dil. NaOH solution containing a drop of phenolphthalein	Pink colour is slowly discharged	Esters
10.	On heating the compound with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated hydrocarbons Saturated aliphatic hydrocarbons or ethers

Type II: Compounds containing C, H and halogens with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	On boiling the compound with alcoholic $AgNO_3$,	(i) White ppt. soluble in NH_4OH (ii) Ligth yellow ppt. Partially soluble in NH_4OH	Chloro compounds Bromo compounds

		(iii) Deep yellow ppt. insoluble in NH_4OH	Iodo compounds
2.	If the compound is heated with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated alkyl halides Saturated aliphatic alkyl halides

Type III. : Compounds containing C, H and N with or without oxygen.

S.N.	**Experiment**	**Observation**	**Inference**
1.	The compound is boiled with aq. NaOH,	Smell of ammonia is noticed	Amides
2.	The compound is treated with dil. HCl followed by $NaNO_2$ drowse in cold,	(i) Brisk effervescence occurs (ii) Brown or green ppt. is formed (iii) Blue colouration appears	Amides, amino acids, primary amines or urea
3.	On treating the above contents with alkaline β - naphthol solution ,	Bright orange-red dye in formed	Aromatic primary amines
4.	The compound is boiled with water,	Yellow colouration	Nitro phenols or nitro compounds

5.	The compound is boiled with zinc dust and aq. NH_4Cl, filtered and filtrate is treated with Tollen’s regent,	Grey precipitate is formed	Nitro compounds

Type IV (A) : Compounds containing C, H and S with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	To the aq. solution of the substance is added few drops of $FeCl_3$ solution,	Violet or red colour is observed	Sulphonic acids of phenols or hydrdro carbons
2.	Equal quantities of substance and animal charcoal are mixed and filled one third of the ignition tube with it and heated,	Disagreeable garlic like odour is noticed	Sulphones

(B): Compounds containing C, H, S and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	2ml. of NaOH solution are added to a trace of the substance in a test tube, heated to boiling, cooled and added 2 drops of aq. lead acetate,	Brown or black colour or precipitate appears	Thioureas

2.	A trace of the substance is dissolved in 2ml. of water by boiling in a test tube and a piece of blue litmus paper is introduced in it,	(i) If colour changes to red. (ii) If no change in colour	Test (a) given below is performed Test (b) is performed as given below
(a)	A trace of the substance is dissolved in 3ml. of dil. HCl, cooled in ice cold water and added 3ml. of 2% sodium nitrite solution and then 4ml. of alkaline β naphthol solution	Red colouration appears	Amino sulphonic acids
(b)	5 drops of conc. H_2SO_4 are added to a trace of substance and heated gently for few minutes, cooled and diluted with 2ml. water. Then added flakes of NaOH and a piece of moistened red litmus paper is brought near the mouth of the test tube,	Colour changes to blue and smell of NH_3 is noticed	Sulphonamide or saccharin

Confirmation of Functional Groups.

The functional groups are then confirmed by normal and sometimes by performing some special test.

1. **Carboxylic acid group (-COOH).**

(i) ***Litmus paper test.*** If the blue litmus paper or solution is added to the aq. solution or suspension of the compound, it turns red.

(ii) ***Sodium bicarbonate test.*** If a small amount of the compound is added to about 3ml. of saturated sodium bicarbonate solution, brisk effervescence is noticed.

(iii) ***Fluorescence test.*** 0.2gm. of organic compound is heated gently with 0.5gm. of resorcinol and few drops of conc. H_2SO_4 in a hard test tube for two minutes, cooled and poured the contents into a beaker containing NaOH diluted largly with water. Intense green fluorescence is formed indicating the presence of 1,2 or ortho dicarboxylic group (i.e. phthalic acid)

(iv) ***Ester formation.*** A small quantity of the substance is heated with ethyl alcohol and a little conc. H_2SO_4, cooled and poured in a tube containing water. A fruity smell due to the formation of an ester indicates the presence of carboxylic group.

