CHE(N)-201

B.Sc. IIIʳᵈ Semester

GENERAL CHEMISTRY-I

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

B.Sc. IIIʳᵈ SEMESTER

GENERAL CHEMISTRY-I

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

Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. Mail: info@uou.ac.in
htpp://uou.ac.in

Unit Written by	Unit No.
1. Dr. K.S. Dhami (Ret. Prof.) Department of Chemistry D.S.B. Campus, Kumaun University, Nainital	1, 2, 3
2. Dr. Geeta Tiwari Department of Chemistry D.S.B. Campus, KNianital	04
3. Dr. Bipin Chandra Joshi Department of Chemistry L.S.M. Govt. P.G. College, Pithoragarh	05, 06
4. Dr. Neeta Joshi Department of Chemistry P.N.G. Govt. P.G. College Ramnagar	07,08
5. Dr. K. B. Melkani(Retd. Professor) Department of Chemistry D.S.B. Campus Kumaun University, Nainital	09, 10
6. Dr. Baleshwar Prasad Yadav Department of Chemistry Meerut College, Meerut	11
7. Dr. Renu Loshali Department of Chemistry Govt. Degree College, Bazpur	12
8. Dr. Vinod Kumar Department of Chemistry, Uttarakhand Open University, Haldawani (Nainital)	13
9. Dr. K.S. Dhami (Retd Professor) Department of Chemistry, D. S. B. Campus Kumaun University, (Nainital)	14
10. Dr. Girdhar Joshi Assistant professor, Department of Chemistry Govt. P.G. College Gopeshwar	15
11. Dr. Namrata Ghildiyal Department of Chemistry, H.N.B. Garhwal University, Shrinagar	16
12. Dr. Ruchi Pandey Department of Chemistry Uttarakhand Open University, Haldwani (Nainital)	15, 16 (Unit Rewrite)

Course Unit Compilation

Dr. Vinod Kumar
Assistant Professor
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Deep Prakash
Assistant Professor
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Charu C. Pant
Assistant Professor (AC)
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Ruchi Pandey
Assistant Professor (AC)
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Course Editors

Dr. Vinod Kumar
Assistant Professor
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Deep Prakash
Assistant Professor
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

CONTENTS

BLOCK-I

UNIT 1: CHEMISTRY OF THE ELEMENTS OF FIRST TRANSITION (3-d) SERIES

CONTENTS:

1.1   INTRODUCTION

The d-block elements are "the elements whose atoms receive the last electron in the d-subshell belonging to the penultimate or $(n-1)^{th}$ shell". The d-block elements are also called transition elements or metals. This is because they exhibit gradual transitional behaviour between highly reactive s-block (electropositive) and p-block (electronegative) elements, i.e. their properties are intermediate between those of the s-block and p-block elements. Thus, these elements are in the middle of the periodic table and are the members of Groups 3 to 12 (IIIB to VIII to II B) in the modern periodic table. According to IUPAC definition, "a transition element is an element which has an incomplete d-subshell in either a neutral atom or in ions in chemically significant (or common) oxidation state". According to this definition zinc (Zn), cadmium (Cd) and mercury (Hg) are excluded from the list of transition elements as they neither have partly filled d-subshell in their atoms or ions nor they show the usual properties of transition elements to an appreciable extent. Still to rationalize the classification of elements, they are studied along with other d-block elements.

There are four series of elements which constitute the *d*-block elements. Each series comprises ten elements as given below:

1. Elements of the First Transition series or 3d-Transition series: The elements from scandium (Sc, Z = 21) to Zinc (Zn, Z = 30) form the 3d-series.

2. Elements of the Second Transition series or 4d-Transition series: This series consists of the elements from yttrium (Y, Z = 39) to cadmium (Cd, Z = 48).

3. Elements of the Third Transition series or 5d-Transition series: The elements lanthanum (La, Z= 57) and hafnium (Hf, Z= 72) to mercury (Hg, Z = 80) constitute the 5d-Transition series.

4. Elements of the Fourth Transition series or 6d-Transition series: The elements actinium (Ac, Z = 89) and rutherfordium (Rf, Z = 104) to copernicium (Cn, Z = 112) are the members of this series. All these elements are radioactive and do not occur in nature. These have been artificially made in the laboratory.

1.2 OBJECTIVES

In this unit you will be able to:

- The characteristic properties of the d-block elements, in general, such as their general electronic configuration and variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions/compounds, catalytic activity, etc. and periodic properties, *viz.*, atomic radii, atomic volume, ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potentials and reducing properties, etc. along with their periodic variation along the series.

- It is also aimed at throwing light on the above properties of the first transition series, in particular, to illustrate the relative stability of the oxidation states of these elements along with to discuss the coordination number and geometry of their complexes and the binary compounds of these elements.

1.3 CHARACTERISTIC PROPERTIES OF D-BLOCK ELEMENTS

Some of the important characteristics of the d-block elements are summarized as follows:

1.3.1 Electronic Configuration and Variable Oxidation States

The d-block elements have a valence shell electronic configuration of $(n-1)d^{1-10}ns^{0-2}$ where (n-1) stands for the inner shell whose d-orbitals may have one to ten electrons and the s-orbitals of the outermost shell (n) may have no electron or one or two electrons. The filling of d-orbitals takes place after the s-orbital of the next higher shell has already been filled as has been discussed in Aufbau principle in the previous unit. This is because ns orbitals have lower energy than (n- 1) d orbitals. But during ionization of the elements (oxidation), the electrons are first lost from ns level followed by the expulsion from (n-1) d subshell (deviation from the expected behaviour) because (n-1) d subshell becomes of the lower energy than ns subshell once the filling of electrons commences in (n-1) d subshell.

Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises the two subshells, *viz.*, (n-1) d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of

electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state. As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

1.3.2 Complex Formation Tendency

The cations of d-block elements are unique in their tendency to form complexes with several molecules such as ammonia, water, etc. or different ions such as cyanide, NO_2^-, halide ions, etc. These molecules or ions are called ligands. The complex forming tendency of these elements is attributed to the following factors:

(a) Small size and high positive charge density,
(b) Availability of vacant d-orbitals of right energy to accept the lone pairs of electrons from the approaching ligands,
(c) Exhibition of variable oxidation states.

A detailed account of this tendency will be given in the respective sections mentioned ahead.

1.3.3 Magnetic Properties

Many compounds of d-block elements exhibit magnetic properties. Qualitatively speaking, there are several kinds of magnetism. The substances which are weakly repelled by the strong magnetic field are termed as **diamagnetic** while those which are weakly attracted by the strong magnetic field are called **paramagnetic.** These substances lose their magnetism by removing the magnetic field. Diamagnetism is the property of the filled electronic subshells and is shown by all substances to more or less extent. Paramagnetism is produced by the presence of unpaired electrons and because most of the d-block metal atoms and ions have unpaired electrons, they are paramagnetic in behaviour.

In some transition metals (e.g. Fe, Co, Ni) unpaired electron spins are more pronounced and show much more paramagnetism than the other d-block metals. Such metals are called **ferromagnetic** metals and the magnetic property shown by them is known as ferromagnetism. Such metals can be permanently magnetized. The detailed account will be given in section 1.4 of this unit and subsequent units.

1.3.4 Formation of Coloured Ions/ Compounds

The majority of compounds of d-block elements, whether ionic or covalent, are colored in solid or solution state. This property of d-block elements is in marked difference from those of s or p-block elements which are white or light coloured.

The colour of a substance arises from the property of the substance to absorb light of a certain wavelength in the region of visible light (white light) when the latter interacts with the substance. The coloured of the substance is the colour of the transmitted light component and is complementary to the colour of the light component absorbed. The colour of d-block metal ions is associated with,

(a) an incomplete d-subshell in the metal ion,
(b) the nature of surrounding groups around the metal ion.

The whole act of exhibition of colour by d-block ions/compounds can be explained as follows. In a free gaseous or isolated ion, the five d-orbitals are degenerate, i.e. of the same energy. Since five d-orbitals are oriented differently in space, the surrounding groups affect the energy of some orbitals more than others in the compounds. This destroys their degeneracy. For example, in the simplest case of an octahedral complex, they form two groups of orbitals of different energy:
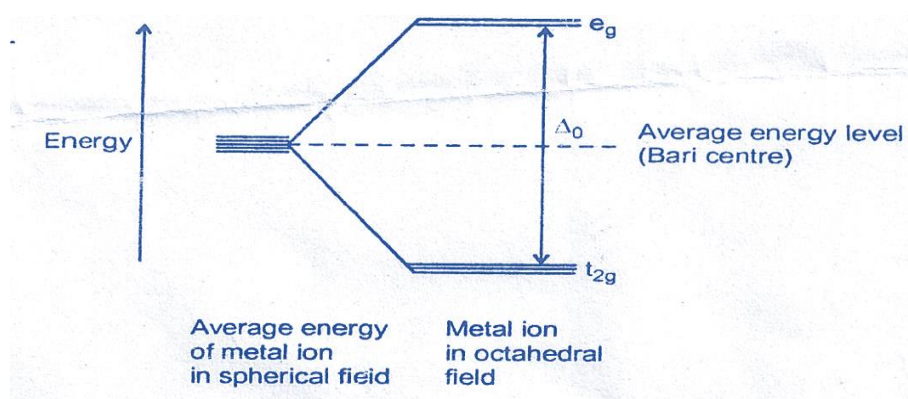

Fig. 1.1 Bary centre

Thus, in d-block metal ions with partially filled d-subshell, it is possible to promote electron(s) from one set of d-orbitals to another set (group) of higher energy by fairly small energy absorbed from the visible light. The colour of the compounds depends on the energy difference

(gap) between the two groups (sets) of d-orbitals. This in turn depends on the nature of ligands and their arrangement around the metal ion in the compound / complex.

1.3.5 Catalytic Activity

The catalytic activity of d-block elements and their compounds is associated with their variable oxidation states and their capability of forming interstitial compounds. Several d-block metals and their compounds are known to catalyze various reactions of industrial importance, e.g., vanadium (V) oxide in the manufacture of sulphuric acid by contact process, etc. An important view of the mechanism of catalysis is that at solid surface of the catalyst, bonds would be formed between the molecules of the reactants and atoms of the catalysts thereby increasing the concentration of the reactants at the surface. This weakens the bonds of the reactant molecules due to lowering of the activation energy.

1.3.6 Formation of Interstitial and Non-stoichiometric Compounds

The d-block elements form interstitial compounds with small non-metal atoms such as H, C, N, B, Si, etc. due to the ability of metal lattice to accommodate these non–metal atoms between the metal atoms without distortion of the structure.

One of the striking properties of these metals is the formation of non-stoichiometric compounds which often exhibit semiconductivity, and fluorescence and behave as heterogeneous catalysts. This non-stoichiometry is due to the defects in the solid structures.

1.3.7 Metallic Character and Alloy Formation

All the d-block elements are metals, good conductors of heat and electricity, are malleable and ductile. All are solids except Hg (mercury) which exists as liquid at ordinary temperature.

These metals form alloys with each other due to the almost similar sizes of the atoms. Thus, the atoms of one metal can easily take up positions in the crystal lattice of the other. The alloys are usually harder and have higher melting points than the parent metals, are more resistant to corrosion than their constituents.

1.3.8 Periodic Properties and Their Variation along the Series

The atomic radii, atomic volumes, ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potential and reducing properties, etc. are the important

periodic properties of the d–block elements which vary and have a definite trend, in general, along each series. These will be discussed below:

a) Atomic Radii, Atomic Volumes and Ionic Radii

The atomic radii generally decrease, with a few exceptions, on moving from left to right in each series of the transition elements due to increased nuclear charge at each step and constant value of the azimuthal quantum number (i.e. l) receiving the last electron.

The d-block elements have low atomic volumes as compared to those of the neighbouring s- and p-block elements. This is because in these elements (n-1) d-subshells are being filled and the increased nuclear charge pulls the electron cloud inwards.

The ionic radii of the d-block elements follow the same trend as the atomic radii, i.e. the radii of the ions having the same charge decrease with increasing atomic number. These properties will be discussed in detail for every series.

b) Melting and Boiling Points

The melting and boiling points of these elements are generally very high showing that they are held by strong forces. The melting and boiling points have the highest values in the middle of the series because, perhaps these elements have the maximum number of unpaired d-electrons available for bonding, a detailed account of which will be given ahead for every series.

c) Ionization Energies and Reactivity

The ionization energy values of the d-block elements are fairly high and lie in between those of s- and p-block elements, i.e. these elements are less electropositive than s-block elements and more so than p-block elements. Hence, these elements do not form ionic compounds as readily as s-block elements and form covalent compounds as well. Because of the existence of covalent bonding, they have high heats of sublimation, i.e. a large amount of energy is required to convert them from solid to vapour state. The metal ions also do not get hydrated easily. Due to these parameters, the metal ions have a small tendency to react. Examples will be given in each series.

d) Standard Electrode Potentials and Reducing Properties

The standard reduction potential values of transition elements are generally lower (negative) than that of the standard hydrogen electrode (taken as zero). Thus, they evolve H_2 gas from acids though most of them do that at a low rate.

These metals are poor reducing agents which are contrary to the expected behaviour because of the high heat of vaporisation, high ionization energies and low heat of hydration. An example, if available will be given in each series.

1.4 PROPERTIES OF THE ELEMENTS OF FIRST TRANSITION SERIES

As has already been mentioned in the beginning that the first transition series is also known as 3d-series because the last or the differentiating electron in the atoms of these elements enters the 3d-subshell. This series starts at scandium, the element of Group 3 and ends at zinc, the element of Ggroup 12, containing a total of ten elements. Thus, this series of elements lies in between calcium (Ca, Z=20) and gallium (Ga, Z=31), the elements of Group 2 and Group 13. The ten elements of the first transition series are scandium (Sc, Z=21), titanium (Ti, Z=22), vanadium (V, Z=23), chromium (Cr, Z=24), manganese (Mn, Z=25), iron (Fe, Z= 26), cobalt (Co, Z= 27), nickel (Ni, Z=28), copper (Cu, Z= 29) and zinc (Zn, Z= 30). These elements are much more important than those of the second transition series. All the characteristics and properties of the d-block elements are shown by the elements of the first transition series which are given below:

1.4.1 Electronic Configuration and Variable Oxidation States

The general valence shell electronic configuration of these elements is $3d^x4s^y$ where x=1 to 10 and y =1 or 2, i.e. the 3-d subshell has one to ten electrons from Sc to Zn and 4s-subshell, in general, has two electrons (i.e. $4s^{2)}$ except in Cr and Cu which have only one 4s electron (i.e. $4s^{1)}$. The exceptional valence shell configuration of Cr and Cu is attributed to the exchange energy effect and the extra stability of the resulting half–filled and completely–filled subshells. "The shifting of an electron from one subshell to another of similar or slightly higher energy to achieve the half-filled or completely-filled subshell is known as **exchange energy effect**". The state of affairs can be shown as follows:

Cr (Z= 24): $3d^44s^2$ (expected but unstable) $\longrightarrow$ $3d^54s^1$ (actual, more stable).
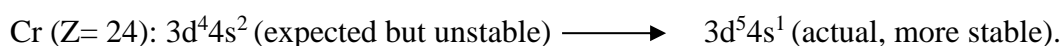
Cu (Z=29): $3d^9 4s^2$ (expected but unstable) $\longrightarrow$ $3d^{10} 4s^1$ (actual, more stable).

As is evident, there is an exchange of electrons from 4s to 3d subshells thereby increasing the stability of the valence shell configuration in Cr and Cu atoms. Thus, among 3d-series elements, only Cr and Cu exhibit irregular/anomalous electronic configurations.

The first transition series elements generally show variable (many) oxidation states in their compounds / ionic forms. The cause of showing different oxidation states is that these elements have several 3d electrons which are quite close to 4s – electrons in energy. The minimum oxidation state shown by all the elements of this series is +2 except Cr and Cu which show +1 oxidation state as well. The number of oxidation states shown increases from Sc to Mn and then decreases till Zn which shows the +2-oxidation state only. As a result, among these elements, Cr and Mn show the maximum number of oxidation states from +1 to +6 and +2 to +7, respectively. From Sc to Mn, the highest oxidation state shown by any element is equal to the group number but the latter elements do not follow this trend. This is evident from the following table:

Elements:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Group number	3	4	5	6	7	8	9	10	11	12
Lowest oxidation state	+2	+2	+2	+1	+2	+2	+2	+2	+1	+2
Highest oxidation state	+3	+4	+5	+6	+7	+6	+4	+3	+2	+2

It has been observed that the lower (+2, +3, etc.) oxidation states generally dominate the chemistry of the first transition series. For an element the relative stability of various oxidation states can be explained based on the stability of d^0, d^5 and d^{10} configurations, e.g. Ti^{4+} ion ($3d^0 4s^0$) is more stable than Ti^{3+} ($3d^1 4s^0$) because the presence of $3d^0$ subshell. Similarly, Mn^{2+} ($3d^5 4d^0$) ion is more stable than Mn^{3+} ($3d^4 4s^0$) ion since Mn^{2+} ion has $3d^5$ subshell.

It has also been observed that first transition series elements form ionic oxides and chlorides in the lower oxidation states which are basic. As the oxidation state of the elements increases, the covalent character and acidic nature of these compounds also increase, e.g., MnO (+2) is basic, Mn_2O_3 (+3) and MnO_2 (+4) are amphoteric and Mn_2O_7 (+7) is acidic. Similarly, CrO (+2) is basic, Cr_2O_3 (+3) is amphoteric and CrO_3 (+6) is acidic. Also, VCl_2 (+2) is basic and $VOCl_3$ (+5) is acidic.

1.4.2 Complex Formation Tendency

The elements of the first transition series fulfil all conditions of complex formation and are, thus, most suitable for this purpose. As a result, the cations of these elements have a strong tendency to form complexes with certain molecules (e.g. CO, NO, NH_3, etc.) or several ions (e.g. F^-, Cl^-, CN^- etc.). These molecules and ions are called ligands (L) and have one or more lone pairs of electrons on their donor atom (usually the central atom) which they donate to the metal ion/atom (M) during the process of complex formation via M←L coordinate covalent bonds. This happens because the metal ions are electron deficient in most of their oxidation states or even the atoms are electron acceptors. Small size and high charge density of the metal ions facilitate the formation of the complexes which also depends on the basicity of the ligands. The complex formation tendency increases as the positive oxidation state of the metal ion increases.

The nature of the complexes depends on the orbitals available on the metal ion/atom for bonding. These orbitals are s, p and d type. The structures commonly found in the complexes of the elements of the first transition series are linear, square planar, tetrahedral and octahedral. This shows that the metal orbitals are hybridized before bonding with the ligand orbitals, e.g. $[Ni(CN)_4]^{2-}$ ion is square planar while $[NiCl_4]^{2-}$ ion is tetrahedral (details of the complexes have been given ahead in this section).

1.4.3 Magnetic Behaviour

As has been mentioned earlier, there are several kinds of magnetism observed in the ions /compounds or complexes of transition metals. Among the transition metal compounds, paramagnetism is common though some metals in the elemental form also show ferromagnetism.

1.4.3.1 Origin of Paramagnetism

The electrons being charged particles act as tiny magnets (or micro magnets) by themselves and determine the magnetic properties of the substances in two ways:

(a) Spin motion or spinning of the electron on its axis produces spin magnetic moment and

(b) Orbital motion or the movement of the electron round the nucleus produces orbital magnetic moment.

The resultant of the above two moments gives the total moment produced by an electron. The observed magnetic moment of the compounds is the sum of the moments of all the electrons present in them. If the two electrons with opposite spins are paired in the same orbital, the magnetic moment produced by one electron is cancelled by that caused by the other electron because both the electrons will have equal but opposite moment thereby giving zero resultant magnetic moment. Such substances which have paired electrons will not show paramagnetism, rather they are diamagnetic.

But if there are unpaired electrons in the ions/atoms of the substance it has the moment produced by all the unpaired electrons. The resultant or total moment in them is sufficiently high to overcome the magnetic moment induced by an approaching magnetic field. Hence, such substances instead of experiencing repulsion, are attracted in a magnetic field and are called paramagnetic substances.

The magnetic moments of atoms, ions and molecules are expressed in units called **Bohr Magneton** (B.M.) which is defined in terms of the fundamental constants as

$$1 \text{ B.M.} = \frac{eh}{4\Pi mc}$$

where h = Planck's constant, e = electronic charge, c = velocity of light and m = mass of electron.

The magnetic moment of a single electron is given by the expression

$$\mu s \,(\text{B.M.}) = g\sqrt{S(S+1)} \quad \text{(According to wave mechanics)}$$

Where S= resultant spin quantum number and g = gyromagnetic ratio (called g-factor). The quantity $\sqrt{S(S+1)}$ is the value of the spin angular momentum of the electron and thus g is the ratio of magnetic moment to the angular momentum. For a free electron, g value is nearly 2 (i.e. 2.00023).

In transition metal compounds/complexes, the unpaired electrons are present in the outer shell of metal ions and in such cases the spin component is much more significant than the orbital contribution because the orbital motion of these electrons is said to be quenched or suppressed. Therefore, the latter can be neglected in comparison to the former. In such cases, the total magnetic moment is, therefore, considered entirely due to the spin of the unpaired electrons and μ_s is given by

$\mu_s = 2\sqrt{S(S+1)} = \sqrt{4S(S+1)}$ BM (By putting the value of $g = 2$)

Now S= n×s where n= number of unpaired electrons and s= spin quantum number (irrespective of its sign)

$$S= n \times \frac{1}{2} = \frac{n}{2}$$

Putting this value of S in the above expression

$$\mu_s = \sqrt{4 \, \frac{n}{2} \, \left(\frac{n}{2} + 1\right)} = \sqrt{2n \, \left(\frac{n+2}{2}\right)} \text{ B.M.}$$

$$\text{Or } \mu_s = \sqrt{n \, (n+2)} \text{ B.M.}$$

μ_s is also expressed as $\mu_{eff.}$, i.e. effective magnetic moment which is dependent only on the number of unpaired electrons and their spins. Hence, this formula of magnetic moment is also called **spin only formula.**

Thus, the permanent magnetic moment of 3d-transition elements gives important information about the number of unpaired electrons present in them and it varies with n. The calculated magnetic moments corresponding to 1, 2, 3, 4 and 5 unpaired electrons will be (using the above formula) $\sqrt{3}$ =1.73 B.M., $\sqrt{8}$ = 2.83 B.M., $\sqrt{15}$ = 3.87 B.M., $\sqrt{24}$ = 4.90 B.M. and $\sqrt{35}$ = 5.92 B.M., respectively.

The number of unpaired electrons evaluated from the magnetic moment value for a compound/complex gives valuable information regarding the type of orbitals that are occupied as well as those available for hybridisation and also the structure of the molecules or complexes provided, we have the idea of strength of the ligands (spectrochemical series). For example, here we discuss the structure of $[MnBr_4]^{2-}$ complex ion in which Mn is in +2 oxidation state and its coordination number is 4.

Mn atom (Z=25): [Ar] $3d^5 4s^2 4p^0$

Ground state of Mn

Excited state of Mn

Hybridization state
of Mn^{+2}

SP^3 Hybridization
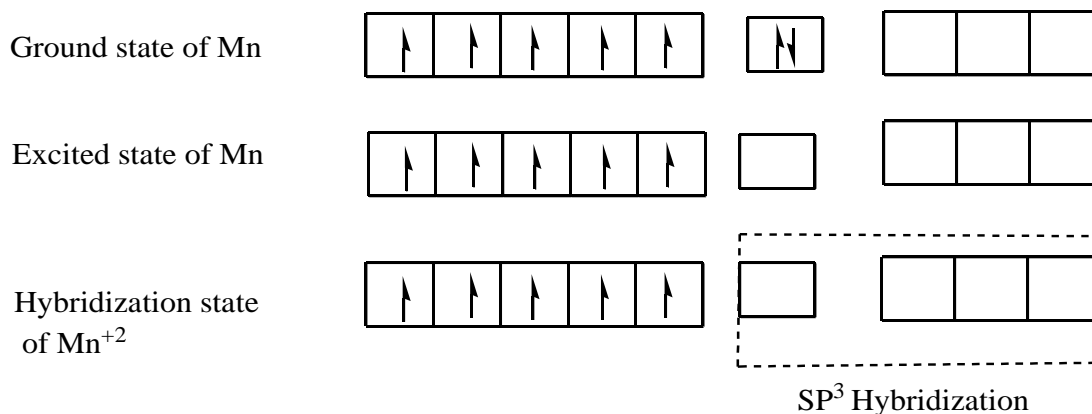
In the complex ion, Mn^{2+} ion is linked with four Br^- ions as ligands which exert weak ligand field on the metal ion orbitals. As a result, the five unpaired d-orbitals remain unaffected and one s and 3p empty orbitals of metal ion (only four hybrid orbitals are required) hybridise before bond formation producing sp^3 hybrid orbitals thus giving tetrahedral structure to the complex ion. The calculated magnetic moment of this complex is nearly 5.92 B.M. which indicates the presence of five unpaired electrons. If that is the situation, the tetrahedral structure of the complex ion is confirmed involving only s and p orbitals.

Similarly for the complexes with coordination number 6, i.e. six ligands are attached to the central metal ion, we can predict whether the complex is outer or inner orbital complex from the knowledge of weak and strong ligands, e.g. $[Co(H_2O)_6]^{2+}$ is an outer orbital complex and $[Co(NH_3)_6]^{2+}$ is an inner orbital complex having the central metal ion, Co^{2+} involving sp^3d^2 and d^2sp^3 hybridisation, respectively.

1.4.4 Formation of Coloured Ions/Compounds

The cause of the exhibition of colour by the ions/compounds/complexes of the d-block elements has been discussed earlier. The elements of first transition series form-coloured ions/compounds/complexes due to the presence of unpaired electrons in them. For example, $[Co(H_2O)_6]^{2+}$ is pink, Cu^+ (d^{10}) ion and its salts are colourless but Cu^{2+} (d^9) ion and its compounds are coloured, $CuSO_4.5H_2O$ is blue which is represented as $[Cu(H_2O)_4]SO_4.H_2O$ and $[Cu(NH_3)_4]^{2+}$ is dark blue (almost violet). Similarly, $[Ni(NO_2)_6]^{4-}$ is red and $[Ni(NH_3)_6]^{2+}$ is blue. Among the other compounds VO_2^+ is pale yellow, CrO_4^{2-} is strongly yellow, MnO_4^- is purple, and $[Ti(H_2O)_6]^{3+}$ is green-coloured.

The colour of the complex ion depends on the nature of the ligands and the type of complex formed. The metal ions with empty or filled d-subshell (as well as their compounds) are colourless, viz., Sc^{3+} ($3d^0$), Ti^{4+}($3d^0$), Cu^+($3d^{10}$), Zn^{2+}($3d^{10}$) etc.

1.4.5 Catalytic Activity

Elements of the first transition (3d) series and their compounds have been used in many industrial processes. Their availability in a variety of oxidation states makes them capable of forming intermediate products with various reactants and their tendency to form interstitial compounds which can absorb and activate the reacting species facilitate their application as catalysts. For example, finely divided Ni is used as a catalyst in hydrogenation reactions; MnO_2 catalyses the decomposition of H_2O_2; $TiCl_4$ is used as a catalyst for polymerisation of ethene in the manufacture of polythene; V_2O_5 is employed in the catalytic oxidation of SO_2 to SO_3 in the contact process of manufacture of H_2SO_4; Fe is used in the manufacture of NH_3 by Haber's process; Cu acts as a catalyst in the manufacture of $(CH_3)_2SiCl_2$ during the synthesis of silicones. Cu/V is used in the large-scale production of Nylon-66. Fe(III) ions catalyze the reaction between iodide and peroxodisulphate ions.

1.4.6 Formation of Interstitial and Non-stoichiometric Compounds

Elements of the 3d-transition series are capable of forming interstitial compounds, e.g., Ti_2C, V_2C, ScN, TiN, Fe_4N etc. These compounds have the properties of alloys being hard and good conductors etc.

These elements also form non-stoichiometric compounds. For example, titanium forms TiO_x (x=0.65 - 1.25 and 1.998 - 2.000); vanadium forms VO_x (x= 0.79 - 1.29); manganese forms Mn_xO (x= 0.848 - 1.00); iron form Fe_xO (x = 0.833 - 0.957), etc. These compounds have a variable composition and are formed due to the variability of oxidation states and solid defects. Sometimes the interstitial and non-stoichiometric compounds are the same.

1.4.7 Metallic Character and Alloy Formation

The metals of the first transition series are hard, malleable and ductile. These exhibit face-centered cubic (fcc), body-centered cubic (bcc) or hexagonal close-packed (hcp) type of lattice structures. These metals are good conductors of heat and electricity. Ccopper and metals of the iron triad are softer than other metals.

The common alloys of these metals are as follows: brass (Cu-Zn), nichrome (Ni-Cr), monel metal (Cu-Ni), German silver (Cu-Ni-Zn), stainless steel (Fe-Cr-Ni-Mn), alnico steel (Fe-Ni-Co-Al), etc. These alloys are harder and have higher melting points than the parent metals. They are also more resistant to corrosion than their constituents.

1.4.8 Periodic Properties and Their Variation along the Series

The melting and boiling points, atomic and ionic radii, atomic volumes, ionization energies and standard electrode potentials along with reducing properties are the main periodic properties of these metals along the series from Sc to Zn, which are discussed below:

a) Atomic Radii, Atomic Volumes and Ionic Radii

As has been discussed earlier for d-block elements, the atomic radii of the elements of first transition series follow the same trend as is applied for other d-block elements. The values generally decrease along the series up to Ni then increase slightly for Cu but pronouncely for Zn. Thus, Zn has exceptional value only lower than those for the first two elements and higher than those of others. This is evident from the following table:

Metal atoms	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii: (pm)	144	132	122	118	117	117	116	115	117	125

This happens due to the increased attraction between the outer electrons and increasing nuclear charge along the period. The close values of the atomic radii from Cr to Cu are due to the existence of increased screening effect of 3d-electrons which are added in each step and which shield the 4s-electrons from the inward pull though the nuclear charge increases continuously in the series from one element to the other. The screening effect in Zn ($3d^{10}$) is maximum and hence has exceptional value.

The atomic volumes of these elements as given below are comparatively low because of the filling of 3d-orbitals instead of 4s which is the subshell of the last shell. This causes increased nuclear pull acting on the outer electrons. The densities of these elements are very high. Atomic volumes decrease up to Cu and increase thereafter for Zn.

Metal atoms	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic volume:(cm^3)	15.0	11.0	8.3	7.2	7.3	7.1	6.7	6.6	7.1	9.2

The ionic radii of these elements follow the same trend as the atomic radii, i.e. the radii of the ions with the same charge generally go on decreasing as we move across the series except only for the last element. Radii of the bivalent and trivalent ions of the elements of this series are listed below:

Bivalent ions	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic radii (pm)	95	90	88	84	80	76	74	72	72	74
Trivalent ions	Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Ni^{3+}	--	--
Ionic radii (pm)	81	76	74	69	66	64	63	62	--	--

b) Melting and Boiling Points

The melting and boiling points of these elements are generally high and have irregular trend in the values as given below:

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point^{0}C	1540	1670	1900	1875	1245	1535	1495	1453	1083	420

As is evident from this table, the highest melting point is for V (1900 ^{0}C) and Zn, the last element has exceptionally low melting point (420 ^{0}C). Among other elements, Mn and Cu

have lower melting points as compared to other members. The boiling points are very high, >2200^{0}C except for Zn (906^{0}C) as expected.

c) Ionization Energies and Reactivity

The first ionization energy values of 3d-series elements show an irregular trend as shown below:

Elements:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I.E. (KJ):	631	658	650	653	717	759	758	737	746	906

But the second and third I.E. values generally show an increasing trend from Sc to Zn. The appreciably higher value of the first I.E. for Zn is attributed to the additional stability associated with a filled 3d-subshell ($3d^{10}4s^2$). The variation or irregularity occurring in the values of I.E. across the series are mainly due to the changes in atomic radii because of the screening effect of extra electrons added to the 3d-subshell which is exerted on the nuclear charge.

On account of the factors given above, the elements of first transition series show less reactivity.

d) Standard Electrode Potentials and Reducing Properties

The standard reduction potentials of the elements of 3d-series except copper are lower than that of standard hydrogen electrodes.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E^o_R (volts)	-2.10	-1.60	-1.20	-0.74	-1.18	-0.41	-0.28	-0.25	+0.34	-0.76

These elements evolve H_2 from acids though at very low rate. $M + 2H^+ \rightarrow M^{2+} + H_2$ (g). Cu does not react with acids. It tends to get reduced, sometimes the metals are protected from the attack of acids by a thin impervious layer of an inert oxide, e.g. Cr. These metals are oxidized easily to their ions and hence are reducing agent though poor due to the obvious reasons given above.

1.5 THE BINARY COMPOUNDS OF FIRST TRANSITION SERIES ELEMENTS

Those compounds which are formed by the combination of two different elements/ions are called binary compounds. For example, oxides, sulphides, halides, phosphides, carbides, nitrides, etc.

1.5.1 Oxides

The elements of the 3d-transition series react with oxygen at high temperatures to give oxides. These oxides are less basic and less soluble in water. Oxides in lower oxidation states are ionic and basic, in the intermediate oxidation states their nature is amphoteric and in higher oxidation states, ionic nature decreases and covalent nature increases thereby increasing the acidic character of the oxides. It means the acidity of a salt depends on its covalent nature which in turn is based on the oxidation state of the element. Thus, oxidation states $\propto$ covalent nature $\propto$ and acidic nature. Accordingly, the oxides may be classified as (a) basic oxides, (b) amphoteric oxides and (c) acidic oxides.

(a) **Basic oxides** are those which are formed by the metals in the lower oxidation states. These are ionic in nature, and soluble in non-oxidising acids, e.g. HCl. For example, TiO, CrO, MnO, FeO, Cu_2O, CoO, NiO, etc.

(b) **Amphoteric oxides** are the oxides containing the metals in the intermediate oxidation states. These oxides are also soluble in non-oxidising acids, e.g., HCl. Examples TiO_2, VO_2, Cr_2O_3, Mn_3O_4, MnO_2, CuO, ZnO, etc.

(c) **Acidic oxides** are of weak acidic nature and are formed by the elements in higher oxidation states. These are soluble in bases. For example, V_2O_5, CrO_3, MnO_3, Mn_2O_7 etc.

Reducing and oxidising nature of oxides. The electron exchange property determines the redox nature of oxides. The oxide containing the metal is lower oxidation state acts as electron donor and hence is a reductant (reducing agent). As atomic number increases, the reducing property in the lower oxidation state also increases, e.g., TiO < VO < CrO. If the metal in the oxide is in a higher oxidation state, the oxide is an electron acceptor or oxidising agent, e.g., CrO_3, Mn_2O_7 etc.

1.5.2 Halides

The elements of the 3d-transition series react with halogens at high temperatures to give halides. The reactivity of halogens goes on decreasing from F_2 to I_2. Fluorides are ionic, others have ionic as well as covalent nature. Halides are formed by many of these elements in different oxidation states, e.g. $TiCl_3$, $TiCl_4$, VCl_3, VCl_5 etc.
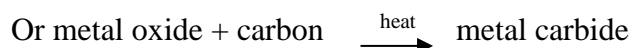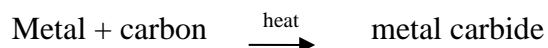
1.5.3 Sulphides

Metal sulphides may either be prepared by direct heating the mixture of metal and sulphur or by treating metal salt solution with H_2S or Na_2S:

$$\text{Metal} + S \xrightarrow{\text{heat}} \text{metal sulphide}$$

Or   metal salt solution + $H_2S/Na_2S \longrightarrow$ metal sulphide
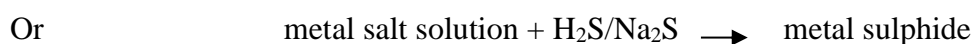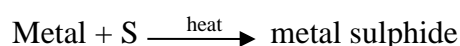
Metals in low oxidation state form sulphides which are insoluble in water.

1.4.4 Carbides

Metal carbides are generally prepared by the following two methods:

$$\text{Metal} + \text{carbon} \xrightarrow{\text{heat}} \text{metal carbide}$$

$$\text{Or metal oxide} + \text{carbon} \xrightarrow{\text{heat}} \text{metal carbide}$$

The carbides of these metals are classified as follows:

(a) Metallic or Interstitial carbides

These carbides are prepared as is given below.

$$V + C \longrightarrow VC$$
$$TiO_2 + 2C \longrightarrow TiC + CO_2$$
$$3Fe + C \longrightarrow Fe_3C$$
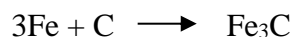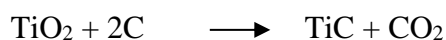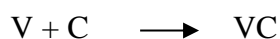
These are hard solids, have metallic properties like lustre, are stable at high temperature, chemically inert and are conductors. Ni does not form carbide. In solid state, these have tetrahedral or octahedral voids which are occupied by carbon atoms.

(b) Salt-like carbides

These carbides are limited to Sc, Cu and Zn only and are ionic:

$$Sc_2O_3 + 7C \longrightarrow 2ScC_2 + 3CO$$
$$ScC_2 + 2H_2O \longrightarrow C_2H_2 + Sc(OH)_2$$

$$Zn \quad + C_2H_2 \longrightarrow ZnC_2 \quad + H_2$$

$$ZnC_2 \quad + 2H_2O \longrightarrow C_2H_2 \quad + Zn(OH)_2$$
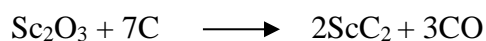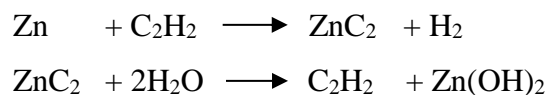
1.5 RELATIVE STABILITY OF OXIDATION STATES OF THE ELEMENTS OF THE FIRST TRANSITION SERIES

The stability of an element is determined by its electronic configuration. The elements of the 3d-transition series, generally exhibit variable oxidation states and are more stable in a particular oxidation state, e.g., $Ti^{4+} > Ti^{3+}$ and $Fe^{3+} > Fe^{2+}$ etc. Generally, lower oxidation states are less stable than the higher oxidation states. This relative stability depends on many factors:

(a) Filled, half-filled and vacant d-orbitals present in the compound, i.e. d^{10}, d^5 and d^0 configurations are more stable than other configurations, e.g. $Ti^{4+}(d^0) > Ti^{3+}(d^1)$; $Mn^{2+}(d^5)$ $> Mn^{3+}(d^4)$. However, it is not always true, e.g. $Cu^+(3d^{10})$ is less stable than $Cu^{2+}(3d^9)$ due to high lattice energy and solvation energies of Cu^{2+} in solid state and in solution.

(b) Higher oxidation states become less stable as atomic number increases. For example, Sc^{3+} $> Ti^{3+} > V^{3+} > ------- > Ni^{3+} > Cu^{3+}$.

(c) In the binary compounds of elements of the 3d-transition series, it has been observed that halogens and oxygen also illustrate the trend in stability. Generally, the group oxidation state for many elements is brought out more readily by oxygen than fluorine, the strongest halogen. This may be because fewer oxygen atoms are required than fluorine atoms to achieve the same oxidation state. For example, the group oxidation state (+7) of Mn is achieved in MnO_4^-, but MnF_7 has never been prepared. In the d-block elements, the oxidation states can be stabilised by complex formation. Low oxidation states are less stable and ligands like CN^-, N_2, NO, CO, C_6H_6, C_2H_4 etc. called π-acceptors form complexes in these low oxidation states to stabilise them. These complexes are known as π-complexes, e.g. $[Ni(CO)_4]$, $[Cr(C_6H_6)_2]$, $[Fe(C_5H_5)_2]$ etc. Higher oxidation states are stabilized by complex formation with highly electronegative ligands.

(d) The compounds in any oxidation state of the metal are regarded as stable if they have free existence, are not oxidised by air, are not hydrolysed by water vapour, do not disproportionate or decompose at normal temperature.

1.6 THE COMPLEXES OF THE FIRST TRANSITION SERIES ELEMENTS, THEIR COORDINATION NUMBER AND GEOMETRY

The elements of first transition (3d) series fulfill all conditions of complex formation and thus are most suitable for this purpose. The general representation for the complexes is as follows:

$[M \longleftarrow L_n]^{x\pm}$ where n represents the number of lone pairs accepted by the central metal atom/ion from the ligands (L) and x is the charge on the metal complex which may be positive or negative or even zero in neutral complexes. All the elements of this series form complexes with a variety of ligands, e.g. $[CrCl_2(H_2O)_4]^+$, $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Co(NH_3)_3(SCN)_3]$, $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$ etc. The elements of this series form stable complexes with N, O, and halogen donor ligands.

1.6.1 Coordination Number (CN)

The number of ligands (monodentate only) directly attached to the central metal atom/ion or more appropriately the number of lone pairs of electrons accepted by the central metal atom/ion from the ligands (mono as well as polydentate) in the process of the formation of the complexes (molecules or ions), is known as the coordination number (C.N.) of the metal. In the above examples, the C.N. of Ag^+ ion is 2, that of Cu^{2+} ion is 4, for Cr^{3+}, Ni^{2+}, Co^{3+}, Co^{2+} and Fe^{3+} ions it is 6. The central metal atom/ion and attached ligands are kept within the square brackets called coordination spheres. With the polydentate ligands the metal atom/ions form ring-type complexes known as **chelates** (meaning claw).

1.6.2 Geometry of the Complexes

The coordination number of the central metal atom/ion of the complex is intimately related with its geometry. The relationship may be shown as follows:

C.N.	Geometry of the complex
2	Linear: Cu^+ and Ag^+ complexes, e.g. $[Ag(NH_3)_2]^+$
4	Tetrahedral: Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} complexes with weak ligands *viz.* H_2O, Cl^-, Br^-, I^- etc., e.g. $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$, $[NiCl_4]^{2-}$, $[CuCl_4]^{2-}$, $[FeCl_4]^{2-}$ etc.

| | Square planar: Ni^{2+}, Cu^{2+} complexes with strong ligands viz. CN^-, NH_3, en, dmg etc., e.g. $[Ni(dmg)_2]$, $[Cu(en)_2]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ etc. |
| 6 | Octahedral: Cr^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+} complexes with weak and strong field ligands, e.g. $[Cr(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ etc. |

It may be recalled that octahedral complexes of the metal ions with weak field ligands are outer orbital (also called high spin) complexes involving sp^3d^2 hybridisation and those with strong field ligands are inner orbital (also known as low spin) complexes, the central ion undergoing d^2sp^3 hybridisation.

1.7 SUMMARY

The summary of the present unit is -:

- In contrast to the main group elements, the last electron in the atoms of d-block elements enters the (n-1) d-subshell which influences the characteristics and periodicity in properties of transition elements. Hence, the text material of this unit is related to characteristic properties in general of d-block elements such as their electronic configuration, variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions/compounds, catalytic activity, formation of interstial and non-stoichiometric compounds, alloy formation, metallic character, melting and boiling points, atomic and ionic radii, ionization energies, reactivity, standard electrode (reduction) potential and reducing properties.

1.8 TERMINAL QUESTIONS

1. Give a brief note on the factor responsible for anomalous electronic configuration of Cr and Cu.

2. What accounts for the complex formation tendency of d-block elements?

3. Write a short note on the paramagnetism shown by d-block elements.

4. Why do 3d-series elements form-coloured ions and compounds?

5. What are the non-stoichiometric compounds?

6. What are alloys? Give any two examples.

7. "Mn and Cr have highest number of oxidation states among first transition (3d) series elements". Comment.

8. Which one is more stable: Ti^{4+} or Ti^{3+}?

9. μ_{eff} for a metal ion with 3 unpaired electrons is

   A. 1.73 B.M.   B. 2.83 B.M.   C. 3.87 B.M.   D. 4.90 B.M.

10. Finely divided Ni is used in

    A. The manufacture of H_2SO_4 B. The manufacture of HNO_3

    C. The manufacture of NH_3 D. The hydrogenation reactions

11. Brass is an alloy of

    A. Cu-Zn   B. Cu-Fe   C. Cr-Ni   D. Mn-Fe

12. MnO_2 is

    A. An acidic oxide   B. An amphoteric oxide

    C. A basic oxide   D. None of the above

1.9 ANSWERS

1 to 7: please refer to the text,   8. Ti^{4+} $(3d^0)$ is more stable than Ti^{3+} $(3d^1)$

   9. c,   10. d,   11. a,   12. A

UNIT 2- CHEMISTRY OF THE ELEMENTS OF SECOND TRANSITION (4d) SERIES

CONTENTS:

2.1 INTRODUCTION

The series of ten elements starting from yttrium, the element of Group 3 and ending at cadmium, the element of Group 12, constitutes the second transition series. These elements with their symbols and atomic numbers are given here:

Yttrium (Y, Z = 39), zirconium (Zr, Z = 40), niobium (Nb, Z = 41), molybdenum (Mo, Z = 42), technetium (Tc, Z = 43), ruthenium (Ru, Z = 44), rhodium (Rh, Z = 45), palladium (Pd, Z = 46), silver (Ag, Z = 47) and cadmium (Cd, Z = 48). These elements are also known as the elements of the 4d transition series because the differentiating or the last electron in the atoms of these elements enters the 4d subshell progressively giving $4d^1$ to $4d^{10}$ configurations, respectively. All the characteristic properties of d-block elements are exhibited by the members of this series also. These elements are the next higher analogues of the first transition series elements and are less important. This series lies between strontium (Sr, Z =38) of s-Block (Group 2) and indium (In, Z = 49) of p-Block (Group 13) so that the gradual transition of properties may occur from s- to p- Block elements in the period.

2.2 OBJECTIVES

In this unit learners will be able to:

- The general characteristics of the elements of the second transition (or 4d) series such as their electronic configuration, variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions/compounds, catalytic activity, formation of interstitial and non-stoichiometric compounds, metallic character and alloy formation as well as other periodic properties such as atomic and ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potential and reducing properties, etc. with their variation along the series.

- The comparative study of some of the above periodic properties, *viz.*, ionic radii, oxidation states and the magnetic behaviour of these elements with those of their 3d analogues is also aimed at. The spectral properties ad stereochemistry of these elements and their compounds or complexes is also to be discussed to make the readers familiar with these fascinating aspects.

2.3 GENERAL CHARACTERISTICS OF SECOND TRANSITION (4D) SERIES ELEMENTS

All the general characteristics of the d-Block elements apply to the elements of the second transition series though to a lesser extent. These are discussed below:

2.3.1 Electronic Configuration and Variable Oxidation States

In yttrium 4d-subshell begins filling, its valence shell configuration being $4d^1 5s^2$. The filling of the 4d-subshell continues as we move along the series towards the last element, Cd which has $4d^{10} 5s^2$ valence shell configuration. There are observed pronounced irregularities in the valence shell configurations of these elements which have the general valence shell configuration $4d^{1-10} 5s^{1,2}$. Except for the last three elements, *viz.*, Pd, Ag and Cd which have completely filled 4d-subshell ($4d^{10}$), all have incomplete d-subshells. Y, Zr, Tc and Cd have 2 electrons in 5s-subshell ($5s^2$) but Nb, Mo, Ru, Rh and Ag have only one electron, i.e., $5s^1$, in the last shell and Pd does not have any 5s- electron ($5s^0$). The anomalous valence shell configuration of Pd (i.e. $4d^{10} 5s^0$) is due to the shifting of both 5s-electrons to 4d-subshell so that it has completely filled state (i.e., $4d^{10}$) and becomes stable, though no satisfactory explanation is available for this shifting. For the elements which have partly filled 4d-subshell but still have only one electron in 5s subshell ($5s^1$), the anomalous behaviour has not been explained with effective reasoning, only it is said for these elements that the nuclear-electron and electron-electron interactions play significant role for this behaviour. In Mo ($4d^5$) and Ag ($4d^{10}$), one electron is said to have shifted from 5s to 4d subshell to make the atoms of these elements extra stable due to exchange energy effect as has been given earlier for Cr and Cu elements of 3d- transition series.

Like the elements of first transition (3d) series, the elements of this series also exist in various oxidation states in their compounds. This is because of the availability of several electrons in 4d and 5s subshells whose energies are fairly close to each other. Hence, under different experimental conditions different number of electrons can be used from both the subshells for bonding.

It has been found for second transition series elements that the higher oxidation states become more stable. This can be illustrated by taking Fe and its next higher analogue, Ru. Fe shows +2 and +3 stable oxidation states and +4 and +6 unstable states but Ru has +2, +3, +4 and +6 as

stable oxidation states while +5, +7 and +8 are unstable states for this element. The first element Y (+3) and the last element Cd (+2) exhibit only one oxidation state (though Sc in 3d transition series has also been assigned a very uncommon oxidation state of +2) because of the stable valence shell configuration of the ions, *viz.,* Y^{3+} $[Kr]4d^05s^0$ and Cd^{2+} $[Kr]4d^{10}5s^0$. All other elements show a variety of oxidation states, both stable and unstable, the variability being the maximum towards the middle of the series as happens in case of elements of 3d-transitin series. Ruthenium, lying almost in the middle of the series, exhibits maximum number of oxidation states (i.e. 7) among all the elements of the series, including the unstable ones, ranging from +2 to +8 (i.e.+2, +3, +4, +5, +6, +7, +8). Up to Ru, the next higher member of Fe group, the highest oxidation state is equal to the group number, e.g., Sc: + 3 (Group 3); Zr: +4 (Group 4); Nb: +5 (Group 5), Mo: +6 (Group 6), Tc: +7 (Group 7) and Ru: +8 (Group 8) but the latter members of the series do not follow this trend. The lowest oxidation state is +1 only for Ag, the next congener of Cu. For Ru, Pd and Cd, the lowest oxidation state is +2, and +3 is the lowest oxidation state for other members of the series. This has been shown in the table below.

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Group number	3	4	5	6	7	8	9	10	11	12
Lowest oxidation State	+3	+3	+3	+3	+4	+2	+3	+2	+1	+2
Highest oxidation state	+3	+4	+5	+6	+7	+8	+6	+6	+3	+2

Thus, it is concluded that the electronic structure of the atoms of the second transition series elements does not follow the pattern of the elements of the first transition series and also among the 4d series elements, the higher oxidation states become more pronounced and stable.

2.3.2 Complex Formation Tendency

The availability of various oxidation states facilitates the complex formation tendency. The complex formation tendency is found in the elements of the second transition series also though it is less pronounced. These metals are weakly electropositive and do not form stable complexes with wide range of ligands as is found in the case of first transition series elements. These

elements from stable complexes with P, S and heavier halogens as donor atoms in the ligands in contrary to the elements of 3d sereis. They also form π complexes with CO as ligand. The 4d series elements show the common as well as unusual coordination numbers in their complexes which may be 4, 6 and even more than six. The examples are available for most of the second transition series elements in various oxidation states.

Yttrium forms complexes readily with NCS^-, acac, EDTA etc., *viz.*, $[Y(NCS)_6]^{3-}$, $[Y(acac)_3.H_2O]$, $[Y(EDTA)]^-$, respectively. Its complexes with C.N. 8 are also known.

Zirconium usually gives halo complexes of the type $[ZrX_6]^{2-}$ and $[ZrX_7]^{3-}$ (X = halide ions), $[Zr(acac)_4]$, $[Zr(C_2O_4)_4]^{4-}$, $[Zr(bipy)_3]$ and also $[Zr_2F_{13}]^{5-}$ and $[ZrCl_4]_3(POCl_3)_2$ type.

Niobium forms clusters only, e.g. $[Nb_6X_{12}]^{n+}$, where n = 2, 3 or 4; $[Nb_6X_{14}]$, $[Nb_6X_{15}]$ and $[Nb_6X_{16}]$, etc.

Molybdenum forms a variety of complexes having Mo in different oxidation states and coordination numbers. For example, $[Mo_2Cl_8]^{4-}$, $[Mo_2Cl_9]^{3-}$, $[MoCl_6]^{2-}$, $[Mo(CO)_5]^2$, $[Mo_2(CO)_{10}]^{2-}$, $[Mo(CO)_6]$, $[Mo(CNR)_7]^{2+}$, $[Mo(CN)_8]^{4-}$, $[Mo(S_2CNMe_2)_4]$, etc.

Technitium also forms many complexes though not as many as are formed by manganese and rhenium. For example, $[Tc(CO)_4]^{3-}$, $[Tc(CO)_5]^-$, $[Tc_2(CO)_{10}]$, $[Tc(CN)_7]^{4-}$, $[Tc(CN)_6]^-$, $[Tc(NCS)_6]^-$, $[TcH_9]^{2-}$ etc.

Ruthenium forms a variety of complexes both with normal and π-ligands, such as N_2, CO etc. For example, $[Ru(NH_3)_5N_2]^{3+}$, $[Ru(NH_3)_6]^{3+}$, $[Ru(CO)_5]$, $[Ru_3(CO)_{12}]$ etc. The first complex further gives ploynuclear complex (N_2 is weak π- ligand):

$[Ru (NH_3)_5 N_2]^{3+} + [Ru (NH_3)_5. H_2O]^{3+} \rightarrow [(H_3N)_5 Ru-N_2-Ru (NH_3)_5]^{4+} + H_2O$
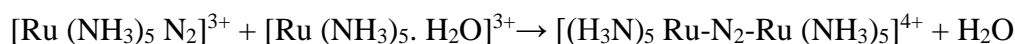
The complexes of Rh, Pd and Cd are as follows:

$[Rh(CO)_4]^-$, $[Rh_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$, $[Pd(NH_3)_2Cl_2]$, $[Pd(NH_3)_4]^{2+}$, $[Cd(CN)_4]^{2-}$, $[Cd (NH_3)_4]^{2+}$ and $[[Pd(NH_3)_6]^{2+}$ etc.

2.3.3 Magnetic Properties

The elements of second transition series exhibit paramagnetism due, obviously, to the presence of unpaired d-electrons in elemental or ionic forms. It has been observed that the magnetic moment, a measure of magnetism in the substances, increases with the number of unpaired

electrons (the relationship of magnetic moment, μ_{eff} and number of unpaired electrons has been given in Unit 1 under magnetic properties of 3d-series elements). The relationship is called **spin only formula** because only spin contribution towards the total magnetic moment is considered and orbital contribution is regarded as quenched. However, if the orbital contribution is also considered in its full capacity to the total magnetic moment, then the magnetic moment of the substance can be calculated by the formula:

$$\mu_{eff} = \sqrt{4S\,(S+1) + L(L+1)}$$

Where S is resultant spin angular momentum and L is the resultant orbital angular momentum.

In the ions/compounds/complexes of second transition series elements, the spin only formula is used to calculate the number of unpaired electrons from μ_{eff} values.

2.3.4 Formation of Coloured Ions / Compounds

The elements of the second transition series also form coloured ions/compounds / complexes whether in solid or in solution state, due to usual reasons as have been given for those of first transition series as well as for general d-block elements. The cations having vacant or completely filled d-orbitals (d^0 or d^{10}) are colourless in the case of this series also. But, those with partly filled d-orbitals (d^1, d^2, d^3……..d^9) are coloured. It means the cations having all the electrons paired in d-orbitals or no electrons in this subshell are colourless but those cations/compounds having unpaired (some or all) in d-orbitals are coloured. If n is the number of unpaired electrons in d-subshell, then the ions having n = 0 are colourless while those having n = 1, 2,….,5 are coloured. In addition to the presence of unpaired electrons in d-subshell or incomplete d-subshell, the nature of atoms (in the compounds) or ligands (in the complexes) attached to central metal ion determines the colour of the compounds as a whole.

As has been explained earlier, the colour in the substances is developed due to the movement of electrons from one d-orbital to another under the influence of visible light falling on the substance. The colour is intense if the transition is allowed but becomes dull if it is forbidden. If in place of inter orbital transition, inter atomic transitions take place, intense colours are produced because such transitions are not affected by the selection rules (*viz.* spin, Laporte and symmetry selection rules) thereby allowing free transition of electrons.

2.3.5 Catalytic Activity

Like the elements of first transition series, those of second transition series also show catalytic activity, some of them being very important and useful as catalysts in a variety of reactions of industrial importance. This is because these are capable of forming intermediate products with the reactants or have active centres on their surface in the activated state which can activate the reactants for the desired reactions. For example,

(a) Pd is used in the hydrogenation of phenol to cyclohexanol.

(b) Pd/Pt catalyses the hydrogenation of unsaturated hydrocarbons.

(c) Mo is used as a promoter in the manufacture of ammonia by Haber process.

(d) Pt/Rh is used as catalyst in the oxidation of NH_3 to NO (manufacture of HNO_3).

2.3.6 Formation of Interstitial and Non-stoichiometric Compounds

The metals of second transition series, in general, form interstitial compounds with small non-metallic elements such as H, N, C etc. The lattice of these metals is capable of accommodating these small atoms between the metal atoms with no change in the lattice structure. Examples are: $PdH_{0.6}$, $ZrH_{1.98}$, ZrC, NbC, MoC, Mo_2C, ZrN, NbN, Mo_2N etc. These compounds have conductivity properties and are hard, thus behaving as alloys.

These elements also form non-stoichiometric compounds which often exhibit semi conductivity, fluorescence and have centres of colours. The above examples of PdH and ZrH_2 also furnish examples of non-stoichiometry. The molecular formula of these compounds does not correspond to the M: H ratio of 1:1 and 1:2. Actually, the M: H ratio in these compounds is 1: 0.6   and 1:1.98, respectively.

2.3.7 Metallic Character and Alloy Formation

All the elements of second transition series are metals which are hard, some of them malleable and ductile (e.g., Ag), fairly good conductors of heat and electricity. They crystallize in one of the following lattice structures: body-centred cubic (bcc), face centred cubic (fcc) or hexagonal close-packed (hcp).

The elements of this series also form alloys though to a lesser extent than the elements of first transition series due to the obvious reasons as given earlier. These alloys are also usually harder and have higher melting points than parent metals. They are also corrosion-proof/resistant.

These metals are less important than those of the first and third transition series.

2.3.8 Periodic Properties and Their Variation along the Series

The periodic properties of second transition series elements such as the atomic radii, ionic radii, atomic volumes, ionization energies, melting and boiling points, standard electrode potentials, reactivity and reducing properties also vary along the series from the first element Y to the last element Cd. These have been discussed below along with their variation in the series.

(a) Atomic Radii, Atomic Volumes and Ionic Radii

It has been observed that the atomic radii of the elements of second transition series, though not known with certainty, decrease from the first element, Y to Rh, the next congener of Co and increase thereafter up to the last element, Cd. The values are very close from Mo to Pd because of the increased screening effect of the 4d electrons which more or less counter balance the nuclear pull exerted on the 5s electrons. Then the screening effect becomes more and more pronounced thereby decreasing the attractive force between the nucleus and the outer electrons. As a result, atomic radii of Ag and Cd are increased. Cd has next highest atomic radius which is only lower than that for Y. These values have been given below:

Elements	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic radii (pm)	162	145	134	130	127	125	125	128	134	148

The atomic volumes of these elements which are dependent on the atomic radii show the same trend in their variation. The atomic volumes are being listed below:

Elements	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic volume (Cm^3)	19.8	14.0	10.8	9.4	-	8.3	8.3	8.9	10.3	13.0

For Tc, its value has arbitrarily been calculated but is not known with certainty. The values decrease from the first element, Y, up to Rh and then increase due to the obvious reason, i.e. increasing atomic radii values.

The ionic radii follow almost the same trend as the atomic radii at least for the few elements. These elements form ions of variety of oxidation states but only those ions may be considered which bear the same charge. This analogy does not apply to the ions of these elements. For various ions, the ionic radii are listed here:

Ions	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{4+}	Tc^{4+}	Ru^{3+}	Rh^{3+}	Pd^{2+}	Ag^+	Cd^{2+}
Ionic radii (pm)	104	86	70	79	-	81	80	80	123	97

As is evident from this table, ionic radii values are showing an irregular trend particularly for the later elements.

(b) Melting and Boiling Points

The melting and boiling points of these elements are generally very high, almost similar to those of the elements of first transition series except for a few elements which have very high values, e.g., Nb to Ru (see the table given below). The last element Cd, has exceptionally low value of melting point even lower than that of Zn. This may be attributed to its high atomic volume, almost one and a half times to that of Zn. This results in weaker metallic bonding in the metal lattice of Cd. The melting point values of these elements are as follows:

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Melting point (^{0}C)	1490	1860	2415	2620	2200	2450	1970	1550	960	321

The highest melting point is for Mo followed by Ru and other elements have comparable values of melting point. Cd has the lowest value. These elements have very high boiling points, greater than 2200 ^{0}C except for Cd (765^0C).

(c) Ionization Energies and Reactivity

The first ionization energies of these elements generally increase from the first element to the last one with a marked drop in the value for Ag. The values are listed below:

Element	Y	Zr	Nb	Mo	Tc	Ru	Ph	Pd	Ag	Cd
First ionization energy (kJ/mol)	636	669	664	694	698	724	745	803	732	866

These high values of first ionization energies can be correlated with the values of atomic radii which generally decrease along the series and the screening effect increases; therefore, the elements accordingly have higher values. For Ag low value is attributed to a slightly higher atomic radius and availability of a single 5s electron. An appreciably higher value of ionization energy for Cd is due to the stability associated with filled 4d and 5s subshells ($4d^{10}5s^2$).

As discussed in section 1.3 above, various factors are responsible for the low reactivity of the elements of the second transition series. They are even less reactive than those of the first transition series.

(d) Standard Electrode Potentials and Reducing Properties

As is well known that the standard electrode potential (reduction) is related with the reducing properties of the elements, in general. Metals with negative values of standard electrode potential as compared to standard hydrogen electrode for which E^0 value is taken as zero, act as reducing agents. Such metals can displace hydrogen gas from dilute acids. For the metals with negative E^0 values but not reacting with acids, some other factors also play an import role such as formation of protective coating on the metal surface and making it unreactive. Strong reducing properties of metals make them displace other metal ions from their solutions. Though standard electrode potential values are available only for a few elements of this series, these are given below:

$$Cd^{2+} + 2e \rightarrow Cd, E^0 = -0.40 \text{ V (can displace } H_2 \text{ from dilute acids)}$$

$$Ag^+ + e \rightarrow Ag, E^0 = +0.80 \text{ V}   \text{ (does not react with dilute acids)}$$
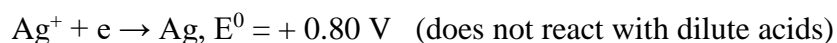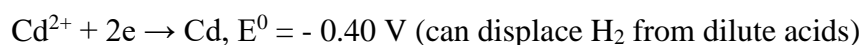
From the above, it can be concluded that Cd^{2+} ions can give up the electrons and act as reducing agents while Ag^+ ions do not give the electrons, rather take up the electrons easily. Hence, act as oxidizing agents when react with reducing ions, e.g.,

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag.$$
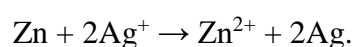
2.4 COMPARATIVE STUDY OF THE ELEMENTS OF THE SECOND TRANSITION SERIES AND THOSE OF FIRST TRANSITION SERIES

(a) Oxidation States

The elements of both the transition series exhibit variable oxidation states. Some of them are common and the others are uncommon or unfamiliar oxidation states. It may be recalled that for the elements of first transition (or 3d) series, generally lower oxidation states (*viz.* +2, +3, etc.) are most stable while the higher oxidation states are less stable. That is why their compounds in the higher oxidation states are less stable and more reactive. For example, $Cr_2O_7^{2-}$ (Cr in +6 oxidation state) and MnO_4^- (Mn in +7 oxidation state) are strong oxidising agents and in their reactions get reduced to Cr^{3+} and Mn^{2+} states, which are stable, respectively. We can say that lower (+2 and +3) oxidation states generally dominate the chemistry of the first transition series elements, e.g., Co^{2+} ion is quite stable in aqueous medium as well as Co^{3+} in $[Co(NH_3)_6]^{3+}$ ion is highly stable. On the other hand, Rh^{2+} ion, next congener of Co is hardly known. Similarly, no such complex of Rh^{3+} is known as is formed by Co^{3+} ion with NH_3.