(v) ***Ferric chloride test.*** 0.5gm. of the acid is neutralised with excess of ammonia in a boiling test tube, the solution is boiled to remove excess of ammonia, cooled and added few drops of neutral $FeCl_3$ solution:

If reddish brown precipitate is formed: aliphatic carboxylic acids; Buff ppt. is formed: Aromatic acids and certain dibasic acids; If violet colour appears: Aromatic hydroxy acids

Note. Phenols and α-naphthylamine also produce colour with $FeCl_3$.

2. Alcoholic –OH group.

(i) ***Ceric ammonium nitrate test.*** 2drops of the organic substance are treated with 0.5ml. of ceric ammonium nitrate solution, then diluted with 2ml. water. A red colouration is observed.

(ii) ***Sodium test.*** About 2ml. of the compound are taken in a test tube, added to it a piece of anhyd. $CaCl_2$ to absorb any water if present. The clear liquid is transferred to another dry test tube and added to it a dry piece of sodium. The effervescence appears due to liberation of hydrogen.

Distinction among primary, secondary and tertiary alcohols.

If 2ml. of the compound is treated with about 5ml. of Lucas reagent (8 gm of anhyd, Zn Cl_2 in 5ml. conc. HCl) and shaken, an insoluble layer at once is formed by a tertiary alcohol, cloudiness within 4-5 minutes appears in case of a secondary alcohol and the solution remains clear for a primary alcohol.

2. Phenolic –OH group.

(i) ***Ferric chloride test.*** On adding 2-3 drops of ferric chloride to 2ml. of aqueous or alcoholic solution of the compound, a green, blue or violet colour shows the presence of phenolic –OH group but nitro phenols do not show this test.

Exceptions. A-naphthylamine and benzoic acid also respond to this test as follows:

α - naphthylamine - blue colour

Benzoic acid - buff coloured ppt.

(ii) ***Liebermann's test.*** A little amount of the compound is fused with a crystal of sodium nitrite in a tube, the mixture is cooled and to it added 1ml. conc. H_2SO_4, a deep green to blue solution is formed which turns red when poured in large excess of water. The red aqueous solution again becomes deep green or blue if made alkaline with NaOH.

(iii) ***Azo-dye formation.*** 2drops of aniline are treated with 0.5ml. conc. HCl in a test tube, diluted with water and cooled in a freezing bath, then added dil. $NaNO_2$ solution while shaking. This diazotized solution is poured to that of phenol in excess of 2N-NaOH solution. Formation of a dye or orange or red colour indicates the phenolic group.

(iv) ***Phthalein test.*** 0.5gm. of compound is heated with 1gm. phthalic anhydride and 2drops of conc. H_2SO_4 for 1minute, cooled and made alkaline with dil. NaOH solution. If few drops of this alkaline liquid are poured in 20ml. water, characteristic colour appears due to phenolic group:

Phenol, O-Cresol - red colour
Catechol, m-Cresol - blue colour

Resorcinol - fluorescent green

p-Cresol - no colouration

Hydroquinone - deep blue

α – Naphthol - green

β – Naphthol - light green

3. **Aldehyde group (-CHO)**

(i) ***Test with Schiff's reagent.*** 5-6 drops of liquid or (0.1gm) of compound are added to 2ml. of the reagent, contents are shaken vigorously, a deep red or violet colour after waiting for 2-3 minutes. (no heating)

(ii) ***Test with Tollen's regent.*** 0.1gm. of solid or 0.1ml. of liquid compound is added to 2ml. of Tollen's reagent, warmed and allowed to stand for 2-3 minutes when a silver mirror or a grey precipitate is formed.

(iii) ***Test with Fehling's solution.*** 0.1gm. of soid or 0.2ml. of liquid compound is added to 5ml. of fehling's solution and the mixture is boiled when red precipitate is formed.

(iv) ***Test with Benedict's solution.*** 0.1gm. of the compound is boiled with 2-3ml. of Benedict's solution for few minutes while a red yellow precipitate appears.