For the elements of second transition series, lower (+2 and +3) oxidation states are of relatively little importance but the higher oxidation states (e.g., +5, +6, +7, etc) are stable and important. For example, in manganese group (Group 7), Mn^{2+} ion is stable while Tc^{2+} ion is unstable; Tc^{3+} occurs in some π-complexes and clusters only. In Group 6, Cr (III) forms a large number of compounds and complexes, while Mo (III) forms only a few. Cr (VI) ions are less stable (as discussed above), but Mo (VI) ions are highly stable: $[MoO_4]^{2-}$ ion is not easily reduced. In Group 7, again $[MnO_4]^-$ is unstable but $[TcO_4]^-$ is stable and very weak oxidising agent. Similarly, FeO_4, $CrCl_6$ and NiF_6 are not known, while RuO_4, $MoCl_6$ etc. are quite stable. The highest oxidation state for 3d-series elements is +7 (in MnO_4^-), but for 4d-series members it is +8 (in RuO_4).

(b) Ionic Radii

In terms of the ionic radii, it has been observed that the radii of 3d-series elements are smaller than those of 4d-series elements, i.e. r_{3d} ions < r_{4d} ions. The comparative table of ionic radii of the elements of the two series is being given here:

Ions:	Sc^3	Ti^{4+}	Cr^{4+}	Zn^{2+}
Radii (pm):	81	75	68	74
Ions:	Y^{3+}	Zr^{4+}	Mo^{4+}	Cd^{2+}
Radii (pm)	104	86	79	97

This is due to the change in the value of n from 3 to 4 for the two series of elements.

(c) Magnetic Behaviour

It has been observed that the magnetic properties of the first transition series elements could be easily interpreted and the magnetic moment of their ions/atoms or compounds can be represented by the spin only formula which gives the idea of the number of unpaired electrons in them. From this, the geometry of the complexes of these elements could be explained.

But the magnetic behaviour of the second transition elements is more complex and difficult to use the spin-only formula to get the number of unpaired electrons or the magnetic moment because the orbital contribution could not be ignored outrightly for the compounds / complexes of these elements.

This is because 4d-orbitals are too much spread out in space and as a result the inter electronic repulsions in these are much less as compared to first transition series orbitals. A given set of ligands produces very large crystal field splitting energy in 4d-orbitals than in 3d-orbitals. Therefore, heavier elements of this series will tend to give low-spin or inner orbital complexes as compared to those of first transition series which form mainly high-spin (or outer orbital) complexes.

2.5 SPECTRAL PROPERTIES AND STEREOCHEMISTRY OF THE ELEMENTS OF THE SECOND TRANSITION SERIES

We know that the electromagnetic radiations of white light such as sunlight consist of a continuous spectrum of wavelengths corresponding to different colours. If such a light falls on a compound, the light-matter interaction results in the absorption of either all the radiations giving black colour to the compound, or that of one radiation of a particular colour. In the latter

case, the light of different colour is transmitted or reflected which is the complementary colour of the absorbed colour and is the colour of the compound. If the compound does not absorb in the visible region, it appears white.

The transition metal ions / compounds / complexes show a variety of colours depending on the nature of metals and ligands. The colour of a compound arises due to the transition of electron(s) from ground state (lowest energy) to the excited state (higher energy). When a photon having energy equal to the difference between the two states, i.e., ground and excited state, strikes the compound or the ion, electronic transition (here promotion) takes place. In the complexes of the transition metals, this transition occurs from t_2g to e_g level in octahedral field and from e to t_2 level in tetrahedral ligand environment. The energy difference between the two states involved in electronic transition is given by (as given in the figure 2.1) the following:

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda} = h\nu \ (\because \nu = \frac{1}{\lambda})$$

Where ΔE = energy, h = Planck's constant, c = velocity of light, λ = wavelength of light absorbed, ν = frequency of light absorbed and ν = wave number.
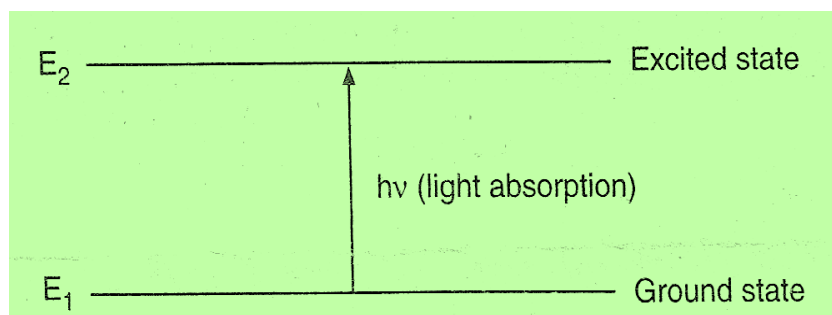
Fig. 2.1

The colour of the compound / complex exhibited due to the above transition is called the colour due to d-d transition. The examples of compounds / complexes which are coloured due to d-d transitions are provided by first transition (3d) series elements and a few heavier elements. Greater is Δ, more energy is required to cause the d-d transition. For 4d-series elements, increasing Δ value in octahedral field is: $Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+}$ etc.

The other types of electronic transitions which are responsible for the colours of the ions / compounds / complexes, particularly, of second transition (4d) series elements are the

charge transfer processes (C.T.) from metal to ligand or ligand to metal. The electronic spectra of the complexes/compounds of second and third transition series elements are less important than those of the complexes of first transition series elements because in the former case the d-d and C.T. bands cannot be separated but this is possible in the latter case. In the compounds/complexes of heavier elements of 4d series because of the larger magnitude of Δ (Crystal field splitting energy), the d-d bands are found at lower wavelengths and hence overlap with the C.T. bands. The charge transfer process is similar to the internal redox process because electron transfer takes place during this process from metal to ligand or ligand to metal within a complex/compound. In heavier transition metal complexes, the latter is generally observed. Thus, it is possible to classify and rank the metal ions according to their oxidising power Rh^{4+} > Ru^{4+} > Ru^{3+} > Pd^{2+} > Rh^{3+}, etc. Greater the oxidising power of the metal ion and also greater the reducing power of the ligands, lower the energy at which the C.T. bands appear.

Charge transfer transitions are Laporte and spin allowed, unlike d-d transitions, i.e., $\Delta l = \pm 1$ and $\Delta s = 0$ because in these transitions, there occurs a transition of electron(s) between the orbitals of different atoms, *viz.,* metal and ligand. These give rise to more intense or strong absorptions. When these transitions occur in visible region, the compound / complex shows intense colour.

These transitions are of four types:

(a) Ligand to metal transitions

(b) Metal to ligand transitions

(c) Intervalence or metal-to-metal transitions

(d) Intra ligand charge transfer

Among the oxo ions of 4d series elements, the decreasing order of energy of ligand to metal charge transfer is as follows:

$$NbO_4^{3-} > MoO_4^{2-} > TcO_4^{-}$$

But, the energy of charge transfer increases for the similar ions of 5d-series elements. For the above ions. The energy difference between 2p-orbitals of oxide ion and 4d-orbitals of the metal ions is very large lying in UV region and hence these ions are colourless.

An example of metal-metal (or inter valence) charge transfer is the Ru-complex given below: (Fig. 2.2)
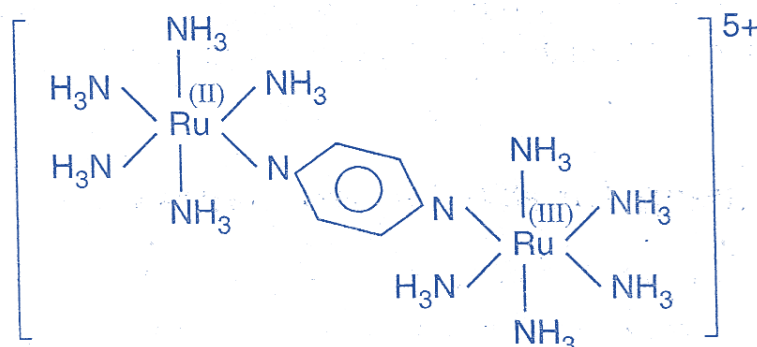
or $[(NH_3)_5Ru^{II} - Pyz - Ru^{III}(NH_3)_5]^{5+}$ where bridging ligand is pyrazine group. In this complex electronic transition occurs from Ru(II) to Ru(III) through Pyz-bridging ligand and gives intense colour. The compounds with M-M bonds also give intense colour, e.g., $[Mo_2Cl_8]^{4-}$ is red in colour. Also, the metal carbonyls with M-M bonds are often intensely coloured (e.g., polynuclear carbonyls).

Stereochemistry of the compounds and complexes

The stereochemistry of the compounds and complexes of the elements of this series may be summarized groupwise. The elements exhibit different stereochemistry depending on the oxidation state, coordination number and ligand in the particular compound/complex. For example, the stereochemistry of zirconium (Group 4) is tabulated below in Table 2.1.

Table 2.1: Oxidation states and stereochemistries of zirconiium compounds

Oxidation state	Coordination number	Geometry	Examples
Zr^0	6	Octahedral	$[Zr(bipy)_3]$
Zr^{3+}	6	Octahedral	ZrX_3 (X = Cl, Br,I)
Zr^{4+}	4	Tetrahedral	$[ZrCl_4]$, $[Zr(CH_2C_6H_5)_4]$
	6	Octahedral	$[ZrF_6]^{2-}$, $[ZrCl_6]^{2-}$, $[Zr(acac)_2Cl_2]$
	7		$[ZrF_7]^{3-}$

	8	Pentagonal bipyramidal Sqnare antiprism Dodecahedral	$[Zr(acac)_4]$ $[Zr(C_2O_4)_4]^{4-}$, $[ZrX_4.(diars)_2]$

The stereochemistry of niobium (Group 5 element) is being summarized below in Table 2.2.

Table 2.2: Oxidation states and stereochemistries of niobium compounds

Oxidation state	Coordination number	Geometry	Examples
-3	5	Trigonal bipyramidal	$[Nb(CO)_5]^{3-}$
-1	6	Octahedral	$[Nb(CO)_6]^-$
+3	6 8	Trigonal prism Octahedral Dodecahedral	$[NbO_2]^-$ $[Nb_2Cl_9]^{3-}$ $[Nb(CN)_8]^{5-}$
+4	6 7 8	Octahedral Distoted pentagonal bipyramidal Square antiprism Dodecahedral	$[NbCl_6]^{2-}$ $K_3[NbF_7]$ $[Nb(SCN)_4(dipy)_2]$ $K_4[Nb(CN)_8]$
+5	4 5 6	Tetrahedral Trigonal bipyramidal Octahedral	$[NbO_4]^-$ $[NbCl_5]$, $[Nb(NR_2)_5]$ $[NbCl_5.OPCl_3]$, $[NbCl_6]^-$

The stereochemistry of molybdenum (Group 6 element) is given below in Table 2.3.

Table 2.3: Oxidation states and stereo chemistries of molybdenum compounds

Oxidation state	Coordination number	Geometry	Examples
-2	5	Trigonal bipyramidal	$[Mo(CO)_5]^{2-}$
-1	6	Octahedral	$[M_2(CO)_{10}]^{2-}$
0	6	Octahedral	$[Mo(CO)_{6s}]$, $[Mo(CO)_5I]^{-}$
+2	6	Octahedral	$[Mo(diars)_2 X_2]$
	7	Capped trigonal prismatic	$[Mo(CNR)_7]^{2+}$
	9	Cluster compound	Mo_6Cl_{12}
+3	6	Octahedral	$[Mo(NCS)_6]^{3-}$, $[MoCl_6]^{3-}$
	8	Dodecahedral	$[Mo(CN)_7(H_2O)]^{4-}$
+4	6	Octahedral	$[Mo(NCS)_6]^{2-}$
	8	Dodecahedral	$[Mo(CN)_8]^{4-}$
+5	5	Trigonal bipyramidal	$MoCl_5$
	6	Octahedral	$[Mo_2Cl_{10}]$, $[MoOCl_5]^{2-}$
	8	Dodecahedral	$[Mo(CN)_8]^{3-}$
+6	4	Tetrahedral	$[MoO_4]^{2-}$, $[MoO_2Cl_2]$
	6	Octahedral	$[MoO_6]$, $[MoF_6]$

The stereochemistry of technetium (Group 7 element) is not much explored. Only very few examples of this element are known. Still, some of them are given in Table 2.4.

Table 2.4: Oxidation states and stereochemistries of technetium compounds

Oxidation state	Coordination number	Geometry	Examples
0	6	Octahedral	$[Tc_2(CO)_{10}]$
+2	6	Octahedral	$[Tc(diars)_2Cl_2]$
+3	6	Octahedral	$[Tc(diars)_2Cl_2]^+$
+4	6	Octahedral	$[TcX_6]^{2-}$
+5	5	Square pyramidal	$[TcOX_4]^-$
	8	Dodecahedral	$[M(diars)_2Cl_4]^+$
+6	6	Octahedral	$[TcF_6]$
+7	4	Tetrahedral	$[TcO_4]^-$, $[TcO_3Cl]$

The stereochemistry of ruthenium (Group 8 element) is being given in Table 2.5.

Table 2.5: Oxidation states and stereochemistries of ruthenium compounds

Oxidation state	Coordination number	Geometry	Examples
-2	4	Tetrahedral	$[Ru(CO)_4]^{2-}$
0	5	Trigonal bipyramidal	$[Ru(CO)_5]$, $[Ru(CO)_3(PPh_3)_2]$
+2	6	Octahedral	$[RuNOCl_5]^{2-}$, $[Ru(dipy)_3]^{2+}$
+3	6	Octahedral	$[Ru(NH_3)_5Cl]^{2+}$, $[Ru(H_2O)Cl_5]^{2-}$
+4	6	Octahedral	$K_2[RuCl_6]$
+5	6	Octahedral	$K[RuF_6]$, $[RuF_5]_4$

+6	4	Tetrahedral	$[RuO_4]^{2-}$
	5	Trigonal bipyramidal	$[RuO_3(OH)_2]^{2-}$
	6	Octahedral	$[RuF_6]$
+7	4	Tetrahedral	$[RuO_4]^-$
+8	4	Tetrahedral	$[RuO_4]$

The stereochemistry of rhodium (Group 9 element) has been given in Table. 2.6.

Table 2.6: Oxidation states and stereochemistries of rhodium compounds

Oxidation state	Coordination number	Geometry	Examples
-1	4	Tetrahedral	$[Rh(CO)_4]^-$
+1	3	Planar	$[Rh(PPh_3)_3]ClO_4$
	4	Tetrahedral	$[Rh(PMe_3)_4]^+$
	5	Trigonal bipyramidal	$[HRh(PF_3)_4]$
+3	5	Square pyramidal	$[RhI_2(CH_3)(PPh_3)_2]$
	6	Octahedral	$[Rh(H_2O)_6]^{3+}$, $[RhCl_6]^{3-}$
+4	6	Octahedral	$K_2[RhF_6]$
+6	6	Octahedral	$[RhF_6]$

The stereochemistry of less explored element palladium (group 10) has been given in Table. 2.7.

Table 2.7: Oxidation states and stereochemistries of palladium compounds

Oxidation state	Coordination number	Geometry	Examples
0	3	Planar	$[Pd(PPh_3)_3]$
	4	Tetrahedral	$[Pd(PF_3)_4]$
+2	4	Planar	$[Pd(NH_3)_4]Cl_2$
+4	6	Octahedral	$[PdCl_6]^{2-}$

The stereochemistry of silver (Group 11element) is being given below: Table. 2.8.

Table 2.9: Oxidation states and stereochemistries of silver compounds

Oxidation state	Coordination number	Geometry	Examples
+1	2	Linear	$Ag(CN)_2^-$, $Ag(NH_3)_2^+$
	4	Tetrahedral	$[Ag(SCN)_4]^{3-}$, $[Ag(py)_4]ClO_4$
	6	Octahedral	AgCl, AgF, Ag Br, (NaCl structure)
+2	4	Planar	$[Ag(py)_4]^{2+}$
+3	4	Planar	$[AgF_4]^-$
	6	Octahedral	$[Ag(IO_6)_2]^{7-}$, $[AgF_6]$

2.6 SUMMARY

- In this unit, an effort has been made to discuss the general characteristics of the elements of the second transition series such as their electronic configuration and variation in the oxidation states, magnetic behaviour, complex formation tendency, colour of the compounds/complexes, catalytic activity, formation of interstitial and non-stoichiometric compounds, metallic character and alloy formation along with the periodic properties and their variation across the period.

- A comparative account of these elements with their 3d analogues in respect to their ionic radii, oxidation states and magnetic behaviour has also been given. A brief discussion of spectral properties and a tabular account of the stereochemistry of the compounds of the elements of this series have also been recorded.

2.7 TERMINAL QUESTIONS

1. What are the transition elements? Why are they called so?
2. Mention three main factors that enable transition elements to form complexes.
3. Write down the names and symbols of 4d and 5d congeners of element manganese.
4. Which ion is more stable Ag^+ or Ag^{2+} and why?
5. Write down the valence shell electronic configuration of Pd (Z = 46).
6. Write down two applications of Pd as catalyst.

2.8 ANSWERS

3. Technetium (Tc) and rhenium (Re)

4. Ag^+ ion due to $4d^{10}$ configuration   5. $4d^{10} 5s^0$

UNIT-3 CHEMISTRY OF THE ELEMENTS OF THIRD TRANSITION (5d) SERIES

CONTENTS:

3.1 INTRODUCTION

The third transition series also contains ten elements and starts at lanthanum (La, Z = 57), the element of Group 3, with $5d^1 6s^2$ valence shell configuration. The next element of this series is hafnium (Hf, Z = 72), the element of Group 4, with $5d^2 6s^2$ configuration in the valence shell. In between these two d-block elements, there occurs a series of 14 elements (from Z = 58 to 71) which are called lanthanides because they succeed La and are closely related with it. These fourteen elements are also known as elements of 4f series. Thus, 5d series element La precedes and Hf succeeds the lanthanides. After Hf the filling of 5d subshell continues in tantalum (Ta, Z = 73), tungsten (W, Z = 74), rhenium (Re, Z = 75), osmium (Os, Z = 76), iridium (Ir, Z = 77), platinum (Pt, Z = 78), gold (Au, Z =79) and mercury (Hg, Z=80), the element of Group 12, with $5d^{10} 6s^2$ valence shell configuration. All the elements of this series have 2 electrons in 6s subshell and 5d subshell is being progressively filled with 1 to 10 electrons, except Au which has one electron ($6s^1$) due to the shifting of one s-electron to (n-1)d subshell to completely fill it (exchange energy effect). Because the last or the differentiating electron in the atoms of these elements enters the 5d subshell, the third transition series of elements is also known as 5d transition series.

These elements are much more important than those of the second transition series. This series of elements lies between barium (Ba, Z = 56), the elements of Group 2, and thallium (Tl, Z = 81), the element of Group 13 so the gradual transition of the properties occurs in the period. These elements also exhibit all the characteristic properties of the d-block elements as happens for those of first transition and second transition series.

3.2 OBJECTIVES

In this unit is to make the learners understand the :-

- general characteristics of the elements of the third transition (5d) series such as their electronic configuration, variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions/compounds, catalytic activity, formation of interstitial and non-stochiometric compounds, metallic character and alloy formation, their periodic properties such as atomic and ionic radii, melting and boding points, ionisation energies and reactivity, standard electrode potential and reducing property along with their variation in the series.

- The comparative study of ionic radii, oxidation states and magnetic behaviour of these elements with those of the 3d and 4d analogues will also to be given so that the learners may understand the similarity and differences between the elements of the three series. The learners will also be acquainted to the spectral properties and stereochemistry of the compounds of these elements to make them familiar with these aspects.

3.3 GENERAL CHARACTERISTICS OF THIRD TRANSITION (5-d) SERIES ELEMENTS

The general characteristics of these elements are as follows:

3.3.1 Electronic Configuration and Variable Oxidation States

The elements of this series show a regular trend in the electronic configuration of the valence shell like those of first transition series. The general valence shell electronic configuration of these elements is $5d^{1-10}6s^{1,2}$. The last two elements, *viz,* gold and mercury have completely filled 5d-subshell (i.e.$5d^{10}$) whereas all other elements have 1 to 8 electrons, i.e., $5d^{1-8}$ in the d-subshell of penultimate shell. As has been given in the introduction, only Au has $6s^1$ configuration and all other elements have $6s^2$ configuration in the last shell, In Au exchange energy effect plays an important role to cause the sifting of one 6s-electron to 5d-subshell so that it has stable $5d^{10}$ configuration (i.e. $5d^{10} 6s^1$ valence shell configuration) as was the case with copper (3d series) and silver (4d series).

Like the elements of first and second transition series, the elements of this series also exist in various oxidation states in their compounds, i.e., the variation of the oxidation states is equally pronounced in the elements of all the three series (i.e., 3d, 4d- and 5d-). This is due to the availability of several electrons in 5d and 6s sub shells whose energies are fairly close to each other like the elements of other series and under different conditions different number of electrons can be used from both the subshells for chemical bonding.

It has been observed that like the members of second transition series and in contrany to those of first transition series, the higher oxidation states become more stable and pronounced for the elements of this series also. The minimum oxidation state varies from +1 to + 3 for these elements in general La and Hf have +3, elements in the middle have +2 and the last two elements, *viz,* Au and Hg have +1 minimum oxidation states. It is interesting to note that for the elements up to the middle from the left, the highest oxidation state of an element is

equal to the group number of the element but this analogy does not apply to the latter elements as happens for elements of second transition series. This has been shown below:

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Group number	3	4	5	6	7	8	9	10	11	12
Lowest ox. state	+3	+3	+4	+2	+3	+2	+2	+2	+1	+1
Highest ox. state	+3	+4	+5	+6	+7	+8	+6	+4	+3	+2

From this table it is clear that the lowest oxidation state is +1 for both Au and Hg and the highest oxidation state is +8 for Os which is the highest stable oxidation state among all the transition elements.

3.3.2 Complex Formation Tendency

Most of the elements of this series also have the complex formation tendency though to a lesser extent because of the weak electropositive nature and non-availability of wide range of ligands. Still, some of them form complexes with halide, cyanide, NH_3, H_2O and π-ligands (such as CO). The examples of the complexes are given below:

Hafnium gives complexes of the type $[HfCl_4.2POCl_3]$, $[HfF_6]^{2-}$, $[Hf(acac)_4]$, $[Hf(C_2O_4)_4]^{4-}$, etc. Ta forms complexes of the type $[Ta(CO)_6]^-$, $[TaCl_6]^{2-}$, $[TaF_6]^-$, $[TaF_7]^{2-}$, $[Ta(S_2C_6H_4)_3]^-$,etc. and also gives clusters of $[Ta_6X_{12}]^{2+}$ type with halides.

Tungsten, like its 3d and 4d analogues chromium and molybdenum, forms a large number of complexes e.g. $[W(CO)_6]^{2-}$, $[W_2(CO)_{10}]^{2-}$, $[W(CO)_6]$, $[W_2Cl_9]^{3-}$, $[W(CN)_8]^{4-}$, $[WF_6]^-$,etc.

Rhenium gives various complexes with halides, pyridine and CO in different oxidation states, e.g., $[Re_2(CO)_{10}]$, $[ReCl(CO)_5]$, and $[ReCl_2(Py)_2]$, $[Re_2Cl_8]^{2-}$, $[ReF_8]^{2-}$, $[ReH_9]^{2-}$, etc.

The complexes of Ir, Pt and Au in different oxidation states with various ligands are given below:

$[Ir_4(CO)_{12}]$, $[IrCl_6]^{2-}$, $[IrCl_3(H_2O)_3]^+$, $[IrCl_4(H_2O)_2]$, $[Ir(C_2O_4)_3]^{2-}$
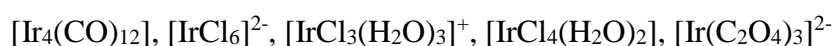
Pt gives complexes in two coordination numbers which are related with the oxidation states, i.e., oxidation state +2, coordination number 4 and oxidation state +4, coordination number 6. For example, $[PtCl_4]^{2-}$, $[Pt(NH_3)_2Cl_2]$, $[PtCl_6]^{2-}$, $[Pt(NH_3)_4Cl_2]^{2+}$, etc. Similarly, gold forms complexes such as $K[Au(CN)_2]$ (oxidation state +1, coordination number 2), $K[AuCl_4]$ (oxidation state +3, coordination number 4), $[AuI_2(diars)_2]^+$ (oxidation state +4, coordination number 6), etc.

The complex formation in the lower oxidation states by these elements provides an excellent tool for stabilisation of these otherwise unstable oxidation states.

3.3.3 Magnetic Properties

As discussed earlier, chemical substances may be diamagnetic, paramagnetic or ferromagnetic. Diamagnetism is inherent in every substance irrespective of the presence or absence of paramagnetism and ferromagnetism. s- and p-block elements always give diamagnetic compounds, the compounds or the ions of ferrous metals, *viz,* iron, cobalt and nickel have ferromagnetism and there is attraction between these substances and the magnetic field. Ferromagnetic ions are permanently magnetized and not demagnetized even after removal from the applied magnetic field. Most of the d-block elements either in the elemental or ionic form (in the compounds/complexes) are paramagnetic due to the presence of unpaired d-electrons in them. The property of paramagnetism, in particular, is expressed in terms of magnetic moment, expressed by the term μ which has the unit of Bohr magneton, B.M. This is related with the number of unpaired electrons, n by the expression:

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \quad \text{B. M.}$$

Based on this expression the magnetic moments for various substances can be calculated and compared with those obtained experimentally. The substance containing the metal ion with the highest number of unpaired electrons will have the maximum magnetic moment.

The above formula of μ has been arrived at by taking into consideration only spin motion of the electrons assuming that in the compounds or complexes of d-block elements, the orbital motion is quenched (or suppressed). If the orbital motion of the electrons is also considered and taken into account, the formula for μ is given as has been mentioned in point 2.3.3 (magnetic properties of second transition series elements).

3.3.4 Formation of coloured Ions/compounds

The analogy given for the elements of the first transition series as well as for those of the second transition series to exhibit colour also applies to the elements of this series. In a solid state or a solution, the compounds or complexes are coloured though only a few such compounds or complexes are known. The elements of the 5d-transition series which have unpaired electrons only can exhibit colour due to the usual reasons as has been discussed above for 3d- and 4d-transition series elements. The attached atoms (in the compounds) or ligands (in the complexes) are also responsible for the type of colour of the compound because these affect the transition of electron (s) within the subshell or between the subshells. The selection rules for electronic transitions also play an important role in determining the intensity of the colour of the ions/complexes/compounds. If any of the selection rules says that a particular transition is forbidden but it occurs due to the breakdown of the selection rule, the intensity of colour produced is low, i.e., dull. But if the transition is allowed, the intensity of the colour is high, i.e., fast. That is why some compounds are dull coloured but some others have very intense colour.

3.3.5 Catalytic Activity

The elements of third transition series and their compounds also show the catalytic activity, some of them being very important and useful catalysts in a variety of reactions used in industry. Some of the examples in which these elements or their compounds act as catalysts are given below:

(a) Pt/PtO is used as Radian's catalyst in the oxidation reactions.

(b) Pt gauze catalyses the oxidation of NH_3 to NO at high temperature and the process is used in the manufacture of nitric acid by Ostwald's process.

(c) Mixture of Pt and Pd is used as a catalyst in the hydrogenation of unsaturated hydrocarbons.

(d) Platinised asbestos catalyses the reaction between SO_2 and O_2 in the manufacture of H_2SO_4 by contact process.

(e) Pt black is used to prepare formaldehyde from methyl alcohol.

(f) Red hot finely divided Pt is used in the preparation of hydrogen halides from hydrogen and halogens.

(g) Finely divided Pt is widely used in many hydrogenation and dehydrogenation reactions.

(h) Large quantities of Pt are also used in petrolium industry, synthetic fiber industry and glass industry.

3.3.6 Formation of Interstitial and Non-stoichiometric compounds

The elements of third transition series also form interstitial compounds with small non-metallic elements such as hydrogen, carbon and nitrogen. During the formation of these compounds, there is no change in the lattice structure of the metal because the non-metallic atoms just fit in the voids of metal lattice. Examples are:

$$TaH_{0.78}, HfC, TaC, WC, W_2C, HgN, TaN, W_2N \text{ etc.}$$
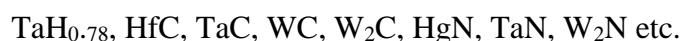
Many of these compounds are non-stoichiometric types like $TaH_{0.78}$, etc. Such compounds have semi-conductivity properties and centres of colour. The non-stoichiometry is, perhaps, due to the defects in the solid structures of transition elements. The apparent molecular formula shows whole number ratio but actually it is not so.

3.3.7 Metallic Character and Alloy Formation

All the elements of this series are metals, most of them hard. Some of them are malleable and ductile (e.g. Au, Pt etc.). All the elements of the series are solids except Hg which among all the d-block elements exists as a liquid at ordinary temperature. These are good conductors of heat and electricity. These elements also crystallise in one of the close lattice structures as has been given for 3d and 4d series elements. Keeping aside Hg, all the metals of the series have high melting points.

In all three series, it has been observed that the metals of Groups 8, 9, 10 and 11 (i.e. those of VIII and IB) are softer and more ductile which can be explained in the light of their crystal structure. These metals crystallize to form face-centred cubic (fcc) lattice type close-packed crystal lattice with a large number of planes where deformation can occur, while others crystallise with hexagonal close-packed (hcp) or body-centred cubic (bcc) lattice type close-packed structure. The hardness of the d-block elements indicates the presence of covalent bonding. The number of covalent bonds gives the measure of the overall bond strength and hardness of the metal. Because the unpaired d-electrons can also take part in covalent bond formation and their number increases from Group 3 to 6 $\{(n-1)d^5ns^1\}$. Hence, the metallic lattice becomes stronger and then strength decreases progressively.

These metals also form alloys but only a few alloys have been prepared and used because of the rare nature of these elements, Na-Hg and Al-Hg alloys have been used as reducing agents called amalgams. Pt-Ir alloy is used to prepare coins, standard weights etc. Pt-Ru & Pt-Cu alloys are also important materials. The metals like Pt, Au and Hg are very important, the first two, i.z., Pt and Au are used in jewellery. Gold is also used as coinage metal and in preparing ornamental vessels.

3.3.8 Periodic Properties and their variation along the Series

The periodic properties of the elements of the third transition series such as the atomic radii, atomic volumes, ionic radii, melting and boiling points, ionisation energies and reactivity, standard electrode potentials and reducing properties etc. vary along the series (period) from the first element to the last one. For some properties the variation is regular and for the other it is irregular, particularly at the end of the series.

(a) Atomic Raddi, Atomic Volumes and Ionic Radii

The values of atomic radii for these elements have been found to decrease from La to Os, the element in the middle and then have an increasing tendency up to the last element, Hg. The values are very close from W to Pt because, perhaps, of the increased screening effect of the 5d-electrons which neutralises the nuclear pull exerted on the 6s- 6s-electrons. Then the screening effect becomes more effective in the later elements that too are still more pronounced in the last element, Hg which has atomic radius only less than that of La and more than that of any element of the series. This trend has been shown below:

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic radius(pm)	169	144	134	130	128	126	127	130	136	150

The atomic volumes of the elements also have a similar trend as is found for the atomic radii. The values first decrease in the series up to the middle and then increase till the last element. Atomic volumes for various elements of the series are being given below:

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Atomic volume(cm^3)	22.50	13.60	10.90	9.52	8.85	8.44	8.54	9.10	10.22	14.80

The ionic radii follow almost the same trend as the atomic radii for most of the elements. Ionic radii of the elements have been obtained in different oxidation states and the trend along the series can only be established for the ions having the same oxidation state. Some values have been given below:

Metal ion	La^{3+}	Hf^{4+}	Ta^{5+}	W^{4+}	Re^{5+}	Os^{4+}	Ir^{3+}	Pt^{4+}	Au^{3+}	Hg^{2+}
Ionic radius (pm)	117	85	70	80	72	77	82	77	85	106

It has been observed that the ionic radii of the cations of different elements in the same oxidation state generally decrease with the increasing nuclear charge or the atomic number. The ionic radii of the elements of the third transition series are almost the same as those of the corresponding cations derived from the elements of the second transition series. The similarity in their ionic radii is due to the presence of fourteen lanthanides between La and Hf.

(b) Melting and Boiling Points

The melting and boiling points of these elements are very high except for Hg, a liquid in physical state with very low melting or freezing point (-38.4^0C). For these elements, the values have been listed below:

Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Melting point (^{0}C)	920	2222	2996	3410	3180	2700	2454	1769	1063	-38.4

From the list, it is clear that Hf, Ta, W, Re, Os, and Ir have very high melting points in comparison to La, Pt, Au & of course Hg. The boiling points of all these elements are above 3000^0C leaving aside Hg which has low boiling point of 357^0C.

(c) Ionization Energies and Reactivity

The first ionization energy values of these elements increase gradually as we move from left to right in the series from La to Hg. The values in kJ/mole have been given below:

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
First ionization energy (kJ/mole)	538	684	761	770	760	840	880	870	890	1008

If compared with the first ionization energies of the elements of the second transition series, it can be observed that Y has a higher value than La (both elements are members of Group 3) due to its smaller size. From Hf to Hg, these elements have higher values of first ionisation energies than those of the elements of the second transition series. This is attributed to the increased nuclear charge in the elements of this series though the atomic sizes of the elements of both the series, *viz*, 4d and 5d series do not vary much. Thus, a higher nuclear charge causes a strong inward pull on the outer electrons which are, therefore, strongly held with the nuclei and their removal becomes difficult. This ultimately results in the higher values of first ionization energies for these elements. Hg has an exceptionally high value of first ionization energy because more energy is required to remove an electron from the stable $5d^{10}6s^2$ configuration of this element.

Due to high ionization energies and other factors discussed in section 1.3 above, these elements show low reactivity, such that some of these elements, *viz*, Ir, Pt, Au, etc. are known as noble metals due to their passive nature towards the chemical reactions with other elements and reagents.

(d) Standard Electrode Potentials and Reducing Properties

The two terms, i.e., standard electrode potentials (reduction) and the reducing properties of the elements are intimately related with each other.

For 3d- and 4d-transition series elements some examples have been given earlier and it has been stated that metals with negative values of standard electrode potential as compared to standard hydrogen electrode, for which E^0 value is taken as zero, act as reducing agents. Such

metals can displace hydrogen gas from dilute acids as well as other metals from their solutions. But there are metals, particularly some d-block elements, which have positive values of standard electrode (reduction) potentials with the tendency to get reduced by H_2 itself or metals with negative standard electrode potential values. Cu and Ag are such metals belonging to 3d- and 4d-transition series. Among the 5d-transition series elements, Pt, Au and Hg provide the excellent examples of such metals as is given below:

$$Au^+ + e \rightarrow Au, \qquad E^0 = + 1.68 \text{ V}$$

$$Au^{3+} + 3e \rightarrow Au \qquad E^0 = + 1.42 \text{ V}$$

$$Pt^{2+} + 2e \rightarrow Pt \qquad E^0 \ = \ + 1.20 \text{ V}$$

$$Hg^{2+} + 2e \rightarrow Hg \qquad E^0 = + 0.85 \text{ V}$$
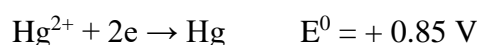
These metals may thus, act as oxidising agents and have a tendency to take up the electrons. They hardly provide electrons for reduction.

3.4 COMPARATIVE STUDY OF THE ELEMENTS OF THIRD TRANSITION SERIES AND THE FIRST TRANSITION SERIES

(a) Oxidation states

It has been observed that the elements of both these transition series exhibit variable oxidation states including both common and uncommon. As has been stated earlier that lower oxidation states are most stable and their chemistry is more pronounced for the elements of first transition (3d) series while their higher oxidation state is less stable. That is why their compounds in the higher oxidation states are more reactive and less stable. This fact can be exemplified by taking the strong oxidising nature of dichromate ($Cr_2O_7^{2-}$, oxidation state of Cr = +6) and permanganate (MnO_4^-, oxidation state of Mn = +7) ions. These ions under suitable conditions take part in redox reactions and get reduced to Cr(III) and Mn(II) states which are stable.

Lower oxidation states are of relatively little importance for most of the elements of third transition series. The Ir^{2+} ion (5d) is hardly known but its 3d analogue, Co^{2+} is quite stable in aqueous medium. Similarly, Ir^{3+} ion does not form complex with NH_3 molecule while $[Co(NH_3)_6]^{3+}$ is highly stable in aqueous medium. In manganese group (Group 7), Mn^{2+} ion

(3d) is stable; Re^{2+} ion (5d) is unstable and occurs only in some complexes with π-ligands and metal clusters. Similarly, Cr^{3+} ion (3d-trasition series) forms a large number of complexes and other normal compounds, W^{3+} ion (5d-transition series) forms only a few complexes.

The higher oxidation state is generally more stable for the elements of the third transition series than that for the elements of the first transition series. For example, OsO_4, WCl_6, PtF_6, etc. are quite stable while FeO_4, $CrCl_6$, NiF_6, etc. are not known. Also, WO_4^{2-} ion is highly stable and is not reduced easily whereas CrO_4^{2-} is strong oxidising agent and is readily reduced to +3 states. Similarly, MnO_4^- is a strong oxidising agent but ReO_4^- is a stable and very weak oxidising agent.

The highest oxidation state for 5d-transition series elements is +8 in OsO_4 while that for 3d-transition series elements is +7 in MnO_4^- ions.

(b) Ionic Radii

It has been observed that the ionic radii of 3d-series elements are smaller than those of the 5d-series elements but there is only a small difference between the radii of the ions of 4d- and 5d-series elements. Thus 3d < 4d < 5d. This has been shown below in the comparative table of the ionic radii of the elements of the two series.

Ions:	Sc^{3+}	Ti^{4+}	Cr^{4+}	Zn^{2+}
Radii (pm):	81	75	68	74
Ions:	La^{3+}	Hf^{4+}	W^{4+}	Hg^{2+}
Radii (pm):	117	85	80	106

The change in the values after lanthanides is small because of the lanthanide contraction.

(c) Magnetic Behaviour

As has been mentioned earlier that the magnetic properties of the elements of first transition series could be interpreted easily and the magnetic moments of their ions/atoms or compounds can be represented by the spin only formula. The calculated magnetic moment in this way gives an idea of the number of unpaired electrons in them as well as the type of geometry of the complexes of these metals can be predicted.

It has been observed that the magnetic behaviour of the elements of third transition series is more complex and difficult to explain by using the spin only formula. Thus, the magnetic moment from the number of unpaired electrons is difficult to find out in the compounds or complexes of these elements. This is because 5d orbitals are too much diffused or spread out in space and hence, the interelectronic repulsions in these are much less in comparison to 3d orbitals (of the elements of the first transition series) Hence, a given set of ligands produces very large crystal field splitting energies in 5d orbitals than in 3d orbitals. The heavier elements of this series will, therefore, tend to give inner orbital or low spin complexes as compared to those of first transition series which generally form outer orbital or high spin complexes.

3.5 SPECTRAL PROPERTIES AND STEREOCHEMISTRY OF THIRD TRANSITION SERIES ELEMENTS

Most of the compounds/complexes of transition metals are highly coloured because the metal ions are capable of absorbing radiant energy in the visible region of the electromagnetic spectrum causing d-d transition.

As has been discussed in Units 1 and 2, the d-d transitions (i.e., the electronic transition between two sets of d-orbitals) are responsible for the electronic spectra and colour of the ions/compounds/complexes of transition metals. But this transition only occurs when the radiation or photon of correct energy interacts with the compound/complex having an energy difference between two d-orbital sets of central metal ions equal to that associated with the photon. This type of transition is called d-d transition and the colours exhibited by the compounds/complexes of the elements of the first transition series are due mainly to these transitions.

It has been observed that the d-d transitions (electronic spectra) of the compounds/complexes of third transition (5d-) series elements are less important than those of the complexes of first transition series elements because more energy is required for causing d-d transitions due to greater value of Δ, the crystal field splitting energy. In the octahedral ligand field, the increasing Δ_0 is as follows: $Ir^{3+} < Re^{4+} < Pt^{4+}$, etc.

The other types of electronic transitions which are encountered in the complexes of the third transition series elements and responsible for their colours are mainly the charge transfer spectra (C.T.) in which electronic transition occurs from metal to ligand or ligand to metal preferably the latter. Sometimes M-M transition is also observed in some polynuclear complexes. In the compounds/complexes of heavier elements of 5d-series, because of the larger magnitude of Δ (crystal field splitting energy), the d-d bands are found at lower wavelengths or higher frequency and hence, overlap with the charge transfer bands. The charge transfer implies the transfer of electron from one atom to another, i.e. from metal to ligand atom or from ligand atom to metal within the complex/compound and thus reflects the internal redox tendencies of both the central metal atoms/ions and ligands. Thus, it is possible to classify and rank metal ions according to their oxidising power:

$$Os^{4+} > Re^{4+} = Os^{3+} = Pt^{4+} > Pt^{2+} > Ir^{3+}$$
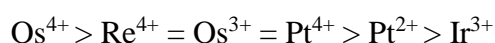
The greater the oxidising power of the metal ion and also greater the reducing power of the ligand, the lower the energy at which the charge transfer (L→M) bands appear.

The compounds with M-M bonds also give intense colour, e.g., $[Re_2Cl_8]^{2-}$ is royal blue. The metal carbonyls of these elements with M-M bonds are often intensely coloured.

Because the d-d transitions may be spin-forbidden as well as are Laporte-forbidden, the breakdown of the selection rules gives light colours to the complexes. But charge transfer transitions give rise to strong absorptions and when these transitions occur in the visible region, the complex/compound shows intense colour, this is because the C.T. transitions are both spin and Laporte allowed.

Stereochemistry of the complexes and compounds

It is easier to summarize the stereochemistry of the compounds and complexes of the elements of this series group-wise. Depending on the oxidation state, coordination number and type of ligands present in the complexes or the atoms in the compounds, the elements show different stereochemistries. The stereochemistry of hafnium though less explored (Group 4 element) is tabulated here Table. 3.1.

Table 3.1: Oxidation states

Oxidation state	Coordination number	Geometry	Examples
0	6	Octahedral	$[(arene)_2HfPMe_3]$
3+	6	Octahedral	$[HfI_3]$
4+	6	Octahedral	$[HfF_6]^{2-}$, $[Hf(acac)_4]$, $[Hf(C_2O_4)_4]^{4-}$
	7	Pentagonal bipyramidal Monoclinic	$[HfF_7]^{3-}$ $[HfO_2]$

The stereochemistry of tantalum (Group 5 element) in different oxidation states is summarized in Table 3.2.

Table 3.2 Oxidation states and stereochemistries of tantalum compounds

Oxidation state	Coordination number	Geometry	Examples
-3	5	Trigonal bipyramidal	$[Ta(CO)_5]^{3-}$
-1	6	Octahedral	$[Ta(CO)_6]^-$
+3	6	Octahedral	$[Ta_2Cl_6(SMe_2)_3]$
+4	6	Octahedral	$[TaCl_4py_2]$, $[TaCl_6]^{2-}$
	8	Square antiprism	$[Ta_2Cl_8(PMe_3)_4]$
+5	5	Trigonal bipyramidal	$TaCl_5$
	6	Octahedral	$[TaO_3]^-$, $[Ta_2Cl_{10}]$, $[TaCl_6]^-$
	8	Square antiprism	$[TaF_8]^{3-}$

The stereochemistry of tungsten (group 6 element in different oxidation states) is tabulated below: Table. 3.3.

Table 3.3 Oxidation states and stereochemistries of tungsten compounds

Oxidation state	Coordination number	Geometry	Examples
0	6	Octahedral	$[W(CO)_6]$
+3	6	Octahedral	$[W(diars)(CO)_3Br_2]^+$
+4	6	Octahedral	$[WBr_4Me_2]$
	8	Dodecahedral	$[W(CN)_8]^{4-}$
+5	6	Octahedral	$[WF_6]^-$
	8	Dodecahedral	$[W(CN)_8]^{3-}$
+6	4	Tetrahedral	$[WO_4]^{2-}$
	6	Octahedral	$[WCl_6]$
	8	Dodecahedral	$[WF_8]^{2-}$

Stereochemistry of rhenium (Group 7 element) in different oxidation states is more pronounced than its 4d congener Tc which has been tabulated below in Table.3.4.

Table 3.4 Oxidation states and stereochemistries of rhenium compounds

Oxidation state	Coordination number	Geometry	Examples
0	6	Octahedral	$[Re_2(CO)_{10}]$
+1	5	Trigonal bipyramidal	$[ReCl(CO)_2(PPh_3)_2]$
	6	Octahedral	$[Re(CO)_5Cl]$, $[Re(CN)_6]^{5-}$

Oxidation state	Coordination number	Geometry	Examples
+2	6	Octahedral	$[ReCl(N_2)(PR_3)_4]^+$, $[Re(bipy)_3]^{2+}$
+3	6	Octahedral	$[ReCl_2(acac)(PPh_3)_2]$
	7	Pentagonal bipyramidal	$[Re(CN)_7]^{4-}$
+4	6	Octahedral	$[ReX_6]^{2-}$, $[Re_2OCl_{10}]^{4-}$
+5	5	Trigonal bipyramidal	$ReCl_5$, ReF_5
	6	Octahedral	$[ReOCl_3(PPh_3)_2]$, $[ReOCl_5]^{2-}$
	8	Dodecahedral	$[Re(diars)_2Cl_4]^+$
+6	4	Tetrahedral (distort.)	$[ReO_4]^{2-}$
	5	Square pyramidal	$[ReOCl_4]$
	6	Octahedral	$[ReF_6]^-$, $[Re(CH_3)_6]^-$
	8	Square antiprism	$[ReF_8]^{2-}$
+7	4	Tetrahedral	$[ReO_4]^-$, $[ReOCl_3]$
	7	Pentagonal bipyramidal	$[ReF_7]$
	9	Tricapped trigonal prismatic	$[ReH_9]^{2-}$

Stereochemistry of osmium (Group 8 element) in various oxidation states is being given in Table 3.5.

Table 3.5 Oxidation states and stereochemistries of osmium compounds

Oxidation state	Coordination number	Geometry	Examples

0	5	Trigonal bipyramidal	$[Os(CO)_5]$, $[Os(CO)_4 X]_2$
+2	6	Octahedral	$[Os(CN)_6]^{4-}$
+3	6	Octahedral	$[OsCl_6]^{3-}$, $[Os(dipy)_3]^{3+}$
+4	4	tetrahedral	$[OsPh_4]$
	6	Octahedral	$K_2[OsCl_6]$
	7	Distorted pentagonal bipyramidal	$[OsH_3(PPh_3)_4]^+$
+5	6	Octahedral	$Na[OsF_6]$
+6	5	Square pyramidal	$[OsOCl_4]$
	6	Octahedral	$[OsF_6]$, $[OsO_2Cl_4]^{2-}$, $[OsO_2(OH)_4]^{2-}$
+7	4	Tetrahedral	$[OsO_4]^-$
	6	Octahedral	$[OsOF_5]$
+8	4	Tetrahedral	$[OsO_4]$
	6	Octahedral	$[OsO_3F_3]^-$, $[OsO_4(OH)_2]^{2-}$

Stereochemistry of iridium (Group 9 element) in various oxidation states has been summarized in Table 3.6.

Table 3.6 Oxidation states and stereochemistries of iridium compounds

Oxidation state	Coordination number	Geometry	Examples
-1	4	Tetrahedral	$[Ir(CO)_3PPh_3]^-$

+1	4	Planar	$[IrCl(CO)(PR_3)_2]$
	5	Trigonal bipyramidal	$[HIr(CO)(PPh_3)_3]$
+3	5	Trigonal bipyramidal	$[IrH_3(PR_3)_2]$
	6	Octahedral	$[IrH_3(PPh_3)_3]$, $[IrCl_6]^{3-}$
+4	6	Octahedral	$[IrCl_6]^{2-}$, $[Ir(C_2O_4)_3]^{2-}$
+5	6	Octahedral	$Cs[IrF_6]$
+6	6	Octahedral	$[IrF_6]$

The stereochemistry of platinum (Group 10 element) in different oxidation states is being given in Table 3.7.

Table 3.7 Oxidation states and stereochemistries of some platinum compounds

Oxidation state	Coordination number	Geometry	Examples
0	4	Tetrahedral	$[Pt(CO)(PPh_3)_3]$
+2	4	Square planar	$[PtCl_4]^{2-}$
	6	Octahedral	$[Pt(NO)Cl_5]^{2-}$
+4	6	Octahedral	$[Pt(en)_2Cl_2]^{2+}$, $[Pt(NH_3)_6]^{4+}$, $[PtCl_6]^{2-}$
+5	6	Octahedral	$[PtF_6]^{-}$
+6	6	Octahedral	$[PtF_6]$

The stereochemistry of gold (element of Group 11) is being given in Table 3.8.

Table 3.8 Oxidation states and stereochemistries of some gold compounds

Oxidation state	Coordination number	Geometry	Examples
+1	2	Linear	$[Au(CN)_2]^-$
	3	Trigonal planar	$[AuCl(PPh_3)_2]$
	4	Tetrahedral	$[Au(diars)_2]^+$
+3	4	Planar	$[AuBr_4]^-$, $[AuPh_4]^-$
	5	Trigonal bipyramidal	$[Au(diars)_2I]^{2+}$
	6	Octahedral	$[AuBr_6]^{3-}$,

3.6 SUMMARY

In this unit, you have studied the

- General characteristics of the elements of third transition series, *viz*., electronic configuration and variable oxidation states, magnetic behaviour, complex formation tendency, formation of coloured compounds/complexes, catalytic activity, metallic character and alloy formation, formation of interstitial and non-stoichiometric compounds along with the periodic properties such as atomic and ionic radii, melting and boiling points, ionisation energy and reactivity, standard electrode (reduction) potential and reducing properties etc with their variation along the transition series.

- Efforts has also been made to record a comparative account of these elements with their 3d- analogues in respect to their ionic radii, oxidation states and magnetic behaviour. The spectral properties and stereochemistry of the elements in the form of tables have also been given to make it easy to understand the subject.

3.7 TERMINAL QUESTIONS

1. Write down the names and symbols of the elements of third transition series.
2. The maximum oxidation state of osmium is

    (a) 4   (b) 6   (c) 8   (d) 10

3. The oxidation state of tungsten in [WCl_6] is

    (a) $+2$ (b) $+4$ (c) $+5$ (d) $+6$

4. The formation of coloured compounds/complexes by the elements of 5d-transition series is due to

    (a) d-d transitions   (b) Charge transfer transitions

    (c) ransitions in UV region   (d) None of above

5. The atomic radii of second and third transition series elements are close to one another. True/false

6. Write down two catalytic applications of Pt.

3.8 ANSWERS

1. Please see the text

2. c

3. d

4. b

5. True

6. Please see the text.

UNIT-4 COORDINATION COMPOUNDS

CONTENTS:

4.1   INTRODUCTION

You have already studied in your earlier classes that there are two types of compounds. The compounds that can easily dissociate into their constituent ions in aqueous medium are called simple salts and double salts such as NaCl, $MgCl_2$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, etc. On the other hand, the compounds which donot dissociate into their constituent ions in any solvent are known as coordination or complex compounds such as $[Cu(NH_3)_4]^{2+}$. Transition metals can form several coordination compounds due to their small size, high charge and presence of empty d orbitals on the metal ion. A compound formed from the union of metal ion (an electron-deficient species, central metal atom/ion; Lewis's acid) and electron rich species (ligand; Lewis's base) which can donate one electron pair is called coordination compound or complex compound. The   coordination compounds can be represented by the general formula, $[ML_n]^{\pm m}$, where M is a metal ion, L is electron rich species; n is the number of L attached to the metal atom/ion and m is the charge on complex ion.

Some metal complexes were prepared and used in the eighteenth century in the form of metal salts and vegetable extracts as paints. The first well known coordination compound was Prussian blue, $Fe_4[Fe(CN)_6]_3$ in the beginning of eighteenth century. In 1798, $CoCl_3.6NH_3$ was discovered. Werner gave a theory to understand the bonding in such compounds about a century later in 1893. We are studying chemistry of coordination compounds because they have many applications in analytical / environmental chemistry, metallurgy, biological systems, industries and medicine.

4.2 OBJECTIVES

By the end of this Unit, you will be able to define the following terms:

* What is Coordination compound, Ligand, Coordination number (CN), Complex ion, Coordination sphere, Chelate, Primary valency, Secondary valency,
* Effective Atomic Number (EAN),
* Applications of coordination compounds,
* Name of coordination compounds,
* How to determine oxidation state of metal ion in a coordination compound.

4.3 LIGANDS AND THEIR TYPES

The electron rich species, which may be charged species, e.g. Cl^-, CN^-, NO_2^-, etc or neutral species e.g. H_2O, NH_3, $NH_2CH_2C_2NH_2$, CO, NO, etc., that can donate an electron pair to the metal atom/ion are called ligands.

4.3.1 Types of ligands

The ligands can be classified in the following ways:

4.3.1.1 Type I- Based on electron accepter/donor properties of the ligand

- **σ (sigma) donor ligands** are those ligands which can only donate electron pair to the meal ion, e.g. H_2O, NH_3, F^-. These ligands are also known as weak field ligands.

- **σ (sigma) donor and Π (pi) accepter ligands** are those ligands which can donate electron pair and also have a tendency to accept electrons in their empty antibonding π molecular orbitals (MO). Such ligands can be involved in back bonding (π bond) with the metal ion. For example, CO, CN^-, NO, etc. These ligands are also known as strong field ligands.

- **Π (pi) donor ligands are ligands** like benzene and ethylene, which do not have lone pair of electrons but only π electrons for donation to the metal atom/ion.

4.3.1.2 Type II- Based based on number of donor atoms in the ligand

- **Monodentate or unidentate ligands:** The ligands that bound to a metal ion through a single donor atom are called as monodentate or unidentate ligands, e.g. Cl^-, H_2O or NH_3. These ligands can be further divided into the following subclasses based on charge (**Figure 6.1**).

- **Ambidentate ligands:** Some ligands have two or more than two different donor atoms. These ligands can attach through any of the donor atoms. They are given different names depending upon the nature of the donor atom linked to the metal atom. These ligands are known as ambidentate ligands e.g. NO_2 (donor atom may be either N or O), SCN^- (donor atom may be either S or N), CN^- (donor atom may be either C or N), $S_2O_3^{2-}$ (donor atom may be either S or N). These are also monodentate ligands.
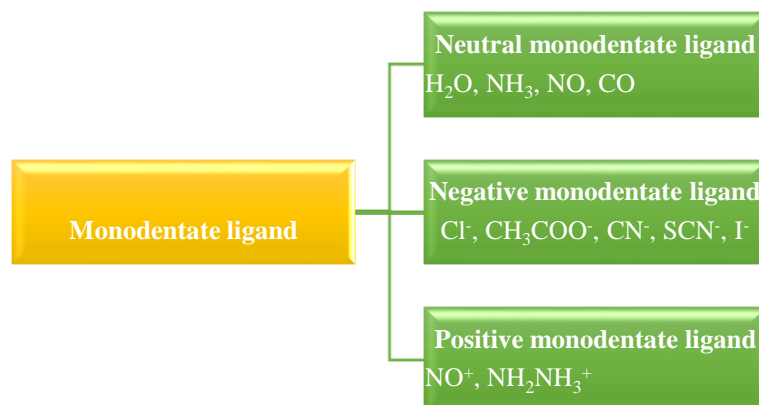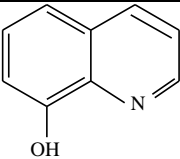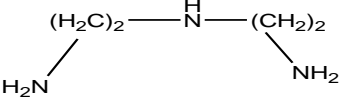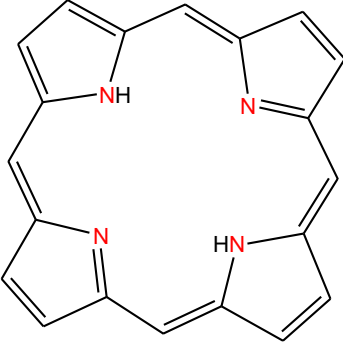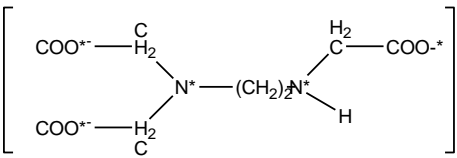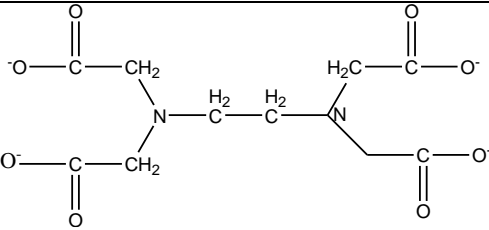
Figure 4.1: Classification of monodentate ligands

- **Polydentate (bidentate, tridentate, tetradentate, pentadentate, hexadentate) ligands**

These ligands bind to a metalatom/ion through two, three, four, five and six donor atoms, respectively. These ligands are also known as chelating ligands. These ligands form ring-type (chelates) compounds (**Table 4.1**).

Table 4.1: Polydentate ligands

Ligand type	Ligand name	Ligand formula/structure
Bidentate	oxalate ion	
	1,10-phenanthroline	
	ethylenediamine (en)	
	dimethylglyoxime	

	8-hydroxyquinoline	
Tridentate	diethylenetriamine	
Tetradentate	triethylenetetramine	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$
	porphyrin ring	
Pentadentate	ethylenediaminetriacetato	
Hexadentate	ethylenediaminetetraacetate (EDTA)	

Red colour letter in the structure represents the donor atom of the ligand.

4.3.1.3 Type III- Based on size of ligand

- **Chelating ligands** are those ligands that bind via more than one atom and form chelate complexes (ring complexes). These complexes are more stable than complexes formed from <u>monodentate</u> ligands. The enhanced stability is known as the <u>chelate effect</u>.
- **Macrocyclic ligands** are the chelating ligands that can form a large ring and surround the central atom or ion partially or fully and bond to it. The central atom or ion resides at the centre of the large ring. This complex formed is more rigid and inert as compared to the

chelate compound and is known as macrocyclic complex. <u>Heme</u> is a macrocyclic complex in which the central <u>iron</u> atom is present at the centre of a <u>porphyrin</u> macrocyclic ring. Dimethylglyoximate complex of nickel is a synthetic macrocycle formed from the reaction of nickel ion with dimethylglyoxime (**Fgure 4.2**) in ammonical medium.
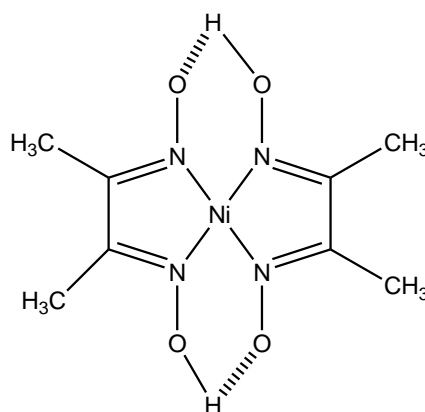
Figure 4.2: Nickel(II) bisdimethylglyoximate

The order of ligands to form stable compounds

Macrocyclic > Chelate > Monodentate

4.3.1.4 Type IV- Based on their use in reactions

- **Actor ligands** are those ligands which take part in a chemical reaction.

- **Spectator ligands are tightly coordinating polydentate liangds** which do not take part in a chemical reaction. Phosphines, allyl groups in catalysis, trispyrazolylborates (Tp), cyclopentadienyl ligands (Cp) and many chelating diphosphines such as 1,2-bis(diphenylphosphino) ethane ligands (dppe) are spectator ligands.

4.3.2 Complex ion

A complex ion is an ion in which the metal ion is present at the center and a definite number of ligands surround it. The complex ion is enclosed in a large bracket. e.g.

$[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$
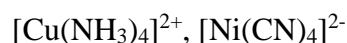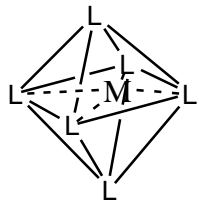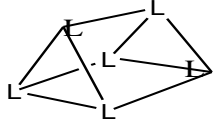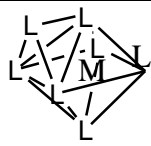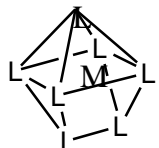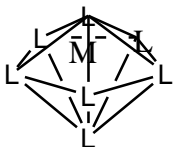
4.3.3 Coordination number (CN)
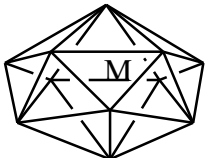
The coordination number of a metal atom/ion is the number of ligands attached to it in a complex compound. Coordination number may be two, three, four, five, six, seven, eight, nine or even higher in case of lanthanides and actinides (**Table 4.2**). Coordination number depends on size, charge and electronic configuration and nature of meal/ion and ligands. For example,

– large metal atoms show high CN

– bulky ligands reduce coordination number

– Lewis bases easily donate electrons to metals and metals with lesser number of electrons can accept electrons.

Table 4.2: Coordination numbers (CN) and geometry of coordination compounds

S.N.	CN	Metals	Ligands	Type of geometry	Geometry of complex
1	2	d-electron rich metals like Cu^+, Ag^+ $[Ag(NH_3)_2]^+$ $[Cu(NH_3)_2]^+$ (uncommon)	Large ligands CH_3	Linear	
2	4	Small, high oxidation state, lower d metals d^8 metal atoms or ions such as Ni^{2+}, Rh^+, Ir+, Pt^{2+}, Pd^{2+}, $Au^{3+, 6+}$ $[Cu(NH_3)_4]^{2+}$ $[Zn(CN)_4]^{2-}$	Large Pi bonding ligands	Tetrahedral Square planar	
3	5	Allows fluxionality and Berry pseudorotation $[Ni(CN)_5]^{3-}$ (Rare)		Trigonal bipyramidal Square pyramidal	

4	6	$[Fe(H_2O)_6]^{2+}$ $[Ni(NH_3)_6]^{2+}$ $[Fe(CN)_6]^{4-}$ (Very common) (Rare)	All types of ligands	Octahedral	
			Three bidentate ligands such as dithiolates or oxalates	Trigonal prismatic	
5	7	Generally shown by rare earths $K_3[NbOF_6]$ (Very rare)		Capped octahedron	
				Capped trigonal prism	
		Uncommon		Pentagonal bipyramid	
6	8	Generally shown by rare earth metal ions (Very rare)	For eight equivalent ligands	Dodecahedron	
				Cube	
		Large metal ions (Rare)			
		Uncommon		Square antiprism	
		Common		Hexagonal bipyramidal	

7	9	Very rare		Three-face centred trigonal prism (Tricapped trigonal prism)	
8	10	Generally shown by rare earth elements		Bicapped square antiprism	
AA	11	Very rare		All-faced capped trigonal prism (Octadecahedron)	
10	12	Generally shown by rare earths		Icosahedron	

4.3.4 Coordination sphere

The coordination sphere of a coordination compound comprises the central metal atom/ion and ligands attached to it. The coordination sphere is enclosed in brackets [ ].

Coordination sphere $[Co(NH_3)_6]^{3+}$

4.3.5 Counter ions

The ions excluding the coordination sphere are called as counter ions. In $K_4[Fe(CN)_6]$ compound, K^+ is the counter ion.

4.4   WERNER'S   COORDINATION   THEORY   AND   ITS EXPERIMENTAL VERIFICATION

Alfred Werner in 1893 suggested a new theory for explaining the nature of bonding in coordination compounds known as Werner's theory. According to this theory, there are two kinds of valences of metal atoms/ions in coordination compounds: primary and secondary valences

- The attachment of species that satisfy both primary as well as secondary valences is shown by ------ solid-broken line

Explanation of structure of Co(III) complexes based on Werner's theory (**Figure 4.3**).

(a)   (b)   (c)   (d)
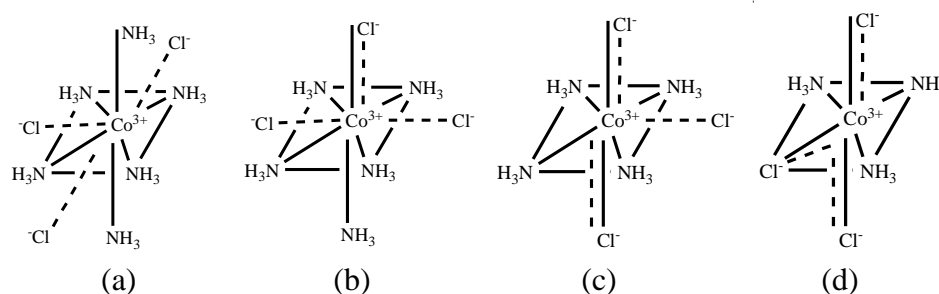
Figure 4.3 Structure of Co(III) amine complexes based on Werner's theory. In all the complexes the primary valency of Co is 3 and secondary valency is 6. (a) $CoCl_3.6NH_3$ $[Co(NH_3)_6]Cl_3$ (b) $CoCl_3.5NH_3$ $[Co(NH_3)_5Cl]Cl_2$ (c) $CoCl_3.4NH_3$ $[Co(NH_3)_4Cl_2]Cl$ (d) $CoCl_3.3NH_3$ $[Co(NH_3)_3Cl_3]$

4.4.1 Werner's theory can be explained based on experimental evidence

- **Molar conductivity measurement method**

Compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ show decreasing order of conductivity due to the formation of 4 ions, 3 ions, 2 ions and no ions, respectively in solution.

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (1 complex ion + 3 chloride ions)

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (1complex ion +2chloride ions)

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$ (1 complex ion+1chloride ion)

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$ (No ions)
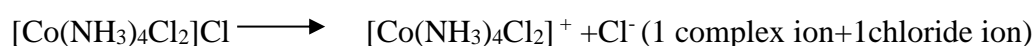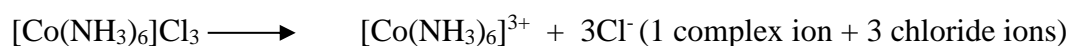
- **Precipitation method**

When cobalt ammine chloride complexes react with $AgNO_3$, some of the Cl^- ions get precipitated with $AgNO_3$ to form $AgCl$. The number of Cl^- ions that are ionizable and present outside the coordination sphere can react with $AgNO_3$. Thus, coordination compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ react with 3, 2 and 1 mole of $AgNO_3$ to form 3, 2 and 1 mole of $AgCl$, respectively as there are 3, 2 and 1 ionisable Cl^- ions, respectively.

4.4.2 Defects of Werner's theory

- Although the theory describes the structure of many compounds, it can't explain the nature of bonding between metal atom/ion and ligands.

  - Werner's theory was unable to explain why 4- and 6-coordination numbers are the preferred coordination numbers.

4.5 EFFECTIVE ATOMIC NUMBER CONCEPT (EAN CONCEPT)

This rule is given by English Chemist Nevil V. Sidgwick. Effective atomic number (EAN) is the total number of electrons in metal atom/ion (atomic number) plus the electrons gained from ligands. This EAN is the atomic number of a noble gas. Therefore, EAN decides stability of the coordination compound. If a coordination compound follows EAN rule, than it is stable one.

EAN= Atomic number of metal atom/ion + number of e^- donated by ligands or 2 x number of ligands (as each ligand can donate two electrons to metal atom/ion).

For $[Co(NH_3)_6]^{3+}$

Atomic number of Co=27; Atomic number of Co^{3+}=24; there are six ligands hence electrons donated by 6 ligands = 6 x 2

EAN = 24 + (6 x 2) = 36 (atomic number of Krypton; Kr)

For $[Ni(CO)_4]$

Atomic number of Ni=28; there are four ligands hence electrons donated by 4 ligands = 4 x 2

EAN = 28 + (4 x 2) = 36 (atomic number of Krypton; Kr)

For $[Fe(CN)_6]^{4-}$

Atomic number of Fe=26; Atomic number of Fe^{2+}=24; there are six ligands hence electrons donated 6 ligands = 6 x 2

EAN = 24 + (6 x 2) = 36 (atomic number of Krypton;

For $[Ag(NH_3)_4]^+$

Atomic number of Ag=47; Atomic number of Ag^+=46; there are four ligands, hence electrons donated by 4 ligands = 4 x 2

EAN = 46 + (4 x 2) = 54 (atomic number of Xenon; Xe)

= 54 (atomic number of Xenon; Xe)

For $[V(CO)_6]^-$

Atomic number of V=23; Atomic number of V^- = 24; there are six ligands hence electrons donated 6 ligands = 6 x 2

EAN = 24 + (6 x 2)

= 36 (atomic number of Krypton; Kr)

For $[Mn(CN)_4]^{2-}$

Atomic number of Mn=25; Atomic number of Mn^{2+} = 23; there are four ligands hence electrons donated 4 ligands = 4 x 2

EAN = 23 + (4 x 2)

= 31

Not obeying EAN rule as 31 is not the atomic number of any noble gas

4.6 CHELATE

A chelate is a stable coordination compound in which a metal atom/ion is attached to ligand (s) with more than one donor site producing one or more rings (**Figure 4.4**). These compounds are also called as cyclic or chelated complexes and the formation of such rings is called as chelation or cyclisation. Classification of chelates depends upon the type and nature of chelating ligands such as bidentate chelates (with bidentate ligands), tridentate chelates (with tridentate ligands) etc.
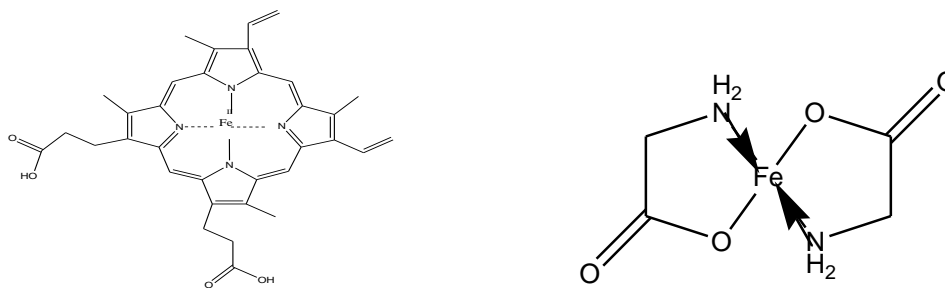
Figure 4.4: Chelates of iron

4.6.1 Applications of chelates

Chelates are useful in water softening, medicical and analytical chemistry and different industries such as chemical and food industry and agriculture.

(i) In water softening: Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions are responsible for the hardening of water. These ions on reaction with soaps precipitate out. In the presence of chelating ligands such as polyphosphates and polydentate amino acids, no precipitation occurs as these ions form chelate complexes with polyphosphate and polydentate ligands present in soap and thus, soften water.

(ii) In food industry: Metal-amino acid chelates help enhance mineral absorption such as Ferrous bis-glycinate. Chelates are also used to preserve fruits, fruit juices, foodstuffs, etc.

(iii) In agriculture: Metal chelates are used as common components of fertilizers in agriculture. Micronutrients such as manganese, iron, zinc, and copper are required for the overall health of the plants. These micronutrients along with EDTA form chelate fertilizers. The presence of chelates enhances the uptake of micronutrients by the plants. Chelating ligands are also used to detoxify poisonous metal such as mercury, arsenic and lead present in polluted water.

(iv) In the medical field: Tetracycline and quinolone can form chelate with Fe^{2+}, Ca^{2+}, and Mg^{2+} ions and thus, these chelates can be used as supplements of these ions. As EDTA softens the dentin, it is used in root canal treatment as an intracanal irritant. Chelates of gadolinium are used as contrast agents in MRI scans. Metal poisoning can be decreased by chelation with EDTA as toxic metals such as mercury, arsenic, lead, and other radioactive metals can be excreted without further interaction with the body by converting them into chemically inert form (EDTA metal complex). Chelation is also used in the treatment for autism.

(v) Chemical applications: Homogeneous catalyst such as ruthenium(II) chloride chelated with BINAP (a bidentate phosphine) is used in Noyori asymmetric hydrogenation and

asymmetric isomerisation for the manufacture of synthetic (–)-menthol. Bio-Rust and Evapo-Rust are chelating agents used for the removal of rust from iron and steel. Metal chelates are also used in dyeing industry.

(vi) Physiological chemistry (in human body): In body fluids, citric, malic, and tartaric acids, the natural chelating agents, keep the metal ions away from precipitation. The other physiologically important chelates are haemoglobin, vitamin B_{12}, chrorophyll, cytochrome and plastocyanine

4.6.2 Stability of chelates

Stability of chelates can be explained based on standard free energy change (ΔG^o), standard entropy change (ΔS^o), steric effect, size of ring and number of rings.

(i) Change in thermodynamic variables: Consider the formation of coordination compounds of cadmium with monodentate and bidentate ligands, e.g.,

$$[Cd(H_2O)_4]^{2+} + 4CH_3NH_2 \longrightarrow [Cd(CH_3NH_2)_4]^{2+} + 4H_2O.....i, \Delta H^o\text{=-ve}$$

Monodentate ligand   Non-chelated compound

1 molecule   4 molecules   1 molecule   4 molecules

$$[Cd(H_2O)_4]^{2+} + 2en \longrightarrow [Cd(en)_2]^{2+} + 4H_2O...............ii, \Delta H^o\text{=-ve}$$

1 molecule   2 molecules   1 molecule   4 molecule

Bidentate ligand   Chelated compound
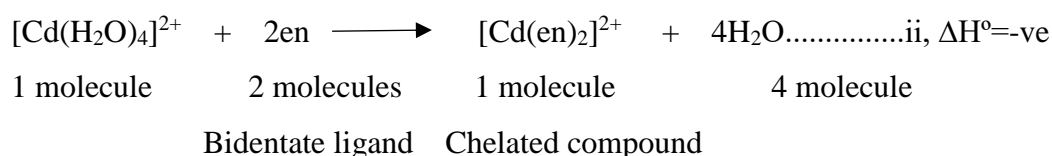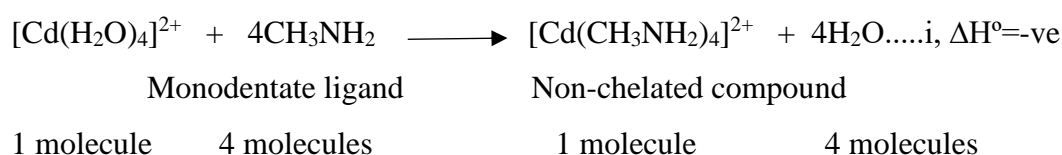
Stability of the product in a chemical reaction can be explained by the following reaction:

$\Delta G^o = (\Delta H^o) - (T\Delta S^o)$ where ΔH^o is the change in enthalpy and T is the temperature.

You already know that a product will be stable if the value of ΔG^o is negative (-ve) and value of ΔS^o is positive (+ve).

During the formation of a nonchelated compound with monodentate ligands (i), the number of molecules on both sides is equal (5 molecules on each side), hence ΔS^o will be zero and the value of ΔG^o will be negative.

With bidentate ligand (ii), number of product molecules (5 molecules) is greater than the number of reactant molecules (3 molecules). Hence, entropy of product is greater than reactants and thus, ΔS^o will be positive and value of ΔG^o will become more negative. Thus, it may be concluded that ΔG^o has a more negative value for chelates which are formed by the reaction of

bidentate or other polydentate ligands and therefore, are more stable as compared to the nonchelated compounds.

(ii) Steric effect: When a group is present on the donor atom or near the donor atom of a ligand, the metal-ligand bonds become weak and thus, lower the stability of that compound. This effect is known as the steric effect or steric hindrance. Among complex compounds I and II, compound II will be more stable as in compound I, there is one methyl group near the donor atom N which causes the steric effect.

(I) and (II)
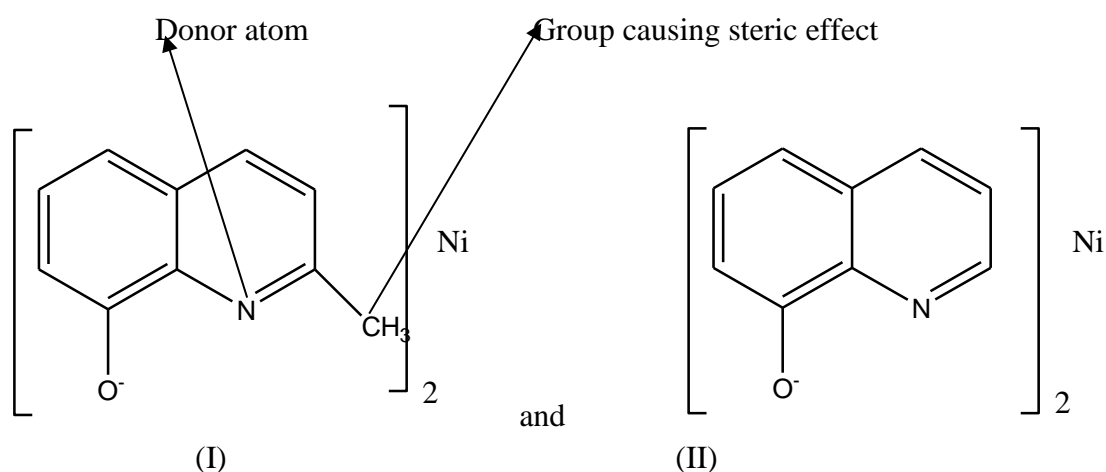
(iii) Size of chelate ring: Chelate ring having 5-members give stable compounds and chelate rings having more or less than 5-members are generally less stable. This happens because the stability constant for 5-membered chelate is the highest.

(iv) Number of rings: The Greater the number of rings, more will be the stability of the chelate. As the number of donor atoms in a chelating ligand increases, stability increase due to the increase in the number of chelate rings.

Stability order of the chelates with the bi- and tridentate ligands.

en (number of rings=1) < trien (number of rings = 3)
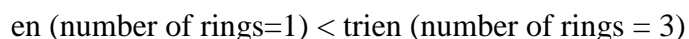
4.7 NOMENCLATURE OF COORDINATION COMPOUNDS

The coordination compounds are named according to the following steps suggested by IUPAC (International Union of Pure and Applied Chemistry) (**Figure 4.5**).

Step I: Naming of ions

- The positively charged metal ion is written first followed by the negative ions in **ionic compounds**.

$FeCl_2$: Iron (II) chloride

KCl   : Potassium (I) chloride

- Names of **non-ionic or molecular complexes** are written as one word without any gap.

$K_4[Fe(CN)_6]$: Potassium (**positive ion**) hexacyano(ligand)ferrate (**central ion**)(III)

(non ionic compound)

$[Pt(NH_3)_4]^{4+}$: Tetraammineplatinum (IV)

The name in red is one word without any gap as it is a complex ion.

Step II: Naming coordination sphere

- In the case of the complex ion (coordination sphere), the name of the ligands written first then only the central metal atom/ion along with its oxidation number in parenthesis should be written.

$[Ni(CO)_4]$ - Tetracarbonylnickel(0)

$[Pt(NH_3)_4]^{4+}$ - Tetraammineplatinum(IV)

Ending of name: If the complex is anionic, the suffix **ate** is added to the name of metal along with the oxidation state in parenthesis.

$K_2[HgCl_4]$ Potassium tetrachloridomercur**ate**(II)

Step III: At the last, the name of anion which is present on the outside of the coordination sphere should be written, e.g.,

$[Pt(NH_3)_4]Cl_4$ - Tetraammineplatinum(IV) **chloride**

$[Co(NH_3)_6]Cl_3$ - Hexaamminecobalt(III) **chloride**

- **Names of some common ligands**

Ligands are named alphabetically along with a prefix (di, tri, tetra, penta etc for simple ligands and bis, tris, tetrakis etc. for complicated ligands) of their number. Some of the common ligands are given in **Table 4.3.**

Table 4.3: Name and abbreviation of ligands

Type of ligands	Category of ligand	Formula	Name
Simple ligands	Neutral (written as a neutral molecule)	H_2O	Aqua
		NH_3	Ammine
		CO	Carbonyl
		NO	Nitrosyl
		F^-	fluorido
		Cl^-	chlorido

	Anionic (-o at the end of ligand's name)		
		Br^-	bromido
		I^-	iodido
		OH^-	hydroxido
		CN^-	cyanido
		$C_2O_4^{2-}$	oxalato
		NO_3^-	nitrato
		CO_3^{2-}	carbonato
		NH_2^-	amido
		H^-	hydrido
		NO_2^-	nitrito-N
		ONO^-	nitrito-O
		O^{2-}	oxido
		O_2^{2-}	peroxido
		N_3^-	azido
		S^{2-}	sulphido
		$C_6H_5^-$	phenyl
		NH_2^-	amido
		NH^{2-}	imido
		$C_5H_5^-$	cyclopentadienyl
	Cationic (-ium at the end of ligand's name)	NO^+	Nitrosonium
		NO_2^+	nitronium
Complicated ligands with abbreviation	en	$C_2H_8N_2$	ethylendiamine
	py	C_5H_5N	pyridine
	ox	$C_2O_4^{2-}$	oxalato
	dmso	$(CH_3)_2SO$	dimethyl sulfoxide
	EDTA	$C_8H_{12}N_2O_8^{4-}$	ethylenediamine tetraacetato
	gly	$NH_2CH_2CO_2^-$	glycinato
	oxine	C_9H_7NO	8-hydroxyquinolinato
	phen	$C_{12}H_8N_2$	1,10-phenanthroline
	dmg	$C_4H_7N_2O_2$	dimethylglyoximato
	ur	NH_2CONH_2	urea
	tu	H_2NCSNH_2	Thiourea
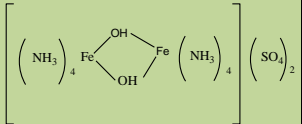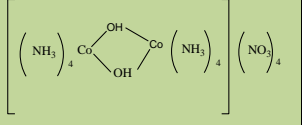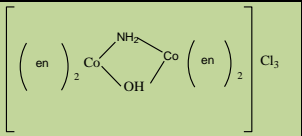
Naming of bridging complexes

The bridging groups in the complexes are written first with the prefix μ by separating it from the complex by a hyphen (-). This μ is used every time for each bridging ligand. Thereafter,

the other liands with number prefix (di, tri or bis-, tris- etc.), metal with oxidation state in the bracket and at last the negative species outside the coordination sphere.

Type of complex/ compound		Formula of compound	Name of compound
Simple (one ion is complex and other simple ion)	Complexes with neutral coordination sphere	[Ni(CO)$_4$]	Tetracarbonylnickel(0)
		[Fe(C$_5$H$_5$)$_2$]	Bis(cyclopentadienyl)iron (II)
		[Pt(en)$_2$Cl$_2$]	Dichlorobis(ethylenediamine)platinum(II)
		[Hg(CH$_3$)$_2$]	Dimethylmercury(II)
		[Mn$_3$(CO)$_{12}$]	Dodecacarbonyltrimanganese (0)
		[Ni(PF$_3$)$_4$]	Tetrakis(trifluorophosphine)nickel(0)
	Complexes with anionic coordination sphere	K$_2$[HgCl$_4$]	Potassium tetrachloromercurate(II)
		K$_4$[Cu(CN)$_6$]	Potassium hexacyanocuperate(II)
		Na$_3$[Co(NO$_2$)$_6$]	Sodium hexanitrito-Ncobaltate(III)
		K$_2$[Fe(CN)$_5$NO]	Potassium pentacyanonitosylferrate(III)
		Na[Au(CN)$_2$]	Sodium dicyanoaurate(I)
		K$_3$[Cr(CN)$_6$]	Potassium hexacyanochromate(III)
		K$_4$[Ni(CN)$_4$]	Potassium tetracyanonickelate(0)
		Na$_3$[Fe(C$_2$O$_4$)$_3$]	Sodium trioxalatoferrate(III)
		Fe[Fe(CN)$_6$]	Iron hexacyanoferrate(III)
		K$_4$[Fe(CN)$_6$]	Potassium hexacyanoferrate(II)
		K$_3$[Fe(CN)$_6$]	Potassium hexacyanoferrate(III)
		Na$_2$[ZnCl$_4$]	Sodium tetrachlorozincate(II)
		[Cr(C$_2$O$_4$)$_3$]$^{3-}$	Trioxalatochromate(III)
		[Co(N$_3$)(NH$_3$)$_5$)]SO$_4$	Pentaammineazidocobalt(III) sulphate
		[Cr(H$_2$O)$_6$]Cl$_3$	Hexaaquachromium(III) chloride
		[Cr(NH$_3$)$_6$]$^{3+}$	Hexaammine chromium(III) ion

		$[Cr(H_2O)_4Cl_2]NO_3$	Tetraaquadichlorochromium(III) nitrate
	Complexes with cationic coordination sphere		
		$[Cu(NH_3)_2(en)]Br_2$	Diammine(ethylenediamine)copper(II) bromide
		$[PtClBr(NH_3)py]$	Amminebromochloropyridinepalatinum(II)
		$[CuCl_2(CH_3NH_2)_2]$ Complex ligand	Dichloro**bis**(methylamine)copper(II) ion
		$[Co(NH_3)_5ONO]SO_4$	Pentaamminenitritocobalt(III) sulphate
		$[Co(NH_3)_2(H_2O)_2(CN)_2]Cl$	Diamminediaquadicyanocobalt(III) chloride
		$[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$	Diamminetriaquahydroxochromium(III) nitrate
Both cation and anion are complex		$[Pt(NH_3)_4][PtCl_4]$ (Firstly complex cation is named then only the complex anion)	Tetraammineplatinum(II) tetrachloropalatinate(II)
		$[Cr(NH_3)_5(NCS)][ZnCl_4]$	Pentaammineisothiocyanatochromium (III) tetrachlorozincate(II)
			Octaaqua-μ-dihydroxo-diiron(III) sulphae or

Bridging complex **????**	 ?????	Tetraammineiron(III)-μ-dihydroxo- tetraammineiron(III) or μ-dihydroxo-octaaquadiiron(III) sulphate or μ-Hydroxo-tetraaquairon(III)μ- hydroxo-tetraaquairon(III) sulphate
		μ-Dihydroxo-octaamminedicobalt(III) nitrate
		μ-Amido-μ-hydroxo- tetrakis(ethylenediamine)dicobalt(III) sulphate

- **Calculation of oxidation number of metal atom/ion**

In coordination compound, $[M(L)_n]^{\pm}$ or $[M(L)_n]$, the oxidation state of M can be calculated as the Oxidation number of M + Oxidation number of L x n = ± or 0

For example,

1) Oxidation number (ON) of Co in $[Co(NH_3)_6]^{3+}$

ON of Co + 0 (ON of NH_3 is 0) = +3

Hence, ON of Co will be +3.

2) Oxidation number (ON) of Ni in $[Ni(CO)_4]$

ON of Ni + 0 (ON of CO is 0) = 0

Hence, ON of Ni will be 0.

4.8 SUMMARY

In this Unit, you have studied the following:

- Simple or double salts dissociate into their constituent ions while coordination compounds break up into complex ions and its counter-charged ion.

- Coordination compounds comprise of two main parts; central metal atom/ion and ligands coordinated to the metal atom/ion.
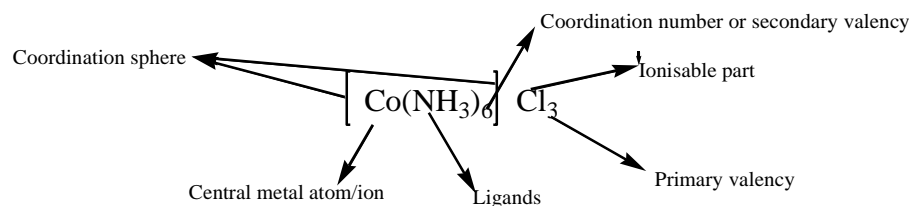
- A wide variety of ligands including monodentae, polydentate, sigma donor, chelating, macrocyclic, actor and spectator ligands are involved in the formation of coordination compounds with metal atom/ion.

- Monodentate lingads can donate a pair of electrons to a central metal atom while a polydentate ligand can donate more than one pair of electrons to the metal atom/ion. Bidentate or polydentate ligands form cyclic compounds called chelates.

- Coordination compounds have various applications in different industries.

- Werner suggested that the coordination number and oxidation number of metal depend on the nature of the metal.

- EAN rule decides the stability of a coordination compound.

- Nomenclature of coordination compounds is systematic.

4.9 DEFINITIONS

Chelate: Chelate is a compound containing a ligand (typically organic) bonded to a central metal atom at two or more points.

Complex ion: A complex ion is an ion formed by the coordination of central metal ion with one or more ligands.

Coordination compound: A compound in which a central atom/ion is bonded to a definite number of ligands.

Coordination number: It is the number of ligands surrounding the central metal ion.

Effective Atomic Number: It is the sum of the electrons of metal atom/ion and electrons donated by ligand.

Ligand- Ligand is a charged or neutral molecule which can done electron pair to the metal atom to form a coordination compound.

Primary valency: Primary valency in a coordination compound is the number of negative ions that satisfy the positive charge on the central metal ion.

Secondary valency: Secondary valency in a coordination compound is defined as the number of ligands that are coordinated to the central metal ion. It is equal to the coordination number.

4.10 TERMINAL QUESTIONS

4.10.1 Short answer questions

1. Which of the following ligands are weak or strong?

CN^-, CO, H_2O, NH_3

2. Classify the following ligands as pi acceptor or sigma donor ligands.

NO, Cl^-, NH_3, benzene

3. Give two examples of each neutral and positive monodentate ligand.

4. What is chelate effect?

5. Select monodentate and polydentate ligands among the following:

NCS^-, NH_3, $C_2O_4^{2-}$, EDTA, en, Cl^-

6. Draw the structures of the following ligands:

EDTA, dmg, porphyrin, 8-quinoline, diethylenetriamine

7. Explain spectator ligand.

8. How chelates are useful?

9. What do you mean by complex ion?

10. Calculate oxidation state and coordination number of Fe in $[Fe(CN)_6]^{4-}$ and $[Fe(C_2O_4)_3]^{3-}$?

11. Draw the geometry that describe five and six-coordinate compounds. Which structures are more common?

12. Give the geometry of the following compounds:

(i) $[Co(NH_3)_6]^{3+}$ (ii) $[Ag(NH_3)_2]^+$ (iii) $[Fe(CN)_6]^{4-}$ (iv) $[Fe(C_2O_4)_3]^{3-}$

13. Define coordination sphere.

14. What is primary valency?

15. What do you mean by secondary valency?

16. On the basis of Werner's theory, draw the structure of $CoCl_3.6NH_3$ and $CoCl_3.5NH_3$.

17. Name the experimental methods to explain Werner's theory?

18. Define EAN rule.

19. Who gave the concept of EAN rule?

20. Calculate EAN for $[Ni(CO)_4]$.

21. Calculate the oxidation number of the metal atom/ ion in the following coordination complexes:

   a) $[CoCl_4]^{2-}$ b) $[Fe(CN)_6]^{3-}$ c) $[Ni(CO)_4]$ d) $[Cr(CO)_6]$

22. Name the following ligands:

        Cl^-, H^-, NO^+, H_2O, NO_3^-, ONO^-, NH_2^-, $C_5H_5^-$
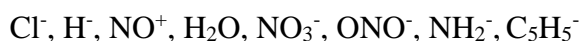
23. Write down the abbreviation and formula of the following ligands: ethylenedimmine, dimethyl sulphoxide, glycine, urea, 1,10-phenanthroline, ethylenediammine tetraacetic acid.

24. Name the following coordination compounds:

  a. $Na_3[Co(NO_2)_6]$,   b. $K_4[Ni(CN)_4]$,   c. $[Mn_3(CO)_{12}]$,   d. $K_3[Fe(CN)_6]$,   e. $[Pt(NH_3)_4][PtCl_4]$

25. Write down the formula of hexamminecobalt (III) chloride and tetracarbonyl nickel (0).

26. Draw the structure of the following complexes:

       a) Sodium hexafluoroslilicate (IV)

       b) Ammonium diamminetetra(isothiocyanato)chromate(III)

27. How does the conductivity of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ differ from each other?

28. Write the formula of the following compounds:

       a) Octaammine-μ-amido-μ-nitridocobalt(III) nitrate

       b) Dichlorobis(ethylenediamine)cobalt(III) chloride

       c) Hexaaquairon(II) sulphate

       d) Tetrachloroplatinate(II)

29. Which of the following complexes follow EAN rule? Give electron count in each case.

 a. $[Cr(NH_3)_6]^{3+}$, b. $[Ni(NH_3)_6]^{2+}$, c. $[Cr(CO)_6]$, d. $[Mn(CN)_6]^{4-}$, e. $[Fe(H_2O)_6]^{2+}$, f. $[Fe(CN)_6]^{4+}$

30. Explain the meaning of the terms monodentate, bidentate and tetradentate.

31. Arrange the following complexes in the increasing order of molar conductivity:

       a) $[Co(NH_3)_6]Cl_3$ b) $[Co(NH_3)_5Cl]Cl_2$ c) $[Co(NH_3)_3Cl_3]$

4.10.2 Long type questions

1. What is the difference between chelating and macrocyclic ligands? Explain with the help of examples.

2. What are chelates? How are they important? Give examples.

3. Define ligand. Give a detailed account of the classification of ligands.

4. How are the coordination compounds named? Describe with the help of examples.

5. What is the EAN rule? Give details with examples.

6. Explain Werner's theory.

7. What do you mean by coordination number? How is it useful in deciding the geometry of

coordination compounds? Explain with the help of examples.

8. What are primary and secondary valencies? Explain by giving suitable examples.

9. Explain in detail about the stability of chelates.

ANSWER

Short answer questions:

1. Weak ligands- H_2O, NH_3; strong ligands - CN^-, CO

2. pi acceptor ligands- NO, C_6H_6; sigma donor ligands- Cl^-, NH_3

3. Neutral monodentate ligands- NH_3, H_2O; positive monodentate ligands- NO^+, $NH_2NH_3^+$.

4. Chelating ligands are those ligands that bind via more than one atom and form chelate complexes (ring complexes). These complexes are more stable than complexes formed from <u>monodentate</u> ligands. The enhanced stability is known as the <u>chelate effect</u>.

5. Monodentate ligands: NCS^-, NH_3, Cl^-; Polydentate ligands- $C_2O_4^{2-}$, EDTA, en. EDTA:

6. EDTA
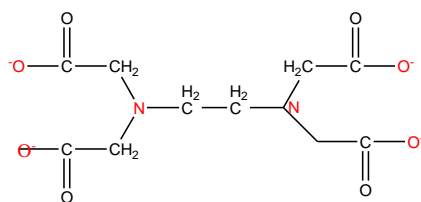
dmg:
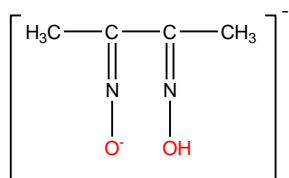
porphyrin:
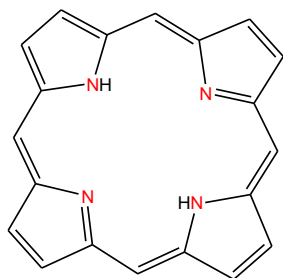
8-hydroxyquinoline:
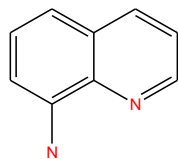
diethylene triamine:
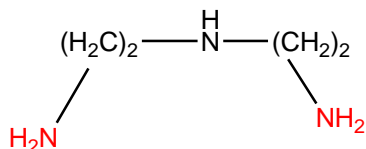
7. Spectator ligand, a tightly coordinating polydentate liangd that do not take part in a chemical reaction.

8. Chelates are useful in water softening, medical and analytical chemistry, and different industries such as agriculture, chemical, and food.

9. A complex ion is an ion in which the metal ion presents at the center and a definite number of ligands surround it. The complex ion is enclosed in a large bracket.

10. The oxidation state and coordination number of Fe in $[Fe(CN)_6]^{4-}$ is +2 and six while in $[Fe(C_2O_4)_3]^{3-}$ is +3 and six, respectively.

11. Geometry that describes five coordinated compounds:

Trigonal bipyramidal and Square pyramidal; Trigonal bipyramidal is the most stable geometry.

Geometry that describes six coordinated compounds.

Octahedral and Trigonal prismatic; Octahedral is the most stable geometry.

12. (i) Octahedral, (ii) Linear, (iii) Octahedral, (iv) Octahedral

13. The coordination sphere of a coordination compound comprises the central metal atom/ion and ligands attached to it. The coordination sphere is enclosed in brackets [ ].

14. Primary valency is the oxidation number or the group valency of the metal atom/ion, for example +2 for copper (Cu).

15. Secondary valency is the coordination number or the number of ligands coordinated to the metal aom/ion such as 6 for cobalt (Co).
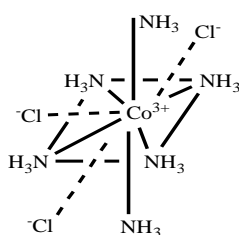
16. $CoCl_3.6NH_3$ $CoCl_3.5NH_3.$
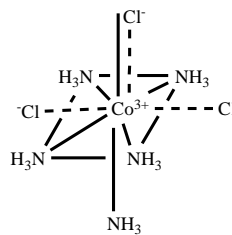
17. Molar conductivity measurement method and precipitation method.

18. Effective atomic number (EAN) is the total number of electrons in metal atom/ion (atomic number) plus the electrons gained from ligands. This EAN is the atomic number of a noble gas. Therefore, EAN decides stability of coordination compound. If a coordination compound follows EAN rule, than it is stable one.

19. English Chemist Nevil V. Sidgwick gave the concept of EAN rule.

20. EAN for $[Ni(CO)_4]$ Atomic number of Ni=28; there are four ligands hence electrons donated by 4 ligands = 4 x 2 = 8

$$EAN = 28 + 8, \quad = 36 \text{ (atomic number of Krypton; Kr)}$$

21. Oxidation number of the metal in the following coordination complexes:

$$a) +2, \qquad b) +3, \quad c) 0 \qquad d) 0$$

22. $Cl^- $ = chloro; H^- = hydrido; NO^+ = nitrosonium; H_2O = aqua; NO_3^- = nitrato; ONO^- = nitrito-N; NH_2^- = amido; $C_5H_5^-$ = cyclopentadienyl.

23. ethylenedimmine = en; dimethyl sulphoxide = dmso; glycine = gly; urea = ur; 1,10-phenanthroline = phen; ethylenediammine tetraacetic acid = EDTA.

24. a. $Na_3[Co(NO_2)_6]$ = Sodium hexanitrito-N cobaltate (III)

b. $K_4[Ni(CN)_4]$ = Potassium tetracyanonickelate (0)

c. $[Mn_3(CO)_{12}]$ = Dodecacarbonyltrimanganese (0)

d. $K_3[Fe(CN)_6]$ = Potassium hexacyanoferrate (III)

e. $[Pt(NH_3)_4][PtCl_4]$ = Tetraammineplatinum(II) tetrachloropalatinate

f. = μ-Dihydroxo-octaamminedicobalt(III) nitrate

25. Hexamminecobalt(III) chloride = $[Co(NH_3)_6]Cl_3$,   tetracarbonylnickel(0) = $[Ni(CO)_4]$

26. a) $Na_2[SiF_6]$,   b) $NH_4[Cr(NH_3)_2(NCS)_4]CrO_4$

27. Compounds $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ show decreasing order of conductivity due to the formation of 4 ions and 3 ions, respectively in solution.

28.

a.
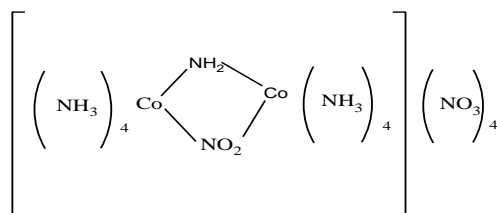
    b. $[Co(en)_2Cl_2]Cl$

    c. $[Fe(H_2O)_6]SO_4$

    d. $[PtCl_4]^{2-}$

29.

a. EAN = 37 (not follow EAN rule),   b. EAN = 38 (not follow EAN rule)

c. EAN = 36 (follow EAN rule)   d. EAN = 35 (not follow EAN rule)

e. EAN = 36 (follow EAN rule)   f. EAN = 36 (follow EAN rule)

g. EAN = 35 (not follow EAN rule)

30.   The ligands that bound to a metal ion through a single donor atom; two donor atoms and four donor atoms are called as monodentate, bidentate and tetradentate ligands, respectively.

31.   c) $[Co(NH_3)_3Cl_3]$ b) $[Co(NH_3)_5Cl]Cl_2$ a) $[Co(NH_3)_6]Cl_3$

4.11. REFERENCES

1.   M. S. Yadav. *Quick Review in Inorganic Chemistry*, Anmol Publications Pvt. Ltd., New Delhi, 2004.

2.   P. Mishra *Advanced Inorganic Chemistry*, Jagdamba Publishing Compan, New Delhi, 2011.

3.   R. Gopalan, and V. Ramalingam. *Concise Coordination Chemistry*, Vikas Publishing House Pvt Ltd., New Delhi, 2005.

4.   R. L. Madan, *Chemistry for degree students, B.Sc. II year*, S. Chand & Company Ltd., New Delhi, 2011.

5.   S. Prakash, G. D. Tuli, S. K. Basu, and R. D. Madan. *Advanced Inorganic Chemistry*, Vol. II, S. Chand & Company Ltd., New Delhi, 2007.

6.   W. U. Malik, G. D. Tuli, and R. D. Madan. *Selected Topics in Inorganic Chemistry*, S. Chand Publication, Delhi, 2013.

BLOCK-II

UNIT - 5 ALCOHOLS

CONTENTS:

5.1 INTRODUCTION

Alcohols are organic compounds in which one or more hydrogen atoms from hydrocarbon have been replaced by hydroxyl (-OH) group. They are some of the most common and useful compounds in nature, in industry, and around the house. The general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$, where n=1, 2, 3, etc. The saturated carbon chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. Alcohols can be viewed as organic analogues of water in which one hydrogen atom is replaced by an alkyl group. The simplest and most commonly used alcohols are methanol and ethanol. They occur widely in nature and have many industrial and pharmaceutical applications.

CH_3OH CH_3CH_2OH

methanol   ethanol   cyclopropanol   cyclohexanol

$CH_3CH_2{-}\overset{\displaystyle OH}{\underset{\displaystyle |}{CH}}{-}CH_3$

isobutanol
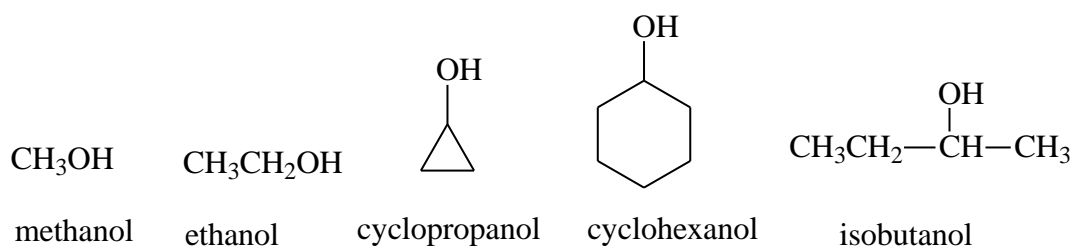
Aromatic compounds, which contain a hydroxy group on a side chain, behave like alcohols are called aromatic alcohol. In these alcohols, the —OH group is attached to a sp^3 hybridised carbon atom next to an aromatic ring.

benzyl alcohol   2- phenyl ethanol   3- phenyl propanol
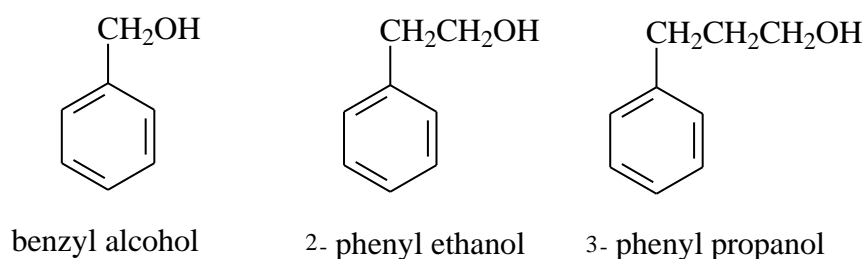
In some alcohols, the —OH group is attached to a sp^3 hybridised carbon next to the carbon-carbon double bond that is to an allylic carbon are known as allylic alcohols. In some alcohols —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols. Allylic and benzylic alcohols may be primary, secondary or tertiary in nature.

$CH_2{=}CH{-}OH$ $CH_2{=}CH{-}CH_2{-}OH$

vinylic alcohol   allylic alcohol   phenol
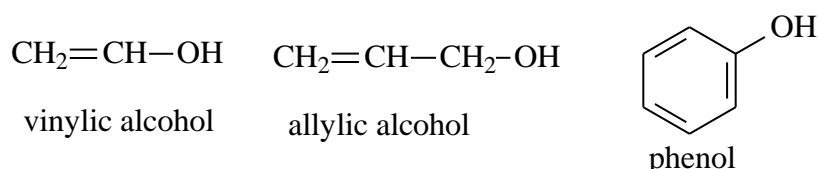
5.2 OBJECTIVES

Objectives of this unit are to study the alcohols, their structures, nomenclature, and classification on the basis of number of –OH groups present like monohydric alcohol, dihydric and polyhydric alcohols. Classification on the basis of nature of carbon attached with –OH group like primary, secondary and tertiary alcohols. This unit also aims on methods of preparation of alcohols with their physical and chemical properties, acidic and basic characters. Chemical reactions of alcohols like Acid-catalyseddehydration etc, Study on chemical properties of dihydric and polyhydric alcohos have also been aimed in this unit

5.3 CLASSIFICATION OF ALCOHOLS

Alcohols are classified into following types on the basis of number of –OH groups present in the molecule and nature of carbon attached with –OH group as follow:

(a) Monohydric Alcohols: These compounds contain only one –OH group.

$$CH_3CH_2OH \quad CH_3CH_2CH_2OH$$

(b) Dihydric Alcohols: These contain two –OH groups.

$$CH_2—OH$$
$$|$$
$$CH_2—OH$$
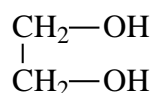
(C) Trihydric Alcohols: These contain three –OH groups.

$$CH_2—OH$$
$$|$$
$$CH—OH$$
$$|$$
$$CH_2—OH$$
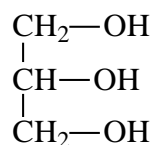
On the basis of nature of carbon atom attached with -OH group the mnohydric Alcohols can be further classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon.

(a) Primary alcohol (1° alcohol): A primary alcohol has one alkyl group attached to the carbon bound to the –OH, *i.e.*, a compound in which the hydroxyl group is bounded to a primary carbon. Primary alcohols have the group –CH$_2$OH, where the carbon atom with the alcoholic hydroxyl group has at least two additional hydrogens attached to that

carbon. Primary alcohol has –OH group bonded to a carbon which is bonded to one other carbon:

$$
\begin{array}{c}
\quad\;\; H \quad\;\; H \\
\quad\;\; | \quad\;\;\; | \\
H-C-C-OH \\
\quad\;\; | \quad\;\;\; | \\
\quad\;\; H \quad\;\; H
\end{array}
$$
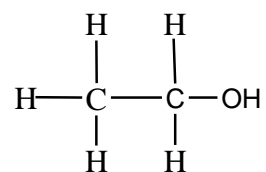
(b) Secondary alcohol (2° alcohol): A secondary alcohol has two alkyl group attached to the carbon bound to the –OH, i.e., the hydroxyl group is bounded to a secondary carbon. Secondary alcohols have the group –CHOH, where the carbon atom with the alcoholic hydroxyl group has only **one** additional H atom attached to it. There are two R groups (R stands for any other organic chain or group), and the alcoholic hydroxyl group is attached to a secondary carbon. Secondary alcohol has –OH group bonded to a carbon which is bonded to two other carbons:

$$
\begin{array}{c}
\quad\;\; H \quad\;\; OH \quad\;\; H \\
\quad\;\; | \quad\;\;\; | \quad\;\;\; | \\
H-C-C-C-H \\
\quad\;\; | \quad\;\;\; | \quad\;\;\; | \\
\quad\;\; H \quad\;\; H \quad\;\; H
\end{array}
$$
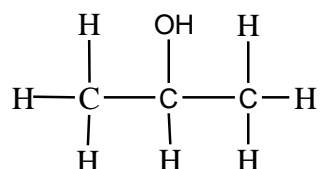
(c) Tertiary alcohol (3° alcohol): A tertiary alcohol has three alkyl group attached to the carbon bound to the –OH, i.e., the hydroxyl group is bounded to a tertiary carbon. Tertiary alcohols have the group –COH, where the carbon atom with the alcoholic hydroxyl group has no additional H atoms attached to it.

$$
\begin{array}{c}
\quad\;\; H \quad\;\; CH_3 \quad\;\; H \\
\quad\;\; | \quad\;\;\; | \quad\;\;\; | \\
H-C-C-C-H \\
\quad\;\; | \quad\;\;\; | \quad\;\;\; | \\
\quad\;\; H \quad\;\; OH \quad\;\; H
\end{array}
$$
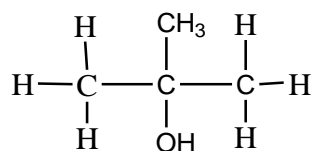
If we replace hydrogen with a –OH group we get the following groups for three alcohols:

$$
-CH_2OH \qquad\qquad -\overset{|}{\underset{}{CH}}-OH \qquad\qquad -\overset{|}{\underset{|}{C}}-OH
$$

primary alcohol   secondary alcohol   tertiary alcohol

primary alcohol   secondary alcohol   secondary alcohol   tertiary alcohol
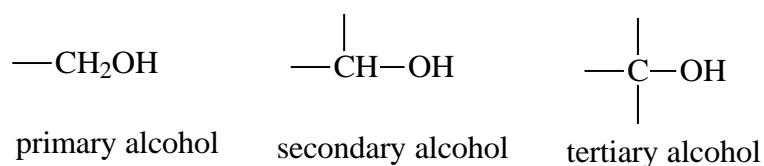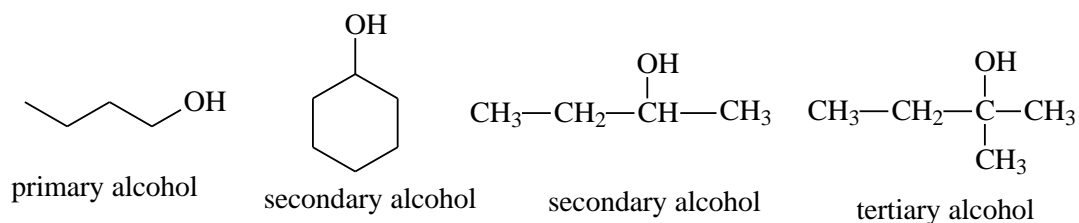
5.4 NOMENCLATURE OF ALCOHOLS

According to the IUPAC system of nomenclature, alcohols are called alkanols. They are named as the derivatives of the corresponding alkane in which the *-e* of the alkane is replaced by *-ol*. The IUPAC have come up with a set of rules that are used to name any alcohol regardless of its complexity. These rules are summarized as follows:

Step 1. Name the longest continuous chain to which the hydroxyl (—OH) group is attached. Count the number of carbon atoms and identify the corresponding alkane. The name for this chain is obtained by dropping the final **-e** from the name of the hydrocarbon parent name and adding the ending **-ol.**

Step 2. Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.

Step 3. Locate the position of the hydroxyl group by the number of the carbon to which it is attached.

Step 4. Number the any other substituents according to their position on the chain.

Step 5. Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

Step 6. If there are more than one –OH group do not remove the –e from the suffix, but add a di- or tri- prefix to the –ol suffix.

Step 7. Identify and locate the other branches on the chain so that they are named alphabetically and their carbon number is hyphenated onto the front of the name.

viz;	Alcohols	Common name	IUPAC name
	CH_3OH	Methyl alcohol	Methanol
	CH_3CH_2OH	Ethyl alcohol	Ethanol
	$CH_3CH_2\ CH_2OH$	n-Propyl alcohol	1-Propanol
	$CH_3CHOHCH_3$	Isopropyl alcohol	2-Propanol
	$CH_3(CH_2)_2CH_2OH$	n-Butyl alcohol	1-Butanol
	$CH_3(CH_2)_3CH_2OH$	n-Pentyl alcohol	1-Pentanol

Other examples:

2 - butanol

5 methyl 2 hexanol

cyclopentanol

1, 2, 3- trihydroxy propane

3-cyclopentyl-1- propanol

3--amino 2- butanol

3 - butene -2 -ol

3 - meyhylcyclohexanol

2.3 - dimethylcyclooctanol
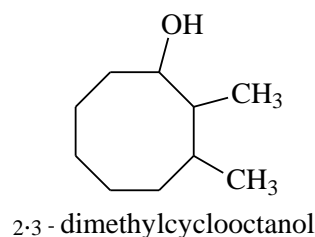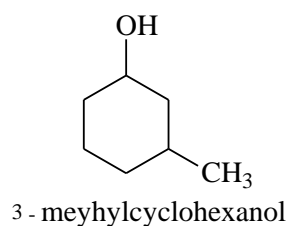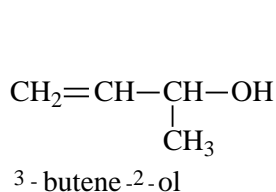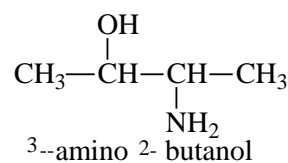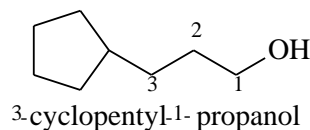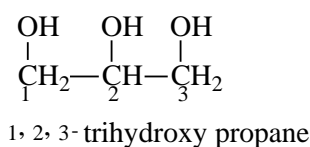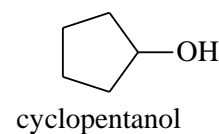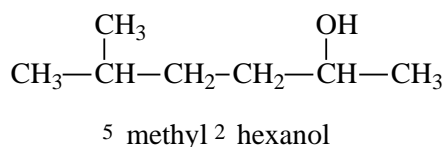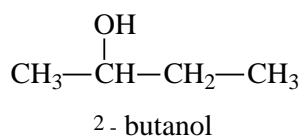
5.5 *METHOD OF PREPARATION OF ALCOHOLS*

The following methods are used for the preparation of alcohols:

1. **Hydrolysis of haloalkanes:** Haloalkanes can be converted to corresponding alcohols using aqueous NaOH, KOH or Ca $(OH)_2$. With this method primary and secondary alcohols are formed from a primary and secondary halogenoalkanes. This is a type of nucleophilic substitution reaction (S_N). This reaction is useful only with reactants that do not undergo E_2 elimination readily.

$$RX \;+\; \overset{\ominus}{O}H \;\xrightarrow{\;H_2O\;}\; ROH \;+\; X^{\ominus}$$

$$CH_3CH_2CH_2Br \;+\; NaOH(aq) \;\xrightarrow{\;H_2O\;}\; CH_3CH_2CH_2OH \;+\; NaCl$$
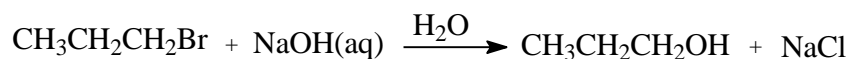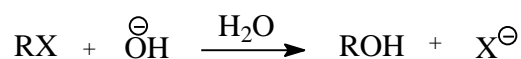
2. Reduction of carbonyl compounds: Carbonyl compounds (which contain –C–O group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols. Aldehydes give primary alcohols while ketones yield secondary alcohols, either by catalytic hydrogenation or by use of chemical reducing agents like lithium aluminum hydride, LiAlH4. Carboxylic acids and esters also give primary alcohols on reduction with hydride reagents such as LiAIH4 and sodium borohydride (NaBH$_4$). NaBH$_4$ does not reduce

3. carbon-carbon double bonds, not even those conjugated with carbonyl groups, and in thus useful for the reduction of such unsaturated carbonyl compounds to unsaturated alcohols. In the above reactions it is observed that only the carbonyl group is reduced and the other functional groups remain unaffected. Highly selective behaviour of NaBH$_4$ makes it the preferred reagent for the reduction of carbonyl groups in sensitive polyfunctional group containing compounds.

$$CH_3COCH_2CH_2COOC_2H_5 \xrightarrow{NaBH_4} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CH_2\text{-}COOC_2H_5$$
Ethyl-γ-ketopentanoate   Ethyl-4-hydroxypentanoate

$$C_6H_5\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow{NaBH_4} C_6H_5\text{-}CH(OH)\text{-}CH_2\text{-}CH_2\text{-}COOH$$
β-Benzoyl propanoicacid   γ-Hydroxy-4-phenylbutanoic acid

$$CH_2\text{-}OH\text{-}(CHOH)_4\text{-}CHO \xrightarrow{NaBH_4} CH_2OH\text{-}(CHOH)_4\text{-}CH_2OH$$
Glucose   Sorbitol

$$C_6H_5\text{-}CH = CH - CHO \xrightarrow{NaBH_4} C_6H_5\text{-}CH = CH\text{-}CH_2OH$$
Cinnamaldehyde   Cinnamyl alcohol

$$NC\text{-}CH_2\text{-}CH_2\text{-}CHO \xrightarrow{NaBH_4} NC\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$
3-Cyanopropionaldehyde   4-Hydroxybutyronitrile

$$RCOCl \xrightarrow{NaBH_4} R\text{-}CH_2OH$$
Acid chloride   Alcohol

$$O_2N\text{-}\langle\text{-}\rangle\text{-}CHO \xrightarrow{NaBH_4} O_2N\text{-}\langle\text{-}\rangle\text{-}CH_2OH$$
p-Nitrobenzaldehyde   p-Nitrobenzyl alcohol

4. **From hydration of alkenes:** Hydration i.e.s addition of H^+ and OH^- across a C=C double bond to give alcohols. This is an electrophilic addition of H_2O to the alkene. Alcohols can be prepared by adding water to an alkene in the presence of a strong acid such as co. H_2SO_4. Because these reactions follow Markovnikov's rule, the product of the reaction is often a highly substituted 2° or 3° alcohol.

$$RCH=CH_2 + H_2SO_4 \rightarrow RCH\text{-}CH_3 \xrightarrow{H_2O} RCHOHCH_3$$

$$CH_2=CH_2 + H_2SO_4 \rightarrow CH_3\text{-}CH_2HSO_4 \xrightarrow{H_2O} CH_3CH_2OH$$

$$CH_3CH=CHCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3$$

$$R_2C=CR_2 + H_2O \xrightarrow{H} R_2CH\underset{\underset{OH}{|}}{C}R_2$$

$$(CH_3)_2C=CHCH_3 \xrightarrow[H_2SO_4]{H_2O} CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_3$$

2-Methyl-2-butene   2-Methyl-2-butanol
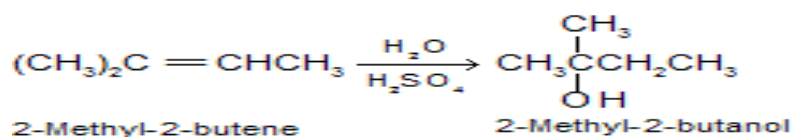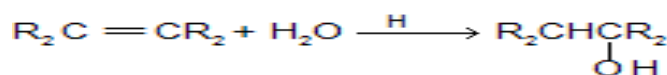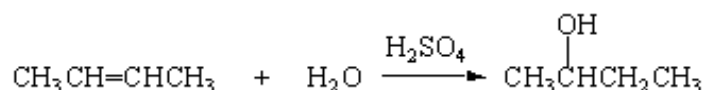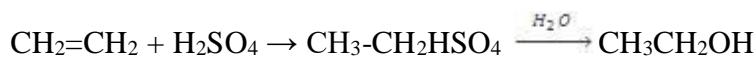
Ease of preparation is tert. > sec. > prim alcohol; ease of dehydration follows   same sequence.

5. **Oxidation of organoboranes:** When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained. Hydroboration followed by oxidation will produce an alcohol. Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane. This is oxidised to alcohol by hydrogen peroxide (H_2O_2) in the presence of aqueous sodium hydroxide. The overall reaction is addition of water across the double bond opposite to that of Markovnikov's rule and the reaction is regioselective producing the least substituted alcohol.

$$R_2C=CR_2 \xrightarrow[\text{2. } H_2O_2, \text{ HO}^-]{\text{1. } B_2H_6} R_2CH\underset{\underset{OH}{|}}{C}R_2$$

$$CH_3(CH_2)_5CH=CH_2 \xrightarrow[\text{2. } H_2O_2, \text{ HO}^-]{\text{1. } B_2H_6, \text{ diglyme}} CH_3(CH_2)_7OH$$

1-Octene   1-Octanol 90%
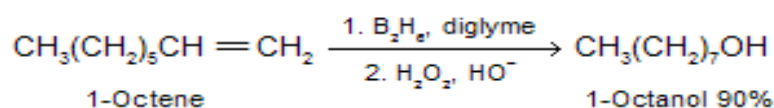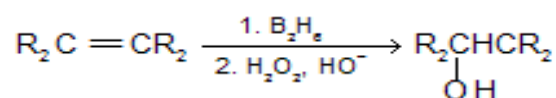
Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes gives primary alcohols.