The compounds can be quickly guessed by the following points:

(a) Smell of bitter almonds – benzaldehyde

(b) If bad pungent odour is there, NaOH is added to the liquid compound and shaken

(i) Brown resin formed – acetaldehyde

(ii) No such change – formaldehyde

4. **Ketone group (>C = O).**

(i) ***2,4- Dinitrophenyl hydrazine test.*** 2drops of the substance are added to about 2ml. of the reagent solution, shaken vigorously and heated if necessary, when a yellow or orange red precipitate separates out.

(ii) ***Sodium bisulphite test***. 0.2gm. or 0.3ml of the compound is added to 1ml. of saturated sodium bisulphite solution and shaken vigorously, a white precipitate is formed.

(iii) ***Sodium nitroprusside test.*** 0.1gm. of solid or 0.2ml. of liquid compound is added to 2ml. of aq. sodium nitroprusside solution and contents are made alkaline with 2-3 drops of sodium hydroxide, a red or purple colour appears (benzophenone does not respond to this test).

Note: The first two tests, i.e. with 2,4 dinitrophenyl hydrazine and sodium bisulphite, are also given by aldehydes but the difference is that ketones do not respond to the tests with Tollen's reagent, Fehling's solution, Schiff's solution, etc.

5. Ester group (RCOOR').

All the esters possess fruity smell.

(i) ***Phenolphthalein test***. To 3ml. of the compound are added 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heated gently, the pink colour is gradually discharged (due to hydrolysis of ester).

6. Carbohydrate.

(i) ***Molisch's test.*** To 1ml. aqueous suspension of compound are added 2drops of 10% alcoholic solution of α – naphthol and shaken well. Now added carefully 2ml. of conc. H_2SO_4 along the side of the test tube, a reddish-violet ring is formed at the junction of two layers in case of carbohydrate.

In the Molisch's test 8ml. conc. HCl is added in place of conc. H_2SO_4 and the solution is boiled, a violet colour is produced immediately for sucrose or fructose but glucose gives this colour after 1-2 minutes of continuous boiling.

(ii) ***Sulphuric acid test.*** A small amount of the powdered compound is treated with 1ml. cold conc. H_2SO_4, colour varying from yellow, brown and black appears.

(iii) ***Test with Tollen's reagent.*** 0.1gm. of the compound is added to 2ml. of Tollen's reagent and heated gently, a silver mirror is obtained inside the wall of the vessel.

(iv) ***Test with Fehling's solution or Benedict's solution.*** 1ml. of the aq. solution of the compound is boiled with 2ml. of Fehling's solution or Benedict's solution for two minutes, red precipitate is formed in case of reducing sugars. If the mixture with Benedict's solution remains blue or only slight turbidity appears then sucrose is present.

7. Hydrocarbon and Ether.

If the compound does not respond to any above test, it may be suspected to be either a hydrocarbon or ether. Ethers are soluble in phosphoric acid while hydrocarbons are rendered insoluble. All ethers are sweet smelling. Liquid benzene and toluene have characteristic sweet petrol like odour.

i. ***Feigl's test for ethers.*** 1-2ml. of ether are taken in a boiling tube and its mouth is covered with a filter paper moistened with a mixture of cupric acetate and benzidine hydrochloride solution. On heating to boiling, a deep blue colour appears on filter paper due to the formation of benzidine blue due to the ether group.
ii. To 0.5 ml. of the compound is added 1ml. of iodine solution in CS_2 and shaken well the purple colour of CS_2 layer changes due to ether group.
iii. 1ml. of compound is mixed with 4ml. of glacial acetic acid and 1ml. conc. H_2SO_4, heated under reflux condenser for about 5 minutes, cooled well and extracted with benzene purple colour appears due to ether group (This test can be applied only when ester group is absent, otherwise not). If the above tests are negative, then the compound is a hydrocarbon.

8. Halogen containing compound.

(i) ***Alcoholic silver nitrate test.*** A little amount of the compound is heated with 2ml. of alcoholic silver nitrate solution for a few minutes and the observed the following:

(a) Formation of a precipitate indicates the presence of aliphatic or reactive halogen.
(b) No precipitate indicates the presence of halogen atom attached to benzene nucleus

(but 1-chloro-2, 4-dinitro benzene does not respond to this test).

Quick guess.

a) If the Cl-containing compound is solid, aliphatic and crystalline containing –CHO group, it is chloral-hydrate.
b) Cl-containing compound is aromatic solid, colourless and crystalline with characteristic smell, it is p-dichlorobenzene.

9. Amide group (-$CONH_2$)

(i) ***Sodium hydroxide test.*** 0.2gm. of the compound is heated with 4ml. of aq. NaOH, ammonia gas is evolved due to amide group.

(ii) ***Nitrous acid group.*** To 0.2gm. of substance is added 2ml. dil. HCl followed by 2ml. of 2% aq. $NaNO_2$ and shaken, brisk effervescence due to the evolution of nitrogen indicates amide group.

(iii) ***Hydroxylamine hydrochloride test.*** In a test tube 0.2gm of the compound, 0.2gm of hydroxylamine hydrochloride and 2ml. ethyl alcohol are taken, boiled for five minutes, cooled and added few drops of $FeCl_3$. Blue-red colour appears indicating an aliphatic amide.

(iv) To the aq. solution of the compound are added 7-8 drops of 6% H_2O_2 and heated nearly to boiling, cooled and added 1-2 drops of 5% $FeCl_3$ solution, Bluish red colour appears in cold within 2mintues or a brown colour on warming shows the presence of an aromatic amide.

(**Quick test**: Compound is dissolved in water by heating cooled and added 1ml. conc. HNO_3

(a) Crystalline ppt formed - urea
(b) No ppt. and aliphatic - acetamide
(c) No ppt. and aromatic - benzamide)

10. Amine groups (-NH_2, > NH and≡ N).

(a) Primary amine.

(i) ***Nitrous acid test.*** 0.2gm. of the compound is dissolved in 10ml. dil. HCl and cooled. Now added 10% aq. $NaNO_2$ solution, brisk effervescence appears-aliphatic primary amine.

(ii) ***Carbylamine test.*** A mixture of 2 drops of the compound, 2drops of chloroform and 2ml. of alcoholic caustic potash (KOH) is boiled. An intolerable offensive odour of carbylamine indicates a primary amine.

(iii)***Diazotisation test.*** About 0.2gm. of the compound is dissolved in dil. HCl, cooled and added to it 10% aq. $NaNO_2$ This is poured into a beaker containing 10% alkaline β – naphthol, a bright orange-red dye appears-aromatic primary amine

(iv) ***Rimini test.*** To about 0.3gm. of the compound taken in a test tube are added 5ml. water, 1ml. acetone and a few drops of sodium nitroprusside, allowed to stand for 2minutes: a violet red colour appears for aliphatic primary amines.

(b) Secondary amine.

(i) ***Nitrous acid test.*** Ice cold dil. HCl is added to a solution of 1% aq. $NaNO_2$. This solution is added gradually to the solution of compound in HCl (0.5gm. in l0ml. HCl). An oily dark coloured liquid or low melting solid is formed due to aliphatic or aromatic secondary amine.

(ii) ***Libermann's nitroso test.*** In the above test, if 1ml. conc. H_2SO_4 is added cautiously to the reaction mixture, a blue colouration which changes to red on dilution with water and blue or green with aq. alkali confirms the secondary amine.

(c) Tertiary amine.

(i) ***Nitrous acid test***. Ice cold dil. HCl is added to 1% aq. $NaNO_2$. To this solution is added gradually 0.2gm. of the compound in 10ml. dil. HCl:

(a) If there is no reaction-tertiary aliphatic amine.

(b) If green or brown coloured salt is produced-aromatic tertiary amine.

11. Nitro group (-NO_2).

Almost all nitro compounds are light yellow or yellow in colour.