5. From Grignard reagents – Alcohol can easily be prepared by using Grignard (RMgX) reagent as follow:

(a)   **By reaction with aldehydes & ketones:** The reaction of Grignard reagents with formaldehyde produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols. In this method alcohol is prepared with the formation of new carbon-carbon bonds.
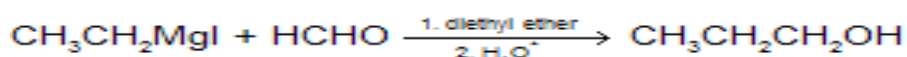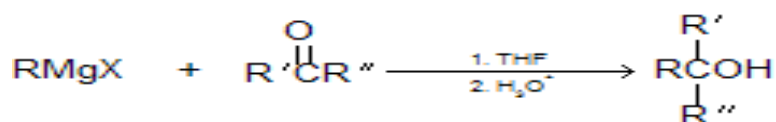
All other aldehydes yield 2^0 *alcohols* on reaction with Grignard reagents.
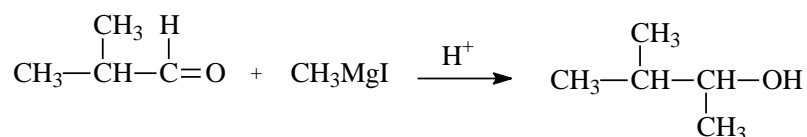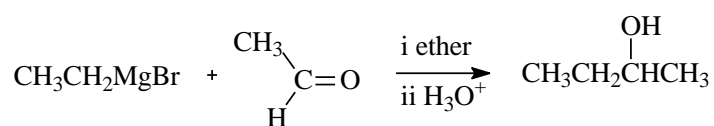
With ketones, Grignard reagents give 3^0 *alcohols*.

cyclopropylethanone   2-cyclopropyl-2-propanol
68%
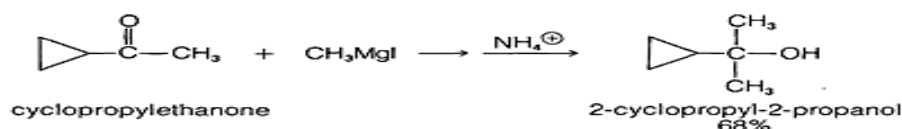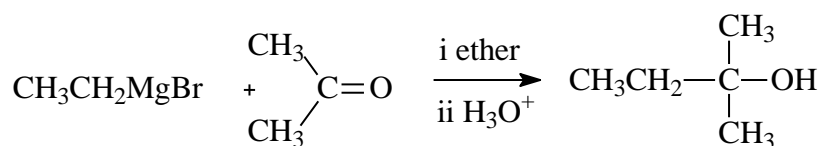
(b) By reaction with esters: Produces tertiary alcohols in which two of the substituents on the hydroxyl- bearing carbon are derived from the Grignard reagent.

$$2RMgX + R'\overset{O}{\underset{\parallel}{C}}OR'' \xrightarrow[\text{2. H}_2\text{O}^*]{\text{1. THF}} R\overset{R'}{\underset{R}{\overset{|}{C}}}OH + R''OH$$

$$2CH_3CH_2CH_2CH_2MgBr + CH_3\overset{O}{\underset{\parallel}{C}}OCH_2CH_3 \xrightarrow[\text{2. H}_2\text{O}^*]{\text{1. ether}} CH_3\overset{OH}{\underset{CH_2CH_2CH_2CH_3}{\overset{|}{C}}}CH_2CH_2CH_3$$

Butylmagnesium bromide   Ethyl acetate
(Excess)

Ter. alcohol
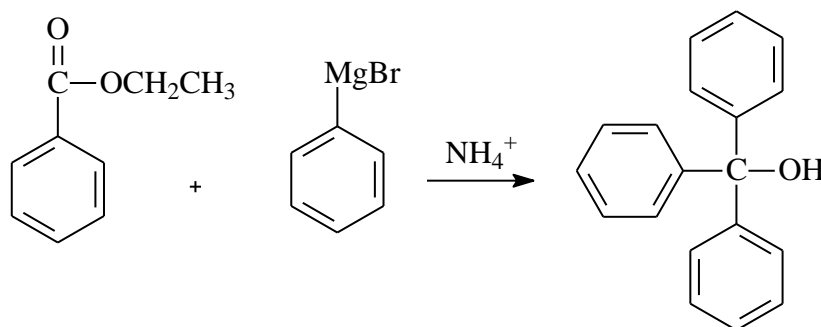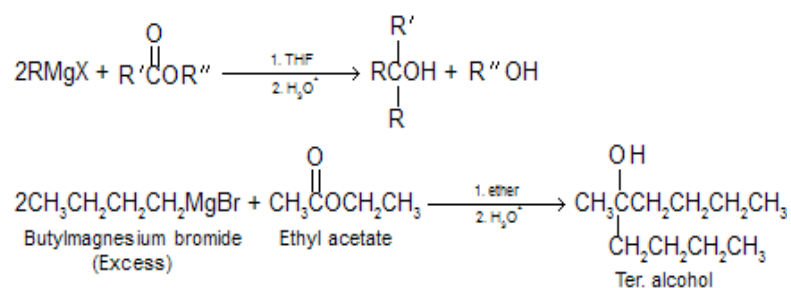
(c) By reaction with epoxides: Grignard reagents react with epoxide to yield primary alcohols containing two or more carbon atoms.

$$CH_3CH\overset{}{\underset{O}{\diagdown\diagup}}CH_2 + C_6H_5MgBr \longrightarrow \xrightarrow{NH_4^{\oplus}} CH_3CH\underset{OH}{\overset{|}{-}}CH_2C_6H_5$$

2-methyloxacyclopropane
(2-methyloxirane)

1-phenyl-2-propanol
60%

$$\overset{-}{R}\overset{+}{MgX} + H_2\overset{\delta+}{C}\overset{}{\underset{O\,\delta-}{\diagdown\diagup}}CH_2 \xrightarrow[\text{2. H}_2\text{O}^*]{\text{1. diethyl ether}} RCH_2CH_2OH$$

Ethylene oxide

$$CH_3(CH_2)_2\overset{-}{C}\overset{+}{H_2}MgBr + H_2\overset{\delta+}{C}\overset{}{\underset{O\,\delta-}{\diagdown\diagup}}CH_2 \xrightarrow[\text{2. H}_2\text{O}^*]{\text{1. diethyl ether}} CH_3(CH_2)_4CH_2OH$$

Ethylene oxide   1-Octanol (71%)
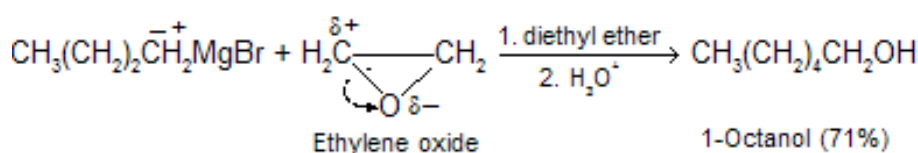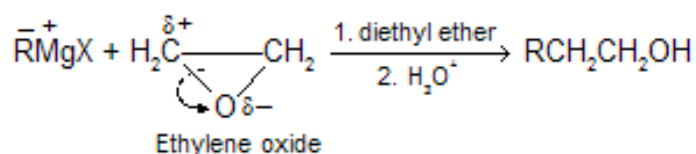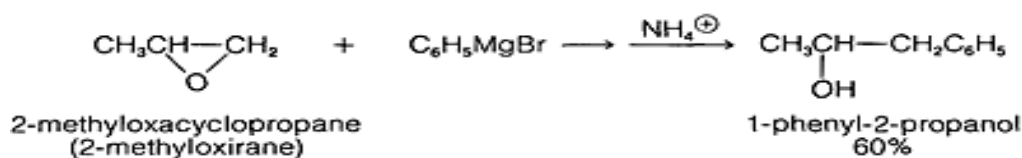
6. **Fermentation:** Ethanol is prepared on a large-scale using fermentation process. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes. Yeast converts the reactant glucose or fructose into ethanol and carbon dioxide in presence of zymase enzyme.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar   Glucose   Fructose

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Ethyl alcohol
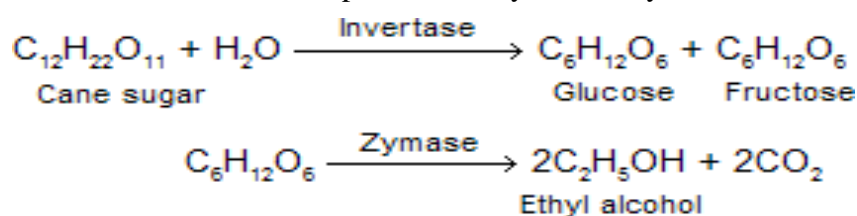
5.6 ACIDIC NATURE OF ALCHOLS

Alcohols can act as Brönsted acids as well as Lewis base due to donation of proton and presence of unpaired electron on oxygen respectively. Alcohols are very weak acids because the alkyl group pushes electrons towards the —OH group, so that the oxygen does not strongly attract the electrons in the —OH bond. Further more once a RO^- ion is formed, it cannot be stabilized by the delocalization of the charge. Thus alcohols react only to a very slight extent with alkali, but will react with very electropositive metals under anhydrous conditions to give alkoxide with the general formula $RO^-\ M^+$.

Example: Reaction of ethanol with sodium

$$2CH_3CH_2OH\ +\ 2Na\ \rightarrow\ 2CH_3CH_2O^-\ Na^+ +\ H_2$$

Addition of water will regenerate the alcohol readily.

$$CH_3CH_2O^-Na^+ +\ H_2O\ \rightarrow\ CH_3CH_2OH\ + NaOH$$

The reaction is much slower than the reaction of water with sodium. Alcohols tend to be slightly less acidic (pKa = 15) compared to water (pKa = 14). The higher the pKa value the lower is the acid strength. The reaction of alcohol with sodium can be used to deposite the excess sodium in the laboratory. Even alcohols are neutral to litmus and do not react with alkali like NaOH but contain active hydrogen atom so reacts with Na or K metal.

$$CH_3CH_2OH\ +\ NaOH\ \rightarrow\ No\ reaction$$

Reactivity of alcohol towards metal: $1° > 2° > 3°$ alcohol. An electron-releasing group (-CH_3, -C_2H_5) increases electron density on oxygen tend to decrease the polarity of O-H bond. For example, with methanol:
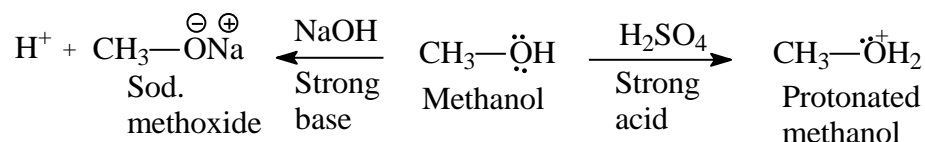
(i) The lower alcohols are colourless liquids with a characteristic smell and a burning taste. The higher members (with more than 12 carbons) are colourless wax like solids.

(ii)   Because of hydrogen bonding, alcohols tend to have higher boiling points than comparable hydrocarbons and ethers of similar molecular weight. Alcohols exists associated molecules due to the association of molecules in the liquid phase through strong intermolecular hydrogen bond between hydrogen atom of one molecule and oxygen atom of another molecule. The oxygen-hydrogen bond is polar because oxygen is much more electronegative than hydrogen. The lowers members have low boiling points. With the increase in molecular weight, the boiling points keep on increasing gradually. For example, the boiling point of butyl alcohol is 118°C whereas the boiling point of the isomeric diethyl ether is 36°C.

(iii)   Solubility: The general rule in solubility is *"like dissolves like."* The hydroxyl group generally makes the alcohol molecule polar and therefore more likely to be soluble in water. Hydrogen bonding also has an effect on water solubility. The OH groups of an alcohol can hydrogen bond with water, and so this portion of the alcohol is hydrophilic. On the other hand, the alkyl chain in an alcohol is similar to hydrophobic molecules like hydrocarbon that do not mix with water. Compounds like alcohols that have hydrophilic and hydrophobic regions are called ambiphilic (or amphiphilic). The water solubility of a given alcohol depends on whether the hydrophilic OH or the hydrophobic alkyl chain dominates. Alcohols with shorter carbon chains (CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$) are usually more soluble than those with longer carbon chains because the increasing size of the nonpolar chain disrupts the hydrogen bonding network. Formation of hydrogen bonds with water will increase their solubility. That is why alcohols are much more soluble in water than their corresponding alkanes, aromatic hydrocarbons, alkyl halides or aryl halides. Amongst isomeric alcohols, the solubility increases with branching.

(iv)The B.P. and M.P. will also increase with carbon chain length. The longer the alcohols carbon chain, the better the chance that the alcohol will be a solid at room temperature. Alcohols show higher boiling points than alkane and ethers of similar mass due to hydrogen bonding. Since there is not any possibility of hydrogen bonding in ether, the forces between the ether molecules are much weaker and can be much more easily vaporized.

CH_3CH_2OH $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$

Soluble in water   Insoluble in water
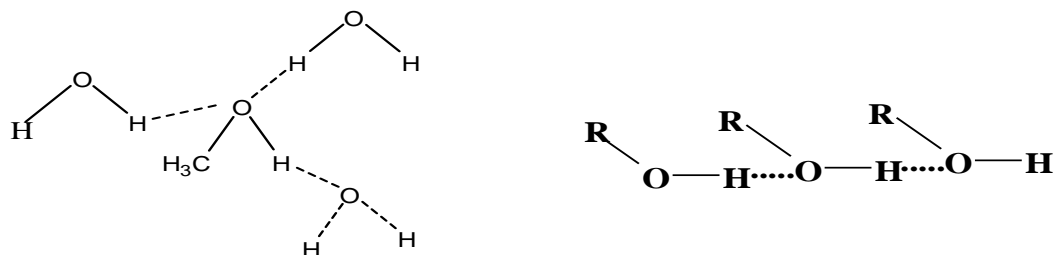
Comparison of boiling points among isomeric alcohols

$CH_3CH_2CH_2CH_2OH$

1−butanol

B.P. $118\ ^0C$

M.Wt = 74

$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2OH$

2− methyl 1− propanol

B.P. $108\ ^0C$

M.Wt = 74

$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$

2− methyl 2− propanol

B.P. $83\ ^0C$

M.Wt = 74
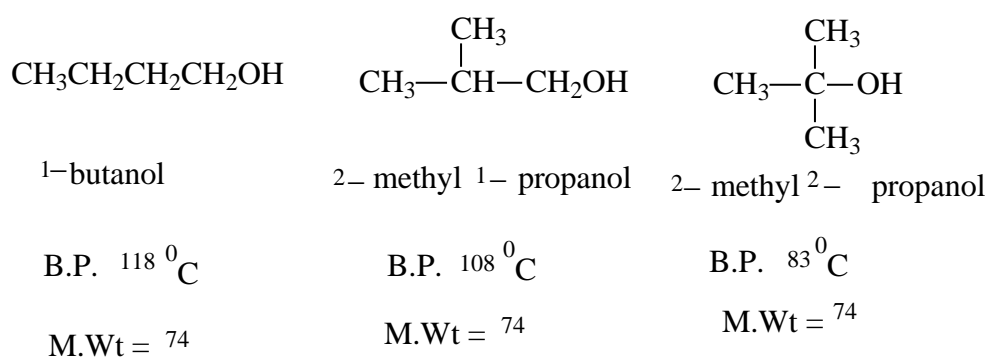
(v)   The viscosity of small alcohols is much higher than the viscosity of alkanes.

(vi) Generally, alcohols are lighter than water, i.e., less dense than water. Density of alcohols increases with molecular mass.

5.7 CHEMICAL REACTIONS OF ALCOHOLS

Alcohols acts both as nucleophiles as well as electrophiles. The bond between O-H is broken when alcohols react as nucleophiles and the bond between C-O is broken when they react as electrophiles. The chemical properties of any given aliphatic alcohol depend on the nature of the alkyl group and on the properties of the hydroxyl group. Based on the cleavage of O-H and C-OH bonds, the reactions of alcohols may be divided into two groups:

(A) Reactions involving cleavage of O-H bond

1. Acylation of alcohol: When alcohol reacts with acylhalide and anhydride substitution of hydrogen atom by acyl group is known as acylation of alcohols.

$$ROH + CH_3COCl \longrightarrow ROCOCH_3 + HCl$$

$$ROH + (CH_3CO)_2O \longrightarrow ROCOCH_3 + CH_3COOH$$
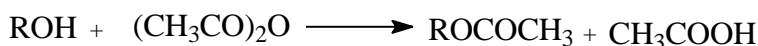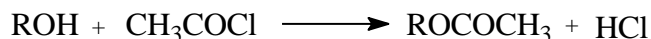
(B) Reaction involving fission of R—OH bond (cleavage of C—O bond): The reactions involving R – OH bond with cleavage of C – O bond is as follow

1. Dehydration: (a) Intramolecular dehydration (forming alkene): Alcohols undergo dehydration to form unsaturated hydrocarbon on treating with a protic acid e.g., con. H_2SO_4or H_3PO_4, or catalysts such as anhydrous $ZnCl_2$or Al_2O_3. In this reaction the OH and an H group removes from an adjacent carbon. Since water is removed from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*). Secondary and tertiary alcohols are dehydrated under much milder conditions. The conditions for dehydrating alcohols depend closely on the structure of individual alcohols.

For primary alcohols, the conditions required are conc. sulphuric acid and temperature of 170^0C.
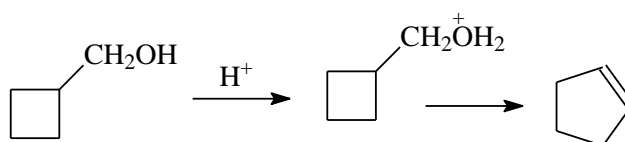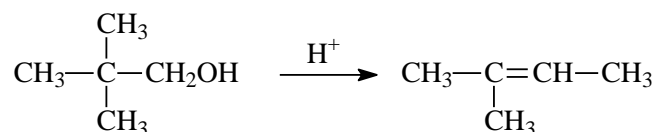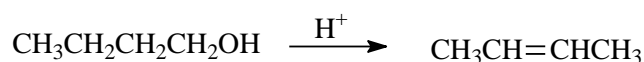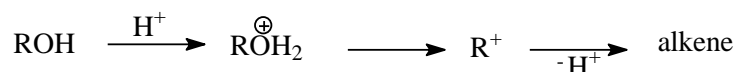
In smaller ring always ring expansion takes place due to molecular strain and they tend to convert to high stability with large ring.
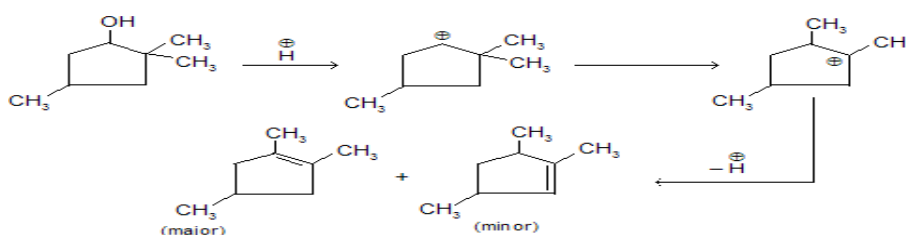
Secondary alcohols dehydrate under milder conditions than primary alcohols.
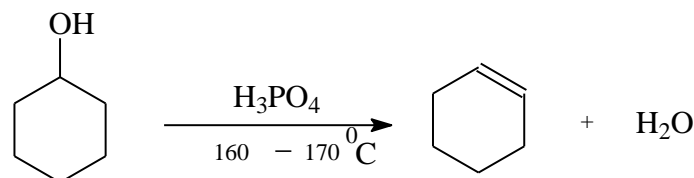
Tertiary alcohols dehydrate under even milder conditions.
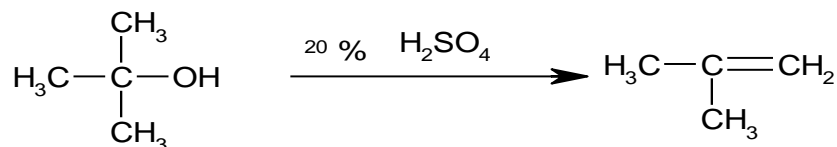
The main function of the acid is to transform the poor leaving group —OH into the very good leaving group $—OH_2$. The order of the relative ease of dehydration of alcohols is: $3^0 > 2^0 > 1^0$

Tertiary carbocations are most stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

The order of stability of the carbocations is:
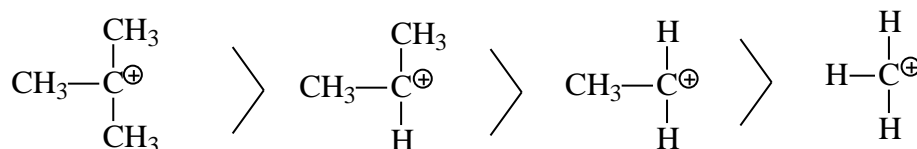
Dehydration of secondary and tertiary alcohols containing more than three carbon atoms will give a mixture of alkenes, the major product can be determined from Satzeff's Rule:

Satzeff's Rule— When an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond i.e., the major product is that contains the higher number of alkyl groups attached to the C=C bond. e.g.
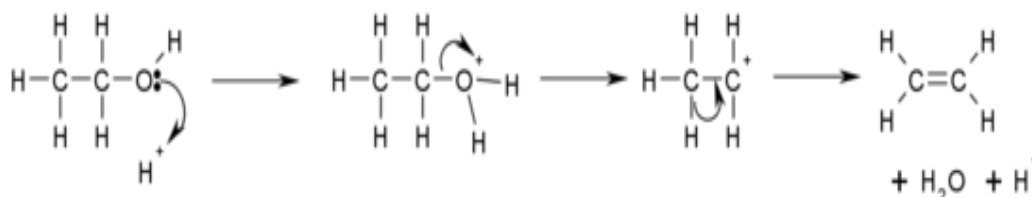
Rearrangement of the alkyl groups of alcohols is very common in dehydration, particularly in the presence of strong acids, which are conducive to carbocation formation. Typical examples showing both methyl and hydrogen migration follow:

Mechanism:
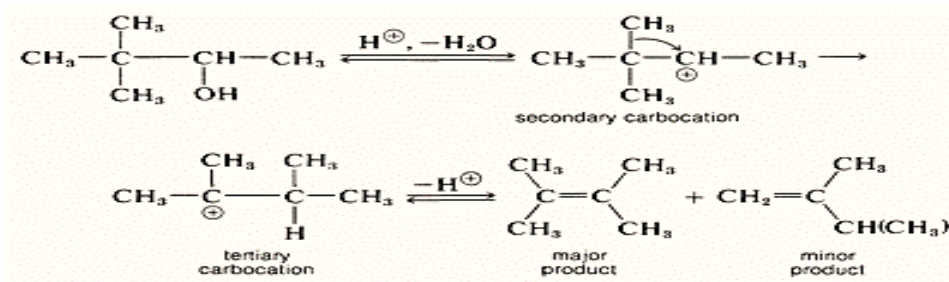
Intermolecular dehydration (**forming ether**):

When the dehydration is carried out at a temperature of 140^0C with an excess of alcohol ether will be formed. This reaction removes a molecule of water from two alcohol molecules, causing the two "R" groups to become attached to an oxygen atom, forming an ether functional group:

$$2\ CH_3CH_2OH \xrightarrow{\text{Con.}H_2SO_4} CH_3CH_2-O-CH_2CH_3\ +\ H_2O$$

2. Halogenation: Alcohols can be converted to alkyl halides using one of three reactions:

(a) Reaction with hydrogen halides: Respective alkyl halides are formed by reacting with the appropriate hydrogen halide, HCl for chlorination, HBr for bromination, and HI for iodination. The reaction involves the initial protonation of the hydroxyl group of the alcohol. This improves the leaving group ability of the hydroxyl group.
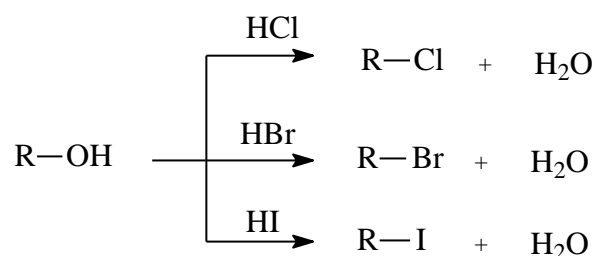
Mechanism:

Step1: Protonation of the alcohols: The alcohol acts as a weak base and accepts the proton donated by the hydrogen halide.
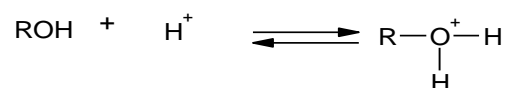
Step 2: Removal of a water molecule and formation of halide through S_N2 mechanism/ S_N1 mechanism as:

(i) For primary and secondary alcohols, it is a S_N2 reaction.
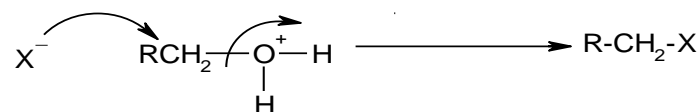
(ii) For tertiary alcohols, it is a S_N1 reaction.
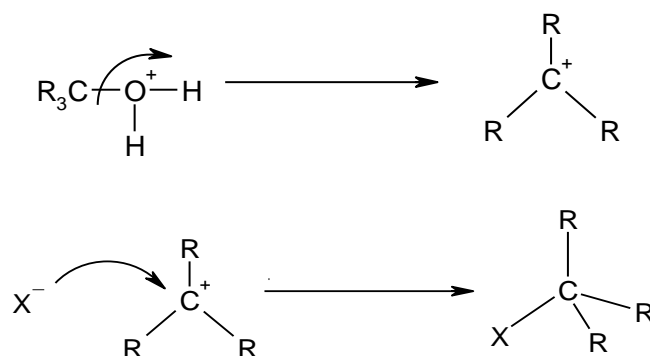
(iii)   Rate of the reaction for 1^0, 2^0 and 3^0 alcohols:

The order of rates of reaction:

$$3^0 \text{ alcohol } > 2^0 \text{ alcohol } > 1^0 \text{ alcohol}$$

The rate can be shown by the turbidity in the aqueous layer since the chloroalkane formed is immiscible with water.

(b) Reaction with thionyl chloride, SOCl₂: Alcohols will react with thionyl chloride to produce alkyl halides. The reaction involves a nucleophilic attack of the alcohol on a $SOCl_2$ molecule displacing one of the chlorides. Then the chloride will act as the nucleophile in a second step and displace the oxygen from the carbinol carbon.

$$R-OH \; + \; SOCl_2 \longrightarrow R-Cl \; + \; SO_2 \; + \; HCl$$
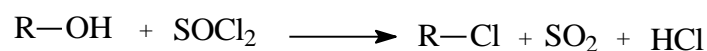
(c) Reaction with phosphorus halides

Alcohols will react with phosphorus tribromide or phosphorus pentabromide to form alkyl bromides.

$$^3 ROH + PBr_3 \longrightarrow {}^3 RBr + H_3PO_3$$

$$^3 ROH + PI_3 \longrightarrow {}^3 RI + H_3PO_3$$
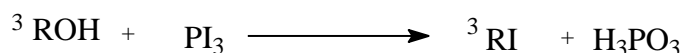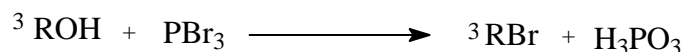
The mechanism is very similar to the thionyl chloride reaction. The alcohol acts as the nucleophile and displaces a halide ion from the PX_3 or the PX_5.

$$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + HCl + POCl_3$$
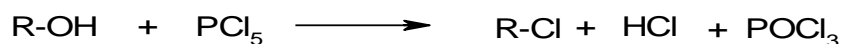
3. Esterification: Alcohol reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride is reversible, and therefore, water is removed as soon as it is formed. Esterification takes place much faster in the presence of a catalyst such as conc. H_2SO_4.

Example :

$$CH_3CH_2COOH + CH_3CH_2OH \xrightarrow[\text{Reflux}]{\text{Con.}H_2SO_4} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3 + H_2O$$
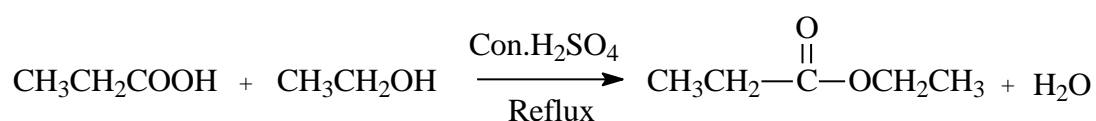
Alcohols can also react with acid chlorides and acid anhydrides to form esters. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation.

Example:

$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C} \quad + \quad CH_3CH_2OH \xrightarrow{\text{Con.}H_2SO_4} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3 + CH_3CH_2COOH$$
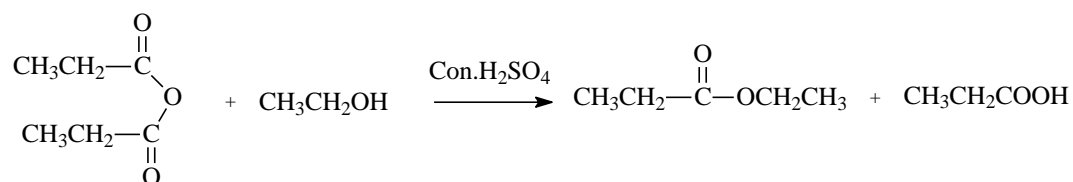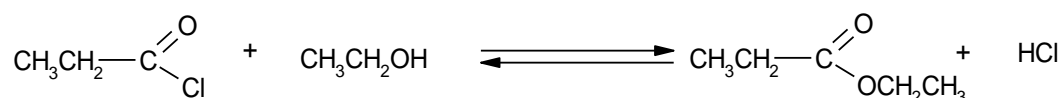
4. Oxidation: Alcohols can be oxidized by various oxidizing agents to aldehyde, ketones or carboxylic acids. Oxidation is the gain of oxygens and /or the loss of hydrogens.
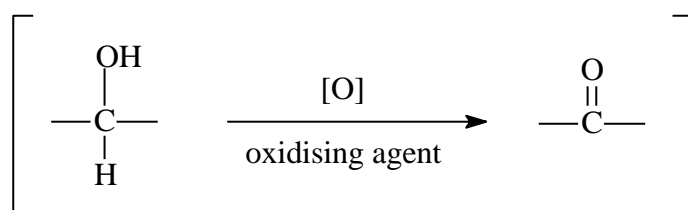
(a) 1^0 alcohol oxidizes readily, first to an aldehyde, then to a carboxylic acid. These two oxidation steps make sense because the primary alcohol functional group has two C-H bonds that can be broken. Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O). Strong oxidizing agents such as hot alkaline $KMnO_4$ or CrO_3 in H_2SO_4 will oxidize primary alcohols right past the aldehyde to the salt of the carboxylic acid in which the acid may be precipitated by acidification. The alcohol, aldehyde and acid retain the same number of carbon atoms.

$$RCH_2OH \xrightarrow[\text{oxidising agent}]{[O]} R-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-H \ + \ H_2O$$

$$CH_3CH_2OH \xrightarrow[\text{oxidising agent}]{[O]} CH_3-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-H \ + \ H_2O$$
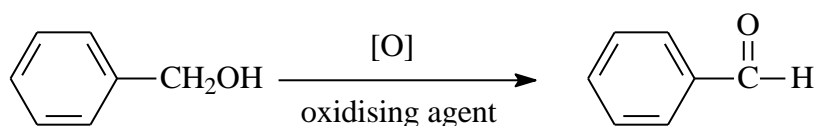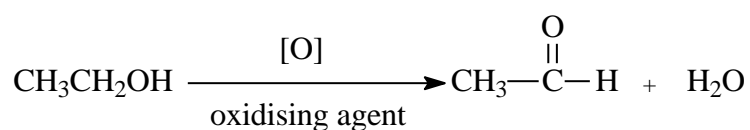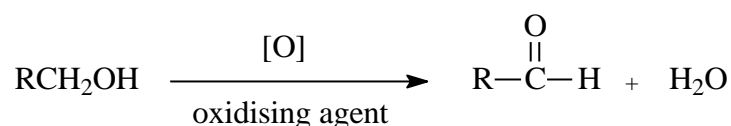
b. 2^0 alcohol has only one C-H bond that can be broken, so it can only oxidize once, to a ketone, which cannot be oxidized any further:
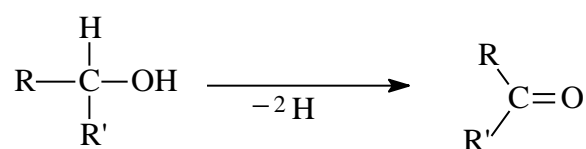
3^0 alcohol   Ketone
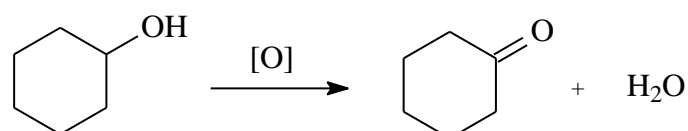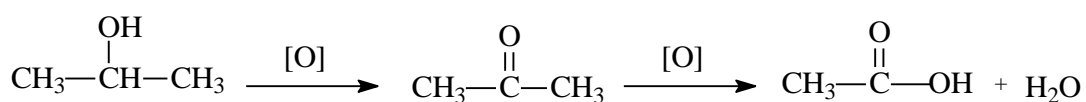
c. 3^0 alcohol has no C-H bonds that can be broken, so it is not oxidized, no matter how strong the oxidizing agent because it would involve the breakage of the high energy C—C bonds in the alcohol molecule.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{\text{[O]}} \text{No oxidation product}$$
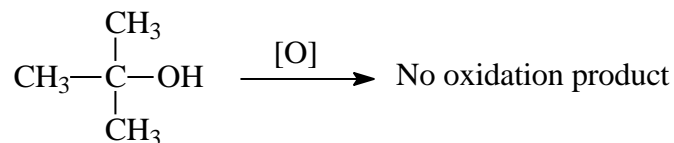
In acidic solutions, 3^0 alcohols can he oxidized to give a mixture of ketone and acid, both with fewer carbon atoms than the alcohol.

$$CH_3-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{\text{[O]}} CH_3-\overset{\overset{O}{||}}{C}-CH_3 \; + \; CH_3COOH$$
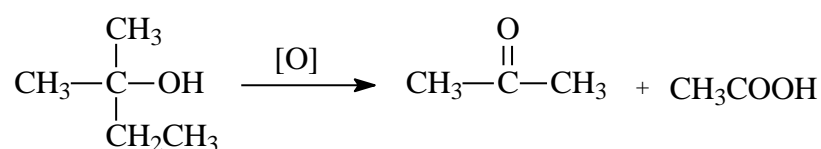
Characterization of the oxidation products of alcohols is a means of distinguishing between primary, secondary and tertiary alcohols.

5.8 DIHYDRIC ALCOHOLS

These compounds contain two hydroxyl (–OH) groups in a molecule. These are dihydroxy components of alkanes. Their general formula is $C_nH_{2n+2}O_2$. The simplest and most important dihydric alcohol is ethylene glycol. They are classified as $\alpha, \beta, \gamma.....$ glycols, according to the relative position of two hydroxyl groups. α is 1, 2 glycol, β is 1, 3 glycol.

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} \qquad\qquad \begin{array}{l} CH_2-OH \\ | \\ CH_2 \\ | \\ CH_2-OH \end{array}$$
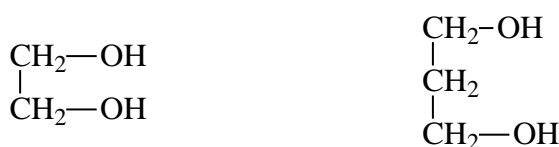
 Nomenclature: For naming polyhydric alcohols, the name of the alkane is retained and the ending -e is not dropped but add a di- or tri- prefix to the –ol suffix. Thus, dihydric alcohols are named as alkane diols and trihydric alcohols are named as alkene triols.

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

eth - 1,2 - diol   trans - 1,2 - cyclobutanediol   2,4 - pentadienol

$$CH_3-\underset{\underset{}{\overset{\overset{OH}{|}}{CH}}}{}-CH_2-\underset{}{\overset{\overset{OH}{|}}{CH}}-CH_3$$
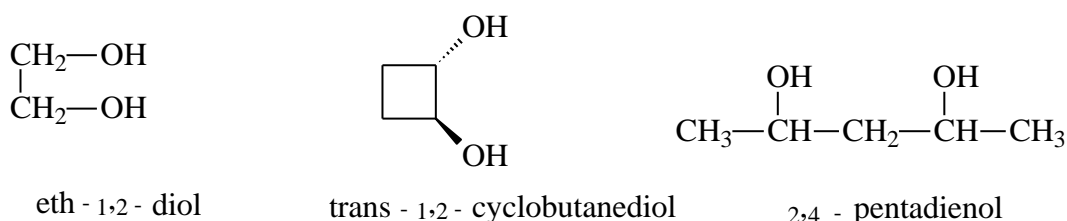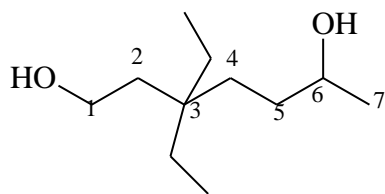
$3,3$ - diethyl - $1,6$ - heptanediol

5.9 METHODS OF PREPARATION

Dihydric alcohols are prepared by following different methods:

From ethylene: (a) through icy dilute alkaline solution of Bayer's reagent.
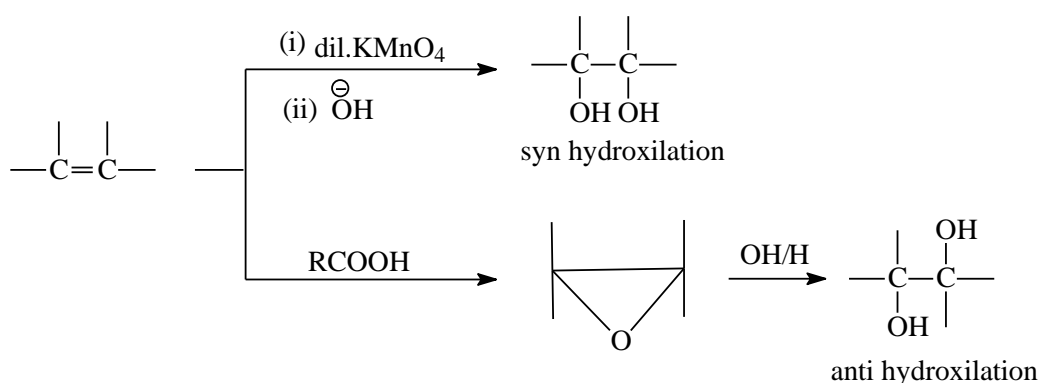
(b) With O_2 in presence of Ag :
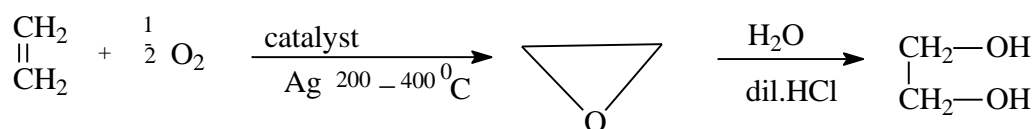
(c) With HOCl followed by hydrolysis:
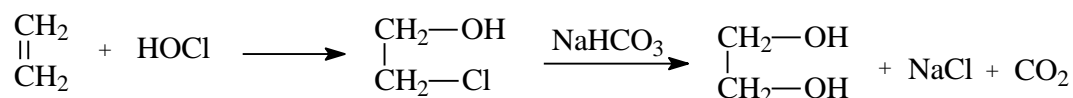
From 1, 2 dibromo ethane
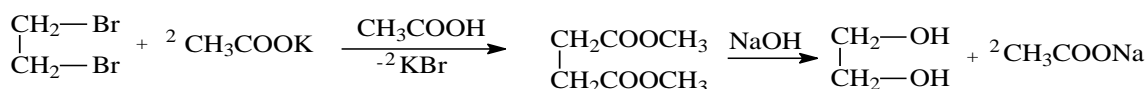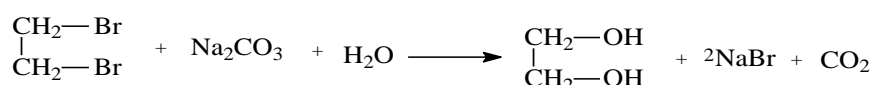
5.10 PHYSICAL PROPERTIES OF DIHYDRIC ALCOHOL

Dihydric alcohol viz; glycerol exhibits the following physical properties:

(i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is $197°C$. melting point -11.5^{0C}

(ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.

(iii) It is toxic as methanol when taken orally.

(iv) It is widely used as a solvent and as an antifreeze agent.

5.11 CHEMICAL REACTIONS OF VICINAL GLYCOLS

Glycerol molecule is made up of two 1^0 alcohol groups joined together its chemical reactions are, therefore those of 1^0 alcohols twice over viz;

1. Action of Sodium: It reacts with Na at 50^0 c to form to form mono and dialkoxide at elevated temperature.

$$\begin{array}{c} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} + Na \xrightarrow{50^0C} \begin{array}{c} CH_2\text{–}ONa^+ \\ | \\ CH_2\text{—}OH \end{array} + \frac{1}{2}H_2$$

$$\begin{array}{c} CH_2\text{–}ONa^+ \\ | \\ CH_2\text{—}OH \end{array} + Na \xrightarrow{160\ ^0C} \begin{array}{c} CH_2\text{–}ONa^+ \\ | \\ CH_2\text{—}ONa^+ \end{array} + \frac{1}{2}H_2$$
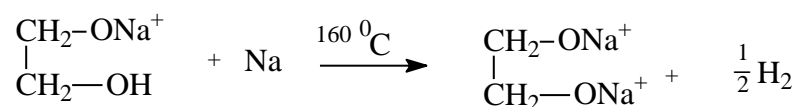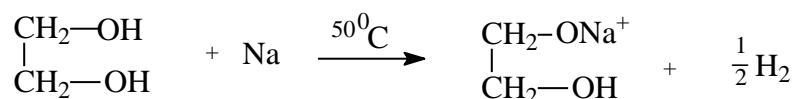
2. Reaction with HC: Ethylene dichloride is formed in two successive steps at elevated temperature

$$\begin{array}{c} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} + HCl \xrightarrow{160^0C} \begin{array}{c} CH_2\text{–}Cl \\ | \\ CH_2\text{—}OH \end{array} + H_2O$$

$$\begin{array}{c} CH_2\text{–}Cl \\ | \\ CH_2\text{—}OH \end{array} + HCl \xrightarrow{200\ ^0C} \begin{array}{c} CH_2\text{–}Cl \\ | \\ CH_2\text{—}Cl \end{array} + H_2O$$
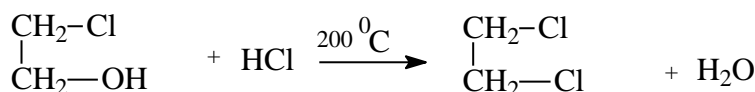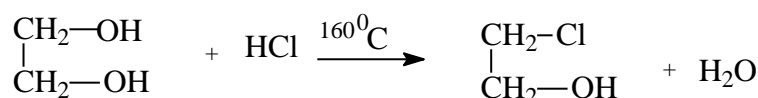
3. Action with phosphorus halides : ethylene dihalides are formed as follow:

$$3 \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + PBr_3 \longrightarrow 3 \begin{array}{l} CH_2-Br \\ | \\ CH_2-Br \end{array} + {}^2 H_3PO_4$$
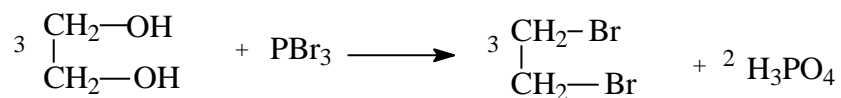
PI_3 produce ethylene diodide which is unstable and split into I_2= and ethylene

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + PI_3 \longrightarrow \begin{array}{l} CH_2-I \\ | \\ CH_2-I \end{array} \longrightarrow \begin{array}{l} CH_2 \\ || \\ CH_2 \end{array} + I_2$$

4. Reaction with carboxylic acid: Gives diester depending upon the amount of glycol and acid taken:

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + CH_3COOH \longrightarrow \begin{array}{l} CH_2-OCOCH_3 \\ | \\ CH_2-OH \end{array} + H_2O$$

glycol monoacetate

$$\begin{array}{l} CH_2-OCOCH_3 \\ | \\ CH_2-OH \end{array} + CH_3COOH \xrightarrow[\text{in excess}]{H_2SO_4} \begin{array}{l} CH_2-OCOCH_3 \\ | \\ CH_2-OCOCH_3 \end{array}$$

glycol diacetate
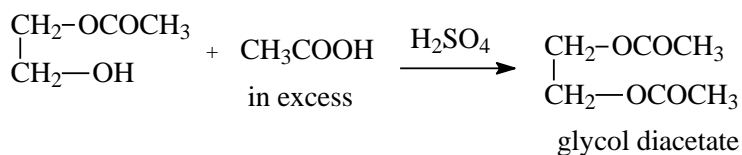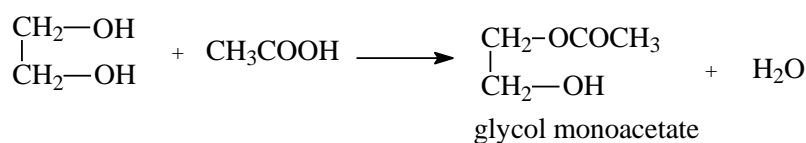
With dibasic acid it form polymer:

$$\left[HOOC-\!\!\!\bigcirc\!\!\!-COOH \right]_n + n\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{-nH_2O} HO\!\!\left[\overset{O}{\overset{||}{C}}-\!\!\!\bigcirc\!\!\!-\overset{O}{\overset{||}{C}}-OCH_2CH_2O \right]_n\!\!H$$

trephthalic acid   terylene
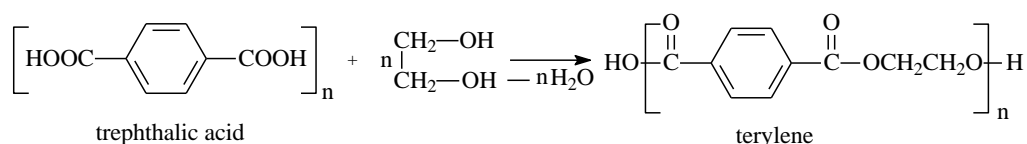
5. Reaction with aldehyde and ketones: Glycol reacts with aldehyde and ketones in presence of p- toluene sulphonic acid to give cyclic acetals/ketals which further may give ketone/aldehyde while treating with HIO_4. This reaction thus can be useful to protect carbonyl group.

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + O=C\!\!\begin{array}{l} R \\ H \end{array} \longrightarrow \text{(cyclic acetal)} + H_2O$$

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + O=C\!\!\begin{array}{l} R \\ R \end{array} \longrightarrow \text{(cyclic ketal)} + H_2O$$

$$\text{(cyclic ketal)} \xrightarrow{HIO_4} {}^2 CHCO + O=C\!\!\begin{array}{l} R \\ R \end{array}$$

---
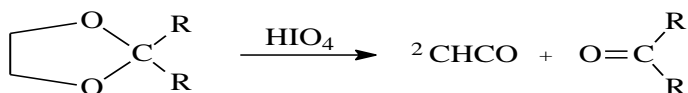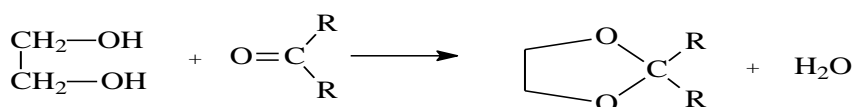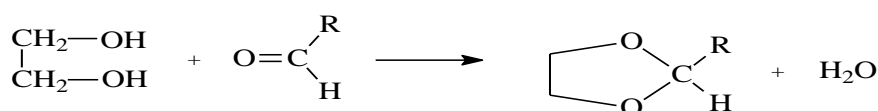
6. (i) The oxidation of ethylene glycol with HNO_3 to yields anumber of substance as follow:
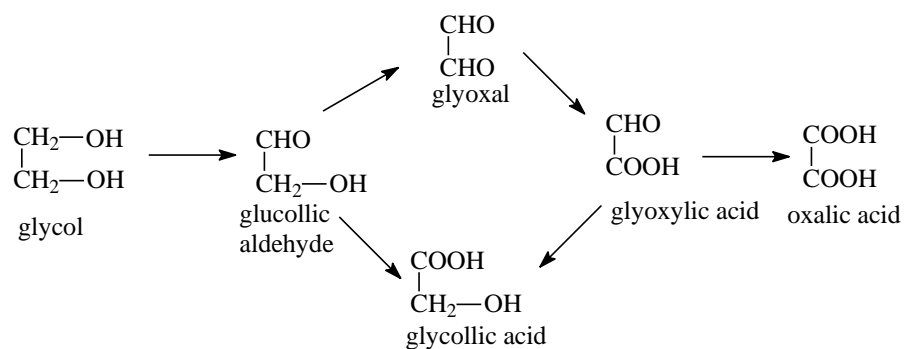
(ii) Oxidation with $KMnO_4$ or $K_2Cr_2O_7$ to form formic acid:
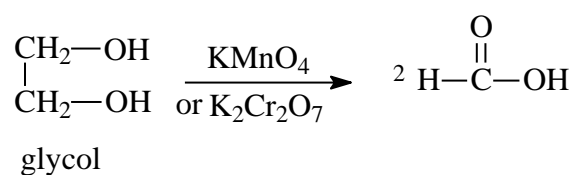
(iii) Oxidation with $Pb (OCOCH_3)_4$ or HIO_4 glycol gives formaldehyde.
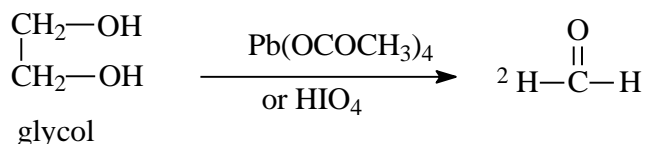
7. Dehydration: (i) Heating wih $ZnCl_2$ glycol gives acetaldehyde
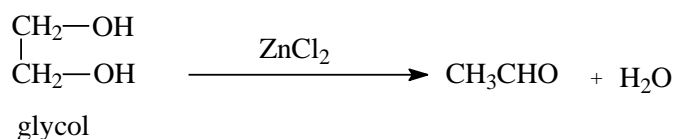
(ii) When heated alone at 500^0C, it gives ethylene oxide.
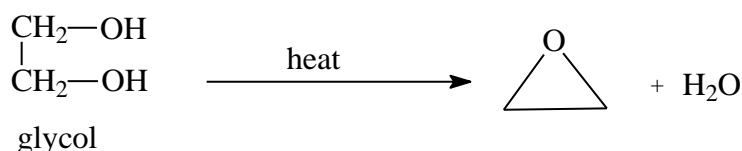
(iii) Dioxane is obtained when glycol is heated with conc. H_2SO_4.
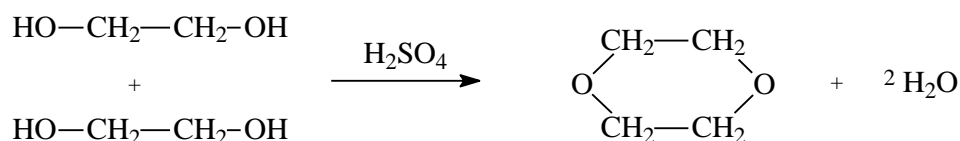
Uses of ethylene glycol:-

1. It is used as antifreeze substance which prevents the freezing of water in car radiators in cold countries.

2. Due it has a high viscosity, so it is used in the hydrolic break, printing ink ball, pen inks, organic solvents.

3. Used in the manufacture of Dacron, dioxane etc.

4. As a solvent and as a preservative.

5. As a cooling agent in aeroplanes.

6. As an explosive in the form of dinitrate.

7. Large amounts of ethylene glycol are converted to polymers (such as polyethylene glycol) used in the manufacture of dacron fibers, photographic films and cassette tapes.

5.12 TRIHYDRIC ALCOHOL

It is a triol. The introduction of third –OH group in diol molecule raises the b.p. about 100^0C, increase viscosity and make the alcohol sweeter. Viz; glycerol

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
$$
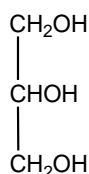
It is desigbated as prop-1, 2, 3-triol in IUPAC nomenclature. It may be considered as derivative of propane, obtained by replacement of three hydrogen atoms from different carbon atoms by three hydroxyl group. In industry, it's known as glycerine. It occurs as glycosides in almost all animal and vegetable oils and fats.

5.13 METHODS OF PREPARATION

Glycerol can be synthesized by following different methods:

1. **From fats and oil:** On hydrolysis of fats and oils, glycerol and higher fatty acids are formed.

$$
\begin{array}{c}
CH_2OOCR \\
| \\
CHOOCR \\
| \\
CH_2OOCR
\end{array}
+ \ 3H_2O \longrightarrow
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+ \ 3RCOOH
$$
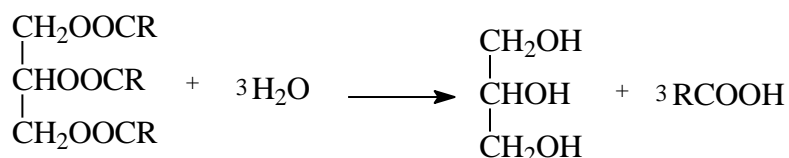
2. **By fermentation of sugars:** Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.

$$C_6H_{12}O_6 \xrightarrow[\text{Na}_2\text{SO}_2]{\text{yeat}} \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + CH_3CHO + CO_2$$
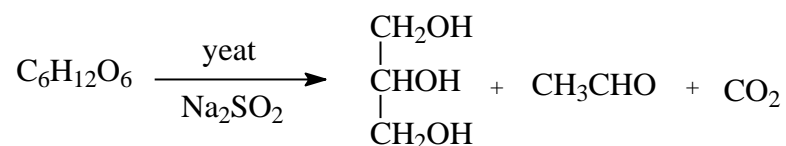
3. **Synthesis (from propene):** Today much of glycerol is obtained from propene.

$$\begin{array}{c} CH_3 \\ | \\ CH \\ || \\ CH_2 \end{array} \xrightarrow[600\,^0C]{Cl_2} \begin{array}{c} CH_2Cl \\ | \\ CH \\ || \\ CH_2 \end{array} \xrightarrow{\text{dil NaOH}} \begin{array}{c} CH_2OH \\ | \\ CH \\ || \\ CH_2 \end{array} \xrightarrow{\text{HOCl}} \begin{array}{c} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array} \xrightarrow{\text{dil NaOH}} \begin{array}{c} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$
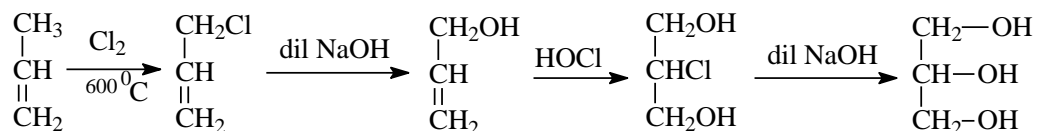
Physical properties: Glycerol is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-oxic in nature. It is soluble in water and ethyl alcohol but insoluble in ether. It has high boiling point, i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding purified in the lab by reduced pressure distillation or vacuum distillation.

5.14 CHEMICAL REACTIONS

Glycerol molecule contains two 1^0 – OH groups and one 2^0 – OH group. Thus, it shows characteristics of both primary and secondary alcohols.

$$\begin{array}{ll} \text{Primary alcoholic group} \longrightarrow & CH_2OH \\ & | \\ \text{Secondary alcoholic group} \longrightarrow & CHOH \\ & | \\ \text{Primary alcoholic group} \longrightarrow & CH_2OH \end{array}$$
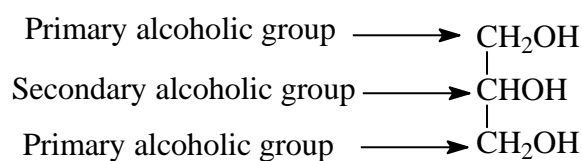
In general, 1^0 – OH groups are more reactive than 2^0 – OH group.

1. Reaction with sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked, Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{Room tem.}]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{High tem.}]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \end{array}$$
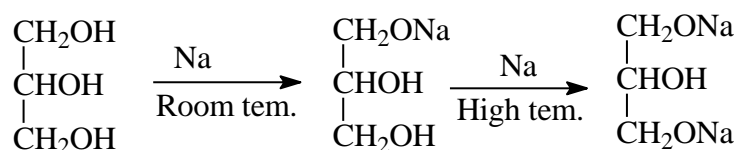
2. Reaction with PCI$_5$: All three OH groups are replaced by Cl atoms.

$$
\begin{array}{c}
CH_2OH \\
| \\
CH_2OH \\
| \\
CH_2OH
\end{array}
\;+\; PCl_5 \;\longrightarrow\;
\begin{array}{c}
CH_2-Cl \\
| \\
CH-Cl \\
| \\
CH_2-Cl
\end{array}
\;+\; 3\,POCl_3 \;+\; 3\,HCl
$$
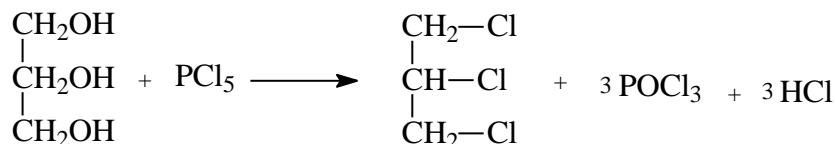
3. Reaction with HCl or HBr: When HCl is passed into glycerol at 110°C, both, α or β glycerol monochlorohydrins are formed. If the HCl gas is passed for sufficient time, glycerol α, α' dichlorohydrin and glycerol, α, β- dichlorohydrin are formed.

$$
\begin{array}{c}
CH_2-OH \\
| \\
CH-OH \\
| \\
CH_2-OH
\end{array}
\;+\; HCl \;\xrightarrow{110\,^0C}\;
\begin{array}{c}
CH_2-Cl \\
| \\
CH-OH \\
| \\
CH_2-OH
\end{array}
\;+\;
\begin{array}{c}
CH_2-OH \\
| \\
CH-Cl \\
| \\
CH_2-OH
\end{array}
$$

$$
\begin{array}{c}
CH_2-Cl \\
| \\
CH-OH \\
| \\
CH_2-Cl
\end{array}
\;+\;
\begin{array}{c}
CH_2-Cl \\
| \\
CH-Cl \\
| \\
CH_2-OH
\end{array}
\;\xleftarrow[110\,^0C]{\text{Excess of HCl}}
$$
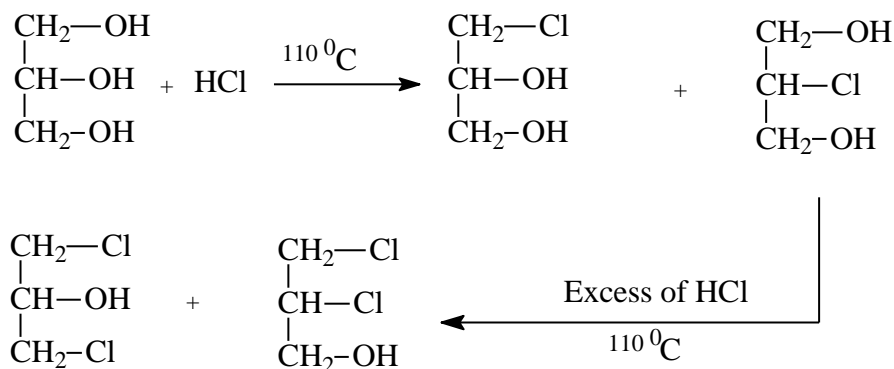
Same reactions occur with HBr.

4. Reaction with HI: Glycerol reacts with HI in two ways:
(a) When glycerol is warmed with a small amount of hydrogen iodide, allyl iodide is formed. First tri-iodide is formed but due to large size of iodine atom I_2 comes out from product.

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\;+\; 3\,HI \;\longrightarrow\;
\begin{array}{c}
CH_2I \\
| \\
CHI \\
| \\
CH_2I
\end{array}
\;\longrightarrow\;
\begin{array}{c}
CH_2 \\
|| \\
CH \\
| \\
CH_2I
\end{array}
\;+\; I_2
$$
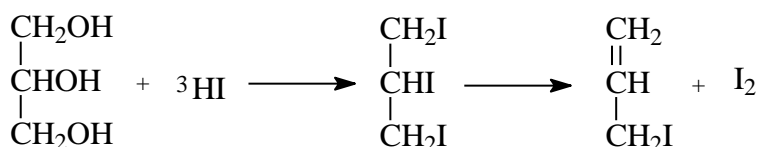
(b) When glycerol is heated with a large amount of HI, the allyl iodide first formed is reduced to propene, which in presence of excess of HI forms iso-propyl iodide.

$$
\begin{array}{c}
CH_2 \\
|| \\
CH \\
| \\
CH_2I
\end{array}
\;+\; HI \;\longrightarrow\;
\begin{array}{c}
CH_3 \\
| \\
CHI \\
| \\
CH_2I
\end{array}
\;\xrightarrow{-I_2}\;
\begin{array}{c}
CH_3 \\
| \\
CH \\
|| \\
CH_2
\end{array}
\;+\; HI \;\longrightarrow\;
\begin{array}{c}
CH_3 \\
| \\
CHI \\
| \\
CH_3
\end{array}
$$
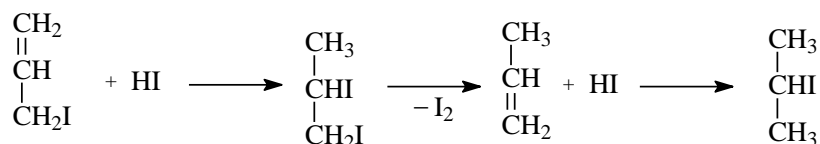
5. Reaction with HNO_3: When one part of glycerol in a thin stream is added to three times conc. HNO_3 and five parts of concentrated sulphuric acid, nitro-glycerine (glyceryl trinitrate) is formed.

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\;+\; HNO_3 \;\xrightarrow{\text{Con. } H_2SO_4}\;
\begin{array}{c}
CH_2-ONO_2 \\
| \\
CH-ONO_2 \\
| \\
CH_2-ONO_2
\end{array}
\;+\; 3\,HCl
$$
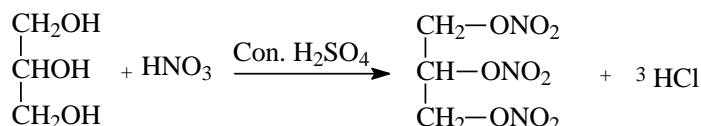
Glyceryl trinitrate is a yellow oily liquid. It is poisonous and causes headache. It explodes violently when heated rapidly or subjected to sudden shock. It becomes a safer explosive when absorbed on kieselguhr. In this form, it is known as **dynamite.** Dynamite was discovered by Alfred Nobel in 1867.

6. Reaction with acetic acid, acetic anhydride or acetyl chloride: Mono-, di- and tri-esters are formed.

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\xrightarrow[\text{or } CH_3COCl]{CH_3COOH}
\begin{array}{c}
CH_2OCOCH_3 \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\xrightarrow[\text{or } CH_3COCl]{CH_3COOH}
\begin{array}{c}
CH_2OCOCH_3 \\
| \\
CHOH \\
| \\
CH_2OCOCH_3
\end{array}
$$

$$
\begin{array}{c}
CH_2OCOCH_3 \\
| \\
CHOCOCH_3 \\
| \\
CH_2OCOCH_3
\end{array}
\longleftarrow
$$
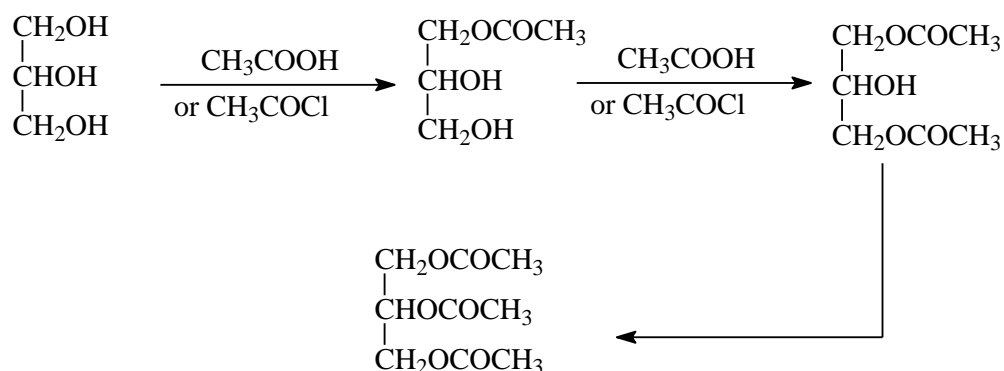
7. **Reaction with oxalic acid:** Different products are formed under different conditions.

   (a) At 100^0C and with excess of oxalic acid, formic acid is formed

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+ HOOC-COOH
\xrightarrow[-H_2O]{100-110^0C}
\begin{array}{c}
CH_2O-\overset{\overset{O}{||}}{C} \\
| \quad\quad | \\
CHOH \quad C-OH \\
| \quad\quad\; || \\
CH_2OH \; O
\end{array}
\xrightarrow{-CO_2}
\begin{array}{c}
CH_2OOCH \\
| \\
CHOH \\
| \\
CH_2OCOCH_3
\end{array}
$$

$$
HCOOH \; +
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\longleftarrow
\begin{array}{c}
H_2O
\end{array}
$$

   (b) At 260^0C allyl alcohol is formed

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+ HOOC-COOH
\xrightarrow[-2H_2O]{}
\begin{array}{c}
CH_2OOC \\
| \quad\quad | \\
CHOOC \\
| \\
CH_2OH
\end{array}
\xrightarrow[-2CO_2]{}
\begin{array}{c}
CH_2 \\
|| \\
CH \\
| \\
CH_2OH
\end{array}
$$
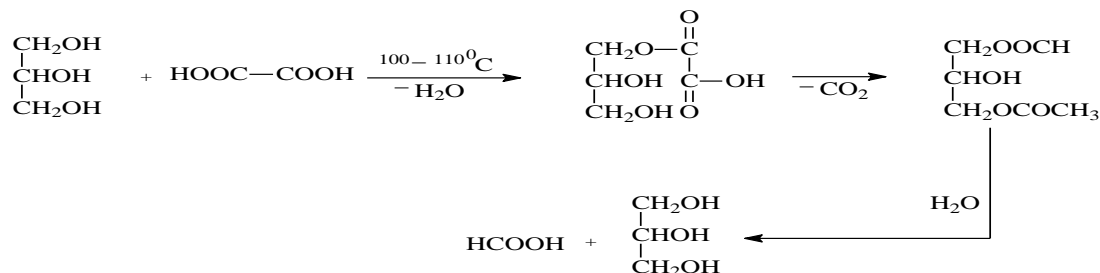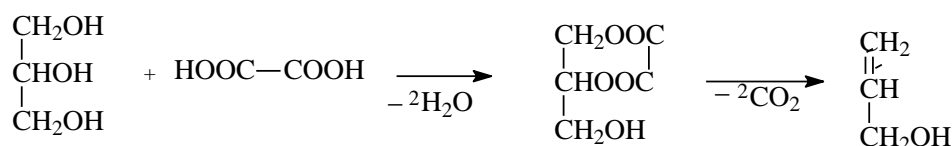
8. Dehydration: Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus penta oxide or conc. sulphuric acid, acrolein or acrylaldehyde is formed which has a characteristic bad smell. This reaction can be used as a test of glycerol.

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
\xrightarrow[P_2O_5 \; heat]{KHSO_4 \; or}
\begin{array}{c}
CH_2 \\
|| \\
CH \\
| \\
CHO
\end{array}
+ \; 2H_2O
$$
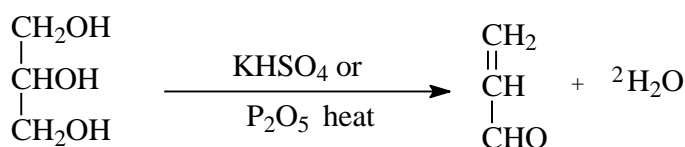
9. Oxidation: Glycerol gives different oxidation products depending on the nature of oxidizing agent. The following products may be obtained during oxidation of glycerol.
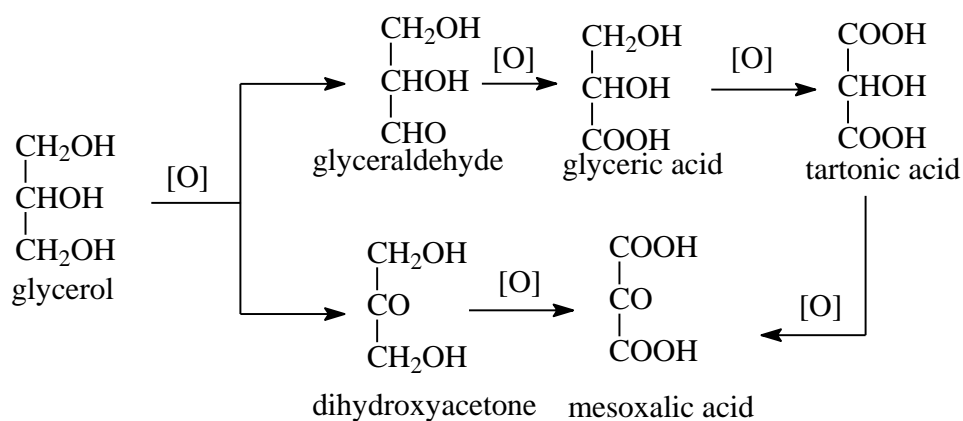
(a) Dilute HNO_3 gives mainly glyceric acid.

(b) Conc. HNO_3 oxidises glycerol into glyceric acid and tartronic acid.

(c) Bismuth nitrate gives mainly meso oxalic acid.

(d) Fenton's reagent (H_2O_2 + $FeSO_4$) or NaOBr or Br_2- water in presence of Na_2CO_3 oxidises glycerol into a mixture of glyceraldehyde and dihydroxy acetone (or glycerose).

10. Formation of resin: Glycerol reacts with phthalic anhydride forming polyesters known as glyptals. Each of the three –OH groups in glycerol forms an ester linkage with the anhydride, giving a thermosetting polymer (plastic) used for making synthetic fibers.
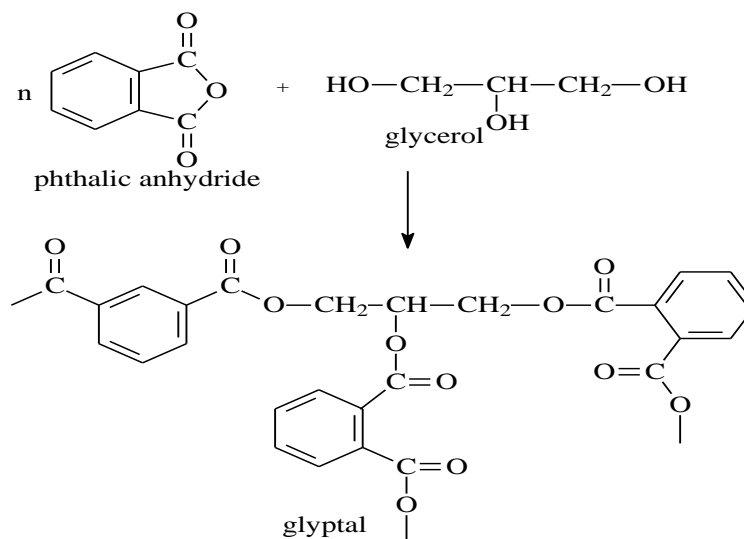
Uses: Glycerol is used: Glycerol is used as a sweetening agent in confectionery, beverages and medicines being non-toxic in nature. It is used as antifreeze in automobile radiators, in the preparation of good quality of soap, hand lotions, shaving creams, tooth pastes and cosmetics and as a lubricant in watches and preservative.

5.15 SUMMARY

In this unit we have learnt that:

- Alcohols are compounds in which a hydrogen of alkane has been replaced by an –OH group and are classified as monohydric, dihydric, trihydric or polyhydric on the basis of –OH group present.

- The monohydric alcohols can be classified into 1°, 2° and 3° alcohols. In IUPAC name alcohols are designated as alkannol by replacing 'e' with –ol from the corresponding alkane.

- This unit also describes the methods of preparation of alcohols by using different methods like; hydrolysis of halogenoalkanes, hydration of alkene, reduction of aldehydes and ketones using Grignard reagents (RMgX), $LiAlH_4$, $NaBH_4$, by fermentation of carbohydrates etc.

- The amphoteric nature of alcohols has also been described in this unit. As an acid, it ionizes to form an alkoxide ion (RO^-) and hydrogen ion, H + in the presence of a base, while in   presence of an acid, the alcohol may function as a base and can accept a proton.

- This unit   makes the readers aware about methods of preparation, physical properties and chemical reactions along with applications of dihydric alcohol glycol and trihydric alcohol glycerol.

5.16 TERMINAL QUESTION

Q. 1. Explain why Alcohols are acidic in nature.

Q. 2. Write the mechanism of dehydration of ethyl alcohol with conc. H_2SO_4.

Q. 3. Why boiling point of alcohols is higher than that of alkanes of corresponding molecular weight.

Q. 4. Explain why polarity of primary alcohol is maximum?

Q.5. Write the major product(s) of the following reaction.

$$\underset{\text{pyridine}}{\xrightarrow{\text{SOCl}_2}}$$

$$\xrightarrow{\text{PBr}_3}$$

$$\underset{\text{H}_2\text{SO}_4}{\xrightarrow{\text{CrO}_3}}$$

$$\xrightarrow{\text{PBr}_3}$$
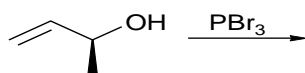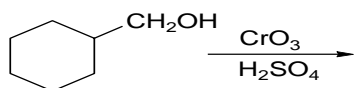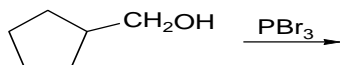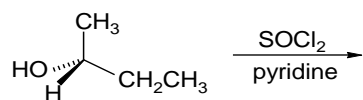
Q.6. Write short note on:-

1. Satuzaff's rule

2. Glyptal

3. Amphoteric nature of alcohols

4. Synthesis of glycerol

5. Applicatoions of glycol and glycerol

6. Classification of monohydric alcohols

7. Oxidation of glycol and glycerol

Q.8. Tick the appropriate option (MCQs)

1. Ethanol containing some methanol is called

    A. Absolute sprit   B. Rectified sprit

    C. Power alcohol   D. Methylated sprit

2. Glycerol is a:

    A. Primary alcohol   B. Monohydric alcohol

    C. Secondary alcohol   D. Trihydric alcohol

3. Which of the following can work as a dehydrating agent for alcohols?

        A. H_2SO_4 B.Al_2O_3

        C. H_3PO_4 D. All.

4. Primary and secondary alcohols on action of red-hot copper give

    A. Aldehydes and ketons respectively   B. Ketones and aldehydes respectively

    C. Only aldehydes   D. Only ketones

5. Which one has highest boiling point?

        A. Butan-2-ol   B.Ethane

        C.Butane   D.Pentane

6. Which of the following has maximum hydrogen bonding?

      A. Ethyl amine   B.Ammonia

      C. Ethyl alcohol   D. Diethyl ether

7. What is the product of the following reaction?
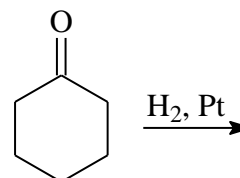
    A. Cyclohexanol   B.Cyclohexane

    C. Cyclohexene   D. 1,2-cyclohexanediol

8. What is the product of the following reaction?
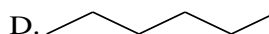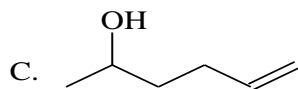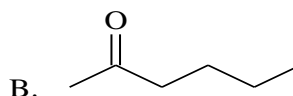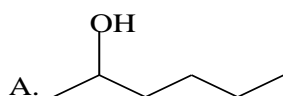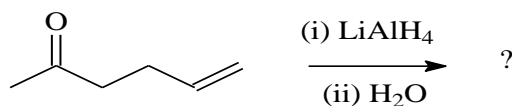
9. What is the product in following reaction?
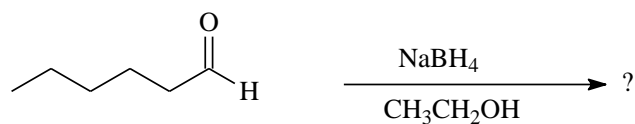
A. 　　　　B.

C. 　　D.

10. What is the IUPAC name of the compound below?
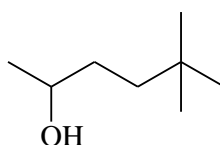
A. 5,5 – dimethyl-2-hexanol　　　　　　B. 5,5-dimethyl- 2- pentanol

C. 2,2- dimethyl-5-hexanol　　　　　　D. 2,2-dimethyl-5-pentanol

11. What is IUPAc name of the following compound?
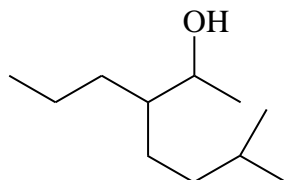
A. 3-isobutyl-2-hexanol　　　　　　　　B. 2-methyl-5-propyl-6-heptanol

C. 2-methyl-5-(1-hydroxyethyl) octane　　D. 6-methyl-3-propyl-2-heptanol

12. What is the IUPAC name of the following compound?
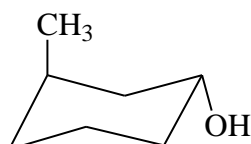
A. *cis*-3-methylcyclohexanol　　　　　B. *cis*-5-methylcyclohexanol

C. *trans*-3-methylcyclohexanol　　　　D. *trans*-5-methylcyclohexanol

13. Identify the tertiary alcohol.

A.

B.

C.

D.
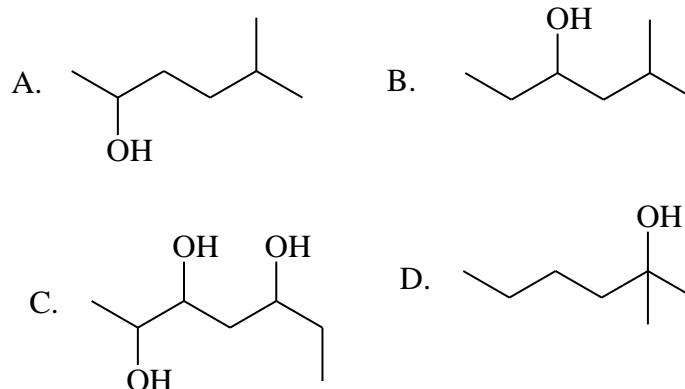
14. What is the hybridization of the oxygen atom in alcohols?

   A. sp   B. sp^2

   C. sp^3 D. sp^3d

15. The compound found in Whisky, Brandy & Bear:

   A. CH_3OH B. CH_3CH_2OH

   C. $CH_3CH_2CH_2OH$ D. $CH_3CH_2CH_2CH_2OH$

16. Which of these five-carbon alcohols would you expect to be most water soluble?
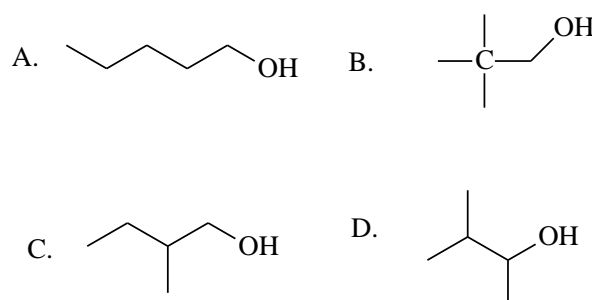
   A.

   B.

   C.

   D.

17. Which is the major product of the following reaction?

   A.

   B.

   C.

   D.

18. Which is the major product of the following reaction?

$$\text{C}_6\text{H}_5\text{CO-CH}_3 \quad + \quad CH_3MgBr \quad \xrightarrow{\text{Ether}} \quad \xrightarrow{H_3O^+}$$

A.

B.

C.

D.
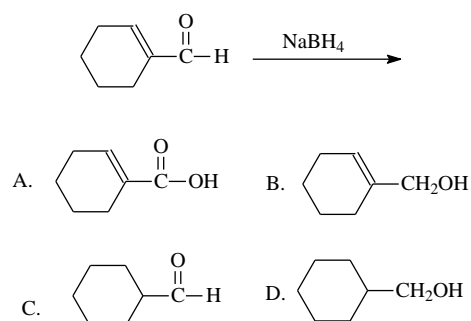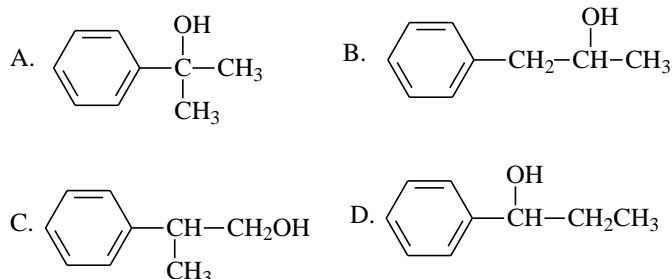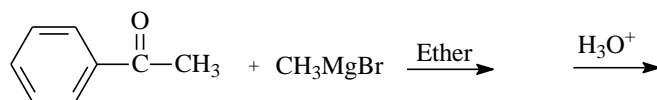
19. Arrange the compounds in order of increasing solubility in water (least first).

$$\underset{\text{I}}{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H} \quad \underset{\text{II}}{CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}H_2} \quad \underset{\text{III}}{CH_3CH_2CH_2CH_2CH_3} \quad \underset{\text{IV}}{CH_3CH_2\overset{O}{\diagdown}CH_2CH_3}$$
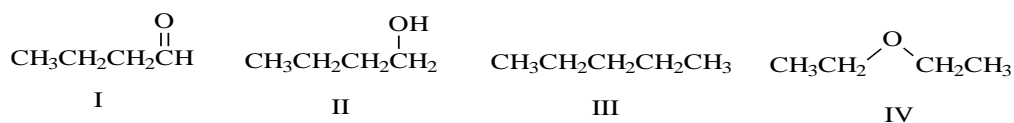
    A. II, I, IV, III   B. I, II, IV, III

    C. III, IV, I, II   D. II, I, IV, III

20. Dynamide is:

    A. Nitroderivative of glycerol   B. Nitro derivative of glycol

    C. Acetyl derivative of glycerol   D. Acetyl derivative of glycol

5.17 ANSWER

1. D   2. D   3. D   4. A   5. A   6. C   7. C   8. C   9. C   10. A   11. D

12. C   13. D   14. C   15. B   16. B   17. B   18. A   19. B   20. B

5.18 REFERENCES

1. Jerry march, Advanced Organic Chemistry, 4th edition, Wiley India,   2010.

2. P.S. Kalsi, Organic Reactions and their Mechanisms, 2nd edition, New age

   International Publishers. 2017

3. S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry. Trinity

Press, 2016

4. Goutam Brahmachari, Organic name Reactions, Narosa publishing house, New

   Delhi. Revised version: 2012.

5. I.L. Finar, Organic Chemistry, Vol. II. 5th edition, ELBS & Longman group Ltd.,

   1974.

6. Organic chemistry, R.T. Morrision and R.N. Boyd, 6th edition, Prentice Hall Private

   Ltd. 1997.

8. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum. 5th Edition,

   2007

9. B.S Bahal and Arun Bahal Advanced Organic Chemistry, 1993, S. Chand & Company
   Ltd. Ram Nagar, new Delhi

UNIT -6 PHENOLS AND ETHER

CONTENTS:

6.1 Introduction

6.2 Objectives

6.3 Nomenclature

6.4 Methods of preparation of phenols

6.5 Commercial preparation of phenols

6.6 Physical properties of phenols

6.7 Acidic character of phenols

6.8 Chenical reactions of phenols

6.9 Substituted phenols

6.10 Introduction of ethers

6.11 Nomencleature of ethers

6.12 Methods of preparation

6.13 Physical properties

6.14 Chemical properties

6.10 Summary

6.11 Terminal questions

6.12 Answers (MCQs)

6.13 References

6.1 INTRODUCTION

Phenols are compounds in which the -OH group is directly attached to an aromatic carbon like benzene ring. Although they share the same functional group with alcohols, where the –OH group is attached to an aliphatic carbon, the chemistry of phenols is very different from that of alcohols. The simplest phenol is hydroxybenzene also called phenol with formula C_6H_5OH. Simple phenol is an antiseptic. A phenolic compound hexachlorophene is a constituent of several mouthwashes, deodorant soaps and medicinal skin cleansers.

Phenol
(hydroxy benzene)

hexachlorophene
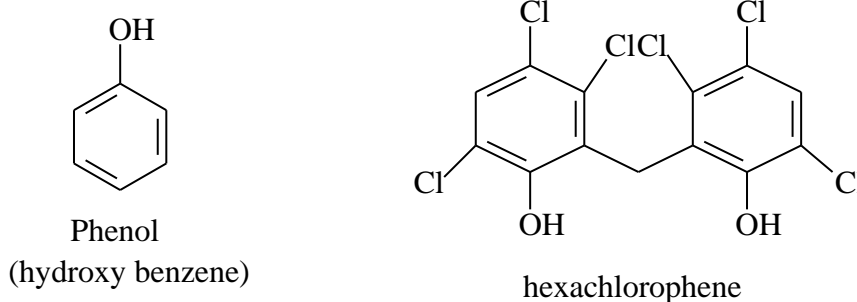
The –OH group consists of an **O** atom bonded to a sp^2-hybridised aromatic **C** atom and a **H** atom via σ bonds as follow. Both the **C-O** and the **O-H** bonds are polar due to the high electronegativity of the **O** atom. Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.

This results in, compared to simple alcohols: - A shorter carbon-oxygen bond distance,

a more basic hydroxyl oxygen, a more acidic hydroxyl proton (-OH)

sp^2
hybridized carbon
with one vacant p orbital

vacant p orbitals

Structure of phenol

C_6H_5OH
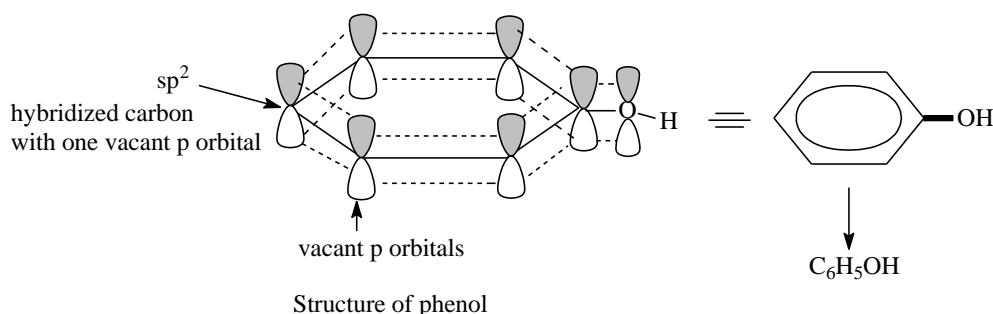
The electronic structure of phenol can be represented as resonance hybrid of the following canonical forms.

I   II   III   IV
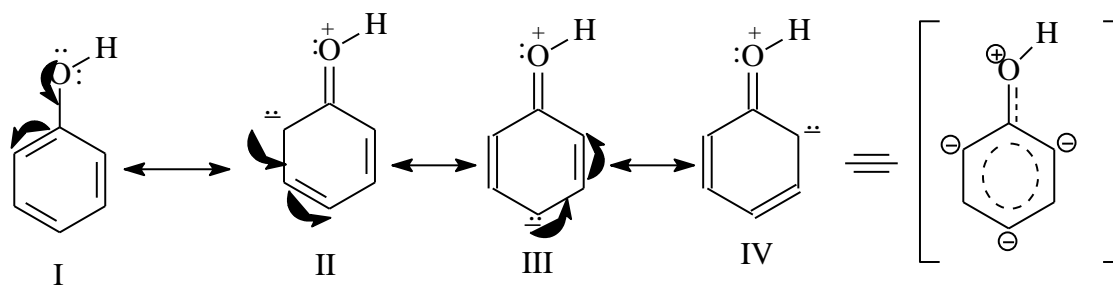
It must be noted that the aromatic compounds in which -OH group is not directly attached to benzene ring are not phenols but are called aromatic alcohols. These may be regarded as aryl derivatives of aliphatic alcohols.
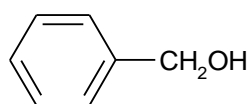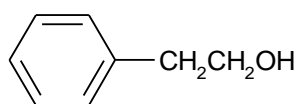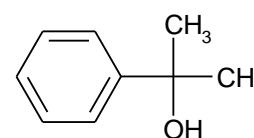
Benzyl alcohol   2-Phenylethanol   2-Phenylpropanol

6.2 OBJECTIVES

The objectives of this unit are; -

- To study the structure and bonding of phenol. To study physical and chemical properties of phenols, their acidic characters.
- Besides these objectives this unit will make aware the students about general methods of preparation of phenols, comparative acidic characters with alcohols, various chemical reactions, characteristic electrophilic substitution reactions and some name reactions involving phenols.

6.3 NOMENCLATURES

Functional group suffix = *-common - phenol, systematic - benzenol*

Functional group prefix = *hydroxy*

The hydroxyl derivatives of toluene have been given the name CRESOLS. If a phenolic moiety is included in a molecule which is named by IUPAC system, the –OH group is specified as a substituent according to the order of precedence. In such a case a substituent

(COOH or –CHO) is assigned number-1. The systematic and common names of some phenols have been illustred as follow.

MOHOHYDRIC PHENOLS:
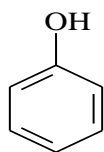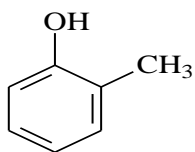
phenol   2- methylphenol   3- methylphenol   4- methylphenol
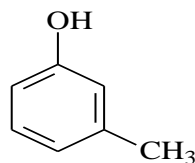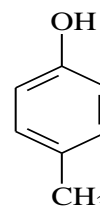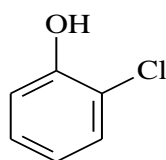
2- chlorophenol

2- chloro -1- hydroxy benzene
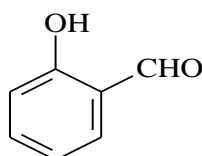
2- hydroxybenzaldehyde
ortho hydroxybenzaldehyde
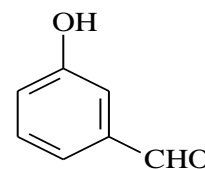
3 - hydroxybenzaldehyde
meta hydroxybenzaldehyde

DIHYDRIC PHENOLS:
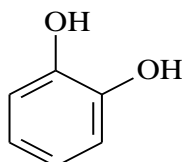
1,2 - dihydroxybenzene
catechol
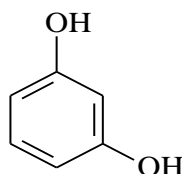
1,3 - dihydroxybenzene
resorcinol
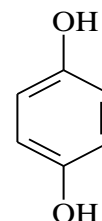
1,4 - dihydroxybenzene
hydroquinone

TRIHYDRIC PHENOLS:
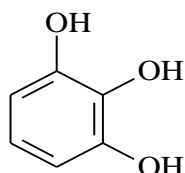
1, 2, 3 - trihydroxybenzene
pyrogallol
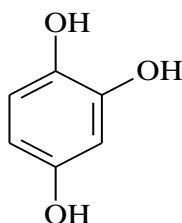
1, 2, 4 - trihydroxybenzene
hydroxyquinone
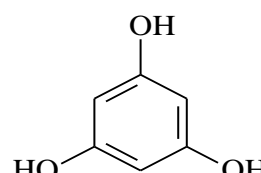
1, 3, 5 - trihydroxybenzene
phloroglucinol

The prfix ortho, meta and para are also used in place of 2, 3 and 4 while naming monohydrin substituted phenols or cresols
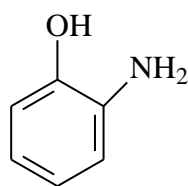
ortho amino
phenol
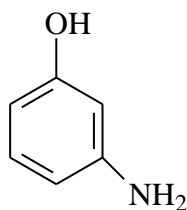
meta amino
phenol
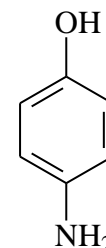
para amino
phenol
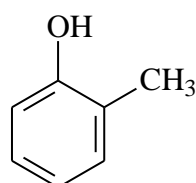
ortho cresol
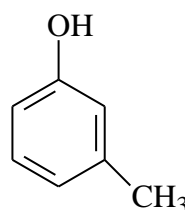
meta cresol
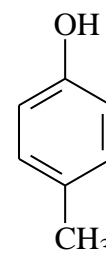
para cresol

6.4 METHODS OF PREPARATION OF PHENOLS

Thre are many methods which are used to prepare phenols viz;

1. From aryl sulphonic acids: An aryl sulphonic acid yields the corresponding phenol on heating it with molten sodium hydroxide at 570 - 620^0 K. The sodium salt is obtained which is hydrolysed with acid to obtain free phenol.
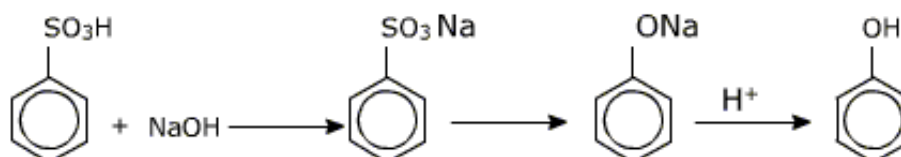
2. From haloarenes: Chlorobenzene (an haloarene) is hydrolysed by treating it with 10% NaOH at 623^0 K and 320 atmospheric pressures in presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.
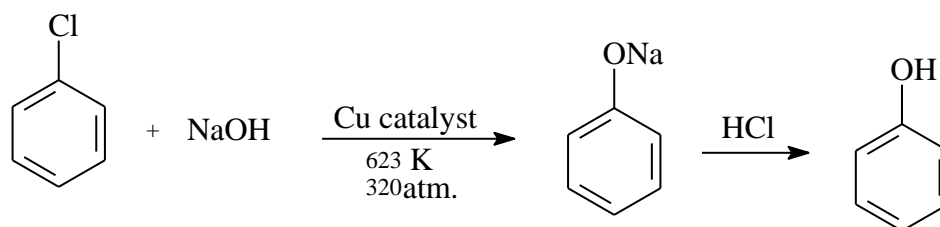
3. Hydrolysis of diazonium salts: A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (obtained from a mixture of $NaNO_2$ and HCl) at low temperature of 273^0 K to 278^0 K. Diazonium salts are hydrolysed to phenols treating with dilute acids.
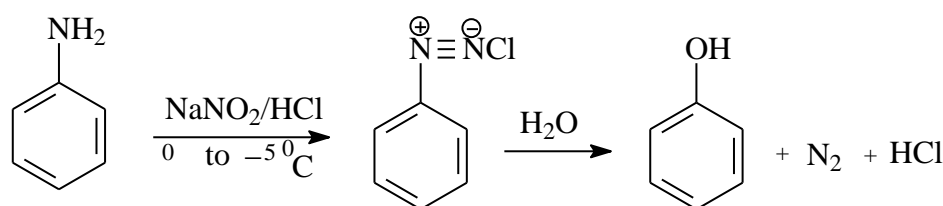
4. Decarboxylation of phenolic acids: Phenolic acids upon distillation with sodalime are decarboxylated to form sodium phenoxide, which upon hydrolysis gives phenols.
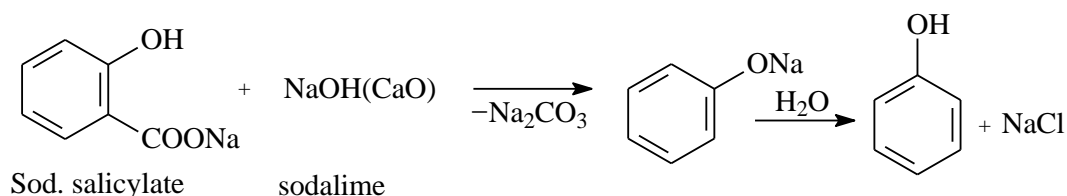
5. Oxidation of Grignard reagent followed by hydrolysis: Aromatic Grignard reagent on treating with O_2 in presence of light followed by hydrolysis in presence of mineral acid gives phenol.
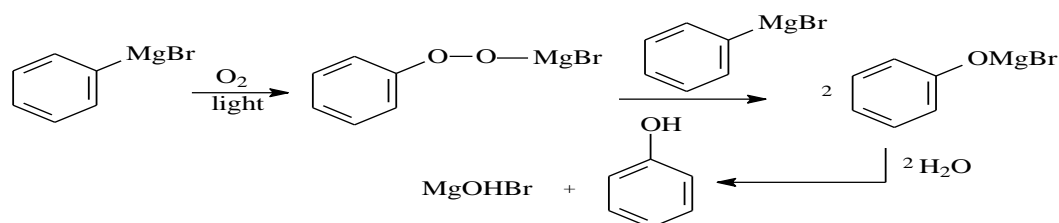
6.5 COMERCIAL PREPARATION OF PHENOLS

Phenols are important class of compounds used commercially for many purposes ance need commercial synthesis in pilot scale. Still some ammount of phenols are obtained from coal-tar, however about 90% are produced synthetically in industries.

1. From coal-tar: generally heavy and middle oil containing phenols and naphthalene in crude oil are subjected to extra cooling as aresult the naphthalene crystals are separated and are removed by filtration. The remaining fraction is treated with NaOH, which dissolve the phenols by making phenoxids. Altimately carbon dioxide gas is blown through the solution in order to liberate phenols. The water layer containing Na_2CO_3 is drawn off, leaving crude phenol behind, which is fractioned to recover the individual phenols as follow
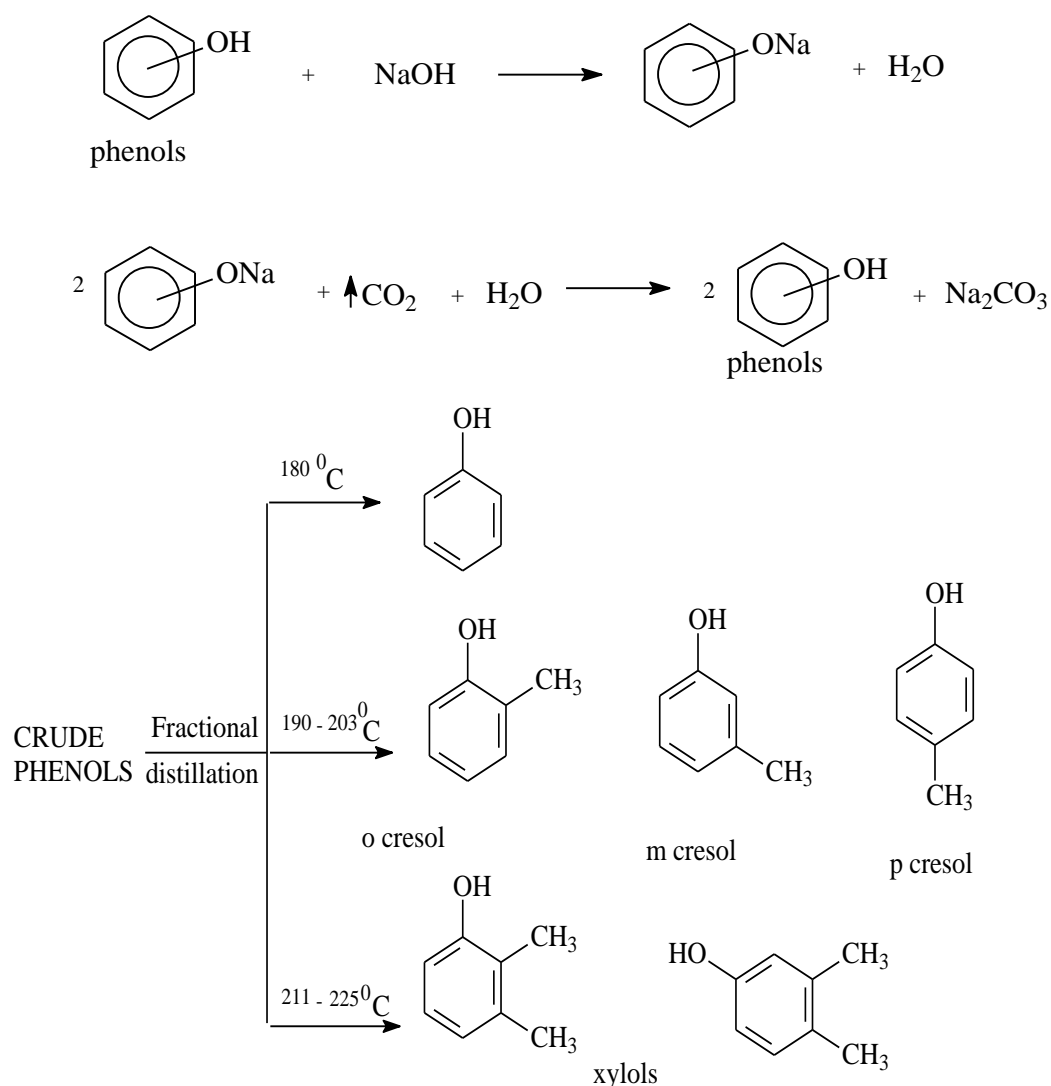
2. From cumene: Commercially phenol can be synthesised from cumene, which in turn is prepared from petrolium using Friedal Craft reaction as follow.
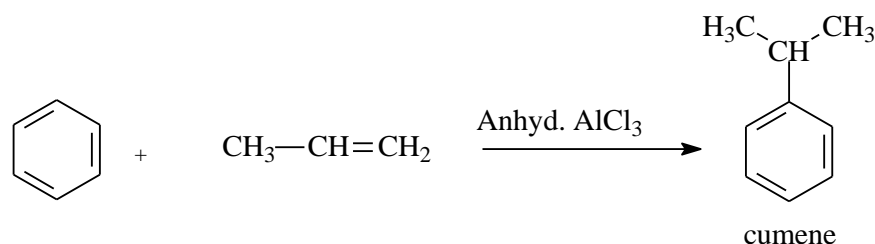
The cumene obtained from petroium as above is oxidised at 130^0C in presence of metal catalyst, which gives phenol as the ultimate product by envolving the intermediate compounds in sequence as follow.
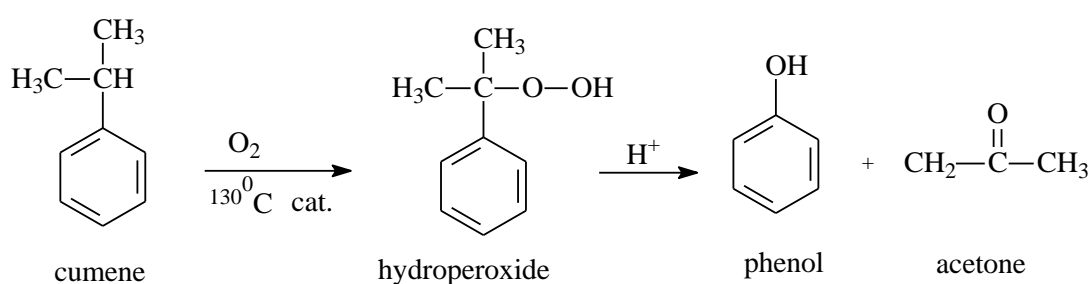
6.6 PHYSICAL PROPERTIES OF PHENOLS

Phenol has higher boiling point than the arenes or haloarenes or ethers of same molecular weight. It is due to the formation of intermolecular hydrogen bond. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discolored. Phenols are sparingly soluble in water but readily soluble in organic solvents such as alcohol and ether. The boiling points of phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding which is responsible for the high boiling point that is lacking in ethers and hydro carbons.
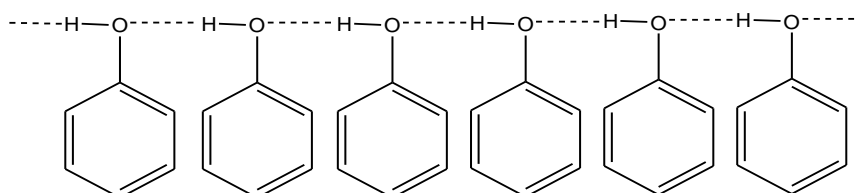
6.7 ACIDIC CHARACTER OF PHENOLS

Unlike alcohols (which also contain an -OH group) phenol is a strong acid. Phenols turn blue litmus red and react with metals liberating hydrogen. Phenols behave as acids because of the presence of more polar O-H group in them. They ionise in aqueous solutions and give H^+ ions to a base. However, they do not react with carbonates or bicarbonates.

The greater acidity of phenols can be attributed to the resonance stablisation of the phenoxide ion formed after losing hydrogen ion. The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions. Phenol is a very weak acid than carboxylic acid and the position of equilibrium lies well to the left.
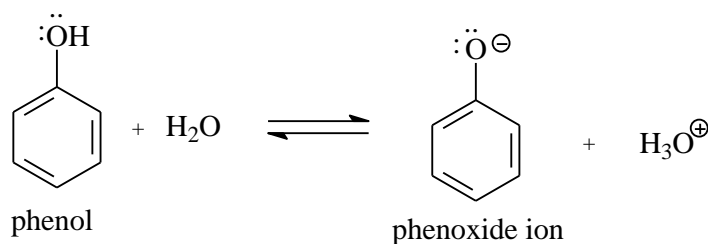
Phenols as well as phenoxide ion both are resonance stabilised. The negative charge on the oxygen atom is delocalised around the ring. The benzene ring helps to stabilise a negative charge on the phenoxide ion, $C_6H_5O^-$, and this makes phenol appreciably acidic (unlike ethanol, which is neutral, a solution of phenol in water has a pH of about 5). The more stable the ion is, the more likely it is to form. Phenol reacts with aq. sodium hydroxide solution to give a colourless solution containing sodium phenoxide.
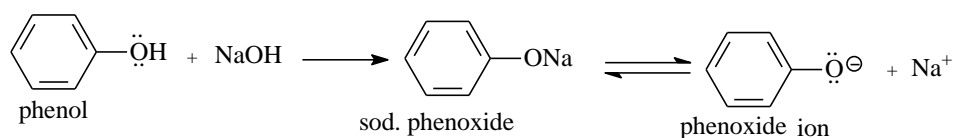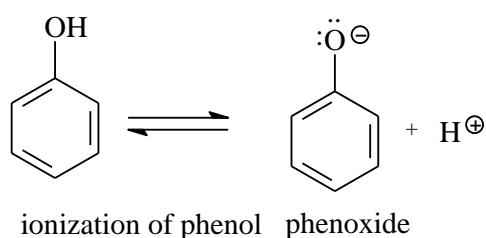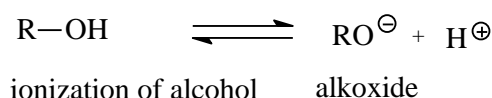

The various contributing structures of phenol and phenoxide ion are given below:
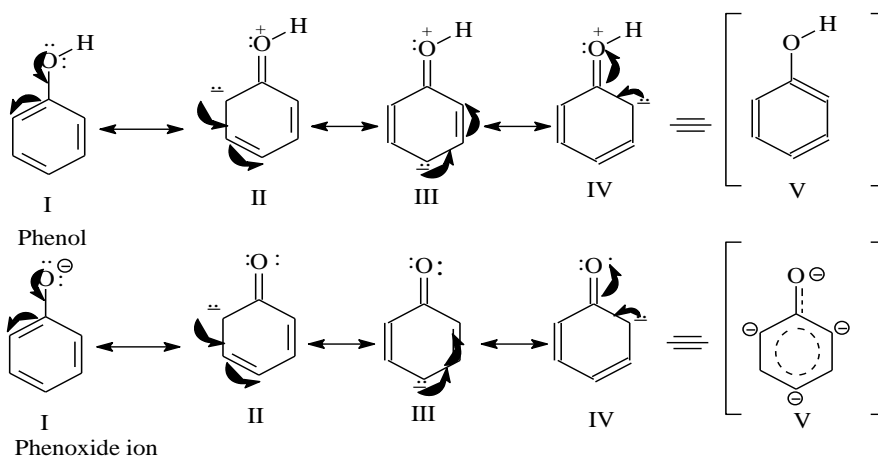

Comparative acidic character of alcohols and phenols

The ionisation of an alcohol and a phenol takes place as shown in equation:

$$R\!-\!OH \rightleftharpoons RO^{\ominus} + H^{\oplus}$$

ionization of alcohol   alkoxide

ionization of phenol   phenoxide

In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes phenoxide ion more stable and favours the ionisation of phenol. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of -OH group to be positive. A compound in which hydroxyl group directly attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group. Acids react with the more reactive metals to give hydrogen gas. Alcohols and phenols react with active metals like Na, K, Al etc to liberate hydrogen gas. The reactions of phenol with metals as well as NaOH indicate it is relatively more acidic than alcohols and also water. The sp^2 carbon of phenol attached to 'O' being more electronegative than sp^3 carbon of alcohols, it decreases the electron density on oxygen. Because of this oxygen develops still more electron seeking character and releases proton by taking the shared pair of electrons with it.

Effect of substituents on acidity of phenol: In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion.On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

picric acid/TNP

more acidic   less acidic
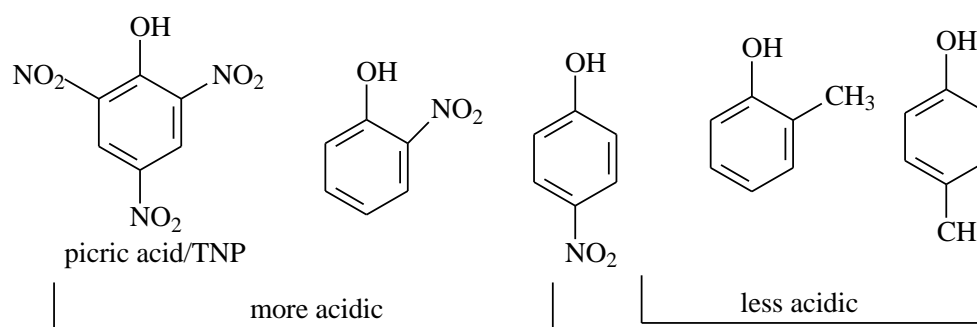
Electron releasing groups like alkyl groups increase the electron density on oxygen and decrease the polarity of O-H bond. This decreases the acidic strength. Hence alkylphenols have greater *pKa* values as compared to phenol itself.

On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents (–Cl, –NO$_2$, etc.) have lower *pKa* values than phenol. In fact, 2,4,6-trinitrophenol / picric acid (TNP) is more acidic than many carboxylic acids.

6.8 CHEMICAL REACTIONS OF PHENOLS

Alcohols and phenols both contain –OH group attached with carbon but in case of phenols the carbon atom is member of phenyl ring as also shown above in resonating structures in phenols the C-O bond acquires double bond character because of delocalization of electrons from oxygen to phenyl ring, which results the C-O stronger than O-H σ bond. The increased electron density in the phenyl ring activates it and gives electrophilic substitution reaction.

Resists cleavage

Easily cleaved

Phenol
Resonance hybrid

Resists cleavage
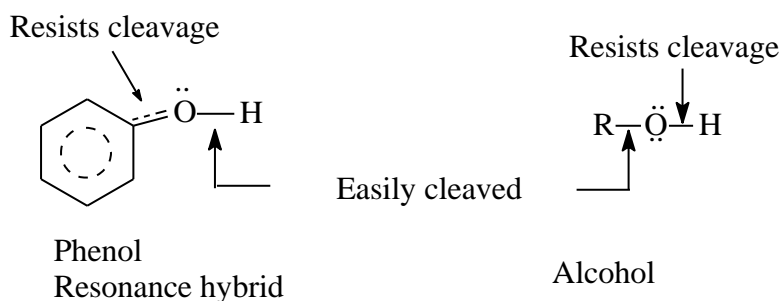
Alcohol

In alcohols no resonance is possible and the non bonded electron pairs remain localized on the oxygen atom. The C-O linkage thus retains its σ-bond character and is weak as compared to that in phenol.

Phenols thus undergo two types of reactions:

A. Reaction involving the –OH group

B. Reaction involving aromatic ring

A. Reactions involving –OH group:

1. Aidic character: Phenols are acidic compared to alcohols as they furnish proton to form phenoxide ion which is stabilized by resonance. Acidity of phenol is less than carboxylic acids.


ionization of phenol   phenoxide
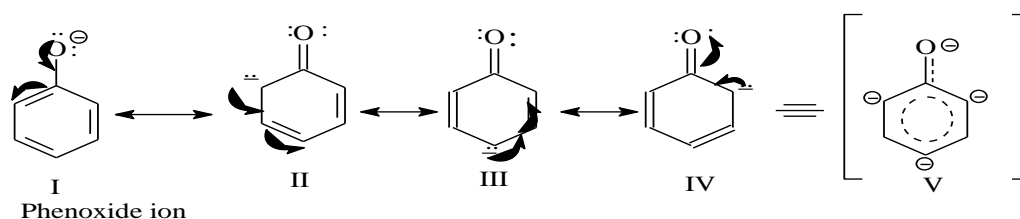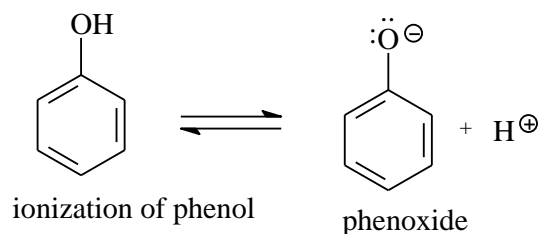
Phenols when react with aq. NAOH or KOH (bot with Na_2CO_3) to form soluble sodium salt known as phenoxides.
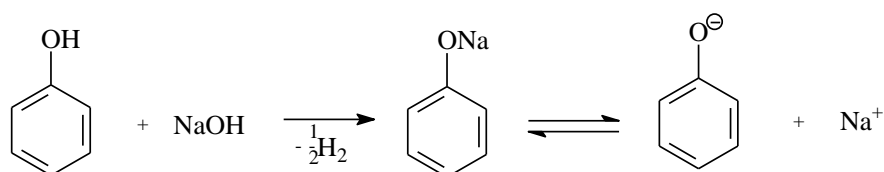
2. Reaction with $FeCL_3$: Phenols give ccolored complex when react with ferric neutral chloride solution

$$6 \quad \text{(OH)} \quad + \quad FeCl_3 \quad \longrightarrow \quad 3\,H^+ \quad + \quad [Fe\,(OC_6H_5)_6]^{3-} \quad + \quad 3\,HCl$$
colored complex
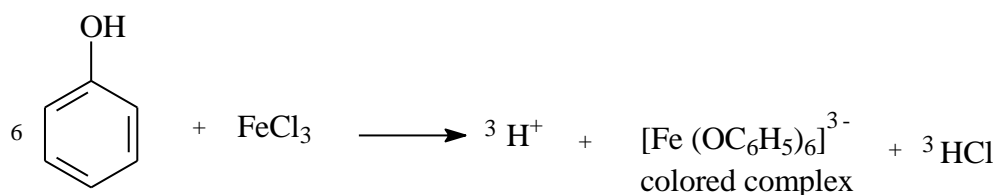
3. Replacement of –OH: When distilled with Zn dust, the –OH group is replaced by hydrogen atom.

phenol diazo methane anisol
methy phenyl ether
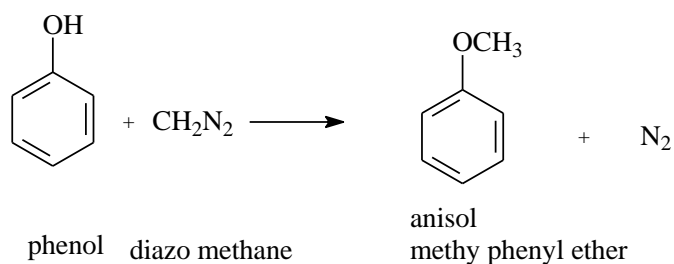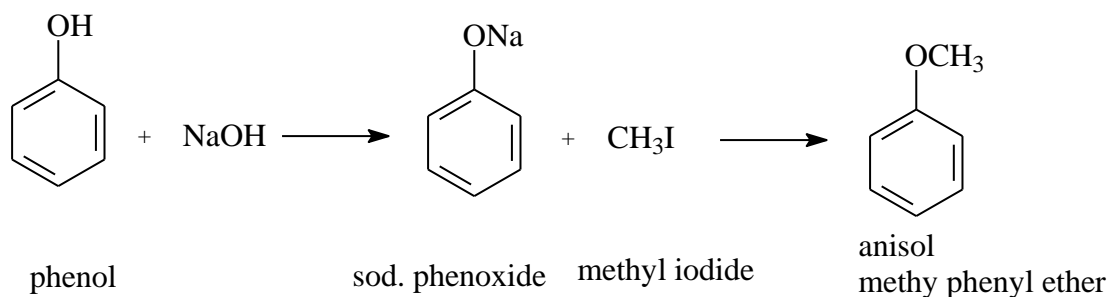
4. Replacement of –OH by halogens: unlike alcohols –OH group cannot be replaced by alkyl halids; however, halogen derivatives are obtained by treating with PBr_3 or PCl_5
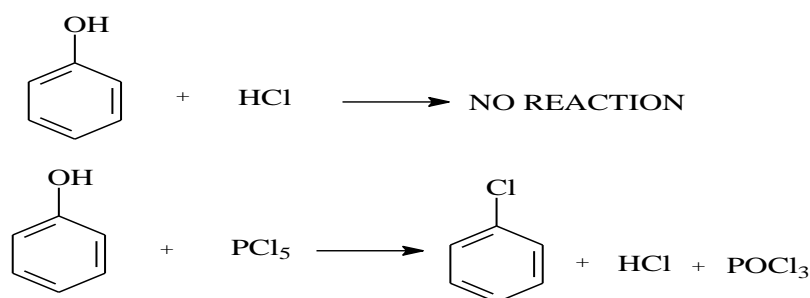
5. Replacement by –NH_2 function:
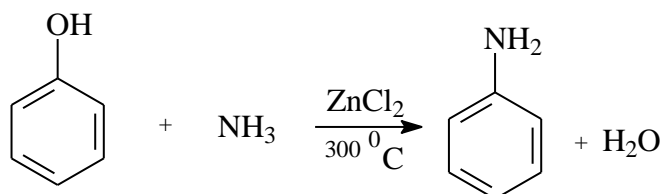
6. Ether formation: The sodium phenoxide of phenol undergoes Williamson synthesis and reacts with alkyl halides to give ether.


phenol sod. phenoxide methyl iodide anisol
methy phenyl ether

unlike alcohol phenols also react with diazomethane and DMSO

hydroquinol   dimethyl sulphoxide
DMSO   hydroquinol dimethyl ether

7. Esterification:

Phenols cannot be esterified directly by using carboxylic acid in presence of mineral acids. This is because of less nucleuphic oxygen of the phenol compared to alcohols

B.   Reactions involving aromatic ring: The aromatic ring in phenols generally undergo electrophilic substitution reaction in which the hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. Phenol is more reactive than benzene towards electrophilic reagents because there is an interaction between the lone pairs on the oxygen atom in —OH or —O and the ring; which increase the availability of electrons in the aromatic ring. Also, it directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by -OH group. In this reaction, an **electrophile** (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are electron rich, the substitution takes place at these positions.

Electophile attack at ortho and para positions

Common electrophilic aromatic substitution reactions taking place in phenol are as follow:

1.Halogenation (Bromination): The -OH group in phenol can donate electrons back to the delocalised π-system, helping to stabilise the intermediates of electrophilic substitution and so making phenol much more reactive than benzene. It will react immediately with bromine water, decolorising it and forming a white precipitate of 2,4,6-tribromophenol. If bromine water is added to a solution of phenol in water, the bromine water is decolourised and a white precipitate is formed. The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$, which polarises the halogen molecule. The faster reaction in water is due to the presence of phenoxide ions.

In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid.

It is due to the highly activating effect of -OH group attached to the benzene ring. Chlorine, in the absence of solvent, gives 2 and 4-chlorophenol. Bromine, in a nonpolar solvent (e.g. CS_2 or CCl_4) gives 2, 4-bromophenol.

phenol   2, 4, 6 - tribromophenol
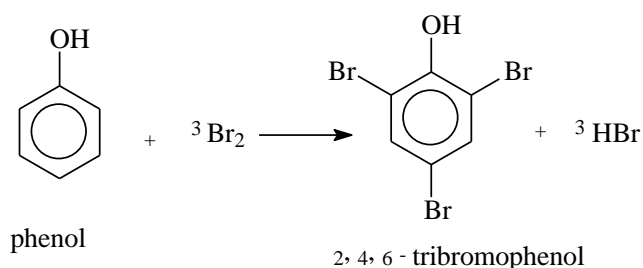
Bromination can be limited to monobromination to give mainly 4-bromophenol using low temprature and less polar solvent such as carbon disulphide. The other product formed in minor quantity is 2-bromophenol.
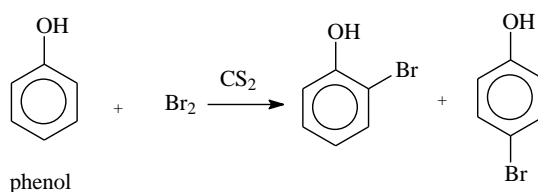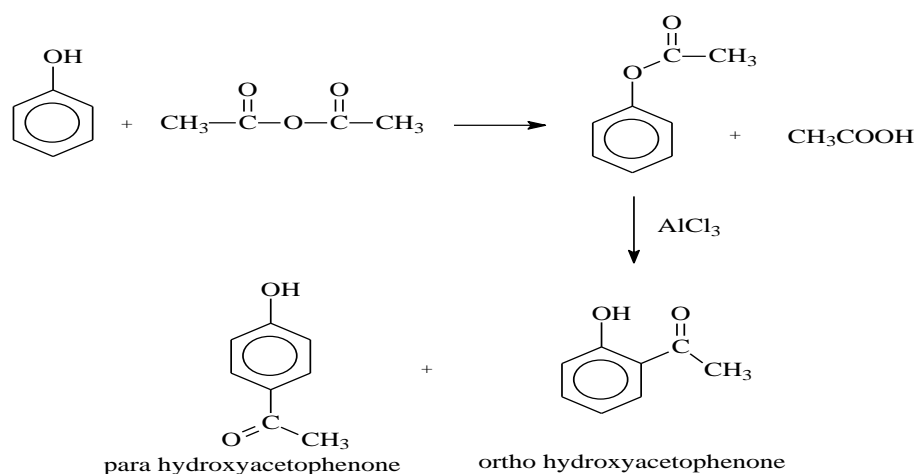

phenol

2. Nitration of Phenol: Phenol can be nitrated with dilute nitric acid. Monosubstituted compound is obtained with dilute nitric acid at room temperature. Phenol reacts with dilute nitric acid at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol.
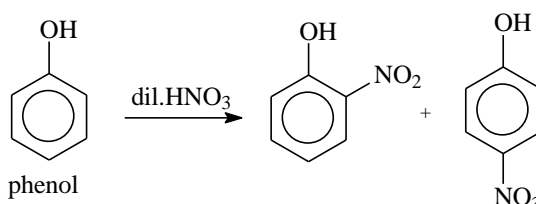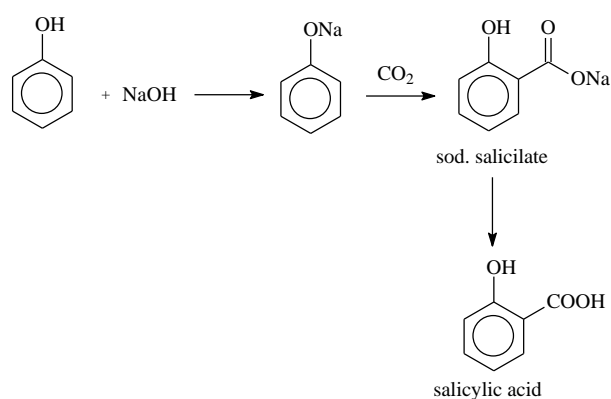

phenol

With concentrated nitric acid trisubstituted product product, 2,4,6-trinitrophenol (picric acid) is obtained readily.


2, 4, 6- trinitrophenol
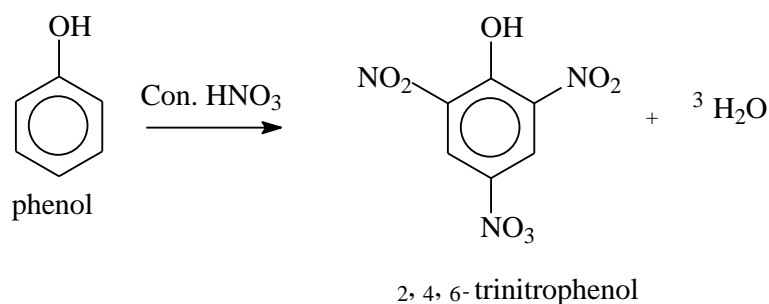
3. Acylation and caboxylation: Ester of phenols are obtainead on treatment with anhydrous aluminium chloride, which further treating with Lewis acid like $AlCl_3$ yields ketones of phenols (Fries rearrangement)


para hydroxyacetophenone   ortho hydroxyacetophenone

4. Kolbe's reaction: On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product. The temperature is 400 K and a pressure of 4-7 atm is required. Sodium salicylates formed which an acidification yields salicylic acid (ortho hydroxy benzoic acid).

sod. salicilate

salicylic acid

5. Fries Rearrangement: The Fries Rearrangement enables the preparation of acyl phenols. The reaction is catalyzed by Bronsted or Lewis acids such as HF, $AlCl_3$, BF_3, $TiCl_4$ or $SnCl_4$. The acids are used in excess of the stoichiometric amount, especially the Lewis acids, since they form complexes with both the starting materials and products. The reaction is *ortho, para*-selective so that, for example, the site of acylation can be regulated by the choice of temperature.
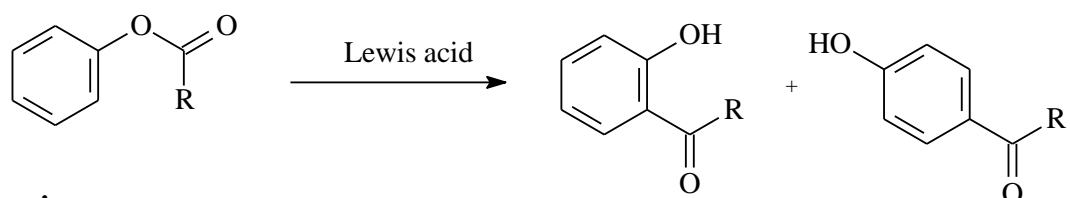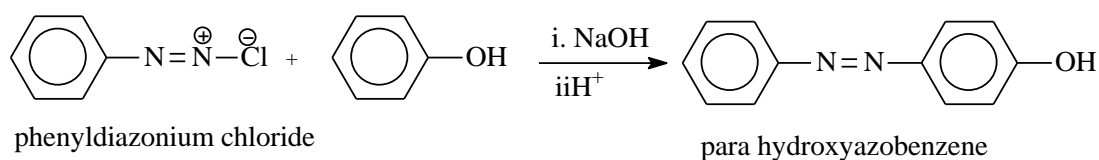

Mechanism
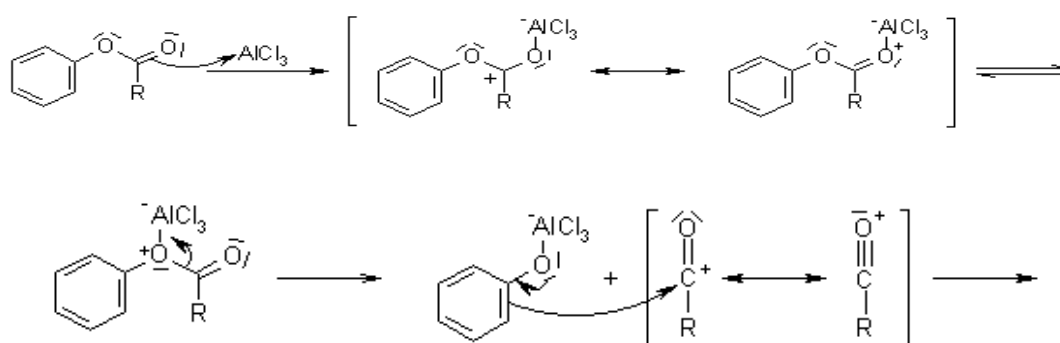
The complex can dissociate to form an acylium ion, which act as an electrophile. After hydrolysis, the product is liberated.