(i) ***Sodium hydroxide test.*** A small amount of the compound is shaken with 2ml. of NaOH solution, yellow, intense yellow or orange colour is produced due to nitro group.

(ii) ***Zinc-ammonium chloride test.*** A small amount of the substance is boiled with 5ml. of 5% alcohol, 0.2gm. each of NH_4Cl and zinc dust, cooled, filtered and added to the filtrate 2 ml. of Tollen's reagent. On heating, a black grey precipitate is formed due to nitro compounds.

(iii) ***Azo-dye test.*** 0.1gm. of the substance is heated with 0.5ml. conc. HCl and 2-3 small pieces of metallic tin for 3-4 minutes, filtered, cooled and added 3ml. of aq. $NaNO_2$ solution. This is poured into a beaker containing alkaline β naphthol solution. An orange red dye is formed.

12. Sulphonic acid group ($-SO_3H$).

The compound having sulphonic acid group gives positive test for S element.

(i) ***Sodium bicarbonate test.*** A little amount of the compound is added to a few ml. of aq. $NaHCO_3$ and the contents are stirred. Brisk effervescence of CO_2 and positive test of element S confirms the sulphonic acid group.

(ii) ***Fusion test.*** Equal amounts of the compound and solid NaOH/KOH are fused and treated with dilute mineral acid. A penetrating smell of SO_2 is noticed. The gas if passed into acidic $K_2Cr_2O_7$ solution, green colour is developed.

15.19 SUMMARY

This unit gives the classification of anions (Acidic Radicals). Preliminary test are given for the identification of class I, class II and class III anions. Basic carbonates of Pb and Bi do not evolve CO_2 with effervescence, but do so gradually. Many sulphides, e.g. those of Ag, Hg, As, Co and Ni do not decompose on heating with dil. HCl or dil. H_2SO_4 . Oxalates of K^+ and NH_4^+ are soluble in water. Soda extract preparation should be used to prepare to prepare solution of anions.The purpose of this lab is to identify the cations present in an unknown solution. Qualitative analysis was used to identify the substances present in the unknown solution. Qualitative analysis is used by reacting the unknown solution with a number of different reagents.

Detection of nitrogen (N), sulphur (S), and halogens (X) is done by Lassaigne’s Test in which these elements are converted into ionisable inorganic substances. This can be done by fusing the substance with metallic sodium in an ignition tube. On fusion with sodium N, S, and halogens are converted to sodium cyanide, sulphide and halides respectively. If N and S both are present in the same compound these are converted into NaCNS (thiocyanate). Functional groups are specific atoms, ions, or groups of atoms having consistent properties. For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne’s test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds. The functional groups are then confirmed by normal and sometimes by performing some special test.

15.20 TERMINAL QUESTIONS

1. Explain the difference between ‘anions’ and ‘cations’ analysis?
2. Explain why a hot solution is used at first during II group precipitation by H_2S. Why it is subsequently diluted with cold water?
3. What is the purpose of preparing sodium carbonate extract for identification of anions?
4. Define any two Confirmation Functional Groups test of, Carboxylic acid (-COOH) and Alcohol (-OH).
5. How we distinguished primary, secondary, tertiary amine by Nitrous acid test?
6. How would you distinguish an aldehyde from a ketone by chemical tests?
7. Name the two solutions that give :

a) A black ppt. on mixing.
b) A yellow ppt. on mixing, which dissolves on heating but reappears on cooling in a golden yellow plate.
c) A white ppt. on mixing, soluble in ammonia.

8. What Is the Lassaigne’s Test? With the help of lassaigne’s test how we detect Nitrogen and sulphur in sodium extract?

15.21 REFERENCES AND FURTHER STUDIES

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UNIT 16: PHYSICAL EXERCISE: DETERMINATION OF VISCOSITY

CONTENTS:

16.1 OBJECTIVES

In this chapter students will learn the following objectives.

- Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the viscosity.
- Explain the use of Ostwald’s viscometer and principal.
- Describe how to determine the viscosity of given liquid like cane sugar solution.
- Determine the composition of the given mixture consisting of two liquids A & B by viscometer.
- Explain the various precautions taken during experiment.

16.2 INTRODUCTION

Some liquids like water, alcohol move very fast, on the other hand liquids like honey, glycerol etc move very slowly. The property of the liquid which determines its flow is termed as viscosity. Thus we can say that viscosity is a property of liquid which retards its flow.

When temperature is applied to the liquid its intermolecular attractions forces are weakened, because kinetic energy of molecules increases. As viscosity depends on intermolecular forces, hence by the application of temperature viscosity decreases.

The unit of viscosity is poise. Scientist Poiseuille, who did pioneer work in the field of viscosity, to honour him unit of viscosity, is poise. Smaller unit of viscosity are centipoise and millpoise. Viscosity is represented as η (eita).

Coefficient of viscosity:

If a liquid is allowed to flow on a surface each layer moves parallel to its adjacent layer without intermixing. The unparallel flow of layers is called turbulent flow. In the laminar flow the force F required to maintain a steady difference v between velocities of two adjacent layers is directly proportional to v, and area A of the surface of contact of two layer and inversely proportional to distance x between them. Hence

$F \propto A.v/x$

or $F = \eta\, Av/x$

Here η is called coefficient of viscosity of the liquid if A= 1 sq. cm., v=1 cm/sec and x=1 cm then F=η. Hence η is defined as the force necessary to maintain a velocity difference of unity between two adjacent parallel layers of liquid, one cm apart and having area of surface of contact unity.

The pressure p at any instant driving the liquid of coefficient of viscosity η through the capillary tube depends upon the difference of the height h, in the levels of liquid in the two limbs, the density d and the gravitational force g.

that is $p \quad hdg$ ……………..16.1

from equation 16.1

$\eta \quad p.t$

$\therefore \eta \quad hdgt$ ……………..16.2

If η_1 and η_2 be the viscosities of the two liquids under study and d_1 and d_2 be their respective densities and t_1 and t_2 be the respective time of flow the same volume

Then $\eta_1 \quad g_1d_1t_1$

And $\eta_2 \quad gd_2\, t_2$

Since same apparatus is used for both the liquids

$$\frac{\eta_1}{\eta_2} = \frac{d_1t_1}{d_2t_2} \qquad \ldots\ldots\ldots\ldots\ldots.16.3$$

Thus by determining the densities and the time of flow of the two liquids, the coefficient of viscosity of one of them can be easily calculated, provided the coefficient of viscosity of the other liquid is known.

Description of the apparatus:

Ostwald's viscometer: The apparatus generally used for the determination of coefficient of the viscosity of liquid is known as Ostwald's viscometer as it was designed by Ostwald. It is shown in fig 16.1.

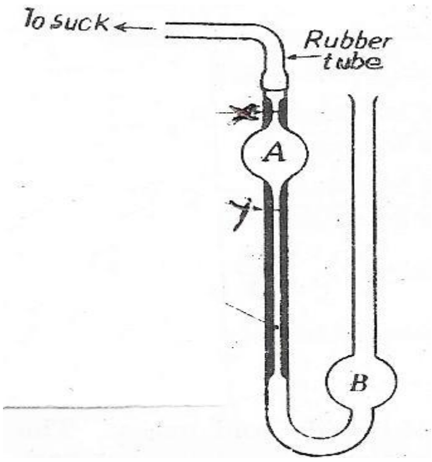

Fig 16.1 Ostwald's viscometer

The viscometer consists of a capillary tube connected at its upper part with a bulb A and at its lower part with a wider U-tube provided with a bulb B. Two marks x and y are etched on the capillary tube above and below the bulb A.

Cleaning of viscometer:

The viscometer should be cleaned thoroughly so that there are no obstructions in the capillary tube. It must be free from any greasy material. The viscometer is cleaned with chromic acid by filling with the acid which is prepared by reaction between potassium chromate and concentrated sulphuric acid.