6. Coupling reaction: Phenols form azo compounds by coupling with aryldiazonium salts in presence of alkali.


phenyldiazonium chloride   para hydroxyazobenzene

7. Gattermann Reaction: Introduction of –CHO group ortho to –OH group by treating phenol with HCN, HCl and $ZnCL_2$ catalyst is known as Gattermabb reaction.

o hydroxybenzaldehyde
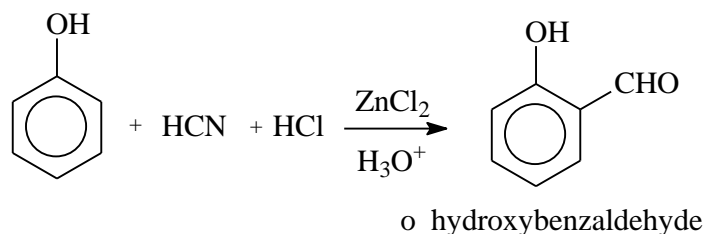
This reaction is used for formylation of aromatic ring

8. Lederer Manasse's Reaction: When phenol is treated with 40% aqueous solution of formaldehyde (formalin) in the presence of a dilute acid or alkali at low temperature, a mixture of o-and p-hydroxy benzyl alcohol is formed.
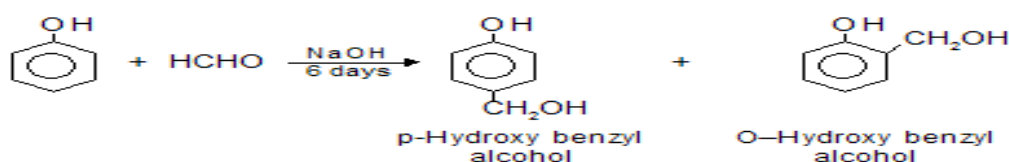
This reaction is called **Lederer-Manasse reaction.** On heating these compounds condense with themselves and give linear polymers by elimination of water.
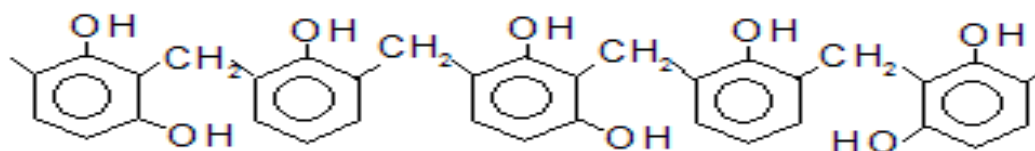

These reactions are the basis of the preparation of phenol formaldehyde resins. These materials were developed by Backland and are hence called **bakelite.** They are thermoplastic solids soluble in many organic solvents. When warmed with hexa methylene tetramine. $(CH_2)_6N_4$, which splits up to formaldehyde and ammonia, further methylene bridges are formed and a three-dimensional polymer results.
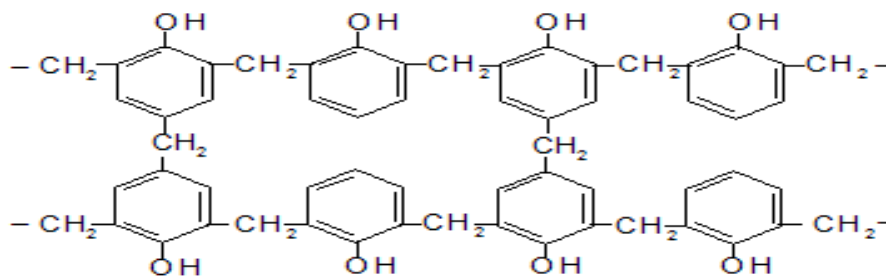

9. Reimer Tiemann Reaction: Process of formylation of phenols with chloroform in alkaline solution is known as **Reimer–Tiemann reaction.** Phenols react with chloroform in

the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.
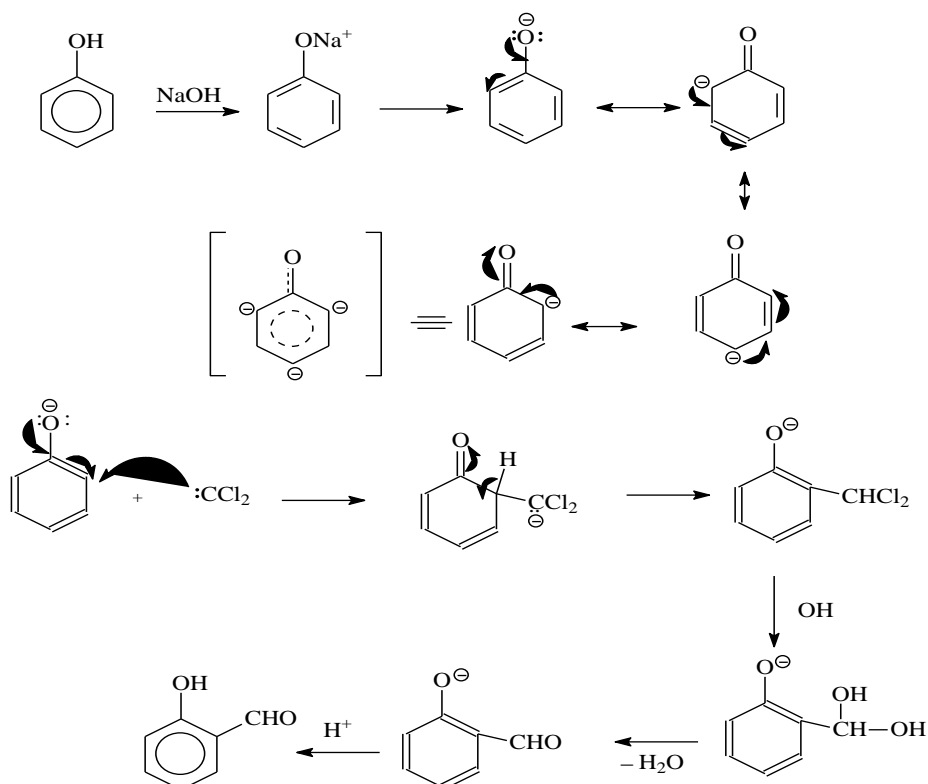

o hydroxybenzaldehyde   p hydroxybenzaldehyde
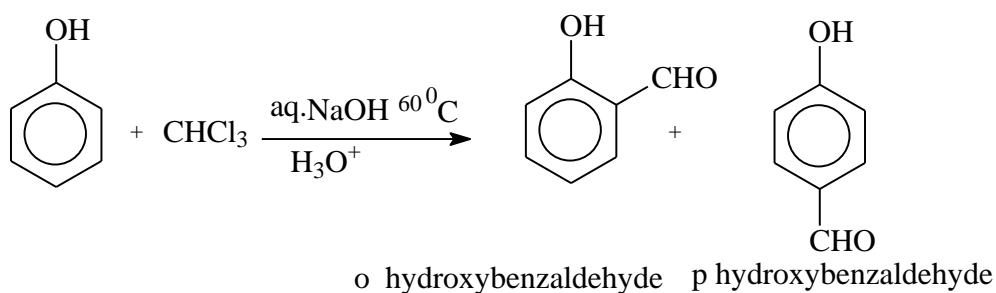
Mechanism: Reimer Tiemenn reaction is an electrophilic substitution reaction. The first step is generation of electrophile.

A   Genertion of dichloro carbene (electrophile)
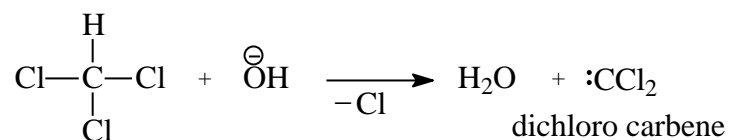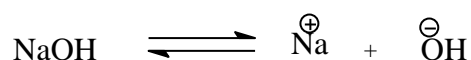

B   Electrophilic substitution in phenol ring

Use of carbon tetrachloride in place of chloroform gives salicylic acid. A mixture of ortho-and para-isomers is obtained in which the ortho isomer predominates due to more thermodynamical stability. If one of the ortho positions is occupied the para-isomer is the major product.

o hydroxybenzoic acid   p hydroxybenzoic acid
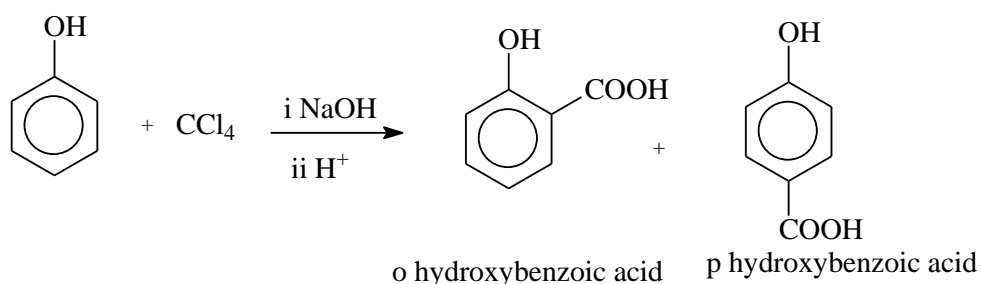
When anisol is treated with $CHCl_3$ in presence of alkali a commercial edible product vanillin is formed as major product


anisol   vanillin
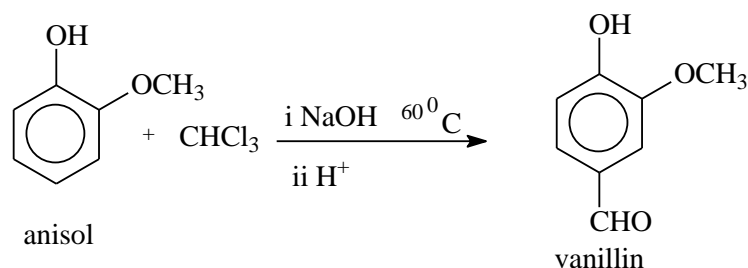
10. Houben –Hoesch reaction: Reactive polyhudric phenols in which –OH groups are *meta* to another may be acylated by treating with alkyl cyanides in the presence of $ZnCl_2$ and HCl. This reaction is known as Houben-Hoesch reaction. The product of the reaction is phenolic ketone.


phenolic ketone

phenolic ketone
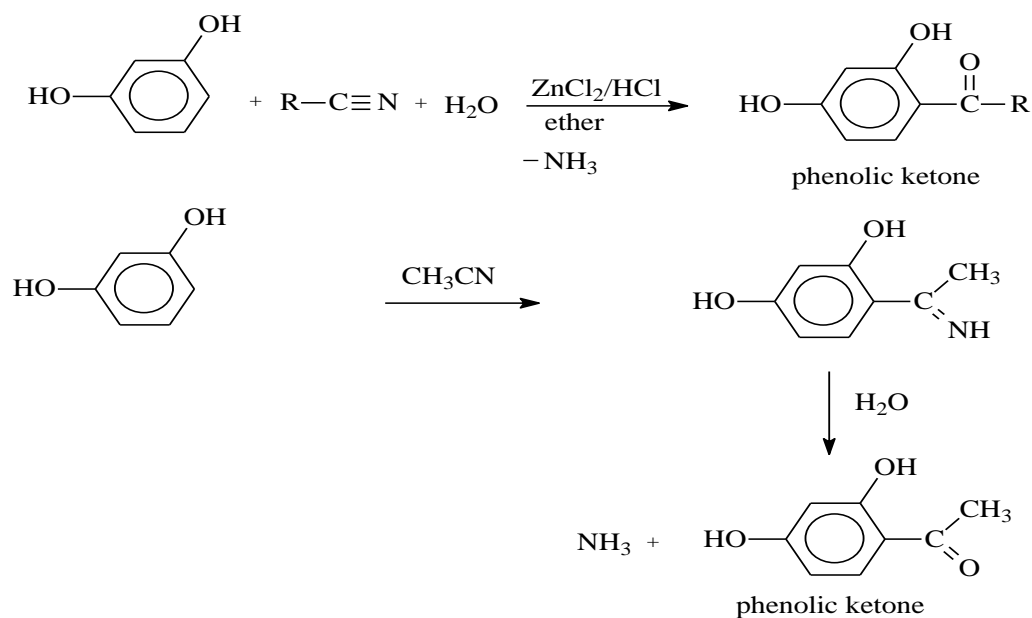
Phenol does not respond to Houben- Hoesch reaction

11. Condensation with phthalic anhydride: Phenol when treated with phthalic anhydride in presence of H_2SO_4 gives phenolphthalein, a colourless compound which produces pink color with alkali solution due to the formation of colored sodi salt. It is a popular indicator used in acid base titrations.

phthalic anhydride

phenolphthalein
colourless/ pale yellow

NaOH

sod. salt of phenolphthalein
mazanta colour
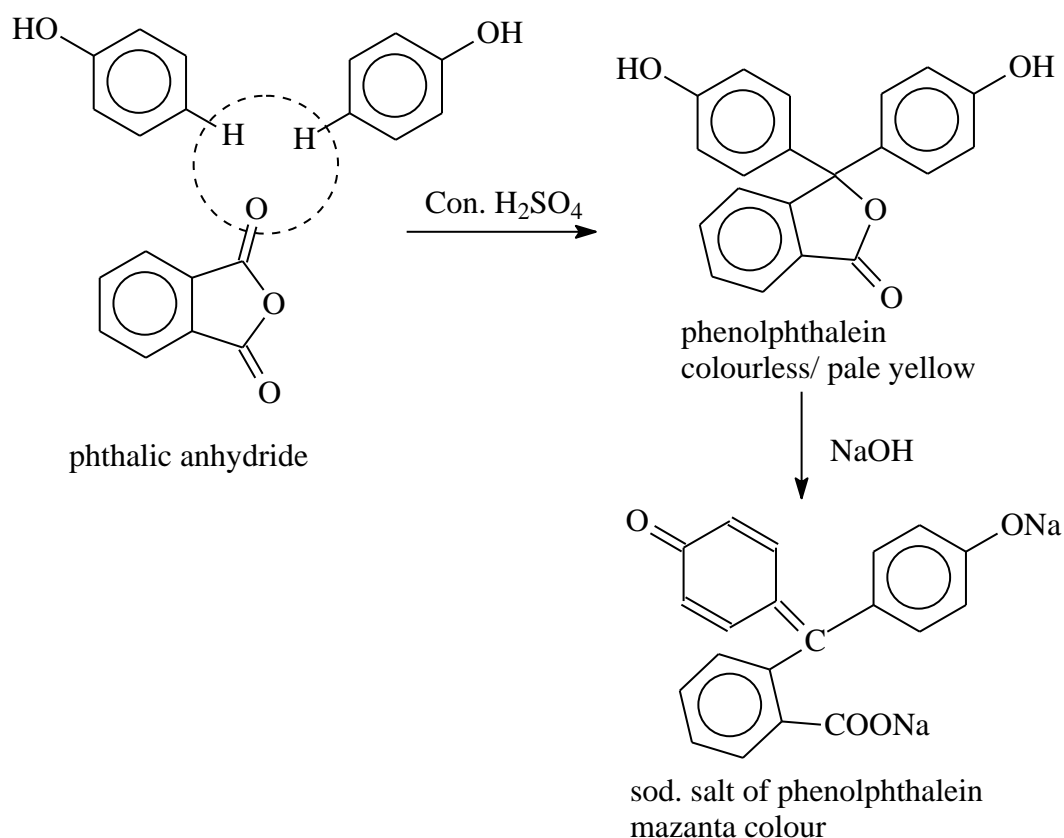
12. Oxidation: Phenol is easily oxidized to p-benzoquinone and similarly hydroquinone on oxidation with silver salt gives p- benzoquinone. This reaction leads to the use of hydroquinone as a photographic developer.

p benzoquinone
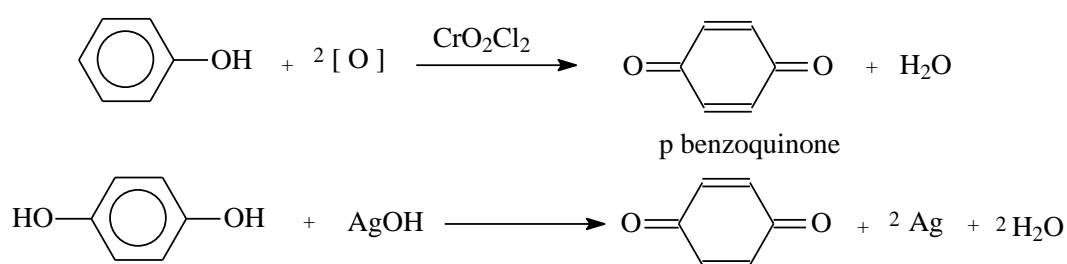
Under drastic condition upon oxidation phenol gives tartaric acid, oxalic acid and carbondioxide
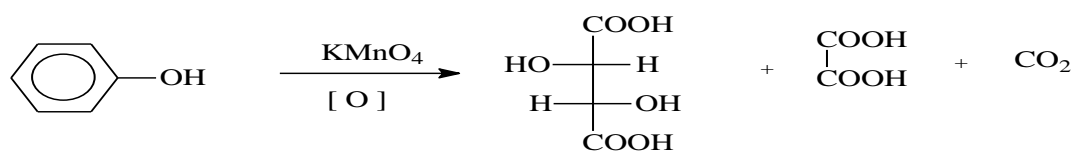
13. Reduction: The –OH group is stable and the catalytic reduction of phenol yields cyclohexanol, Substituted phenols would in same fashion form substituted cyclohexanol

cyclohexanol

methyl cyclohexanol
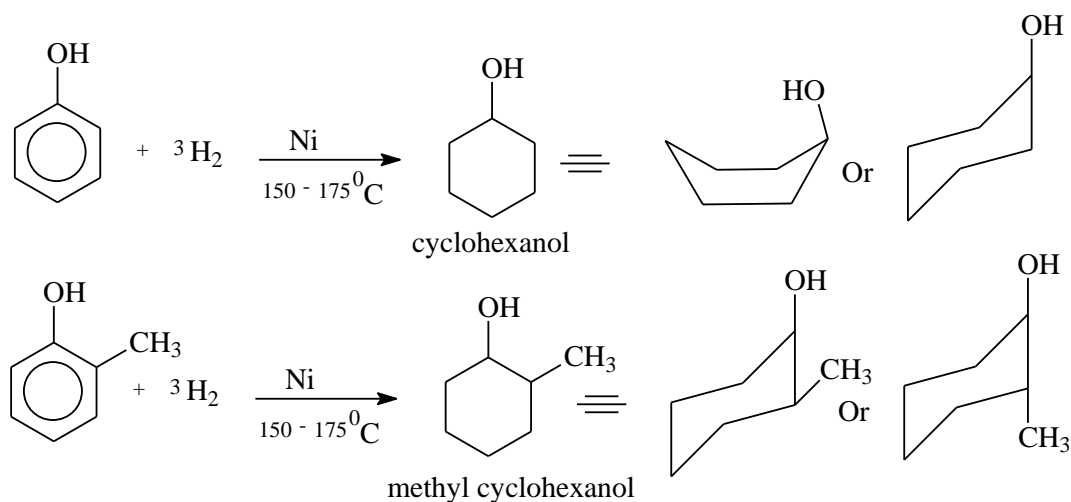
Uses of

phenols: Phenol, in dilute solution, was the first successful antiseptic used by Lister (called *carbolic acid*). Now substituted phenols are used both as **antiseptics** (to keep surfaces free of pathogens) and as **disinfectants** (to kill pathogens already present).

6.9 SUBSTITUTED PHENOLS

Cresols / hydroxytoluene:

o cresol   m cresol   p cresol
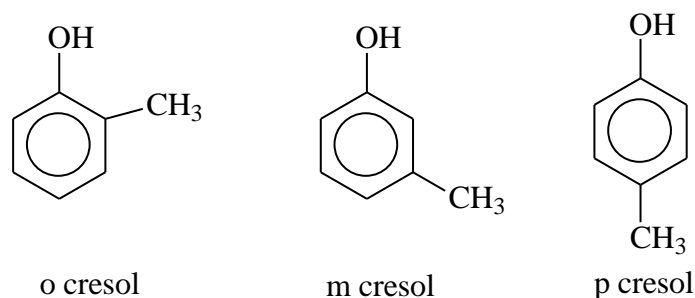
Properties: Cresols are colourless liquids with phenolic smell. Their B.P are o- 191^0C, m- 201^0C and p- 202^0C. They are less toxic than phenol but have greater germicidal activity. Can be oxidized to corresponding carboxylic acid if –OH group is procted.

Uses: As preservative for timber railaway sleepers etc. for making Lysol (a mixture of cresol in soapy water). For the synthesis of dyes, resin, plasticisers and explosive etc.
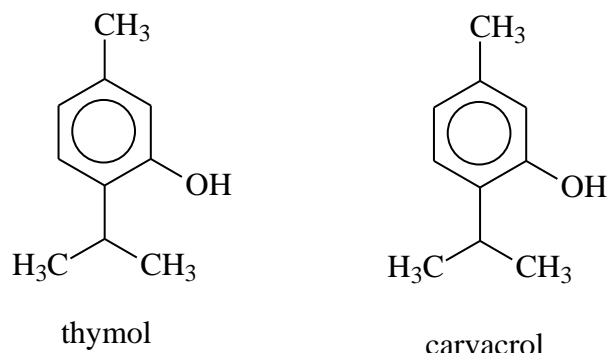
Thymol and cravacrol: These are two isomeric forms of phenol and are extensively used in perfumery and as antiseptics. Thymol occurs in the essential oil of thyme (*Thymus linearis*) carvacrol is obtained by heating camphor with iodine while naturally it occurs in *Mentha spicata* (mint)

thymol   carvacrol

Dihydric member: catechol: it occurs in Indian catechu (*Acasia catechu*) hence is designated as catechol
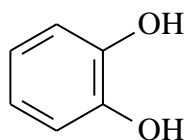
Properties: It is white crystalline solid M.P. 104^0C. Soluble in H_2O ethanol and ether. Gives green color with $FeCl_3$ while condensed with phthalic anhydride it gives alizarin

Uses; As a photographic developer. To manufacture alizarin. As antioxidant in gasoline

Resorcinol:
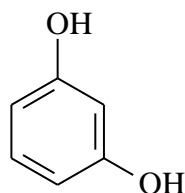
Properties: White solid M.P. 110^0C Turns gray in air, soluble in water, forms 2,4,6-tribromoresorcinol when treated with bromine water. It couplesdiazonium salts to form azo dye and condense with phthalic anhydride to produce fluorescence which show intense green fluorescence when alkalized
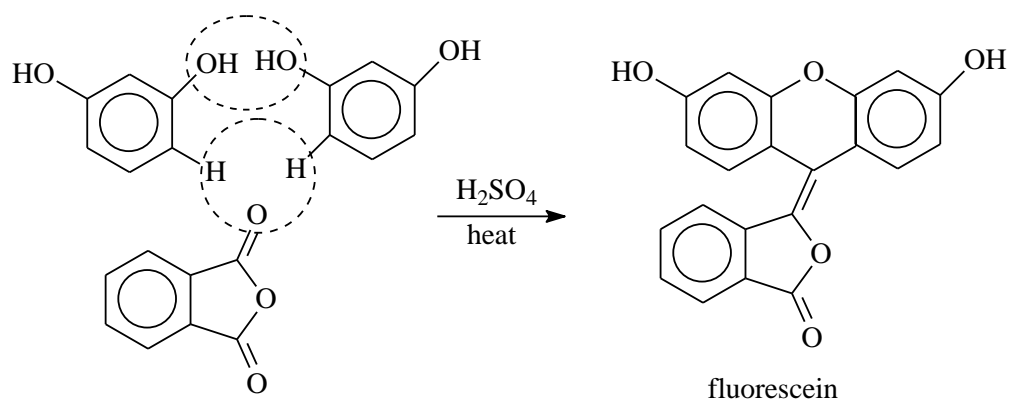
fluorescein

Uses: Used as antiseptic in ointments, for the manufacture of dyes like azo dyes, fluorescein, eosin etc, for preparing drugs used for curing hookworm and urinary disorders etc.

Trihydric phenols:

Pyrogallol: obtained by heating gallic acid
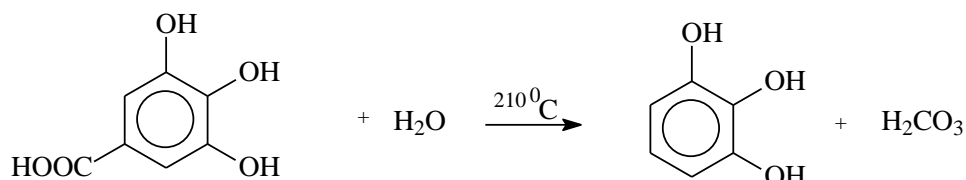
Properties: White crystalline solid, M.P. 133^0C, soluble in water, alkaline solution turns to brown, most powerful reducing agent.

Uses: Excellent photographer developer, for preparing ointments and antiseptic for skin, as hair dyes, for absorbing oxygen in gas analysis

Phloroglucinol: prepared by fusing resorcinol with NaOH in air
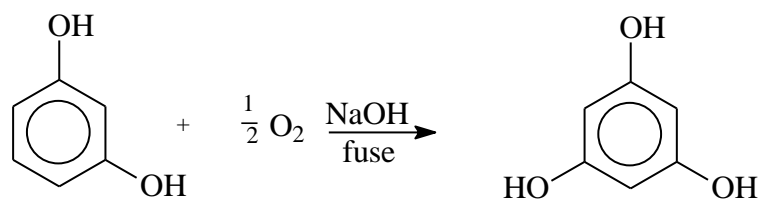
Properties: White crystalline solid, M.P. 218^0C, soluble in water alkaline solution readily darken on exposure to air due to oxidation.

Uses: Used for detecting carbohydrates, producing a red coloration with in presence of H_2SO_4.

6.10 INTRODUCTION OF ETHERS

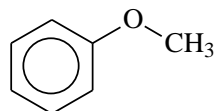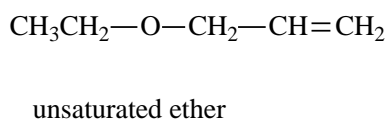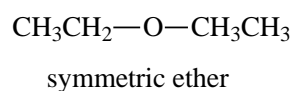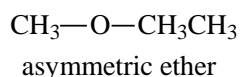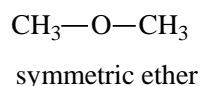Ethers are compounds that containing single oxygen atom bonded to two alkyl groups, two aryl groups or one aryl and one alkyl group. The general formula, of ethers is $C_nH_{2n+2}O$. They are isomeric with the aliphatic monohydric alcohols with the general formula $C_nH_{2n+1}OH$. Thus, ethers can be represented as R -O –R', where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R'are identical, then the ether is called a simple or symmetrical ether, otherwise if these two groups are different, then the ether is known as a mixed or unsymmetrical ether. Diethyl ether, $C_2H_5OC_2H_5$, is symmetrical ether whereas $C_2H_5OCH_3$and $C_2H_5OC_6H_5$ are unsymmetrical ethers. The symmetrical diethyl ether is commonly also referred simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years. Ethers are distinguished from other organic compounds because they lack a continuous chain of carbons.

$$H \overset{\overset{..}{O}}{\diagup\diagdown}_{..} H \qquad\qquad R \overset{\overset{..}{O}}{\diagup\diagdown}_{..} R$$

Ethers are thought of as alkyl analogues of water.

Substitution of the hydroxyl hydrogens of alcohols by hydrocarbon groups gives compounds known as ethers. These compounds may be classified further as open-chain, cyclic, saturated, unsaturated, and aromatic, and so on. The oxygen atom of the ether can also be part of a ring, in which case the ether is known as cyclic ether or also called epoxide. Epoxides are formed when an oxygen atom is linked to carbon atoms of a carbon chain forming a three membered ring. Epoxides are heterocyclic compounds containing oxygen atom as a hetero atom. Epoxides have considerable ring strain. Epoxides are special kinds of ethers. These compounds are special because they have a three-member ring that contains an oxygen atom. They are far more reactive than typical ethers. Tetrahydrofuran is one such cyclic ether which is used as a solvent. Ethers are commonly used as solvents for organic reactions.

CH_3—O—CH_3

symmetric ether

CH_3—O—CH_3CH_3

asymmetric ether

CH_3CH_2—O—CH_3CH_3

symmetric ether

CH_3CH_2—O—CH_2—CH=CH_2

unsaturated ether

aryalkyl ether
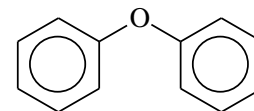
aryl ether
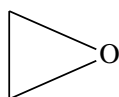
ethylene oxide

trihydrofuran
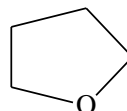
tetrahydrofuran
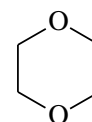
dioxane

Cyclic ethers

6.11 NOMENCLATURE OF ETHERS

There are two methods of naming ethers. The first is the common method and is most useful with simple ethers. Common names "trivial names" of ethers add the suffix ether after naming the two groups on either side of the oxygen. The alkyl groups are listed in alphabetic order. There are spaces between the names of the alkyl groups and the word ether. If the two groups are the same, the prefix "di-" is used, although sometimes this is simply dropped ("ethyl ether").

 e.g. $H_3COCH_2CH_3$ Ethylmethyl ether

                          C_2H_5 - O - C_2H_5 Diethyl ether

                          C_6H_5 - O - C_6H_5 Diphenyl ether

                          C_2H_5 - O - C_6H_5 Ethyl phenyl ether.
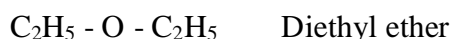
In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane*. Treat the oxygen and the remaining carbons as a side chain and the smaller alkyl group is named as an *alkoxy* (—OR = alkoxy group) substituent on this alkane. The *-yl* ending of alkyl substituents is replaced by *–oxy*.

                  —CH_3 methyl   —OCH_3 methoxy

                  —CH_2CH_3 ethyl   —OCH_2CH_3 ethoxy

For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

$$CH_3OCH_2CH_3$$

Ethylmethyl ether

The remaining portion, *i.e.*, —OCH_3 part in this case, is called the methoxy substituent. Hence, the above ether is called methoxyethane. The numbering of the parent chain is done so that the carbon atom linked to the -O-atom gets the lowest number. Some more examples of IUPAC names of ethers are given below:

Examples:
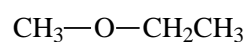
CH_3—O—CH_2CH_3
ethylmethyl ether
methoxy ethane
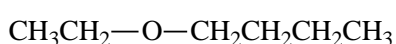
CH_3CH_2—O—$CH_2CH_2CH_2CH_3$
butylethyl ether
1 ethoxy butane
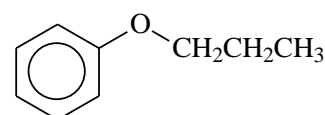
phenylpropyl ether
1 phenoxypropane
O—$CH_2CH_2CH_3$

CH_3—O—$CH_2CH_2CH_3$
1 methoxypropane

CH_2=CH—O—CH_2CH_3
ethoxyethene
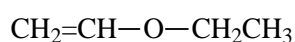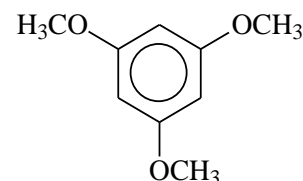
H_3CO OCH_3
OCH_3
1, 3, 5 trimethoxybenzene

diphenyl ether
O

$ClCH_2$—O—CH_2Cl
bis(chloromethyl)ether

CH_3CH_2—O—CH—CH_2CH_3
|
CH_3
2 ethoxybutane

CH_3
|
CH_3CH_2O—C—CH_3
|
CH_3
2 ethoxy 2 methylpropane
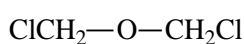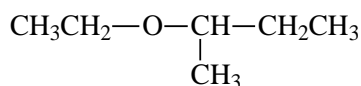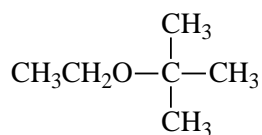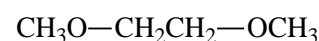
CH_3O—CH_2CH_2—OCH_3
1, 2 dimethoxyethane
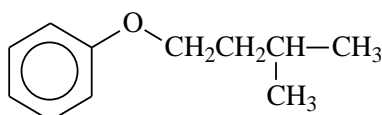
O—CH_2CH_2CH—CH_3
|
CH_3
3 methylbutoxybenzene

Cyclic ethers generally termed as epoxides in IUPAC system. Epoxide contains a 3-membered ring between oxygen and two carbons ethers.
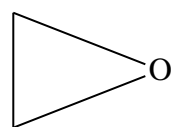
epxyethane

ethylene oxide
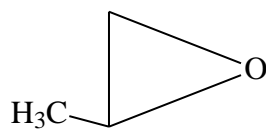
propylene oxide

$_{1,2}$ epoxypropane

6.12 METHODS OF PREPARATION

There are different methods for the synthesis of ethers some of which are being described as follow:

1. By Dehydration of alcohols: (a) The formation of reaction product, alkene or ether depends on the reaction conditions. This method involves heating of excess of primary alcohol with concentrated sulphuric acid and the temperature has to be maintained around 413^0 K to get symmetrical ether. If alcohol is not used in excess or the temperature is higher, the alcohol will preferably undergo dehydration to yield alkene.

$$ROH \xrightarrow[\text{heat}]{H_2SO_4} R-O-R + H_2O$$

$$CH_3CH_2OH \xrightarrow[140^OC]{H_2SO_4} CH_3CH_2-O-CH_2CH_3$$

$$CH_3CH_2OH \xrightarrow[160^O C]{H_2SO_4} CH_2=CH_2 + H_2O$$

Mechanism:

[i] $CH_3CH_2-\ddot{O}H + H^+ \longrightarrow CH_3CH_2-\overset{+}{O}H_2$

[ii] $CH_3CH_2-\ddot{O}H + CH_3CH_2-\overset{+}{O}H_2 \longrightarrow CH_3CH_2-\overset{+}{\underset{H}{\ddot{O}}}-CH_2CH_3 + H_2O$

[iii] $CH_3CH_2-\overset{+}{\underset{H}{\ddot{O}}}-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$
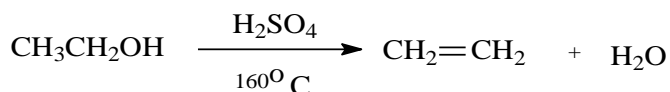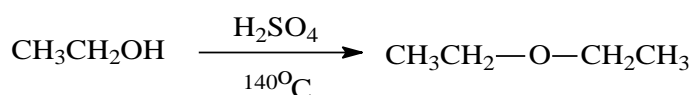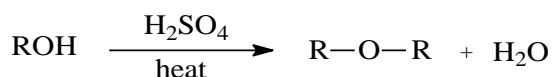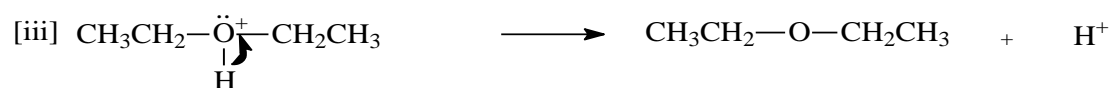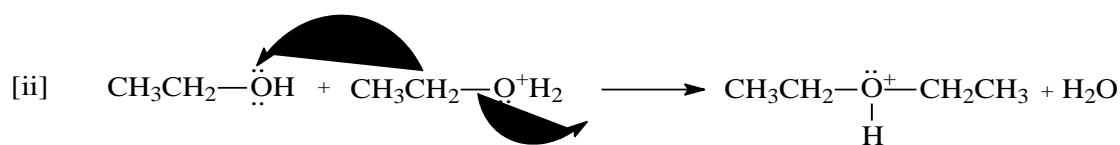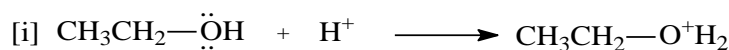
If ethanol is dehydrated to ethene in presence of sulphuric acid at 433K but as 410K ethoxyethane is the main product. The dehydration of secondary and tertiary alcohols to get corresponding ethers is unsuccessful as alkenes are formed easily in these reactions.

$$H_3C-\underset{\underset{H_3C}{|}}{\overset{\overset{H_3C}{|}}{C}}-OH \xrightarrow{\text{Conc } H_2SO_4} CH_2\overset{\overset{CH_3}{|}}{=}C=CH_3 \ + H_2O$$

t-butyl alcohol   Iso-butylene
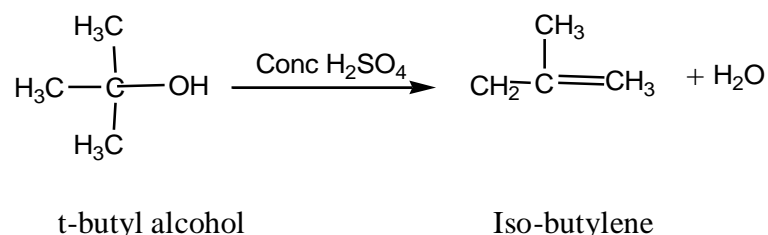
(b) On passing alcohol vapours over heated alumina at 250ºC, dehydration of alcohols leads to the formation of ethers.

$$2 \ ROH \ \underset{vapour}{\xrightarrow[250^O \ C]{Al_2O_3}} \ R-O-R \ + \ H_2O$$
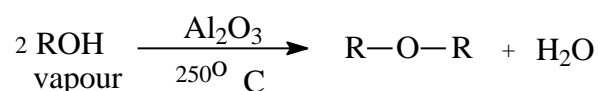
The secondary and tertiary alcohols on dehydration lead to the formation of alkene as main product.

$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{dehydration}} CH_3=CH-CH_3 \ + \ H_2O$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow{\text{dehydration}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \ + \ H_2O$$
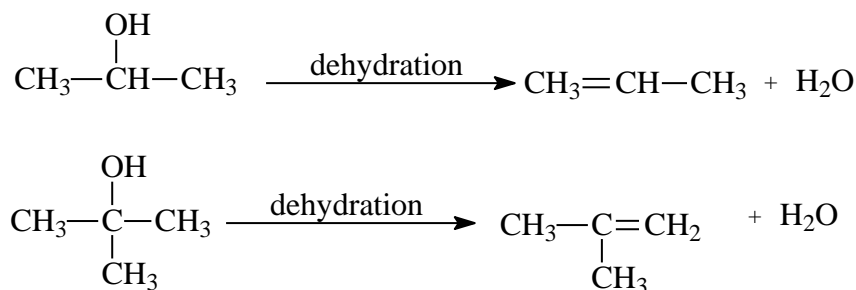
2. By alkyl halides: Alkyl halides on heating with dry Ag_2O (in ether) give ethers.

$$R-X \ + \ Ag_2O \ + \ R-X \xrightarrow{\text{heat}} R-O-R \ + \ 2 \ AgBr$$

$$CH_3CH_2Br \ + \ Ag_2O \ + \ CH_3CH_2Br \xrightarrow{\text{heat}} CH_3CH_2-O-CH_2CH_3 + \ 2 \ AgBr$$
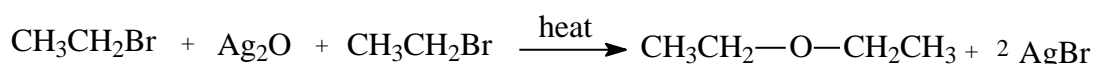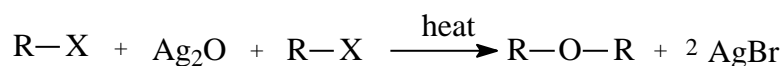
3 Williamson syntheses of ethers: It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. The method involves the treatment of an alkyl halide with sodium or potassium salt of alcohol or phenol. This is a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys S_N2 mechanism. Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves a nucleophilic substitution of halide ion by an alkoxide ion.

$$2\,CH_3CH_2OH + Na \longrightarrow CH_3CH_2ONa + H_2$$

$$CH_3CH_2ONa + R{-}X \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + NaX$$
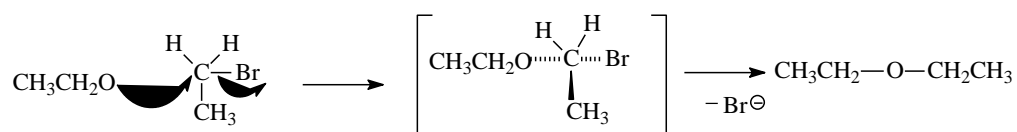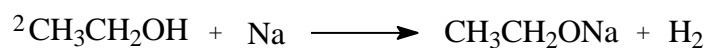
Good results are obtained if the alkyl halide is primary. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

For e.g., the reaction of CH_3ONa and $(CH_3)_3C$-Br gives exclusively 2-methyl propene.
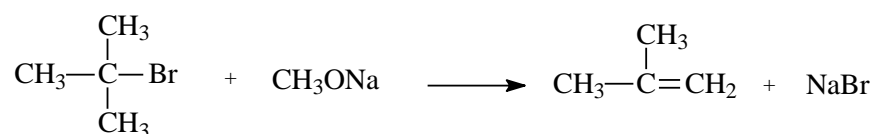
This is because alkoxides are not only nucleophiles but also strong bases as well. They react with alkyl halides leading to elimination reaction.

Phenols are also converted to ethers by this method.
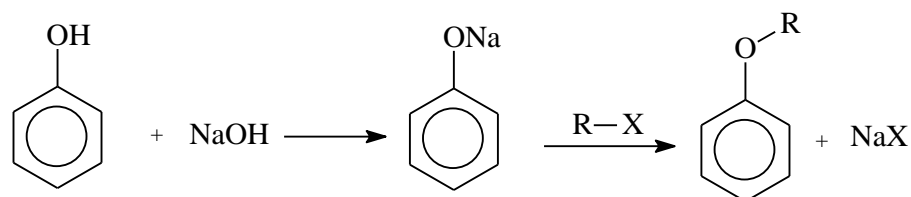
Tertiary alkyl halides undergo elimination reaction with sodium alkoxide to produce
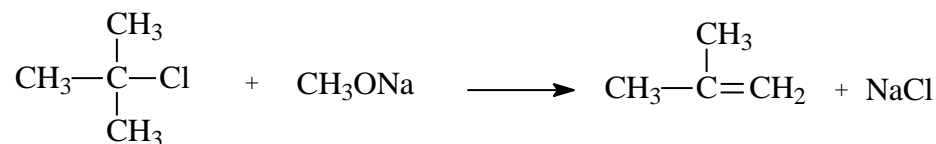
Therefore to prepare t- alkyl-alkyl ether, one must take an alkyl halide with tertiary alkoxide.
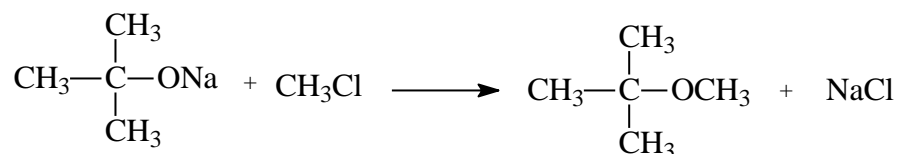
4. From acyl chlorides: Aromatic ketones are formed from acyl chloride by Friedel Craft reaction. This reaction requires excess $AlCl_3$ due to tendency of complexation with carbonyl group and water to hydrolyze the Al salts
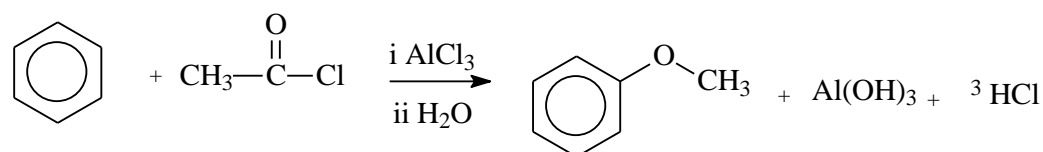
5. From Grignard reagent: This is a good method for the preparation of higher ethjer from lower members, in which a lower halogenated ethers when heated with Grignard reacent we get higher ethers.

CH_3—O—CH_2Cl + $BrMgCH_2CH_3$ $\longrightarrow$ CH_3—O—$CH_2CH_2CH_3$ + Mg(Br)(Cl)

monochlorodimethylether   methylpropylether
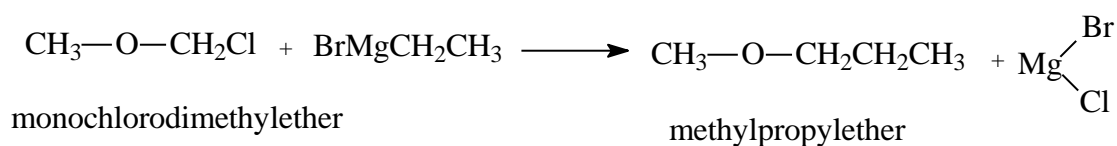
6. Epoxides formation from olefinic peroxidation: The cyclic ether like epoxide can be synthesized by the reaction of peroxides on olefinic compounds to get epoxides or are synthesized by treating alkene with bromine water followed treatment with NaOH.
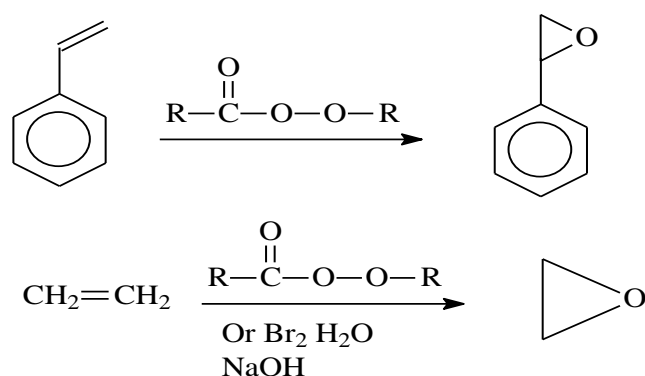
7. By imtramolecular SN_2 reaction: The SN_2 intramolecular reaction of halohydrin in presence of KOH/H_2O gives epoxide.
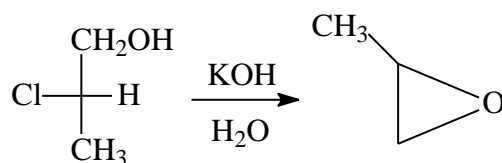
6.13 PHYSICAL PROPERTIES

(*a*) *Physical state:* Dimethylether and ethyl methyl ether are gases at ordinary temperature. The other lower homologes are colourless, pleasant smelling, volatile liquids with typical ether smell.

b) Boiling points: The C - O bonds in ether are polar and thus ethers have a net dipole moment. The weak polarity of ethers does not appreciably affect their boiling points which are comparable to those of the alkenes of comparable molecular mass. Ethers have much lower boiling points as compared to isomeric alcohols. This is because alcohols molecules are associated by hydrogen bonds while ether molecules are not.

Boiling point order: alcohols > ethers > alkanes

$CH_3CH_2—O—CH_2CH_3$
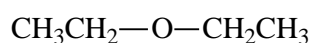
diethylether
ethoxyethane

b. p $35^{0}C$

$CH_3—O—CH=CH_2$
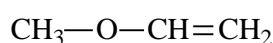
methoxy ethene
methyl ethenyl ether

b. p $12^{0}C$
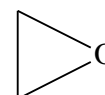
epoxide

b. p $11^{0}C$

c) Solubility: Ethers are slightly polar, and can hydrogen-bond to water, although very weakly, through the oxygen atom. Because ethers have no O-H bonds, they cannot participate in hydrogen bonding to the same extent that alcohols do. Nevertheless, the oxygen in the ether can form a hydrogen bond to the hydrogen in water. The presence of only single site on the ether for a limited kind of hydrogen bonding interaction means that ethers generally have significantly smaller solubilities in water than do alcohols. Still they have higher solubilities than any hydrocarbon. These are extremely volatile and highly flammable (easily oxidized in air).

Ethers containing upto three carbon atoms are soluble in water, due to their hydrogen bond formation with water molecules.
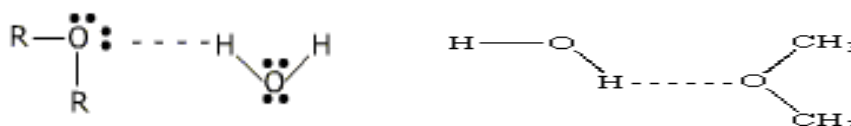
The solubility decreases with increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone etc.

Water solubility order: alcohols > ethers > alkanes

6.14 CHEMICAL PROPERTIES

Ethers have geometry similar to water and alcohols. The oxygen atom is *sp*³ hybridised. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar is nature. Ethers, thus, act as polar solvents. Ethers are quite stable compounds. These are not easily attacked by alkalies; dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

1. Reaction with acids: Being Lewis bases, ethers form complexes with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, etc. These complexes are called etherates.

boron trifluoride etherate (complex)
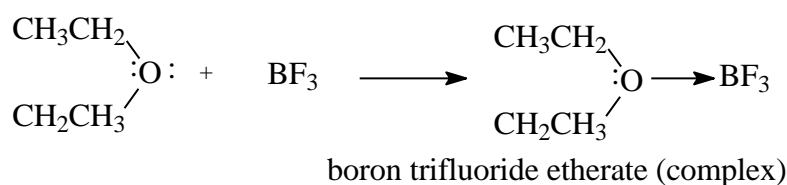
Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.

Grignard reagent eterate
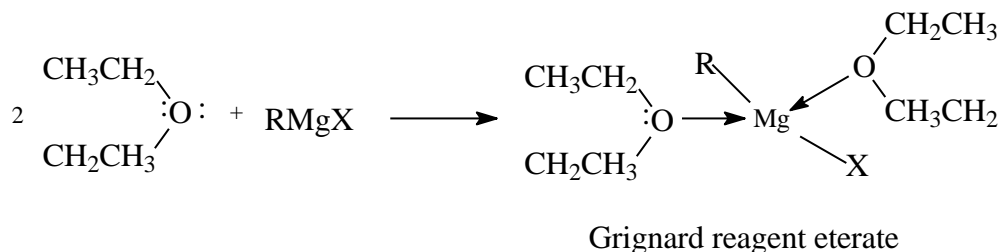
Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

2. Action of hydroiodic acid: Following reactions takes place when ethers are treated with haloacids.

(a) With cold HI

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH$$

Diethyl ether   Ethyl iodide   Ethyl alcohol

(b) With hot HI

$$R - O - R' + 2HI \longrightarrow RI + R'I + H_2O$$
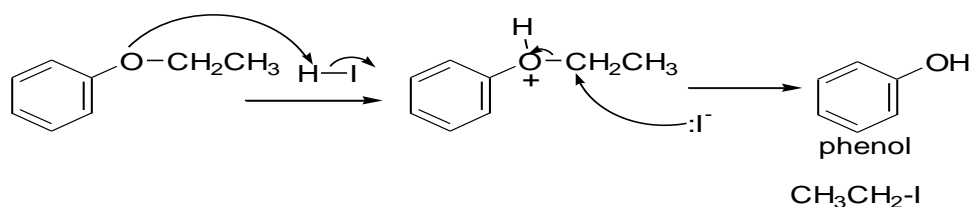
Phenyl ethers are slightly different, and cleave to give alkyl halides and phenols. The reaction stops at the phenol stage since the sp^2 carbon of the C-O bond does not allow the required S$_N$1 or S$_N$2 reactions to generate the second molecule of aryl halide.

3. Reaction wtih HBr:

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature. Ethers are stable to bases, but acidic conditions leads to the protonation of the ether oxygen, which then can undergo substitution reactions.

Grignard reagent eterate
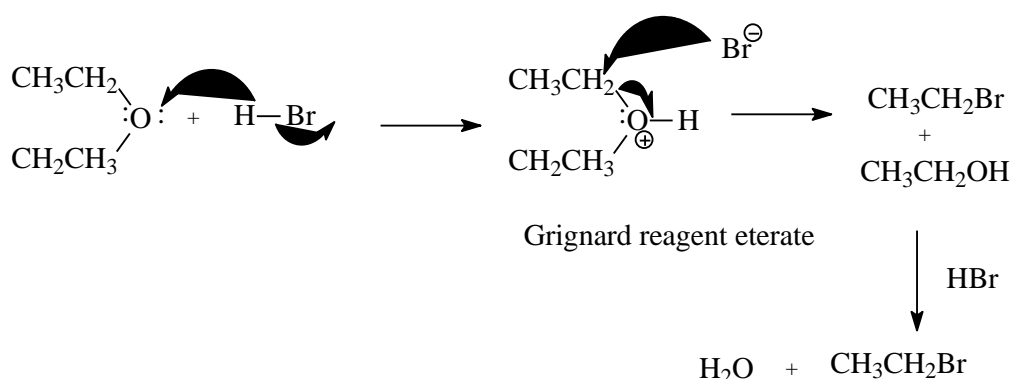
4. Zeisel method:

The compound is heated wih excess hydriodic acid, forming an alcohol and iodomethane. The iodomethane is distilled off and led into an alcoholic solution of silver nitrate, where it precipitates silver iodide.

The silver iodide thus form can be detected and estimated. This is the basis of Zeisel method for the detection and estimation of methoxy (–OCH$_3$) groups in an organic compound. The method was developed by S. Ziesel in 1886.

$$R\text{-}O\text{-}CH_3 + HI \rightarrow ROH + CH_3I$$

$$CH_3I + AgNO_3 \text{ (alc.)} \rightarrow AgI \downarrow + CH_3NO_3$$
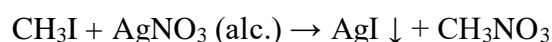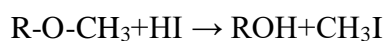
5. Action of PCl$_5$:

Alkyl halides are obtained

$$R - O - R + PCl_5 \longrightarrow 2RCl + POCl_3.$$ There is no reaction in cold.
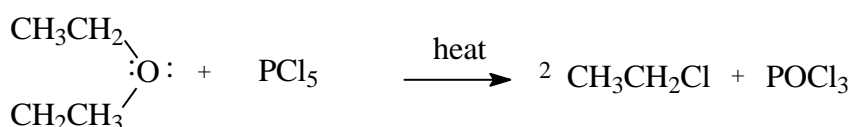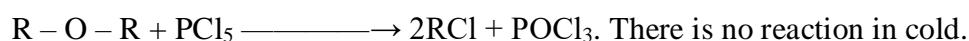
6. Reaction with acetyl chloride: Esters are obtained while treating with acyl halides

$$CH_3COCl \quad + \quad C_2H_5 O C_2H_5 \quad \xrightarrow[\text{heat}]{ZnCl_2} \quad CH_3COOC_2H_5$$

Acetylchloride   Diethyl ether   Ethyl acetate
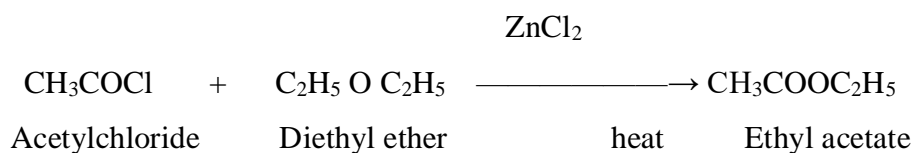
7. Dehydration: Upon dehydration at elevated temperature ethers provide alkenes

$$C_2H_5OC_2H_5 \quad \xrightarrow[300^o]{Al_2O_3} \quad 2CH = CH_2 + H_2O$$
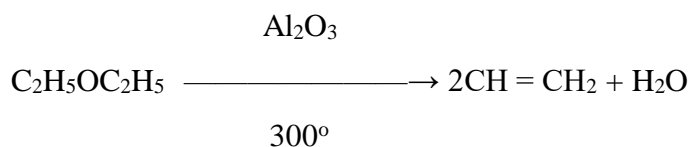
8. Acid and base catalyzed ring opening: Unlike straight chain ethers, epoxides are very reactive and are useful intermediates because of their chemical versatility. Epoxides react to release their considerable strain energy. The acidic hydrolysis of epoxides gives anti diols.
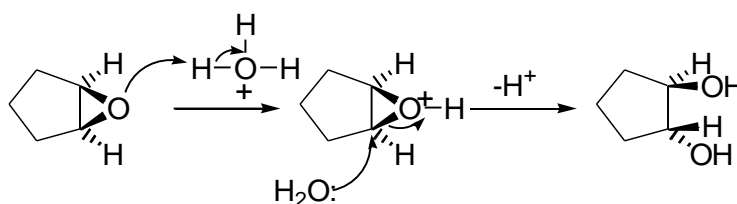
trans-cyclopentane-1,2-diol

Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water. The result is anti-hydroxylation of the double bond. This hydration of an epoxide does not change the oxidation state of any atoms or groups.

Epoxides ring can also be opened by alcohols with acidic catalysis to generate alkoxy alcohols with anti stereochemistry.
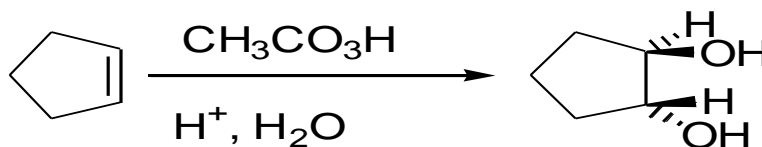
The reaction of hydroxide (or alkoxide) with a symmetric epoxide generates anti diols (or alkoxy alcohols) identical to those produced under acidic conditions.
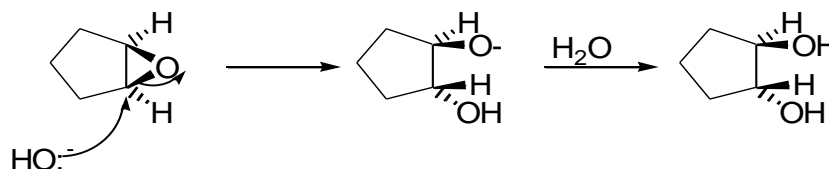
9. Orientation of ring opening: These reactions are no different from the nucleophilic displacements, except that the leaving group, which is the oxygen of the oxide ring, remains a part of the original molecule. The stereochemistry is consistent with an S_N2 mechanism because inversion of configuration at the site of attack occurs. Thus cyclopentene oxide yields products with the trans configuration:

cyclopentene oxide
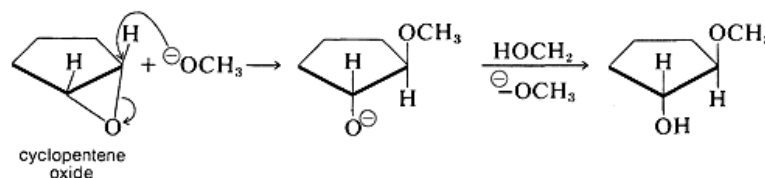
Acidic conditions also can be used for the cleavage of oxacyclopropane rings. An oxonium ion is formed first, which subsequently is attacked by the nucleophile in an S_N2 displacement or forms a carbocation in an S_N1 reaction. Evidence for the S_N2 mechanism, which produces inversion, comes not only from the stereochemistry but also from the fact that the rate is dependent on the concentration of the nucleophile. An example is ring opening with hydrogen bromide:
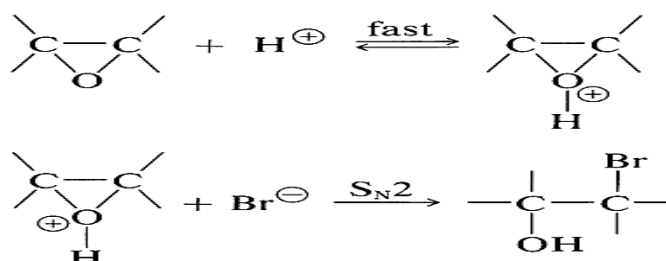
The same kind of mechanism can operate in the formation of 1,2-diols by acid-catalyzed ring-opening with water as the nucleophile.

mixture of cis and trans
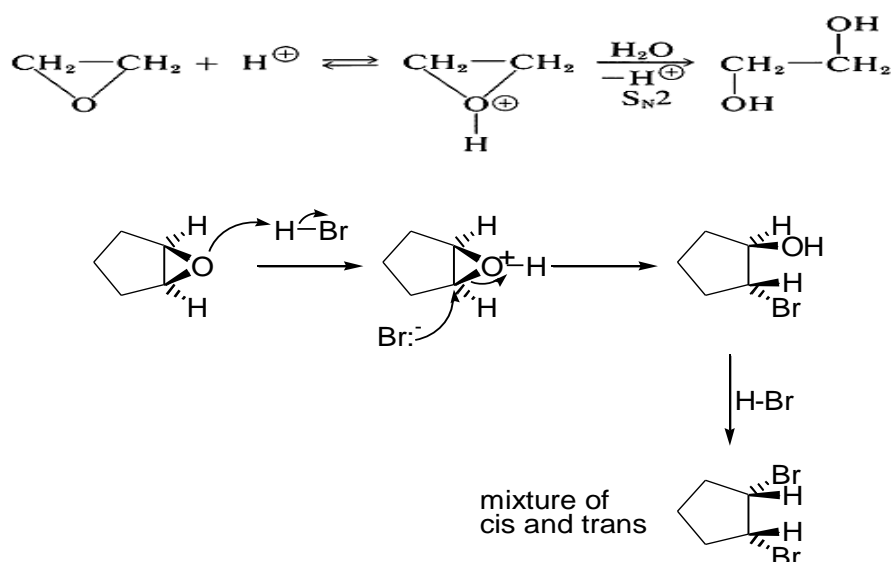
Epoxides react with H-X to produce halohydrins, which react further with H-X to generate 1, 2-dihalides.

Unsymmetrical epoxides give products with different regiochemistry with basic opening compared to acidic opening.
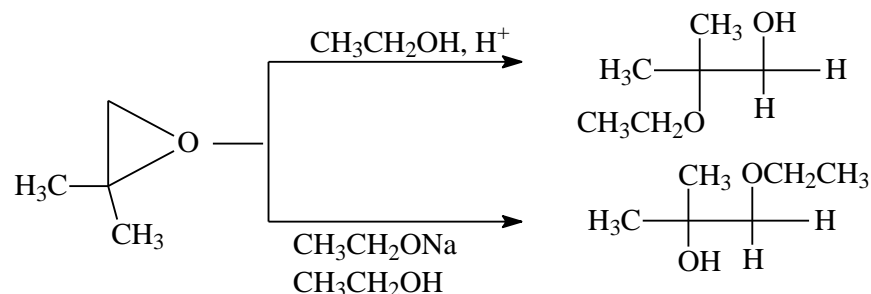
Under basic conditions, the alkoxide simply attacks the least sterically hindered epoxide carbon in an S_N2 displacement.
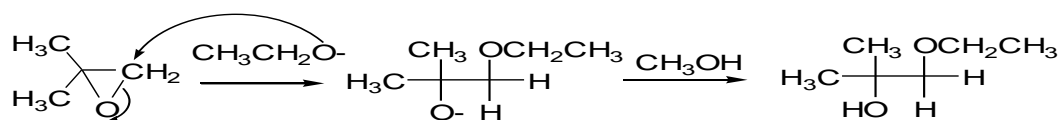
Under acidic conditions, the alcohol *seems* to attack the more hindered carbon, but it is more complicated. The protonated epoxide has several resonance structures.
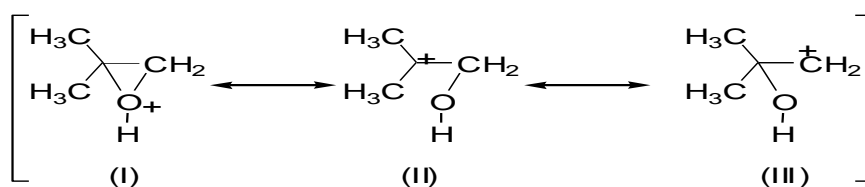
Structure II is a major contributor since the cation is more highly substituted and
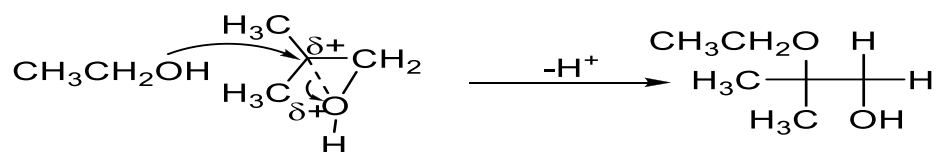
Therefore, more stable. The nucleophile attacks the carbon with greatest positive partial charge.