The acid solution is kept in the viscometer for some hours. It is washed with water then with alcohol. It is then dried.

Density of the liquid is measured with the help of density bottle. Density of the liquid is mass per unit volume. The density at a given temperature means the relative density at that temperature with respect to the density of water. For all practical purposes, the density of water is taken to be unity at all temperatures.

16.3 EXERCISE CANE SUGAR SOLUTION OR GLYCEROL (MORE THAN 5%)

Object: To determine viscosity of the given liquid (say cane sugar solution) at room temperature.
Apparatus: Viscometer, unknown liquid, stop watch, distilled water, density bottle, pipette etc.

Formula used: $\eta_l = (d_l t_l / d_w t_w)\ \eta_w$

Where η_l $d_l t_l$ are coefficient of viscosity, density and time of flow respectively of the experimental liquid and η_w, d_w and t_w are coefficient of viscosity, density and time of flow respectively of water.

Procedure:

Clean the viscometer with chromic acid then wash with distilled water. It is finally washed with alcohol and then dried. A sufficient volume of distilled water is introduced by pipette in bulb B so that bend-portion of tube and half or little more than half of bulb B are filled up. Now suck up water until it rises above the mark x above the bulb A. Now bring water to touch the mark x and hold it there by placing your index finger at the top of the narrow limb. Remove your finger and start the stop watch. Stop it as soon as water touches the mark y. Repeat this process 3-4 times and take the mean value. The viscometer is kept in a thermostat for 10-15 minutes before the mean value, so that the contents acquire the room temperature.

Now remove water from the viscometer and dry it. Introduce in bulb B some cane sugar solution and rinse the viscometer. Now fill the viscometer with the experimental liquid and keep it also in the thermostat for 10-15 minutes, so that cane sugar solution attains room temperature. Note the time during the flow of solution between the marks x and y repeat the process 3-4 times and take the mean value.

Wash the density bottle and dry it. First weight it empty. Then fill it with water and finally with cane sugar solution and weight it both the times. Note the room temperature, by recording the temperature of water in the thermostat.

Observations:

1. Room temperature = t^0
2. Time of flow between x and y

Sl No.	**Water**		**Cane sugar solution**	
	Time of flow	**mean**	**Time of flow**	**Mean**
1		t_w		t_e
2				
3				
4				

16.2 Density of cane sugar solution and water.

Weight of empty density bottle = w_1 gm

Weight of density + water = w_2 gm

Weight of density bottle + cane sugar solution = w_3 gm

Calculation: Weight of water = w_2-w_1 gm

Weight of cane sugar solution= w_3-w_1 gm

Density of glycol = weight of glycol/weight of water x density of water d_w

= weight of glycol/weight of water = $(w_3-w_1)/(w_2-w_1)$

As density of water $d_w = 1$

Coefficient of viscosity of glycol

$$\eta_l = (d_l\, t_l) / (d_w\, t_w)\, \eta_w$$

Now the viscosity of water η_w at t^0C from standard table, and substitute in the above expression, the value of η_l is calculated.

Result: The coefficient of viscosity of the given liquid at t^0C is poise.

Precautions:

1. Viscosity must be kept in vertical position.
2. Some volume of water and glycol should be taken in the viscometer.
3. Observe accurately when the meniscus of glycol and water just passing the upper and lower marks (x and y).
4. Before performing the experiment viscometer should be properly cleaned as described before.

16.4 *EXERCISE DETERGENT/ DETERMINATION OF CMS (CRITICAL MICELLE CONCENTRATION)*

Object: To determine the composition of the given mixture consisting of two liquids A & B by viscometer.

Apparatus: Ostwald viscometer, density bottle, thermostat, thermometer, stop watch, beakers etc.

Theory: By plotting the values of time of flow of solution against their concentrations, we get a curve from which the concentrate of unknown solution is determined.