Some important chemical reactions of epoxide are summarized as follow.
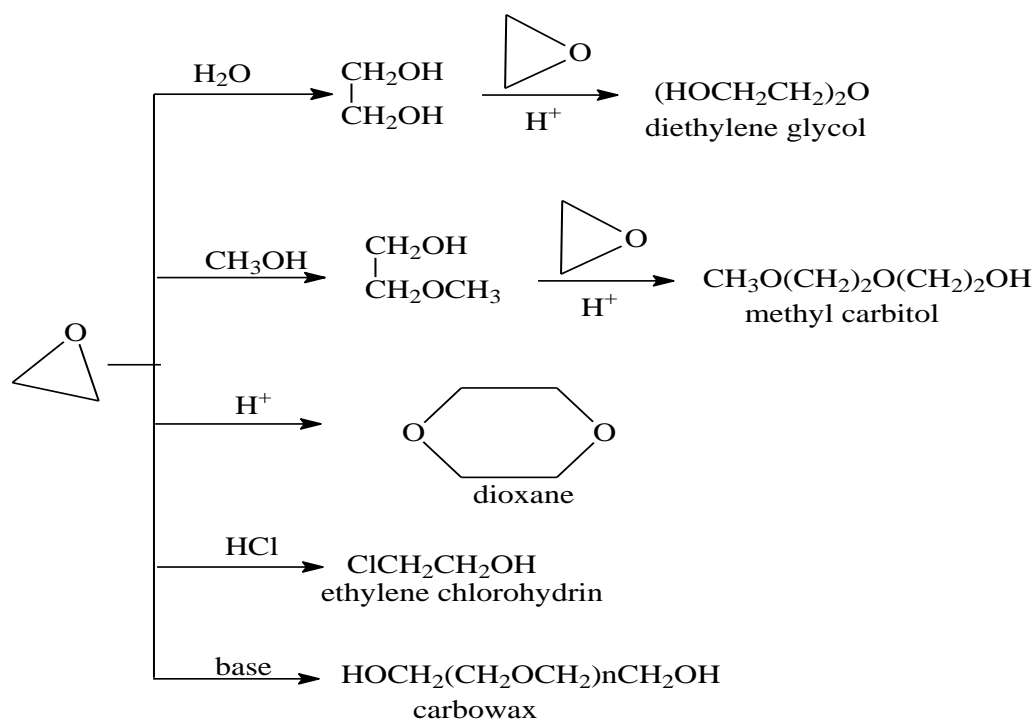
6.15 SUMMARY

In this unit we emphasis has been given to the introduction properties structure, physical properties, chemical properties of phenols. This unit also describes the difference between phenols and alcohols. Acidic character of phenols in comparison to alcohols and carboxylic acids has been described. In chemical reactions both types of reactions, due to – OH group and due to aromatic ring which are basically electrophilic in nature have been described in detail. The important name reactions involving phenols havs been described in this unit. Besides simple phenol, substituted phenols like cresols, pyrogallol, catechol, thymol, carvacrol, resorcinol, flurogocinol etc have been described with their properties and industrial application.

In this unit we also learnet about, Ethers R − O − R' and are compounds having the general formula $C_nH_{2n+2}O$. Ethers are isomeric with the aliphatic monohydric alcohols with the general formula $C_nH_{2n+1}OH$. We learnet that epoxides are the three membered cyclic ethers. This unit also made us aware that the symmetrical or simple ethers have R and R' being identical while unsymmetrical or mixed ethers have different R and R' groups. We learnet that ethers are characterized by the C-O-C bond and can be classified into linear and cyclic compounds. This unit described that in comparision to alcohols, ethers are fairly unreactive except to very strong acids such as HI or HBr. This low reactivity makes them

useful as solvents, *e.g.* diethyl ether, $(C_2H_5)_2O$ and tetrahydrofuran (THF), C_4H_8O. The more reactivity of epoxides over simple ethers due to some ring strain and capability to react with nucleophiles resulting in ring opening reaction has also been described in this unit. It has been described in this unit that under acidic conditions, epoxides open by S_N1 way with the nucleophile attacking the more substituted end. The general modoe of synthesis of ethers and cyclic ethers have been described in this unit besides their important reactions.

6.16 TERMINAL QUESTION

A Tick the correct option (MCQs):

1. Structure of gallic acid is:
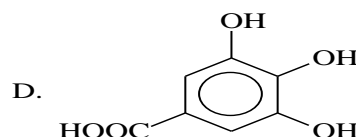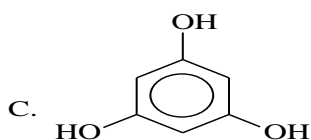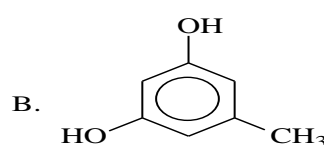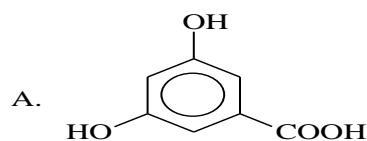
2. Vanillin is obtained by using:

    A. Reimer-Teiman Reaction   B. Hoffman bromide Reaction

    C. Houben-Hosches Reaction   D. Gatterman Reaction

3. Which is most acidic? :
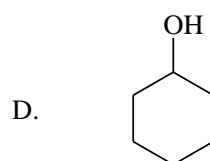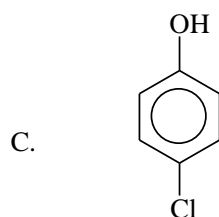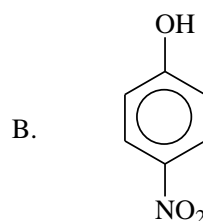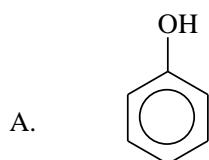
4. Thymol can be obtained naturally from:

    A. Thymus   B. Acasia

    C. Rose   D. None of them

5. Commercially phenols can be obtained from:

    A. Coal- tar   B. Benzene

    C. Gasoline   D. Wood

6. Phenol when treated with ZnO gives.

    A. Cyclohaxenol   B. Benzene

    C. Cyclohexanone   D. hydroquinone

7. Phenol undergoes ionization to become more stable by reacting with

    A. negative ions   B. positive ions

    B. both A and B   D. neutral atoms

8. Condensation of phenol with HCHO to produce Bakelite is an example of:

    A. Aldol condensation   B. Lederer-Manasse reaction

    C. Beckmann reaction   D. Knoevengal reaction

9. Which of the following groups will increase the acidity of phenol?

    A.NO_2 B. CN

    C. halogens   D. all

10. Upon reflexing phenol with $(CH_3COO)_2Hg$ we get.
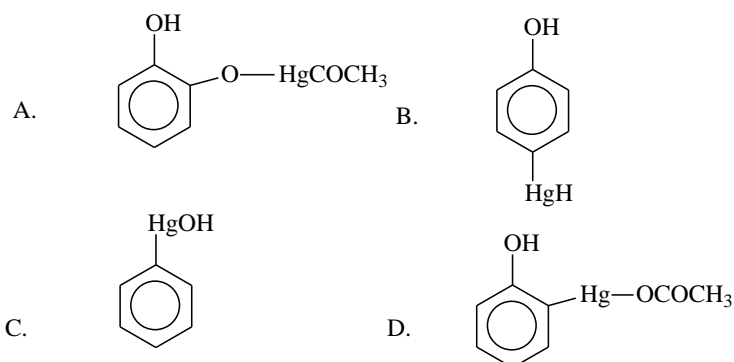
11. IUPAC name of the following compound is

$$CH_3-CH-O-CH_3$$
$$\qquad\ \ \ |$$
$$\qquad\ \ CH_3$$
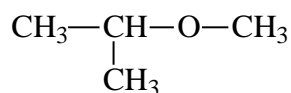
A. 1-methoxy-1-methylethane   B. 2-methoxy-2-methylethane

C. 2-methoxypropane   D. isopropylmethyl ether

12. Ethers can exhibit isomerism

A. Metamesism   B. Functional isomerism

C. Both A and B   D. Geometrical

13. Ethers have:

A. Pungent odour   B. Pleasant odour

C. Fishy odour   D. Vinegar odour

14. When diethyl ether is treated wit hot HI, it forms:

A. Ethyl iodide   B. Acetyl iodide

C. Propyl iodide   D. Ethyl alcohol

15. Ethylisopropyl ether reacts with cold HI gives:

A. $CH_3CH_2CH_2I$ + CH_3CH_2OH B. CH_3-CH-I + CH_3CH_2OH
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\ |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$$

C. $CH_3-CH-OH$ + CH_3CH_2I D. $CH_3CH_2CH_2OH$ + CH_3CH_2I
$$\quad\ \ |$$
$$\quad CH_3$$

16. Because of following properties ether are used as inert (reaction) medium.

A. Neutral and good solvent   B. Neutral and bad solvent

C. Acidic and good solvent   D. Basic and good solvent

17. Ethoxy ethane is hydrolysed by using

A. KOH_{aq} B. H_2O

C. $NaHCO_3$ D. dil H_2SO_4 under pressure

18 Which of the following cannot be considered as use of ether?

A. Inert solvent   B. Anaesthetic

C. Antipyretic   D. Solvent of oil, fats and resins

19. When a mixture of ethyl alcohol and con. H_2SO_4 are heated at 413^0K gives diethyl ether.

This reaction is:

A. Dehydration   B.Desulphonation

C. Intermolecular dehydration   D. Intramolecular dehydration

20. With boiling water or steam diethylether gives.

A. $(C_2H_5)_2SO_4$ B. C_2H_5OH

C. $CH_2=CH_2$ D.$C_2H_5OH + C_2H_5HSO_4$

21. In the reaction:

$$CH_3—\underset{\underset{Br}{|}}{CH}—CH_3 \xrightarrow{\text{Alco. KOH}} [A] \xrightarrow[\text{Peroxide}]{\text{HBr}} [B]$$

$$\xrightarrow{CH_3ONa} [C]$$
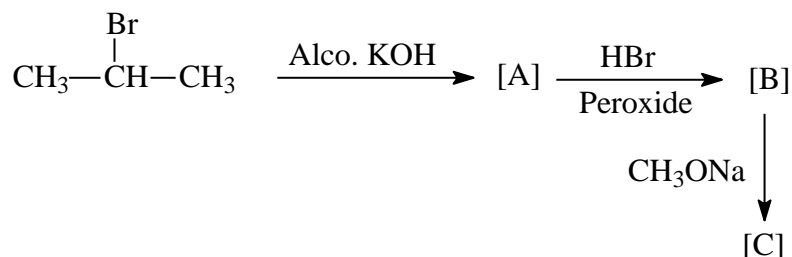
           C is:

A. Diethylether   B. 1-methoxypropane

C.Isopropyl alcohol   D.Propylene glycol

22. The preparation of ether by diazomethane method is known as:

A. Etherification   B. De-etherification

C. Methylation of alcohol   D.methylation

23. Sodium phenoxide reacts with methyl iodide and give anisol. The reaxction is known as:

A. Kolbe's reaction   B.Williamson's reaction

C. Friedel-Craft reaction   D.Reimer-Teiman reaction

24. From the formula C_4H_9OH, the number of isomers of ethers obtained is as follow.

A. Four   B. Two

C. Three   D. One

25. Which of the following is ametamer of methyl isopropyl ether /

A. Butan-2-ol   B.2-methylbutan-1-ol

C. Diethyl ether   D. Bu4tan-1-

B. Discriptive Questions:

   1.   Write the Mechanism of following name reactions

        1. Kolbe reaction

        2. Fries rearrangement

        3. Reimer Tiemann

4. Reimer –Teiman reaction

2. Arrange the following in order of increasing acidic strength. Giving reason:

   p- Nitro   phenol, m-Nitro phenol, o-Nitro phenol.

3. Explain why phenols do not undergo substitution of OH group like alcohol.

4. Explain why phenols are more acidic than alcohols.

5. How will you convert phenol to: -

   (a) Salysilic acid

   (b) Phenolphthalein

   (c) Picric acid

   (d) Ethoxy benzene

   (e) Azo dye

   (f) Catechol

6. Draw structural formulas for these compounds.

(a) 2-(1-Methylethoxy) propane   (b) *trans* -2,3-Diethyloxirane

(c) *trans* -2-Ethoxycyclopentanol   (d) Ethenyloxyethene

(e) Cyclohexene oxide   (f) 3-Cyclopropyloxy-1-propene

(g) 1,1-Dimethoxycyclohexane

7. Predict the products of the following reaction. An excess of acid is available. ethoxycyclohexane + HBr

8. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

   (i) 1-Propoxypropane

   (ii) Ethoxybenzene

   (iii) 2-Methoxy-2-methylpropane

   (iv) 1-Methoxyethane

9. Discuss polarity of ethers and compare it with the polar characters of alcohols.

10. Why Grignard reagent is prepared in ether discuss with reaction and reason.

11. Write a note on: Williamson's synthesis.

12. How is diethyl ether prepared in laboratory? How does it react wit (i) PCl_5 (ii) O_2 (iii) cold concentrated H_2SO_4 (iv) Con. HI

13. Discuss different properties and uses of ether

14. Give general methods of preparation and properties of epoxides.

6.17 ANSWERS (MCQs)

1-D	2- A	3- B	4- A	5- A
6- B	7- A	8- B	9- D	10- D
11-C	12- C	13-B	14 –A	15- B
16– A	17- B	18.- C	19.- D	20.- B
21– B	22- C	23 –B	24- C	25- D

6.18 REFERENCES

1.   Jerry march, Advanced Organic Chemistry, 4th edition, Wiley India, 2010.

2.   P.S. Kalsi, Organic Reactions and their Mechanisms, New Age International Private Limited; Publishing year: 2017.

3.   Goutam Brahmachari, Organic name reactions, Narosa publishing house, New Delhi (Revised version: 2012.

4.   R.T. Morrison and R.N. Boyd Organic Chemistry, 6th edition, Prentice Hall Private Limited, 1997.

5.   Advanced Organic Chemistry by F.A.C arey and R.J. Sundberg, Plenum Pub. 5th Edition, 2007

6.   S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry Trinity Press 2016.

7.   B.S. Bahal, A. Bahal. Advanced organic chemistry. S. Chand & Company Ltd. Ram Nagar, New Delhi 1993

UNIT 7: ALDEHYDES

CONTENTS:

7.1 INTRODUCTION

An aldehyde alkanals are an important class of an organic compounds containing a functional group with the structure −CHO, consisting of a carbonyl center (a carbon double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to an alkyl/aryal group(s). The group—without alkyl/aryl moeity, also known as the formyl group. Aldehydes are common in organic chemistry. Industrially aldehydes are produced in lagre scale as starting material for synthesis of other important chemicals.viz HCHO is produced more than 1.4, million tons/uear for the preparation ofresin.Traces of many aldehydes are found in essential oils (terpenoids) and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin. Possibly because of the high reactivity of the formyl group, aldehydes are not common in several of the natural building blocks: amino acids, nucleic acids, lipids. Most sugars, however, are derivatives of aldehydes. These aldoses exist as hemiacetals, a sort of masked form of the parent aldehyde. For example, in aqueous solution only a tiny fraction of glucose exists as the aldehyde.

7.2 OBJECTIVES

Objectives of this unit are to Study about: -

- Carbonyl Functional groups; molecular orbital structure of functional group, reactivity of carbonyl group, nucleophilicity v_s. basicity, nucleophilicity of carbonyl group, types of reactions carbonyl group undergo, mechanism of name reactions, effect of conjugation on carbonyl group reactivity.

7.3 STRUCTURE AND NOMENCLATURE OF THE CARBONYL GROUP
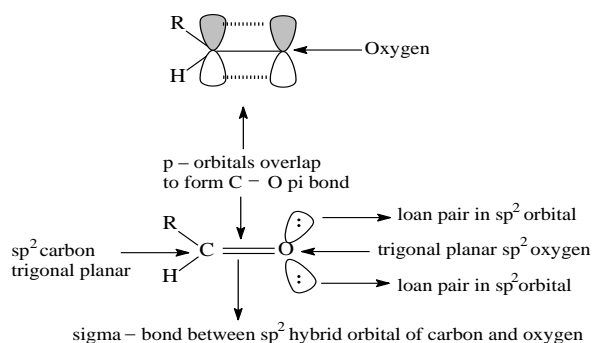
Carbonyl compounds have planar structure. It has a sp^2 hybridized carbon atom and an sp^2 hybridized oxygen atom. The carbon uses two sp^2 hybridized orbitals to form σ- bonds to the substituents. Two lone pairs of electrons are acomodated in sp^2 hybridized orbital of oxygen.

Nomenclature: - Common name for aldehydes is obtained from the names of the corresponding carboxyllic acids.

$$\underset{\text{formic acid}}{H-\overset{\displaystyle O}{\overset{\|}{C}}-OH} \qquad\qquad \underset{\text{acetaldehyde}}{H-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

$$\underset{\text{acetic acid}}{H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-OH} \qquad\qquad \underset{\text{formaldehyde}}{H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

$$\underset{\text{propionic acid}}{CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH} \qquad\qquad \underset{\text{propionaldehyde}}{CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$
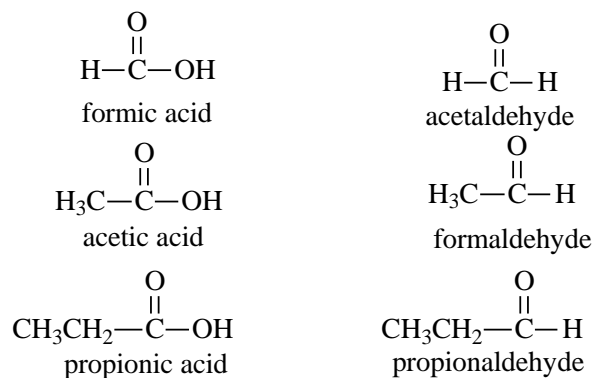
IUPAC names for aldehydes are obtained by replacing the ending –e of the corresponding alkane with –al-. Aldehyde functional group is always terminal in chain. When other substituents are present, the carbonyl carbon is assigned number 1.

$$\underset{\text{methanal}}{H-\overset{\displaystyle O}{\overset{\|}{C}}-H} \qquad \underset{\text{ethanal}}{H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-H} \qquad \underset{\text{propanal}}{CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

$$\underset{2-\text{bromopropanal}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-\overset{\displaystyle O}{\overset{\|}{C}}-H} \qquad\qquad \underset{\text{benzaldehyde}}{C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$
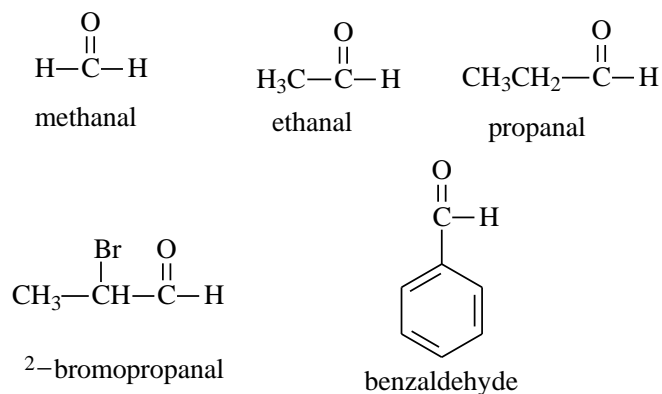
The electronegativity of carbon and oxygen is 2.5 and 3.5 respectively.

Bond energy of C = O bond is 720 kjmol^{-1}, Bond length of C = O bond is 1.21 A^0.

Carbonyl group C = O double bond is shorter than C – O single bond and stronger. C = O bond is polarized and carbon atom has some degree of positive charge and this charge attracts negatively charged nucleophiles and supports nucleophillic addition reaction.

addition product
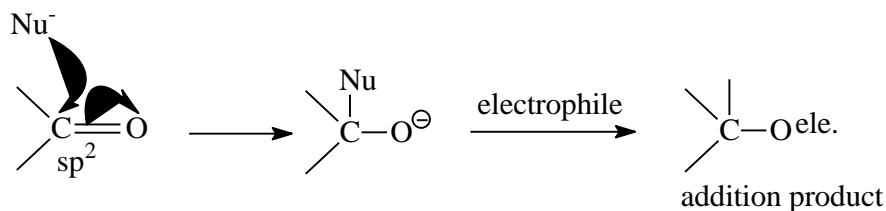
Nucleophillic addition reactions of Aldehydes may be catalysed by acids or bases.

Acid catalysis - Electrophillic protonation Addition:
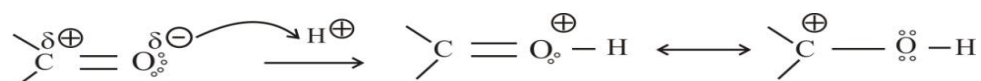
Hydrogen ion of acid attacks negatively charged carbonyl oxygen to give protonated carbonyl group. Protonated carbonyl which is resonance stabilized.
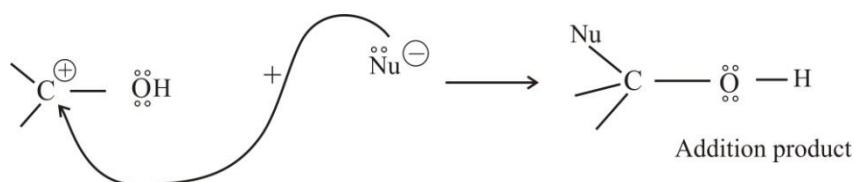
Addition product

The nucleophile attacks the protonated carbonyl group to form the addition product.

Base catalysis – nucleophillic addition – protonation

Bases convert weak nucleophile to a strong one by deprotonation.

addition product
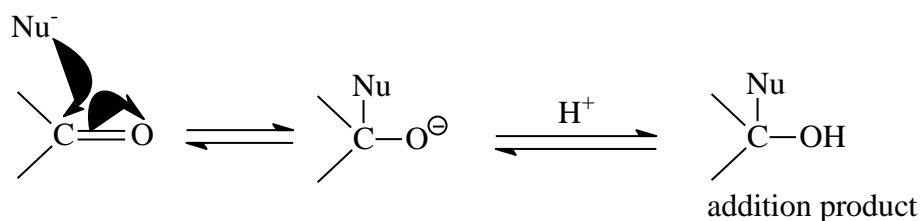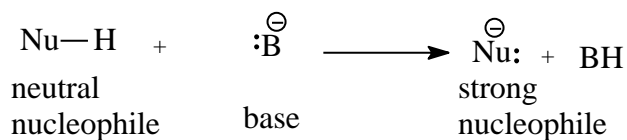
So, in carbonyl carbon two areas of reactivity, i.e. Lewis basic oxygen and electrophillic carbonyl carbon led to addition of carbonyl π bond.

α-hydrogen:- A carbon next to the carbonyl group is called α- carbon and the hydrogen attached with it is referred to as an α-hydrogen. α-hydrogens of carbonyl carbon are acidic in nature with some pK_a values. Abstraction of α hydrogen by a nase (B$^-$) results in the
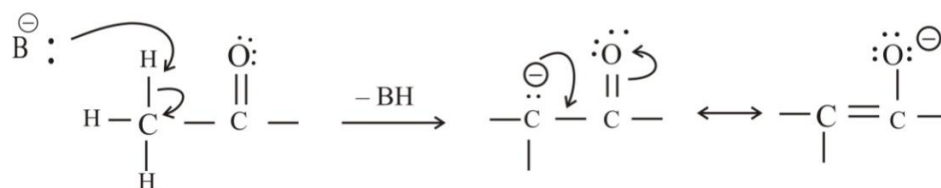
formation of anion (enolate ion) which is reasonance stabilized by delocalisation of charge onto electronegative oxygen.

α- carbon of the enolate ion is an ambident ion. It can act as nucleophile and attack at electrophillic carbonyl carbon of other carbonyl group containing molecules and leads to condensation. Enolate ion can attach an alkyl group to the reactive carbon and it is called **C-alkylation.** Alkylation at oxygen is uncommon but protonition leads to **alkenol**.

7.4 PREPARATION OF ALDEHYDES

There are several reactions which can be used for the synthesis of aldehydes some of them are as follow:-

1. *Oxidation of alcohols*: Oxidation of Primary Alcohols under controlled condition gives aldehyde.
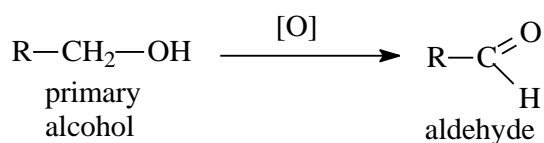
Oxidising agents used are acidified K2Cr2O7 solution, alkaline $KMnO_4$, chromic acid $H_2Cr_2O_7$, pyridine chlorochromate (PCC) $C_5H_6NCaO_3Cl$ in (DCM solvent) CH_2Cl_2.

Mechanism: Mechanism of oxidation of alcohol by dichromate is following:

$$Cr_2O_7^{2-} - H_2O \rightleftharpoons 2H\,Cr\,O_4^-$$

$$RCH_2OH + H\,CrO_4^- + 2H^+ \rightleftharpoons R - \overset{H}{\underset{h}{C}} - O - CrO_3H_2^+ + H_2O$$
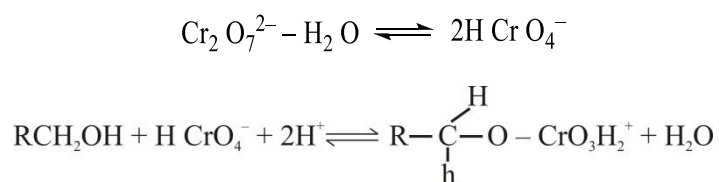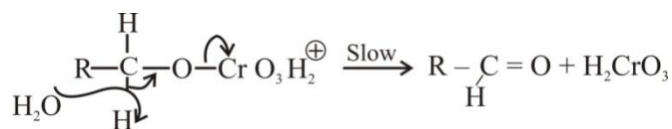
Similar ester intermediate is formed in oxidation with permanganate.

2. *Catalytic dehydrogenation of alcohols*: - Aldehydes may be prepared by dehydrogenation of primary alcohol by passing vapours over copper catalyst at about 300^0C of alcohol.
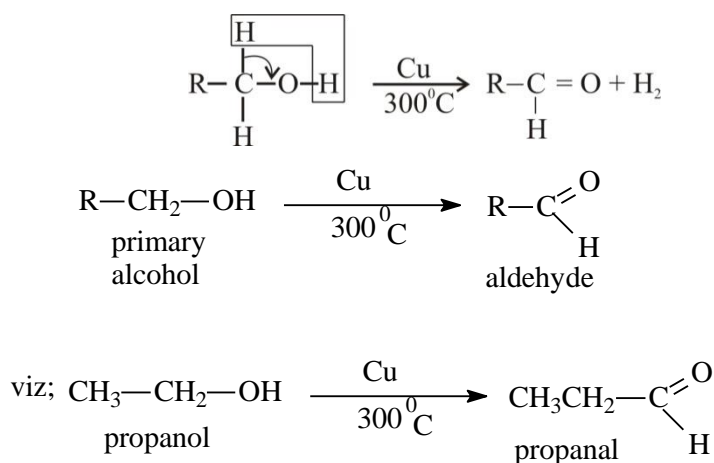
3. By heating a mixture of the calcium salts of formic acid and any one of its homologues
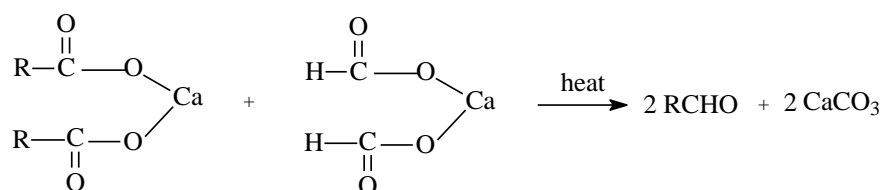
4. By passing a mixture of vapours of formic acid and any one of its homologues over manganous oxide a catalyst at 300^0C.

$$RCOOH + HCOOH \xrightarrow{MnO} RCHO + CO_2 + H_2O$$

$$viz; CH_3COOH + HCOOH \xrightarrow{MnO} CH_3CH_2CHO + CO_2 + H_2O$$
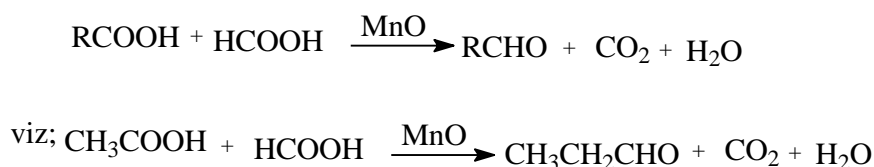
5. *Oxidation of alkenes (ozonolysis)*: - Oxidation of alkene viz;2-pentene with ozone gives ozonides which are often explosive in dry state and they are decomposed with $Zn + H_2O$ to give carbonyl compounds.

$$CH_3—CH_2-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}—CH_3 \quad \xrightarrow[\text{(ii) Zn + H}_2\text{O}]{\text{(i) O}_3} \quad CH_3CH_2CHO \ + CH_3CHO$$

2- pentene
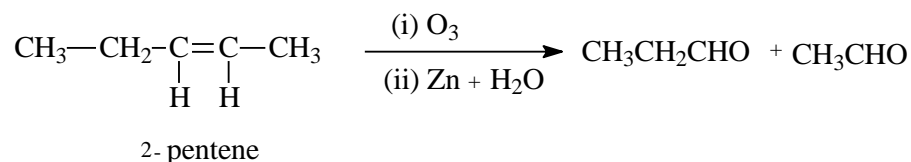
6. Hydration of alkynes: - Acetylene on hydration by passing into hot dilute H_2SO_4 in the presence of $HgSO_4$ as catalyst is converted into acetaldehyde.

$$HC\equiv CH +HOH \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} H-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}—OH \longrightarrow CH_3\ CHO$$

Acetylene   Unstable   Acetaldehyde
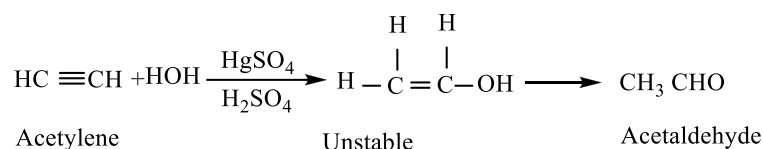
7. Alkaline hydrolysis of gem dihalides: - The germinal dihalides (two halogens' atoms are attached to the terminal carbon atom) gives Aldelyde

$$H_3C—\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}—Cl \quad \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}} \quad H_3C—\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}—OH \ + \ 2\,NaCl$$

unstable

$$\xrightarrow{\hspace{1cm}} H_3C—\overset{\overset{O}{\|}}{C}—H \ + \ H_2O$$
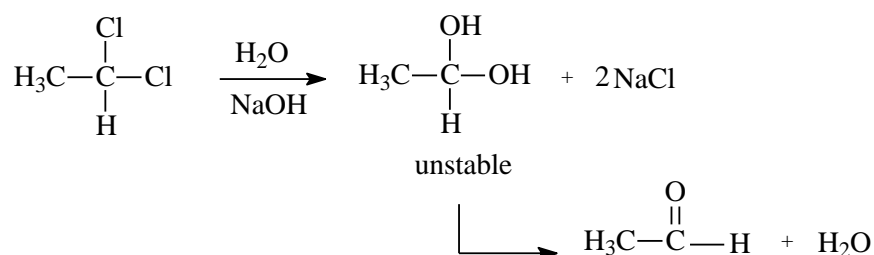
8. Rosenmund's Reduction: - This is one of the most common methods for the synthesis of aldehydes. In this method reduction of an acid chloride with hydrogen in boiling xylene using a poisoned palladium catalyst supported on $BaSO_4$ is used.

$$R—\overset{\overset{O}{\|}}{C}—Cl \quad \xrightarrow[\text{Pd/BaSO}_4]{[H]} \quad R—\overset{\overset{O}{\|}}{C}—H$$

$$CH_3—\overset{\overset{O}{\|}}{C}—Cl \quad \xrightarrow[\text{Pd/BaSO}_4]{[H]} \quad CH_3—\overset{\overset{O}{\|}}{C}—H$$
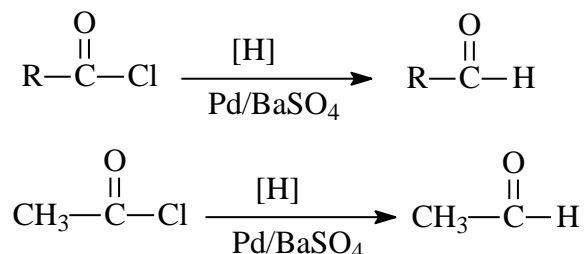
Here $BaSO_4$ prevents further reduction of aldehyde to alcohol as it acts as a poison to Pd catalyst. So small amount of quinoline and sulphur is added to deactivate catalyst partially. Lithium tri-t. butoxy aluminum hydride (LTBA) can also be used as catalyst.

9. Oxo process: - It is an industrially important method to produce aldehydes. Here alkene is treated with carbon monoxide (CO) and hydrogen in the presence of cobalt carbonyl catalysts at high temperature and pressure.

$$R—CH═CH_2 + H_2 \xrightarrow[\text{heat}]{\left[HCO(Co)_4\right]} R—\underset{\underset{H}{|}}{CH}—CH_2—CHO$$
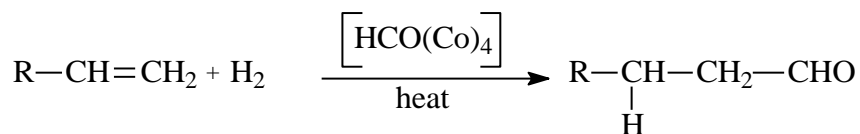
10. Wacker process: - In this process alkene is treated with an acidified aqueous solution of palladium chloride (PdCl$_2$) and cupric chloride (CuCl$_2$).

$$CH═CH_2 + Pd\,Cl_2 + H_2O \xrightarrow{Cu\,Cl_2} CH_3—\overset{\overset{O}{||}}{C}—H + Pd + 2H\,Cl$$

$$Pd + H\,Cl \longrightarrow Pd\,Cl_2$$
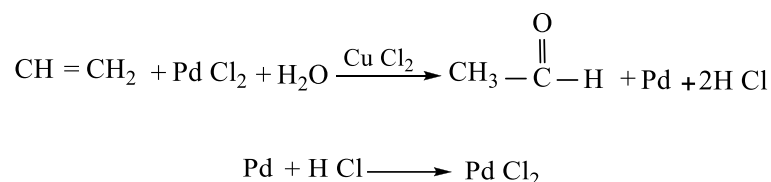
Cu Cl$_2$ promotes regeneration of Pd Cl$_2$ from Pd.

$$Pd + 2Cu\,Cl_2 \longrightarrow Pd\,Cl_2 + 2\,Cu\,Cl$$
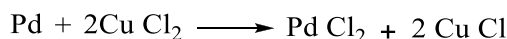
11. Stephen's method: - Here alkyl cyanide is dissolved in ether, or ethyl formate or ethyl acetate and reduced with stannous chloride and hydrochloride acid and then steam distilled.

$$R—C≡N \xrightarrow{HCl} \underset{\text{iminochloride}}{\left[R—C≡NH\right]^{\oplus} Cl^{\ominus}} \xrightarrow[\text{HCl}]{SnCl_2} \underset{\substack{\text{aldemine} \\ \text{stannichloride}}}{\left[R—C═NH_2\right]_2^{\oplus} SnCl_6^{2\ominus}}$$

$$\downarrow H_2O$$

$$RCHO$$
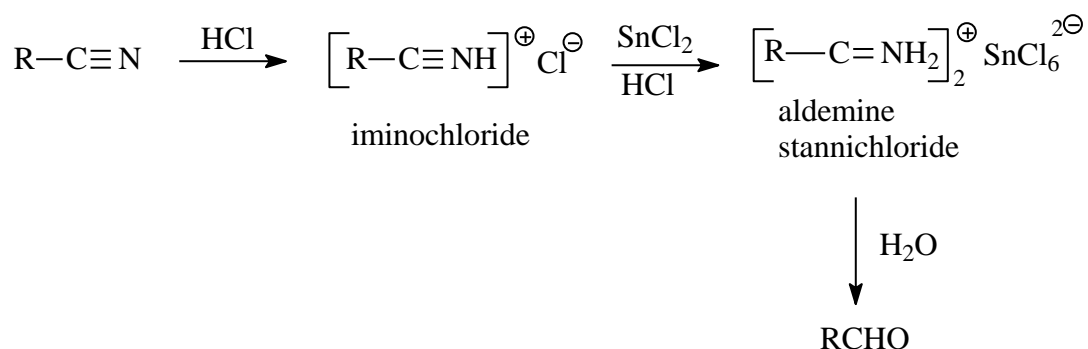
12. Synthesis of aldehyde from 1,3-dithane: 1,3-dithiane has 2 weakly acidic protons that can be removed and alkylation of the carbon is possible. Once alkylated, the 1,3-dithiane becomes a "protected" carbonyl as it can be hydrolyzed to the corresponding carbonyl hydrolyzed to the corresponding carbonyl structure.
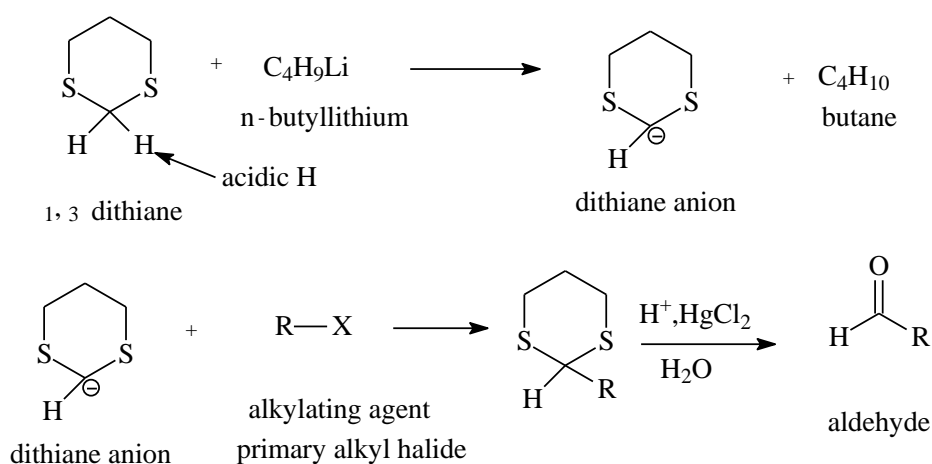
13. Preparative methods of aromatic aldehydes: Aromatic aldehydes are carbony compounds containing CHO functional group attached with phenyl ring /aromatic rings. Like aliphatic aldehydes there are several methods for the synthesis of aromatic adldehydes some of them are being discussed as follow.

i. Oxidation of Toulene with oxygen / air in the presence of vanadium pentoxide catalyst at 350^{0}C.
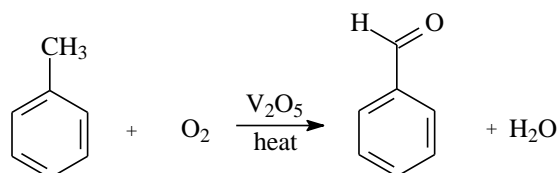
ii.   By hydrolysis of benzylidene chloride with aqueous acid.
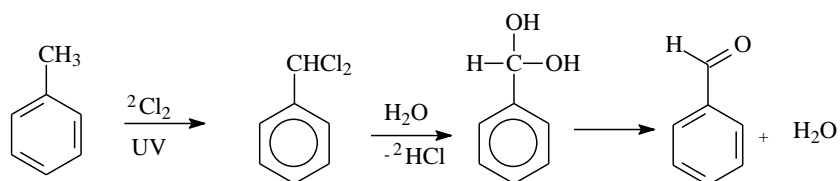
iii.   Boiling of benzyl chloride with aqueous copper or lead nitrate in a current of CO_2 yields benzaldehyde.
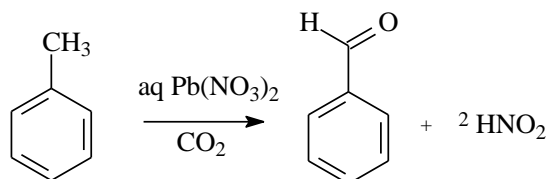
iv. Oxidation of benzylalcohol with acidic $K_2Cr_2O_7$ of with copper catalyst at 350^{0}C.
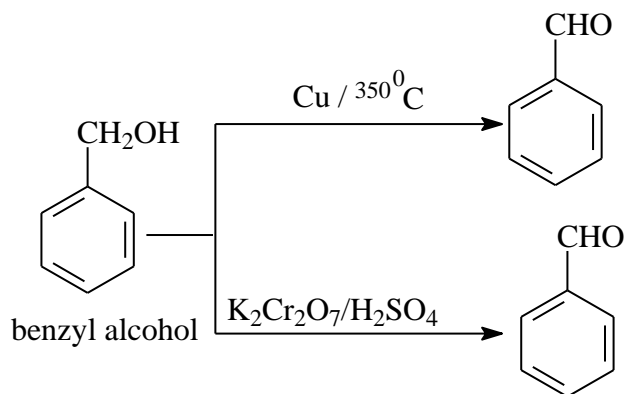
v. Oxidation of alkylbenzene by chromium trioxide in acetic anhydride yields benzylidene diacetate which on hydrolysis with dilute sulphuric acid or hydrochloric acid gives benzaldehyde.
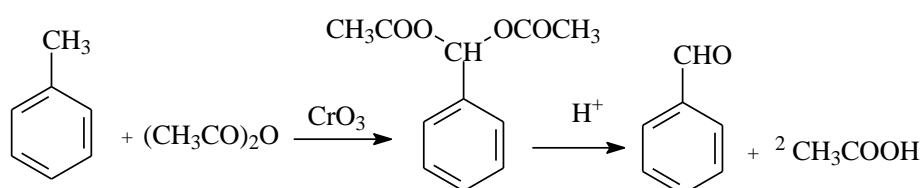
When Toulene is oxidized by chromyl chloride (CrO_2Cl_2) in CCl_4 solution yields complex, which on hydrolysis forms benzaldehyde.
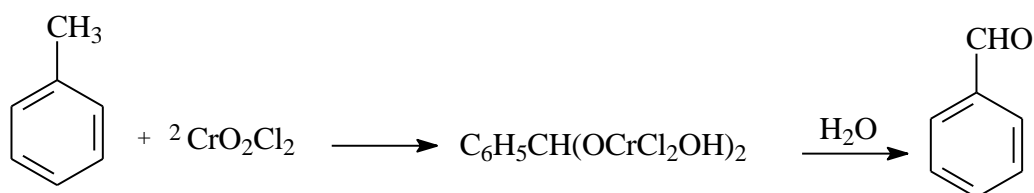
This reaction is known as **Etard** reaction.

vi. **Gattermann Koch aldehyde synthesis:** Benzene is treated with mixture of carbon monoxide and hydrogen chloride in the presence of anhydrous $AlCl_3$ and small amount of cuprous chloride.

$$HCl + \overset{\ominus}{C} \equiv \overset{\oplus}{O} + AlCl_3 \longrightarrow \left[[H - \overset{\oplus}{C} = O] \longleftrightarrow [H - C \equiv \overset{\oplus}{O}] \right] Al\, Cl_4^{\ominus}$$
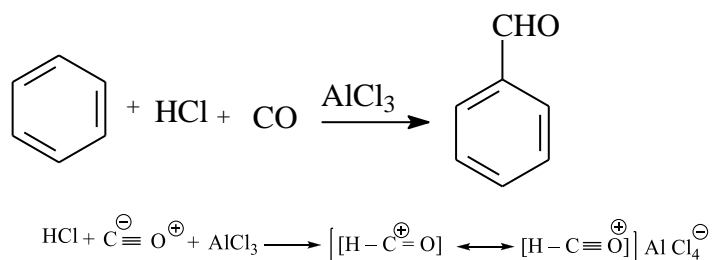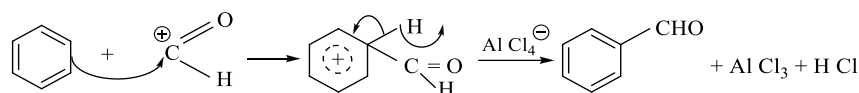
When methyl grp is present in benzene ring then CHO grp is introduced at para position. This synthesis is not applicable to phenols or deactivating grp having benzene.

vii. **Gattermann aldehyde synthesis: -** When Benzene is treated with a mixture of HCN and HCl in the presence of $AlCl_3$, it produces a complex and it is decomposed with water to produce benzaldehyde.
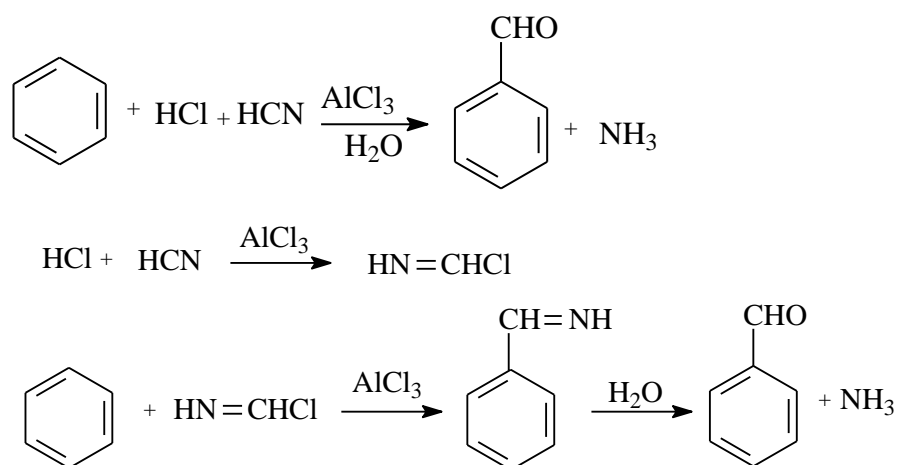
This reaction is applicable to phenols and phenolic ethers, but not to nitrobenzene.

viii. **Sommelet's Reaction: -** Benzyl chloride is refluxed with hexamethylenetetramine in aqueous ethanolic solution, followed by acidification and steam distillation to yield Benzaldehyde.
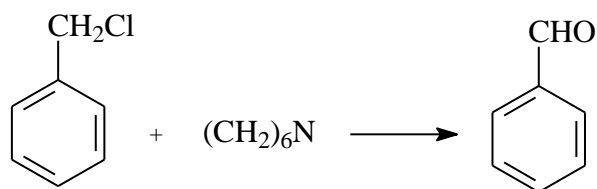
ix. **Rosenmund Reduction: -** Catalytic reduction of benzoyl chloride in the presence of quinoline sulphur poison or $Pd/BaSO_4$ yield benzaldehyde.
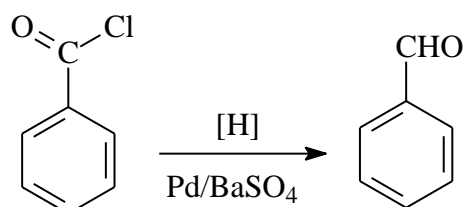
x.   **Stephen's method: -** When phenyl cyanide is reduced with stannous chloride and hydrochloric acid in ethereal solution it gives aldimine stannichloride complex which on hydrolysis with water forms benzaldehyde.
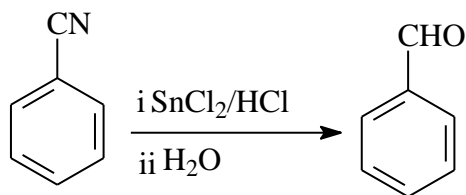
 In ortho substituted cyanides case yield is negligible due to steric hinderance.

xi. When Phenyl magnesium bromide is treated with ethyl formate or ethylorthoformate, it gives Benzaldehyde.
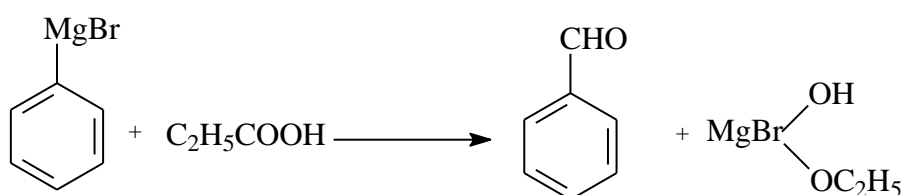
xii. **Reimer Tiemann Reaction: -** When phenol is created with $CHCl_3$ in the presence of alkali forms O-hydroxy formaldehyde.
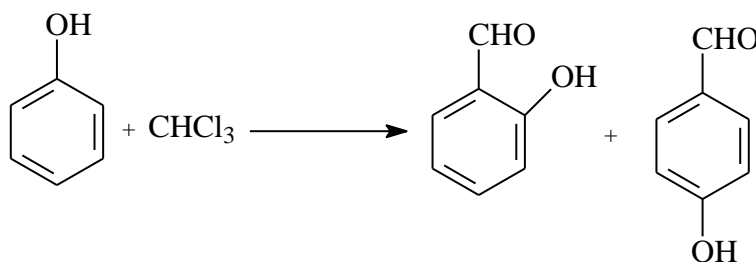
7.5 PHYSICAL PROPERTIES OF ALDEHYDES

1. In aldehyde the first member HCHO is gaseous at room temperature. Acetaldehyde is liquid in nature with b.p. 20^0C. Lower aldehydes are colourless liquids. Benzaldehyde is liquid with characteristic smell of bitter almonds.

2. Lower members of aldehydes possess unpleasant smell.

3. Carbonyl group compounds are polar in nature due to dipole - dipole interactions of partial negative charge of carbonyl oxygen of one molecule and partial positive charge on

the carbonyl carbon of another molecule. So boiling points of aldehydes and ketones are higher than those of alkanes which have comparable molecular weights. However these dipole -dipole interactions are weaker than hydrogen bonding interactions, hence aldehydes and ketones due to lack of intermolecular hydrogen bonding have low boiling points as compared to alcohols of comparable molecular weights.

$$CH_3CH_3 \qquad H-\overset{\overset{\displaystyle O}{||}}{C}-H \qquad CH_3OH$$

	ethane	methanal formaldehyde	methanol
Mol. wt.	30	30	32
b.p.	$-89\,^{0}C$	$-21\,^{0}C$	$64.5\,^{0}C$

4. As aldehydes and ketones can form hydrogen bonds with water so lower aldehydes and ketones are soluble in water.
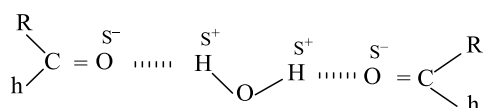
However, solubility decreases as the hydrocarbon part of molecule increases. The lower aldehydes and ketones are soluble in organic solvents such as benzene, ether and CCl_4. Carbonyl compound also form hydrates with water i.e. corresponding germinal diols.

7.5.1 RELATIVE REACTIVITY OF CARBONYL COMPOUNDS

The carbony group of aldehydes is reactive because of electromeric effect. However the electron withdrawing substituents make carbonyl group more electrophilic, as withdrawing groups generates extra positive charge at carbonyl carbon and electron donating alkyl groups reduce positive charge at carbonyl carbon. Increased positive charge at carbonyl carbon destabilize carbonyl compounds and favours attack of nucleophile at electron deficient carbonyl carbon which is followed by the addition of electrophile on negatively charged oxygen.
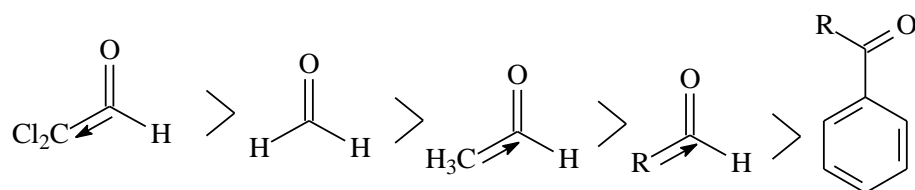
Nucleophile attacks $C = O$ bond prior to electrophile because the produced anion is more stable than the cation resulting due to electrophile attack.

The reactivity of nucleophillic addition is favoured by

i. Electron withdrawing substituent at carbonyl carbon.

ii. Small size of substituent group to avoid sterive hinderance for attacking reagent.

During nucleophilic addition reaction carbonyl carbon transforms from SP^2 hybrid state to sp^3 hybridized state and bond angle reduces from 120^0 approx. to 109.5^0 approx. So transition stage bears steric strain and this steric strain increases with increasing bulk of groups which are already present on carbonyl carbon.

Aromatic carbonyl compounds are less reactive than the corresponding aliphatic carbonyl compounds. Here partial positive charge present on carbonyl carbon is delocalized over benzene ring by resonance.
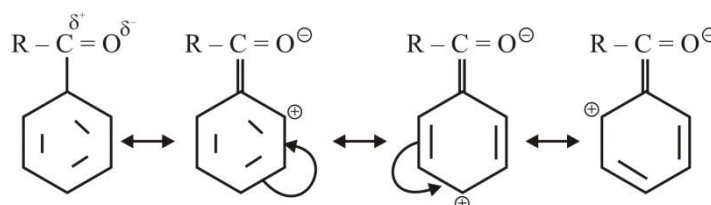
So electrophillic nature of carbonyl carbon which is desired for nucleophillic addition reaction is neutralized and nuclecophillic addition reaction slows down. The acids and bases act as catalyst for a number of carbonyl addition reactions. Here acids catalysts make carbonyl group more electrophillic by protonating carbonyl groups lone pair and base catalysts make nucleophile more nucleophillic by deprotonating nucleophile.

7.6 CHEMICAL PROPERTIES OF ALDEHYDES

The slightly positive carbon atom in the carbonyl group can be attacked by nucleophiles. A nucleophile is a negatively charged ion (for example, a cyanide ion, CN^-), or a slightly negatively charged part of a molecule. Some of the important reactions of adlehydes are being given below

7.6.1 ADDITION REACTIONS

During the reaction, the carbon-oxygen double bond gets broken. The net effect of all this is that the carbonyl group undergoes addition reactions.

(1) **Addition of Sodium Bisulphite** – Aldehydes add on sodium hydrogen sulphite to form bisulphite compounds.
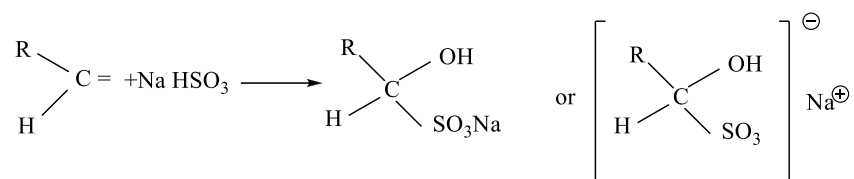
Thus the formed bisuphite compounds are hydroxysulphonic acid salts where sulphur atom is directly attached to the carbon atom. When bisulphate compounds are heated with dilute acid or Na_2CO_3 solution then carbonyl compound is regenerated.

(2) Addition of hydrogen cyanide (HCN) - All Aldehydes add HCN in the presence of base catalyst to form cyanohydrins.

$$HCN + \overset{\ominus}{O}H \longrightarrow H_2O + \overset{\ominus}{C}N$$
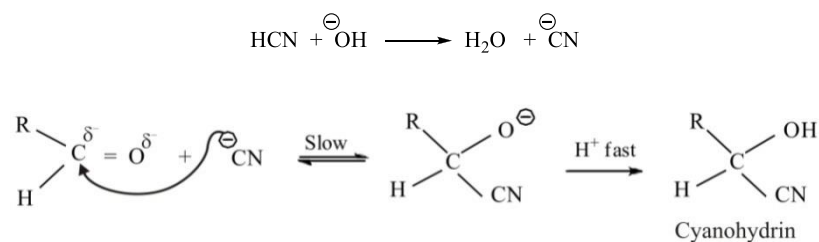
Cyanohydrins can be hydrolysed readily to α hydroxy acids.

$$CH_3CHO + HCN \longrightarrow \underset{\text{cynohydrin}}{CH_3(OH)CN} \xrightarrow{H^+/H_2O} CH_3\overset{\overset{\textstyle OH}{|}}{C}HCOOH$$

$$CH_3CH_2CHO + HCN \longrightarrow \underset{\text{cynohydrin}}{CH_3CH_2CH(OH)CN} \xrightarrow{H^+/H_2O} CH_3CH_3\overset{\overset{\textstyle OH}{|}}{C}HCOOH$$
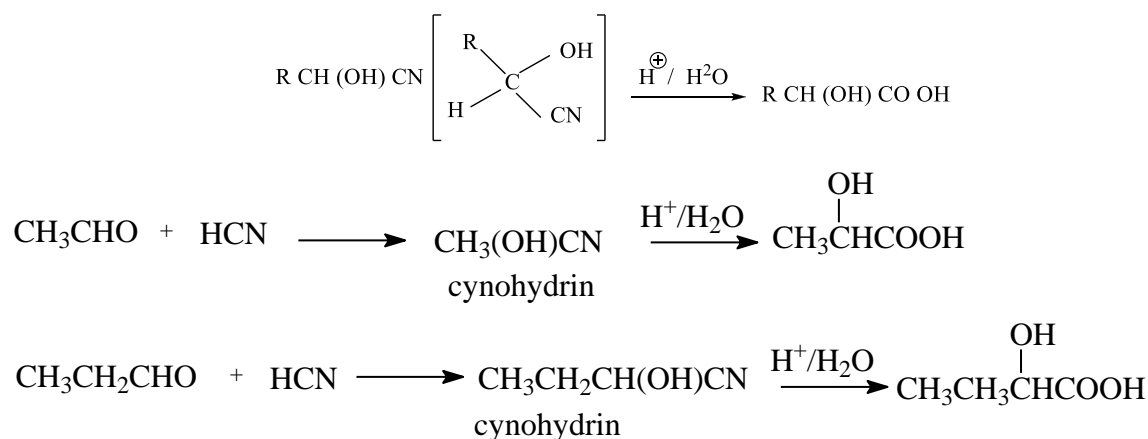
(3) Addition of Grignard Rreagents: Aldehydes react with Grignard reagents to form a complex dilute acid gives alcohol.
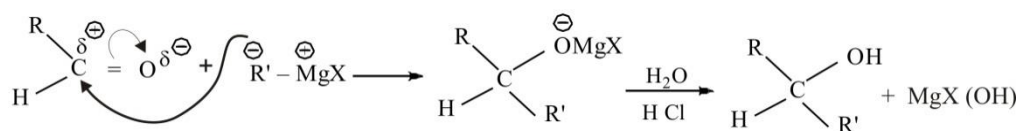
Formaldehyde gives primary alcohol. Other aldehyde gives secondary alcohols.
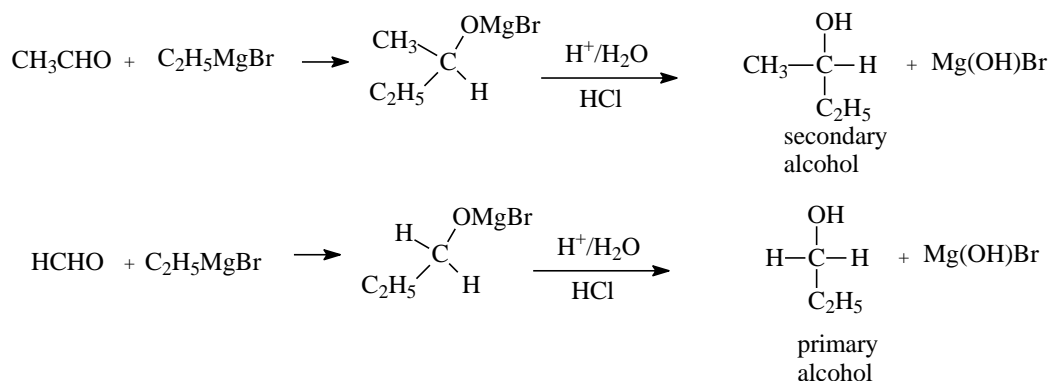
(4) Addition of ammonia – Aldehydes (except HCHO) react with ammonia in other to give aldehyde ammonia.
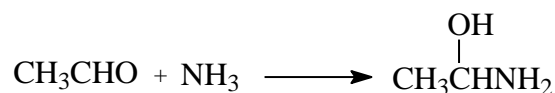
Formaldehyde on treatment with ammonia gives hexamethylenetetratnine.

$$6HCHO + 4NH_3 \rightarrow (CH_2)_6\,N_4 + 6H_2O$$
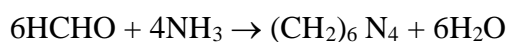
Addition Reactions followed by loss of water

(5) Addition of terminal Alkynes – Sodium salt of terminal alkynes reacts with aldehydes to give alkynol. This reaction is known as Ethinylation.
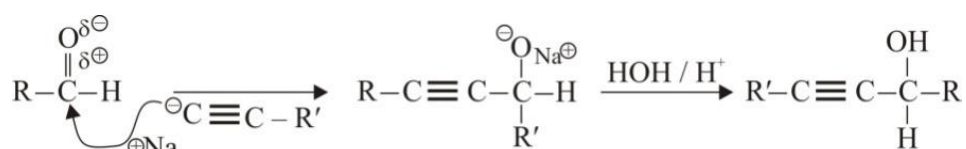
(6) Addition of alcohols – When acetaldehyde is dissolved in methanol it reacts to form hemiacetal which is unstable as compare to parent aldehyde.
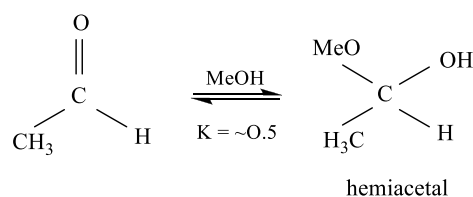
Rate of formation of hemiacetals is greatly increased either by acid or by base.