Procedure: The viscometer is thoroughly cleaned so that there are no obstructions in the capillary tube. It must be free from any greasy material. The viscometer is first cleaned by first keeping it filled with a solution of chromic acid, which is prepared by the reaction between potassium dichromate and sulphuric acid, for some hours. It is then washed with distilled water and finally with alcohol. It is then dried.

Now prepare a number of solutions by mixing the two liquids A and B in different proportions. The solutions are made up with 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10% of A by volume. (90 ml of A and 10 ml of B in first case, 80 ml of A and 20 ml of B in the second case and so on.) The time of flow of each solution noted by means of Ostwald’s viscometer, by allowing the solution to flow from x-mark to y- mark. Repeat this process 3 & 4 times and take the mean value. Before noting the time, the viscometer is kept in a thermostat for 10.to15 minutes, so that the contents acquire the room temperature. The time of flow for the unknown solution is also measured, as usual.

If we are to calculate the viscosity of the liquids then the density of each solution and that of unknown solution is also determined.

Observations:

Room temperature = t^{0}C

Sl. No.	Percentage of components		Time of flow in secs
	A	B	
1	90	10	
2	80	20	
3	70	30	
4	60	40	
5	50	50	
6	40	60	
7	30	70	
8	20	80	
9	10	90	
10	Unknown solution		

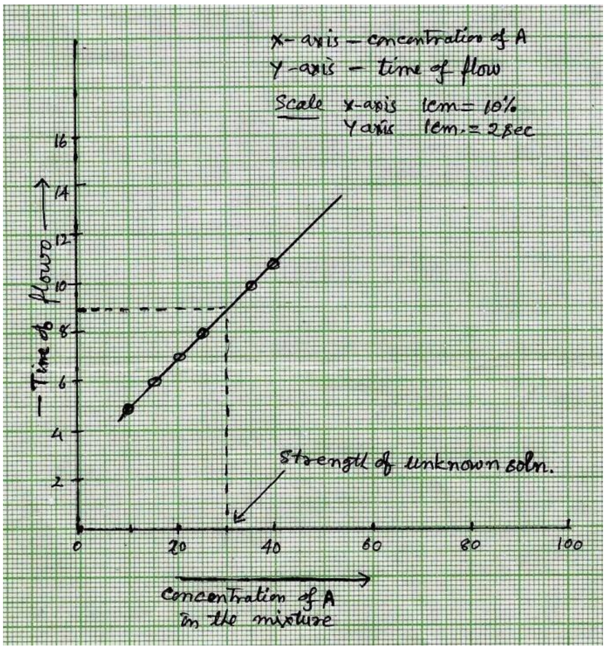

Fig 16.3 strength of unknown solution

Conclusions:

A curve is plotted between the concentration of one component say A and time of flow in seconds. You will see that a straight line is obtained (fig 4.2). The composition of unknown solution is calculated by locating and marking the point on the straight line corresponding to its measured time of flow. A perpendicular is drawn from that point on the concentration axis, from which the composition of unknown solution can be read directly.

Result: The composition of given mixture is ……..% of A and ……..% of B

Precautions:

1. Viscosity must be kept in vertical position.
2. Same volume of liquids should be taken in the viscometer.
3. Observe accurately when the meniscus just passing the upper and lower marks (x and y).
4. Before performing the experiment viscometer should be properly cleaned as described before.

16.5 SUMMARY

In this chapter we have learnt about two important experiments. In first experiment determine viscosity of the given liquid (say cane sugar solution). In the experiment we have understood how coefficient of viscosity of the given liquid at t^0C is poise. In second exercise we learnt the composition of the given mixture consisting of two liquids A & B by viscometer. Both exercise understanding the principles behind these experiments and acquiring skill to perform these experiments will help the students during their research endeavours.

16.6 TERMINAL QUESTIONS

1. Define the term coefficient?
2. What is the unit of coefficient of viscosity?

3. Why relative viscosity has no unit?
4. What is the effect of temperature on coefficient of viscosity? If decreases why?
5. Why unit of viscosity is poise?
6. How does viscosity vary with temperature?

16.7 REFERENCES AND FURTHER STUDIES

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