Acid catalysts increase electrophilicity of carbonyl.
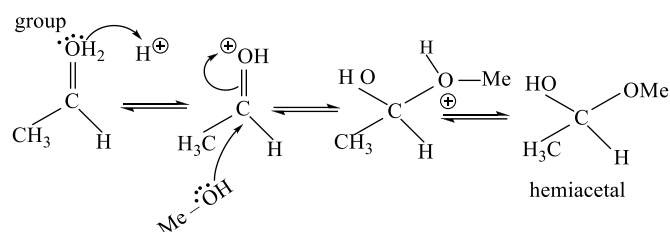
Base catalysts increase nucleophilicity of alcohol by removing the OH proton before it attacks the C = O group.
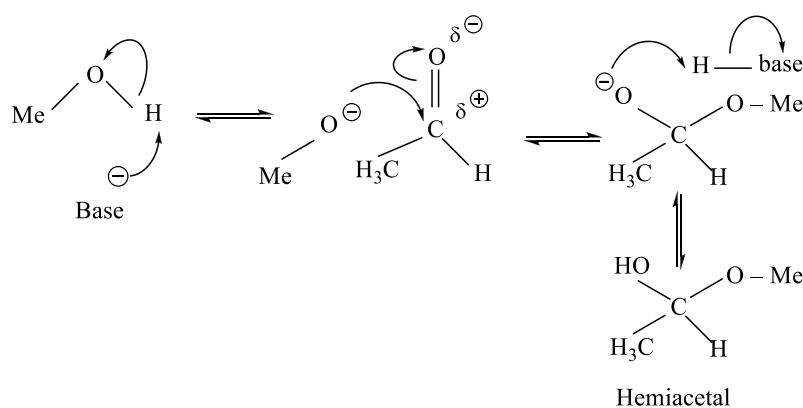
Hemiacetals are unstable. Here acid or base catalyse not only formation of hemiacetals but also decomposition them into aldehyde.
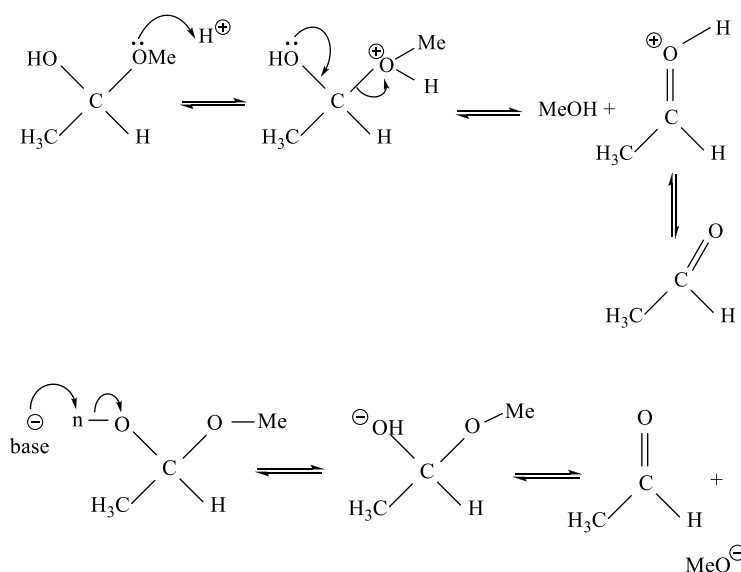
When catalytic acid is added to acetaldelyde-methanol mixture rate of reaction increases and two equivalents of alcohols are added to aldehyde to form new class of compound called acetal.
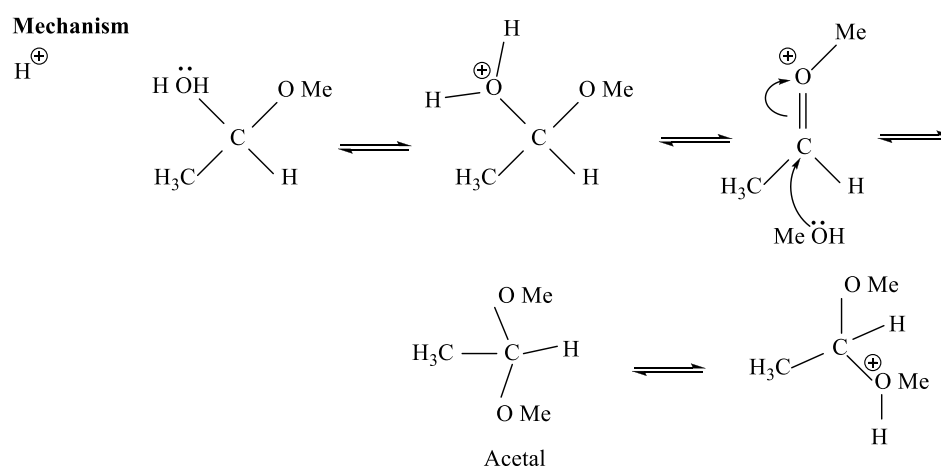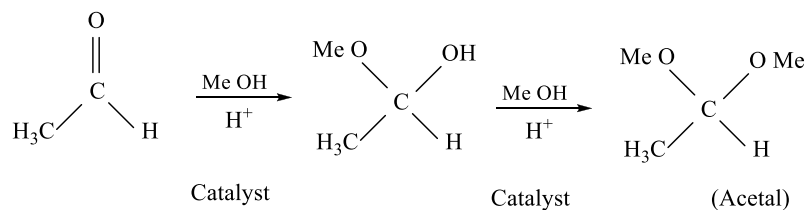
(7) **Addition of mercaptans:** Aldehydes condense with thioalcohols (mercaptans) in the presence of HCl to form mercaptals.
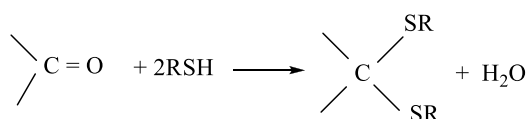
7.6.2 ADDITION REACTIONS FOLLOWED BY ELIMINATION

The addition reactions of aldehydes often followed by the loss of a water molecule. This gives a reaction known as addition-elimination or condensation. The important reactions in continuation to addition reactions as above (4.6.1) given by aldehydes are:

(8) **Addition of ammonia Derivaties** – Aldehydes combines with various compounds of type Y — NH_2 (Y = NH_2, OH, C_6H_5NH etc) to form carbon nitrogen double bonded compounds and a water molecule is eliminated.

Mechanism
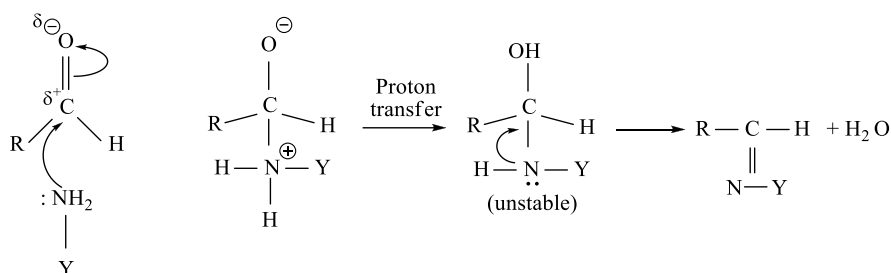
(a) Hydroxylamine (NH_2OH) form oximes with carbonyl compounds

Aldoxime

$$CH_3CHO + NH_2OH \longrightarrow CH_3-\overset{\overset{H}{|}}{C}=NOH + H_2O$$

acetaldehyde oxime
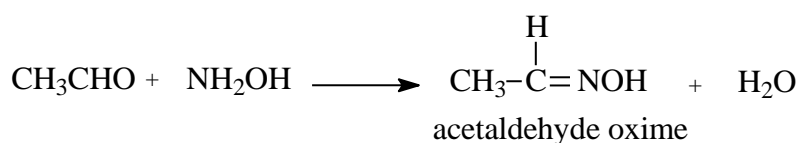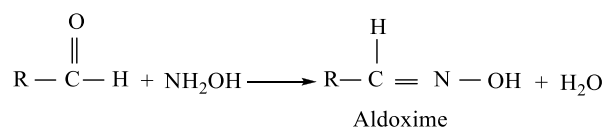
(b) N - substituted hydroxylamines form nitrones which show 1, 3 addtion reactions.
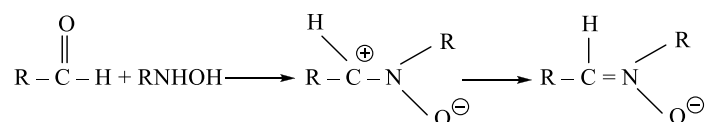
(c) Hydrazines (NH_2NH_2) react with carbonyl compound to give Hydrozones or azines.

hydrazones   azine
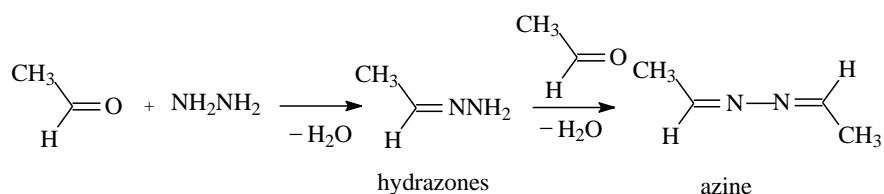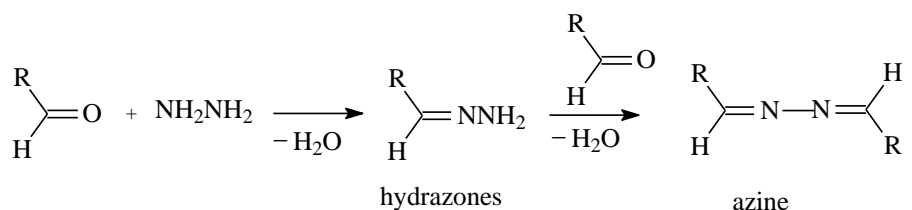
hydrazones   azine

d) Phenyl hydrazine ($NH_2NHC_6H_5$) forms phenyl hydrazones with carbonyl compounds.

phenyl hydrazone
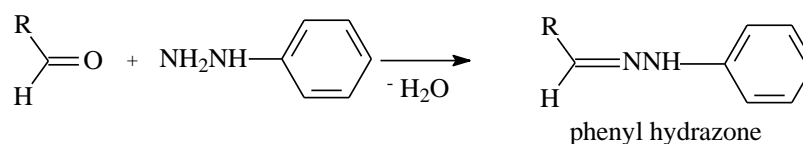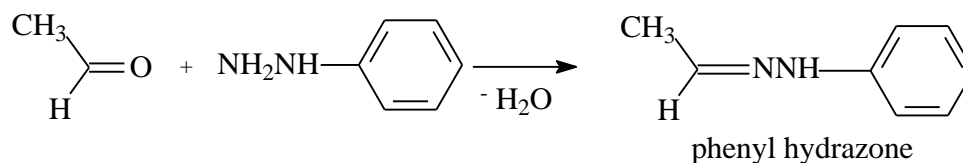
phenyl hydrazone

(e) Carbonyl compounds react with semicarbazides ($NH_2NHCONH_2$) to form semicarbazones.

semicarbazone

semicarbazone
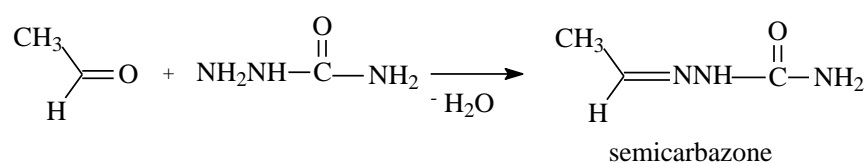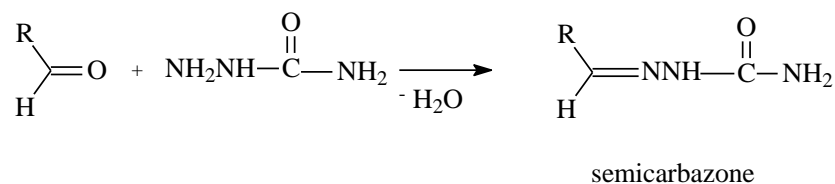
(f)   2, 4 dinitrophenyl hydrazine (DNP) (Braddy's reaction) react with carbonyl compounds to give 2, 4 dinitrophenyl hydrazones.

DNP

DNP
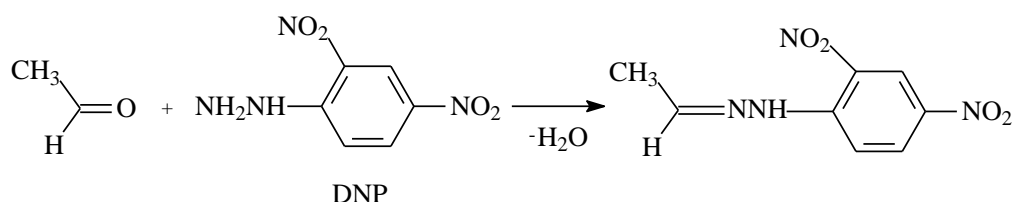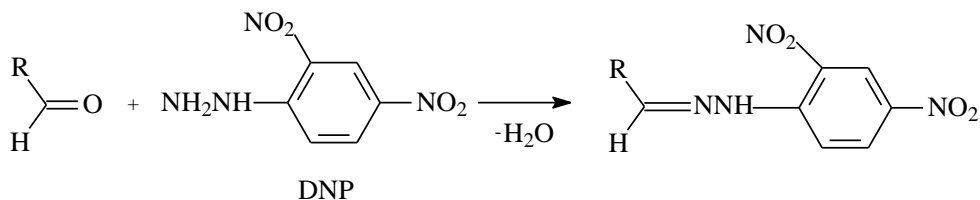
Oximes and hydrazones regenerate carbonyl compound when refluxed with dilute hydrochloric acid. Regeneration from phenylhydrazones is difficult.

(9) Phosphorus pentachloride reacts with simple carbonyl compounds to form 1, 1, dichlorides.

$$\underset{H}{\overset{R}{>}}=O \ + \ PCl_5 \ \longrightarrow \ R-\underset{H}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-Cl \ + \ POCl$$

$$\underset{H}{\overset{CH_3}{>}}=O \ + \ PCl_5 \ \longrightarrow CH_3-\underset{H}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-Cl \ + \ POCl$$
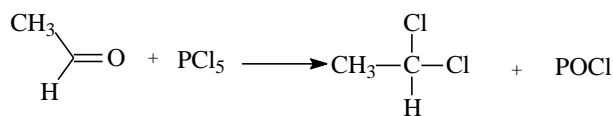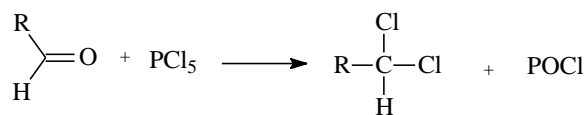
(10) Aldehydes react with aliphatic primary amines to form aldimines.

$$R'\,CHO \ + \ R^2\,NH_2 \ \longrightarrow \ R'\,CH\,(OH)\,NHR^2 \ \xrightarrow{-H_2O} \ R'\,CH \ = \ NR^2$$

$$\underset{H}{\overset{R}{>}}=O \ + \ R'CH_2NH_2 \ \xrightarrow{-H_2O} R-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-NCH_2R \ \xrightarrow{-H_2O} \ \underset{\text{aldimine}}{RCH=N-CH_2R}$$
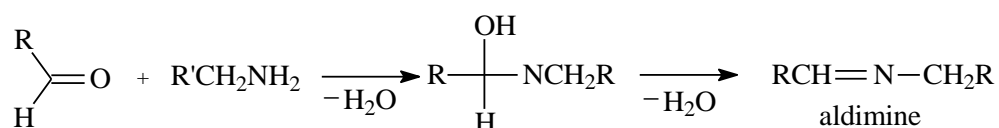
7.6.3 REDUCTION REACTIONS OF ADDEHYDES

Adlehydes can be reduced to alcohols. In continuation to other reactions as discussed above the reduction reactions are being discyssed as follow.

(11) Aldehydes can be reduced to alcohols by treatment with Hydrogen and Ni or Pt catalyst.

$$\underset{H}{\overset{R}{>}}=O \ + \ H_2 \ \xrightarrow{Ni} \ RCH_2OH$$

$$CH_3CHO \ + \ H_2 \ \xrightarrow{Ni} \ CH_3CH_2OH$$
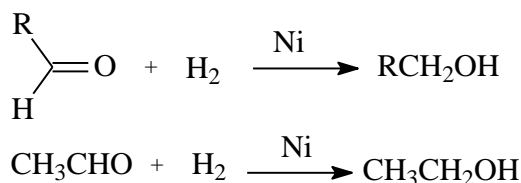
If both double bond and carbonyl groups are present then either both are hydrogenated or preferentially double bond is hydrogenated leaving carbonyl group intact.

$$R-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \ \xrightarrow[25^0C]{Ni\,/\,H_2} \ R\,CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$R-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \ \xrightarrow[\triangle\,/\,Pressure]{Ni\,/\,H_2} \ R-CH_2-CH_2-CH_2-CH_2\,OH$$
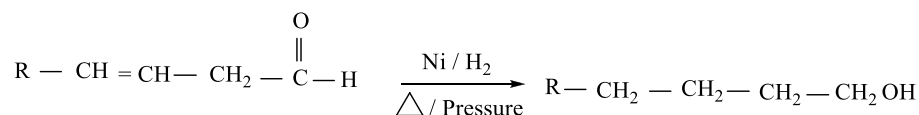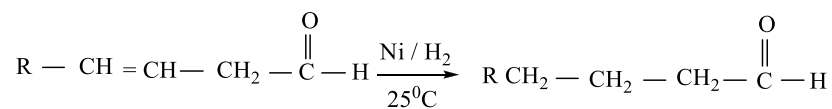
Some metal hydrides as LAH (lithium aluminium hydride) in anlydrous either or THF solvent and $NaBH_4$ (sodium borohydride) in water or alcohol as solvent can be used as reducing agent.
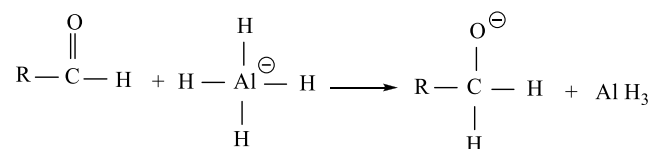
Each hydride ion can reduce one carbonyl group.
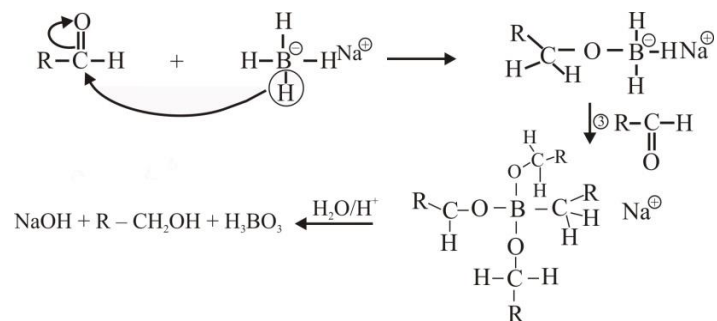
(12) Aldehydes can be reduced to corresponding alcohols by dissolving aldehydes in isopropyl alcohol containing aluminium isopropoxide. Here isopropyl alcohol is converted to acetone. This reaction is known as **Meerwein-Ponndorf-verely (MPV)** reduction.
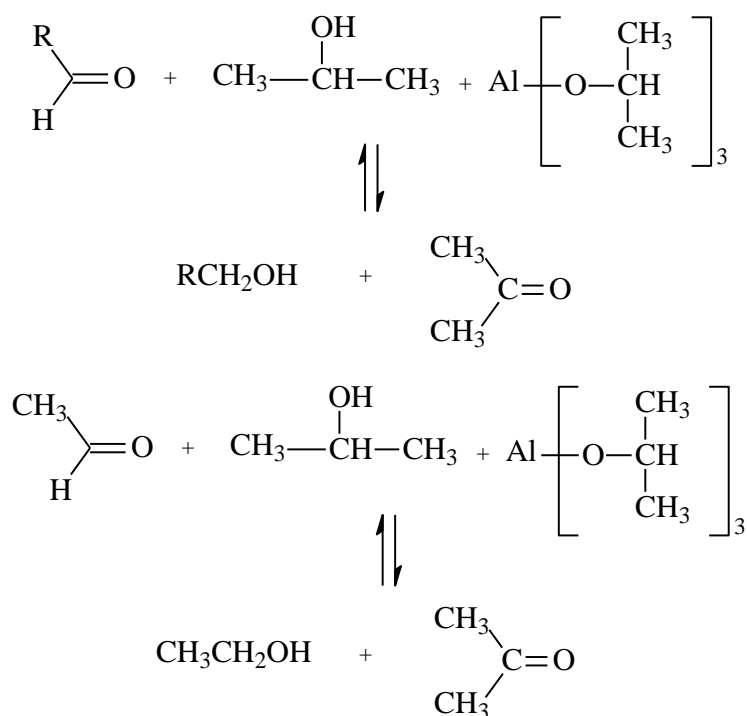
Mechanism:
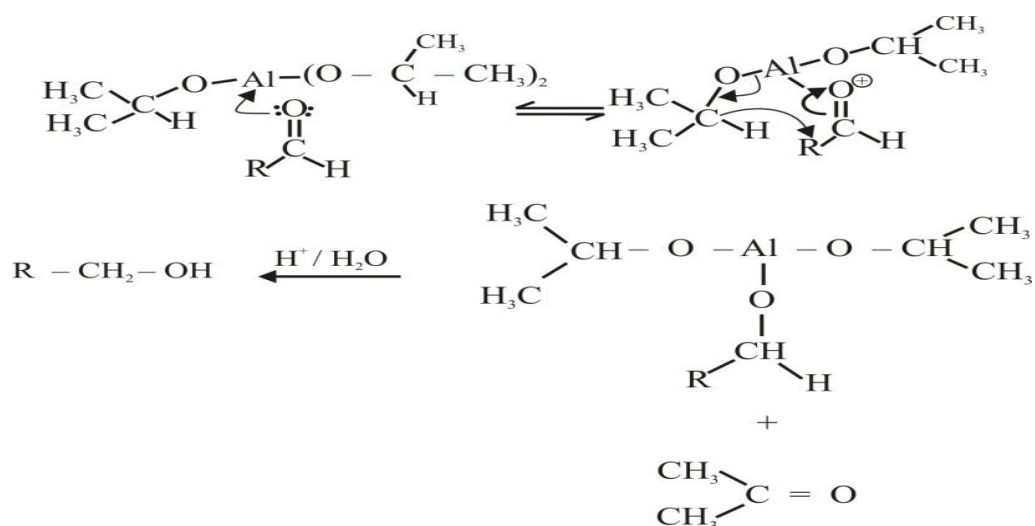
(13) Reduction to hydrocarbon: Carbonyl group of compounds is reduced to methylene group by using zinc amalgam and hydrochloric acid. This reaction is called **Clemmensen reduction**. In this reaction carbonyl group is reduced to $-CH_2-$ group. Ketones are more effective than aldehydes in this reduction. The mercury alloyed with the Zn does not participate in the reaction; it serves only to provide aclean active metal surface. Some times alcohols may be used as the solvent in **Clemmensen reduction**

$$CH_3CHO \xrightarrow[\text{con.HCl}]{\text{Zn/Hg}} CH_3CH_2OH$$
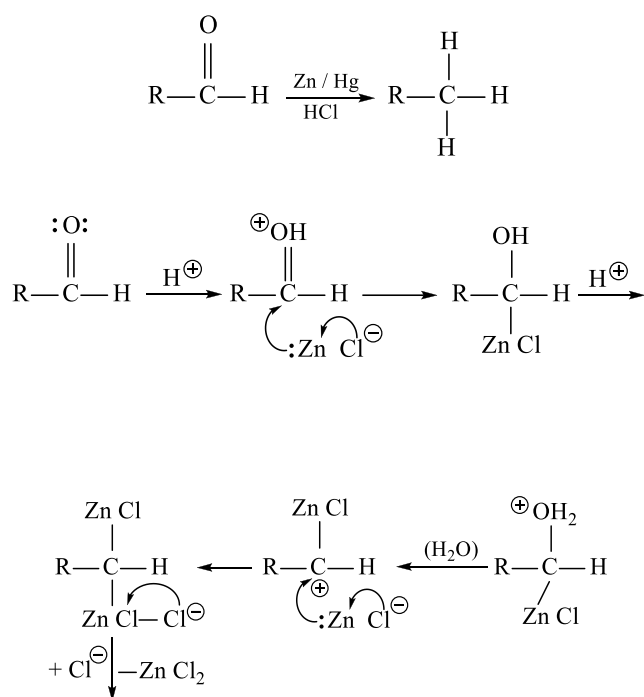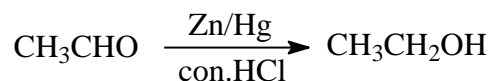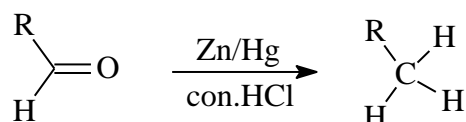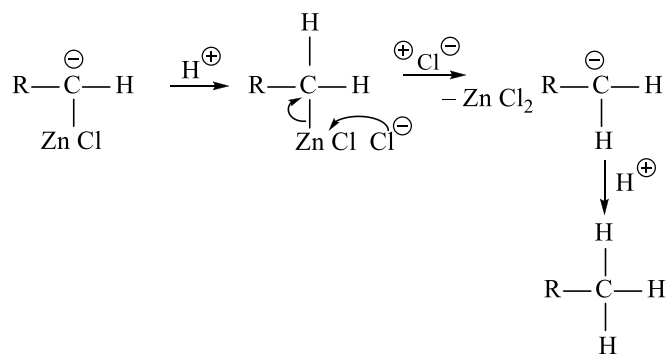
(14) Wolff-Kishner reduction: Hydrazones are hearted with Sodium ethoxide at 180^0C, Nitrogen is eliminated and carbonyl group is converted to methylene group i.e. hydrocarbon.

Hydrazone
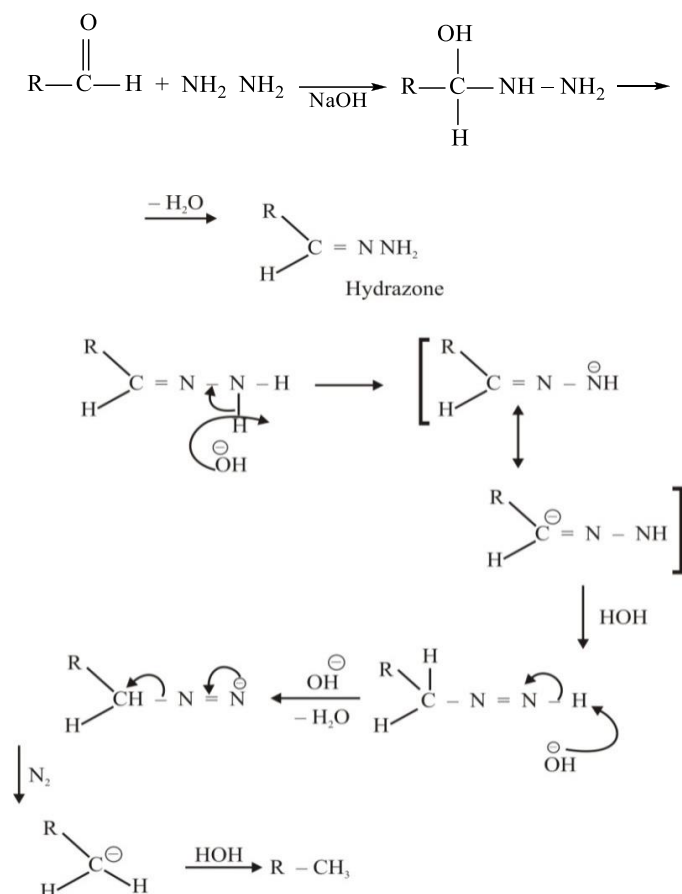
Reaction can be carried out at room temperature in the presence of polar solvents like DMSO. Use of Potassium t-butoxide gives better yield.

7.6.4 OXIDATION REACTIONS OF ADDEHYDES

The aldehydes in presence of oxidizing agent can be oxidized to corresponding carboxylic acids in continuation the reactions are being described as follow.

(15) (i) Aldehydes are easily oxidized with $K_2Cr_2O_7$ in Sulphuric acid, or $KMnO_4$.
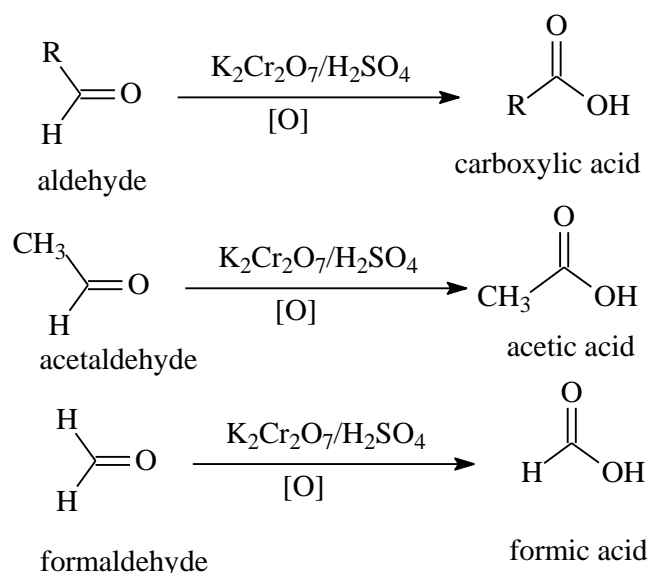
(ii) Aldehydes with methyl or methylene group adjacent to carbonyl group are oxidised to dicarbonyl compounds by Selenium oxide.

$$CH_3CHO + SeO_2 \longrightarrow OHC - CHO + Se + H_2O$$
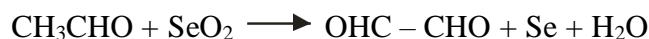
(iii) Mild oxidizing agents like tollen's reagent $[Ag(NH_3)_2OH]$, Fehling's solution i.e. alkaline solution of cupric ion or Benedict's solution i.e. alkaline solution of Cupric ion complexed with citrate ion; oxidize aldehydes.

$$R-\overset{\overset{O}{\|}}{C}-H \ + \ Cu\,(OH)_2 \ + \ NaOH \ \longrightarrow \ R-\overset{\overset{O}{\|}}{C}-\bar{O}\,\overset{\oplus}{Na} \ + \ Cu_2\,O\downarrow \ + \ 3\,H_2\,O$$

<div align="center">redppt
Cuprousoxide</div>
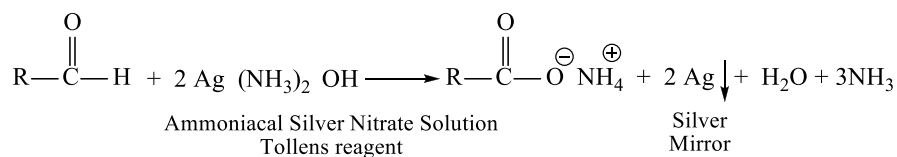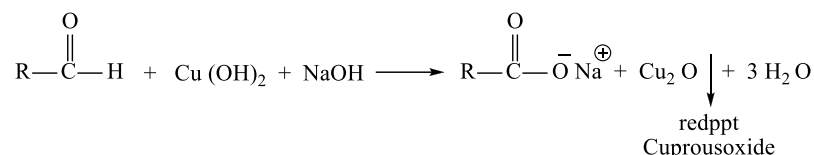
Benzaldehyde gives positive test with Tollen's reagent but not with Fehling's and Benedict's solution because of + Resonance effect of Benzene ring which makes C-H bond stronger and weak oxidizing agents like Fehling and Benedict solutions could not oxidize aromatic aldehydes.

7.6.5 OTHER REACTIONS

The carbonyl groups are polar and this polarity increases acidity of hydrogens of α- carbon. These α- hydrogens may lead to form etholate ions. There enolatic ions are good nucleophile and can attack on electrophiles like protons. The pKa value of aldehyde is lower than that of ethane or acetylene but it is comparable to those of alcohols. So α halogens of aldehydes are removable by strong bases.
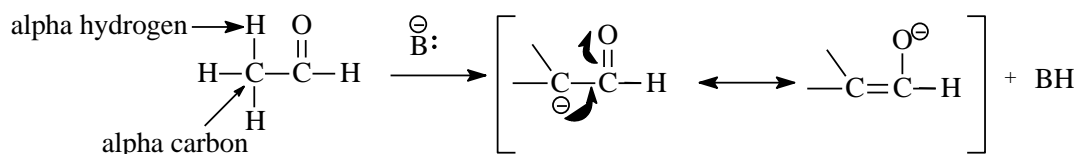
Enolate ion is ambident anion. Here partial negative charge is located on both α carbon and oxygen i.e. two different sites of one molecule are having –ve charges. So this nucleophile can attack eleclrophiles at either of two sites.

If electrophile like alkyl group attacks at carbon, then it is called alkylation or **C-alkylation**, or if it attacks at oxygen, it is **O-alkylation**, O alkylation is uncommon and oxygen site is common for protonation. Protonation leads to unsaturated alcohol called alkenol or enol which are unstable and rapidly isomerizes back to carbonyl compound. Some of the reactions under this had in continuation are being given follow:

(16) Haloform reaction: Acetaldehyde reacts rapidly with halogen (Cl_2, Br_2, or I_2) in the presence of alkali to form haloform.

$$H_3C\ CHO\ +\ 3Br_2\ +\ 3\ NaOH\ \longrightarrow\ H-\overset{\overset{\displaystyle O}{\|}}{C}-CBr_3\ +3H_2O\ +\ 3\ NaBr$$

$$Br_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H\ +\ NaOH\ \longrightarrow\ H-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}\overset{\oplus}{Na}\ +\ CHBr_3$$

Bromoform
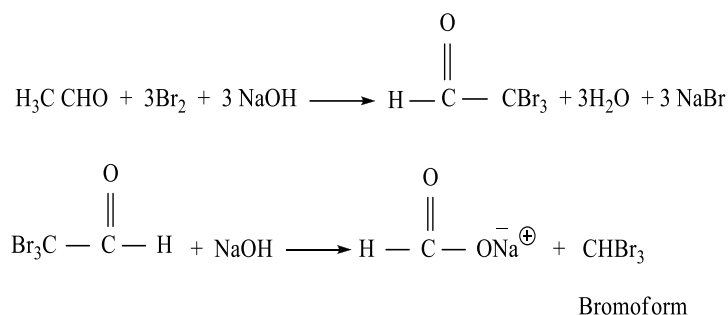
Haloform reaction is useful in identifying the presence of $-COCH_3$ group.

If instead of Bromine, Iodine is used as solution of iodine in aqueous alkali then CH93 yellow precipitate of Iodoform is obtained and reaction is called Iodoform reaction. Ethyl alcohol and secondary alcohols also give this test positive.

17. Cannizaro reaction: Aldehydes that have no α hydrogen atoms undergo disproportionation reaction. Here when aldehydes (with no α hydrogen) are treated with concentrate NaOH, one molecule is converted to alcohol and one molecule to acid.

$$2\ HCHO\ \overset{NaOH}{\longrightarrow}\ CH_3OH\ +\ HCOONa$$
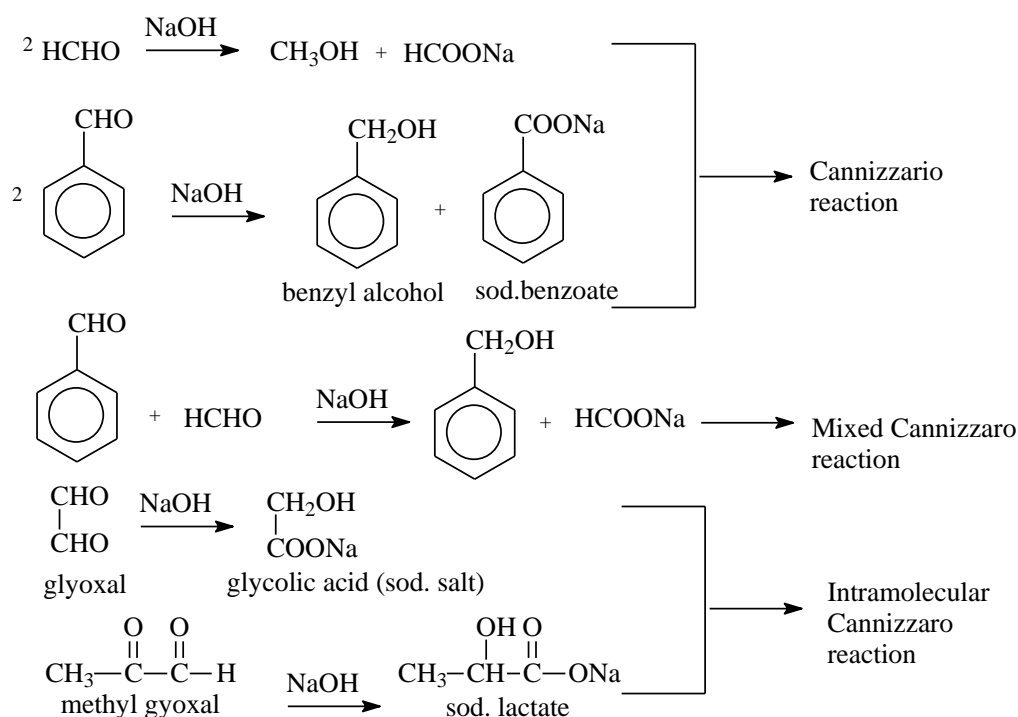
Mechanism : Attack of $OH^{(-)}$ group on the carbonyl group followed by hydride transfer.The sequential mechanism is as follow both forinter and intramolecular Cannizzaro reaction

$$NaOH \rightleftharpoons Na^+ + \overset{\ominus}{O}H$$

The reaction mechanism of formaldehyde with hydroxide ion showing hydride shift, formation of formate ion (H–C–ONa), methanol (CH₃OH), and the intramolecular Cannizzaro reaction of glyoxal (ethanedial) to form hydroxy acetic acid.

glyxol (ethanedial)

hydroxy acetic acid
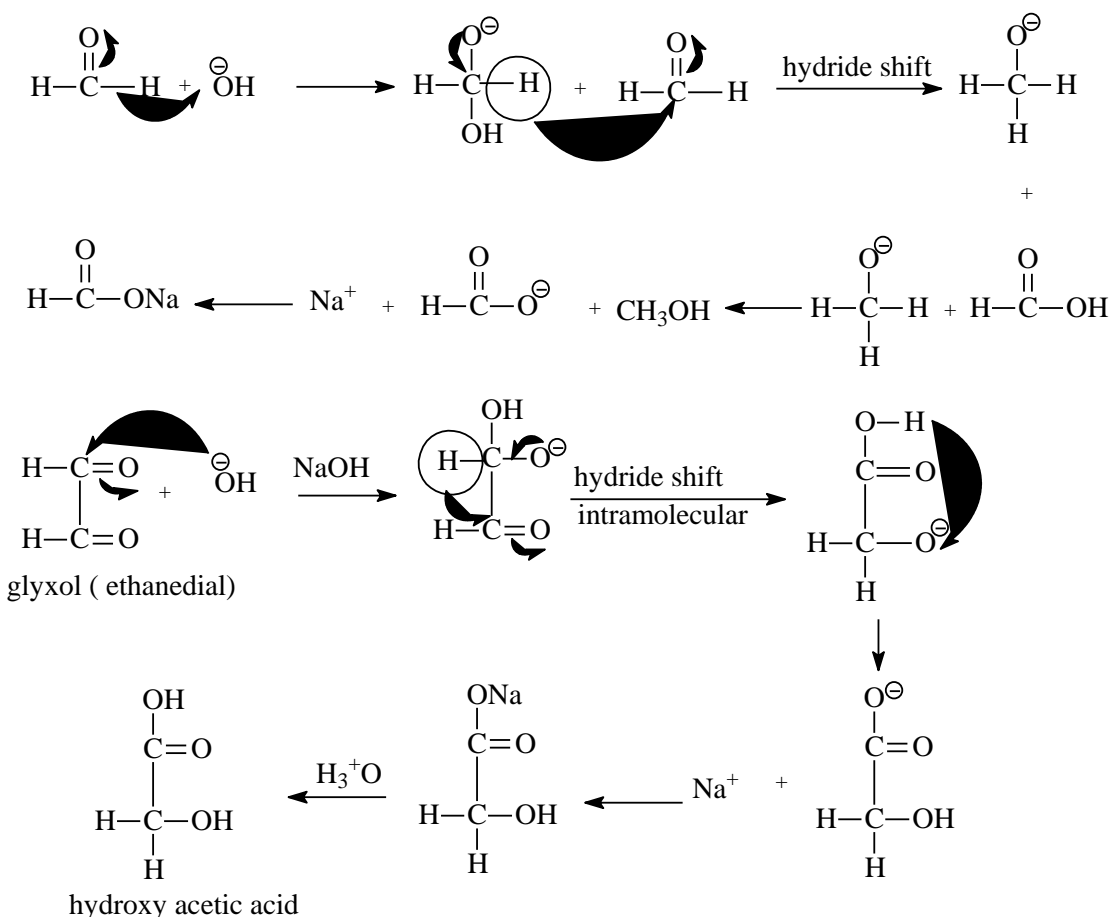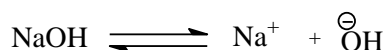
In mixed Cannizzaro reaction it is the formaldehyde that is oxidized to formate ion and other aldehyde viz; benzaldehyde is reduced to alcohol because CHO group of HCHO is the most electrophilic among all the substituted aldehydes and require the least activation energy to react with nucleophile reagent like ⁻OH ion.

18. Reformatsky reaction: Carbonyl compounds on treatment with α- bromoester in the presence of zinc, followed by acid hydrolysis yields β hydroxyl ester.

$$CH_3CHO \quad + \quad BrCH_2COOCH_2CH_3 \xrightarrow[\text{ii } H_2O/H^+]{\text{i Zn, ether}} \quad CH_3{-}\underset{OH}{CH}{-}CH_2{-}\underset{O}{C}{-}OCH_2CH_3$$
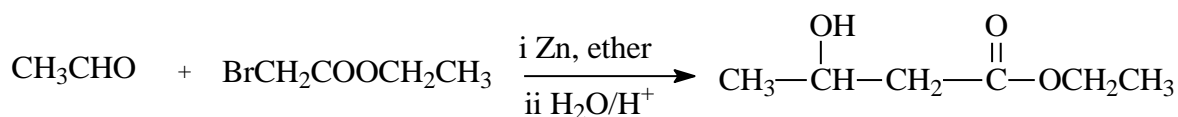
Mechanism:

Zn reacts with α- halo ester to form Zn-enolate reactive intermediate, which is also known as Reformatsky reagent. This enolate react with aldehyde/ketones to give another intermediate which upon hydrolysis gives β-hydroxy ester as follow.
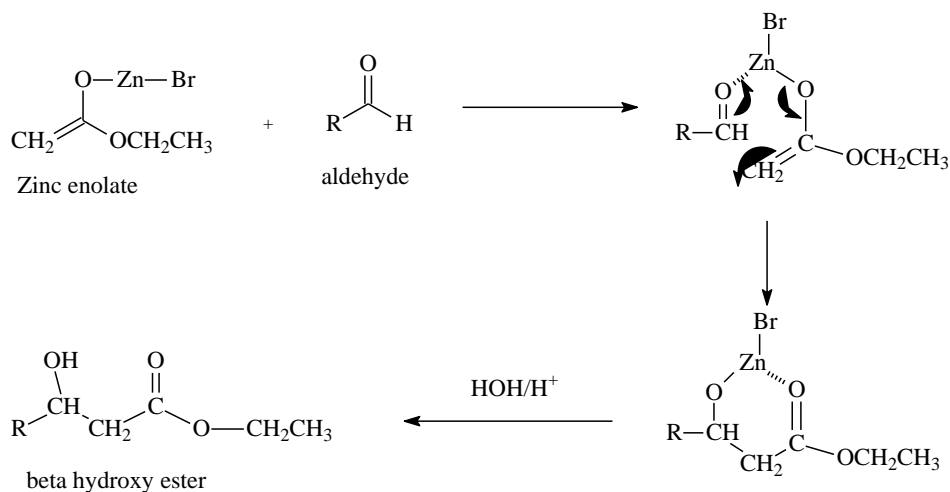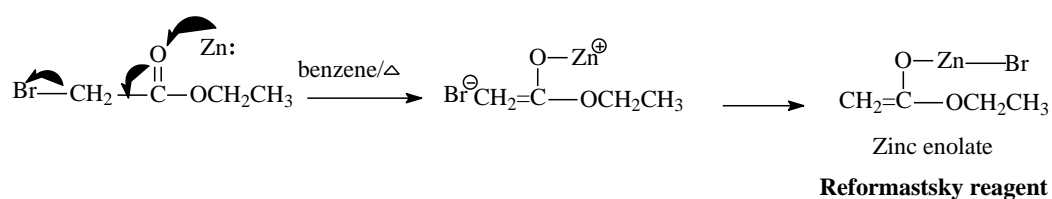
Zinc enolate do not react with ester, hence there is no chance of ester-ester self condensation. Zn also does not form Zn-enolate from a α- bromo ketone or aldehyde. Thus, there is no self condensation between aldehyde or ketone.

The β-hydroxy ester produced in this reaction can easily be dehydrated to α, β – unsaturated ester because dehydration gives a resonance stabilized conjugated system
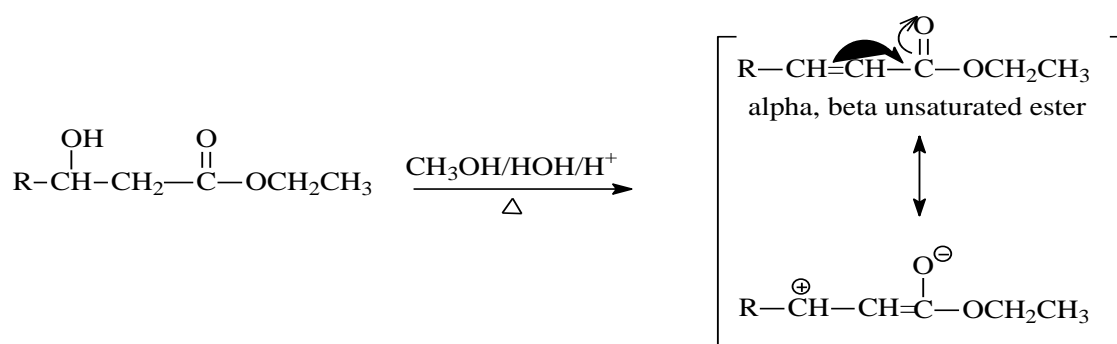
Examples of Reformatsky reaction:

$$CH_3CH_2CHO \ + \ BrCH_2COOCH_2CH_3 \ \xrightarrow[\text{ii } NH_4Cl/HOH]{\text{i } Zn/C/H_6/heat} \ CH_3CH_2\overset{OH}{\underset{}{C}}HCH_2COOCH_2CH_3$$

$$CH_3CHO \ + \ Br\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \ \xrightarrow[\text{ii } NH_4Cl/HOH]{\text{i } Zn/ether/heat} \ CH_3-\overset{OH}{\underset{}{C}}H-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

Benzaldehyde + $Br-\overset{CH_3}{\underset{}{\overset{|}{C}}}H-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$ $\xrightarrow[\text{ii } HOH/H^+]{\text{i } Zn/C/H_6/heat}$

$$\left[\begin{array}{c} \text{Ph-}CH(OH)-\overset{|}{\underset{CH_3}{C}}H-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \\ \updownarrow \\ \text{Ph-}CH=\overset{}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \end{array} \right]$$

$$CH_3-C\equiv N \ + \ Br-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \ \xrightarrow[\text{ii } HOH/H^+]{\text{i } Zn/C/H_6/heat} \ CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

$$CH_3CH_2CHO \ + \ Br-CH_2-\overset{O}{\overset{\|}{C}}-N\overset{CH_3}{\underset{CH_3}{<}} \ \xrightarrow[\text{ii } HOH/NH_4Cl]{\text{i } Zn/ether/C_6H_6/heat}$$

$$\left[\begin{array}{c} CH_3-CH_2-\overset{OH}{\underset{}{C}}H-CH_2-\overset{O}{\overset{\|}{C}}-N\overset{CH_3}{\underset{CH_3}{<}} \\ \downarrow \quad HOH/\overset{\ominus}{O}H/heat \\ CH_3-CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-N\overset{CH_3}{\underset{CH_3}{<}} \end{array} \right]$$

19. Wittig Reaction: Carbonyl compounds react with alkylidenephosphoranes (ylids which is nucleophile) leads to formation of alkene and triphenyl phosphine oxide.

Phosphorus ylids are formed when triphenylphosphine and primary or secondary alkyl halide react in the presence of strong base as NaH, NaNH$_2$ etc.

$$R \ CH_2-X \ + \ \overset{..}{P}(C_6H_5)_3 \ \xrightarrow{SN_2} \ \left[(C_6H_5)_3\overset{\oplus}{P}-C\overset{R}{\underset{H}{\overset{H}{<}}} \right] X^{\ominus}$$

Alkyl Halide   Triphenyl Phosphine   Alkyl triphenyl Phosphonium halide

$$\downarrow \text{RLi (Strong Base)}$$

Phosphorus ylide

$(C_6H_5)_3 \ P = C \ H \ R$

Betaine

Triphenyl Phosphine Oxide

Oxaphosphetane
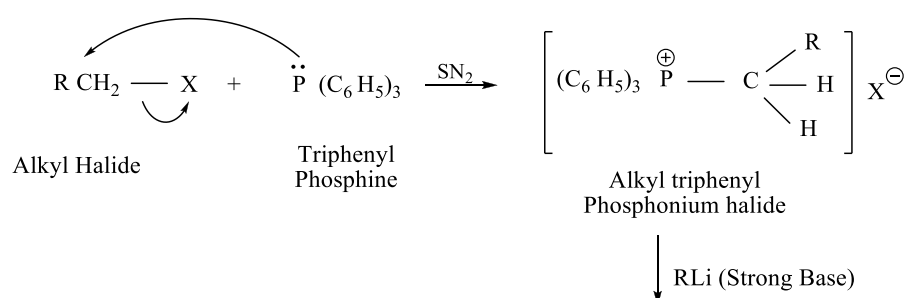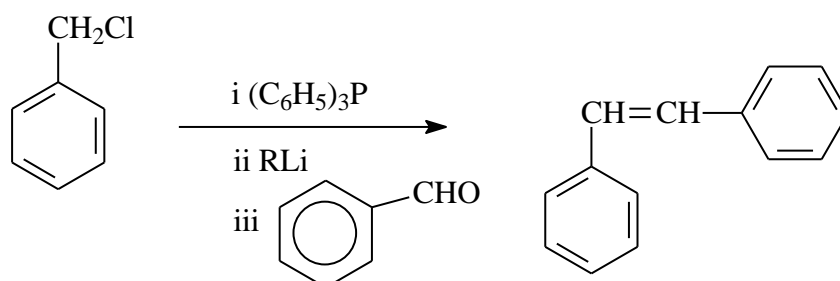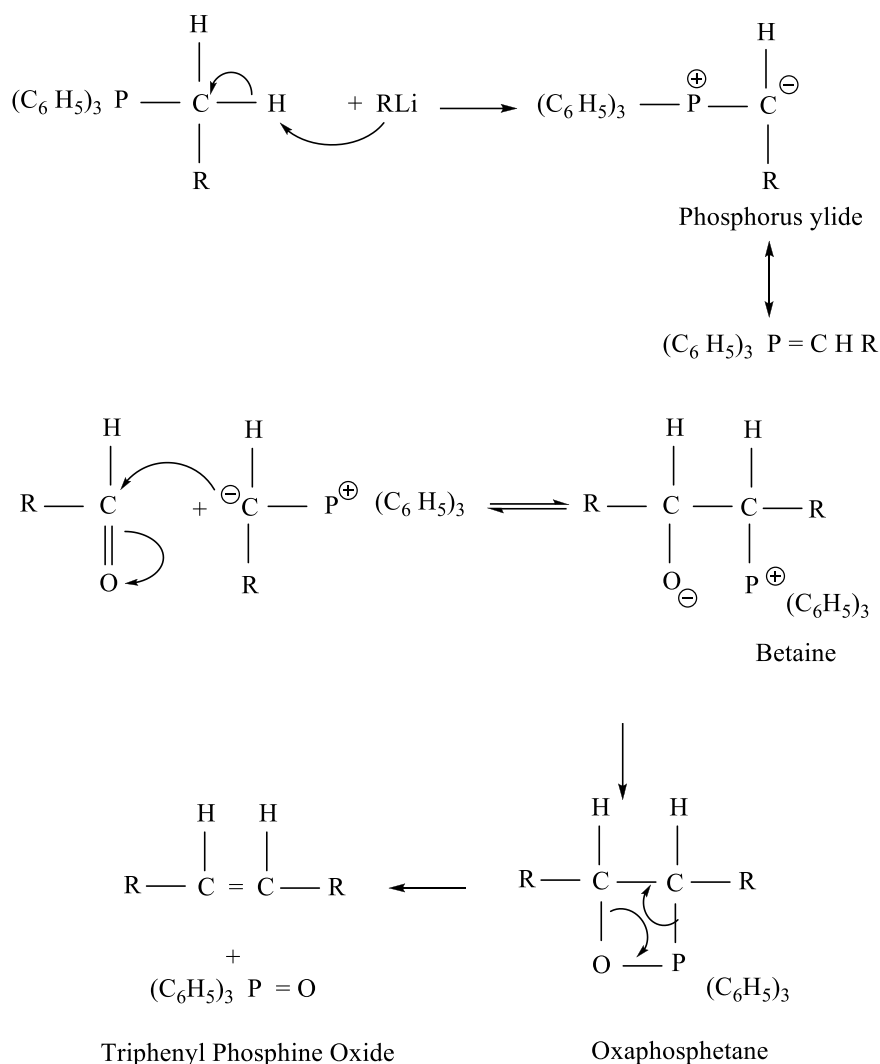
20. Aldol condensation: Carbonyl compounds aldehydes containing α- hydrogens condense in the presence of dilute base form addition product β-hydroxy aldehyde also known as aldols.

alpha carbon with alpha hrdrogens

$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H \; + \; H-\overset{}{CH_2}-\overset{\overset{\displaystyle O}{||}}{C}-H \underset{\longleftarrow}{\overset{NaOH}{\longrightarrow}} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-H$$

beta hydroxy aldehyde
(aldol)
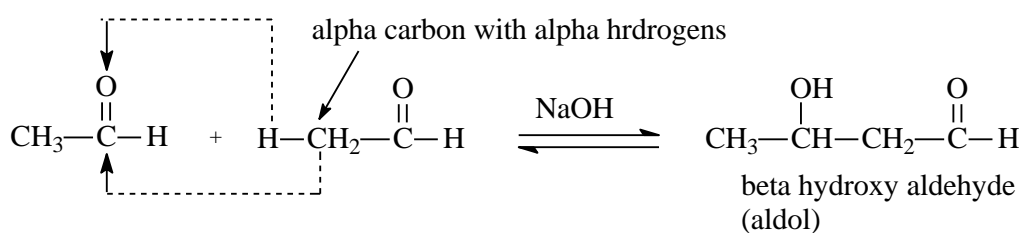
Mechanism: Base generates enolate ion from carbonyl compounds having at least one α hydrogen (acidic α hydrogen). Enolate ion is good nucleophile, attacks carbonyl carbon of other unionized carbonyl compound form alkoxide anion which accepts proton from water to give aldol.

$$H\overset{\ominus}{O} \; + \; H-CH_2-\overset{\overset{\displaystyle }{||}}{\underset{O}{C}}-H \rightleftharpoons \overset{\ominus}{CH_2}-\overset{}{C}-H \; + \; HOH$$

$$CH_2 = \overset{}{\underset{\overset{|}{O^{\ominus}}}{C}} - H$$

$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H \; + \; \overset{\ominus}{CH_2}-\overset{\overset{\displaystyle O}{||}}{C}-H \longleftarrow CH_2 = \overset{\overset{\displaystyle O^{\ominus}}{|}}{C}-H$$

$$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\overset{|}{O^{\ominus}}}{C}}-CH_2-\overset{\overset{\displaystyle }{||}}{\underset{O}{C}}-H$$

(Alkoxide anion)

↓ HOH

$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}-CH_2-\overset{\overset{\displaystyle }{||}}{\underset{O}{C}}-H \; + OH^{\ominus}$$
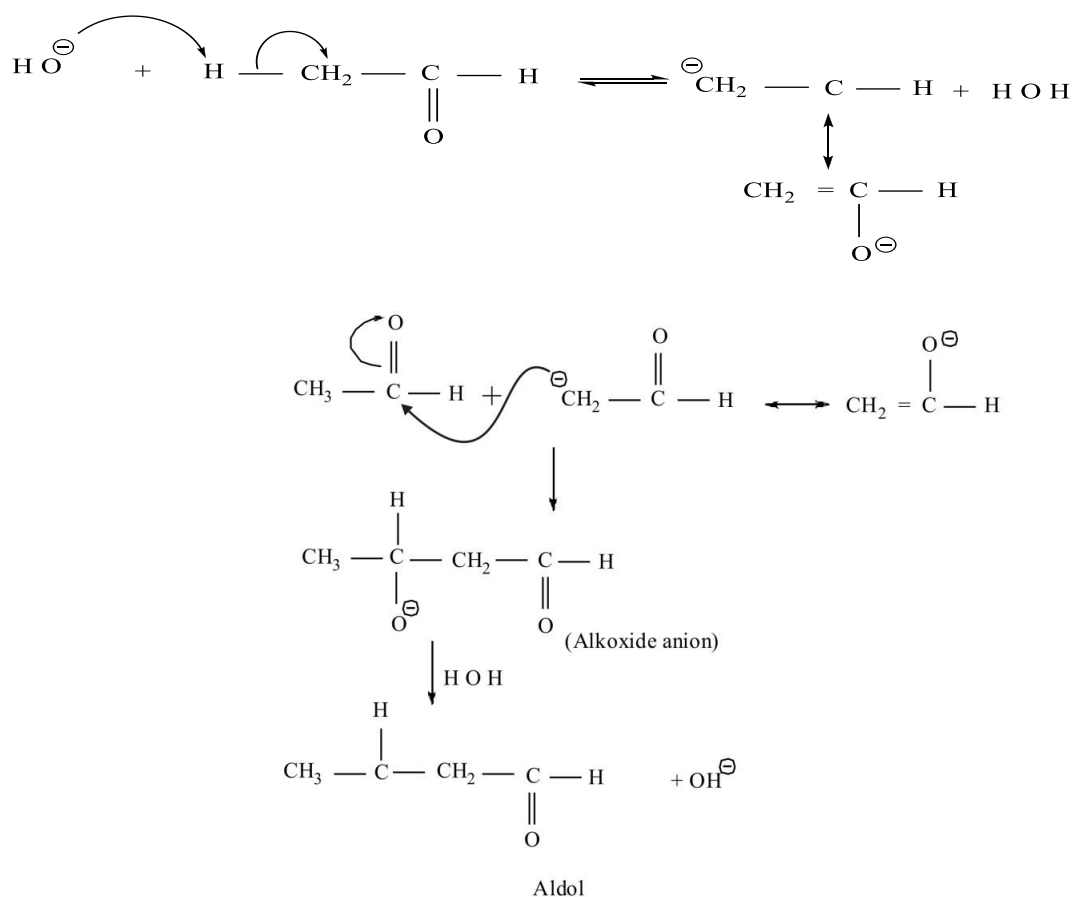
Aldol

Benzaldehyde, formaldehydes type compound (which donot have α hydrogens) donot show aldol condensation.

21. Mannich reaction: A Mannich Reaction is a formation of a β - amino carbonyl compound. The Mannich base is an endproduct in the Mannich reaction, which is formed through nucleophilic addition reaction of a non-enolizable aldehyde (formaldehyde) and any

primary or secondary amine to produce resonance stabilized imine salt. Finally, the addition of a carbanion from compound (any enolizable carbonyl compound, amide, carbamate etc.) to the imine gives the Mannich base.

enolizable carbonyl compound + non enolizable carbonyl compound + amine → beta amino carbonyl compound Mannnich base
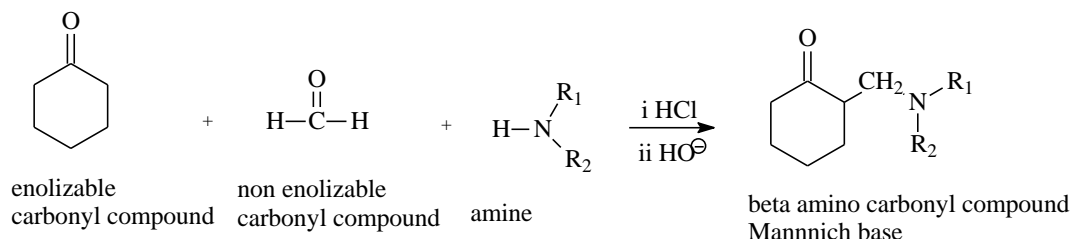
Mechanism:

The mechanism involves the formation of imine salt first from formaldehyde and amine. In this reaction being nucleophilic nature of amine, it attacks the carbonyl group of formaldehyde. No acid is required for that, however the acid-catalysed dehydration of the addition product reveals the imine salt as follow.
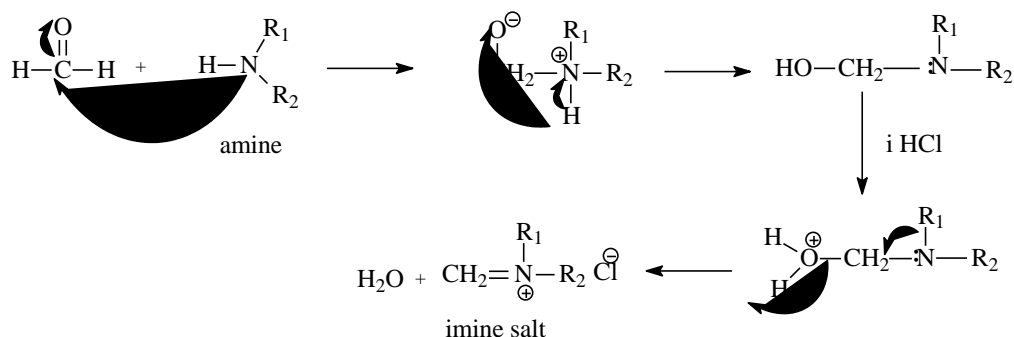
The imine salt is a just intermediate but quite stable. The iodide salt is solid in nature and known as **Ecchenmoser salt**.

$$CH_2 = \overset{\overset{R_1}{|}}{N} - R_2 \ I^{\ominus}$$
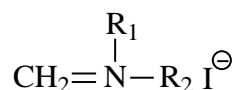
The electrophile imine salt now add to the enol form of carbonyl compound to give the product of the reaction, β- amino carbonyl compound or Mannich base

beta amino carbonyl compound or Mannich base
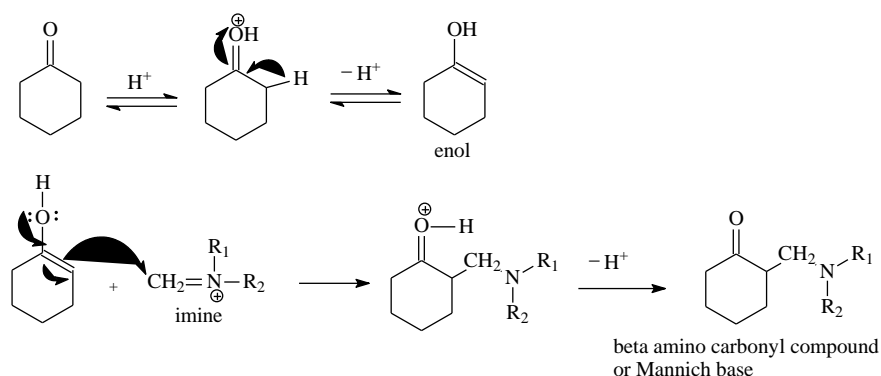
The reaction can further react by three different ways provided that:

1 The Mannich base is 1^0 or 2^0 amines, in such cases it condenses further with two or one additional HCHO and enolizable carbonyl compound.
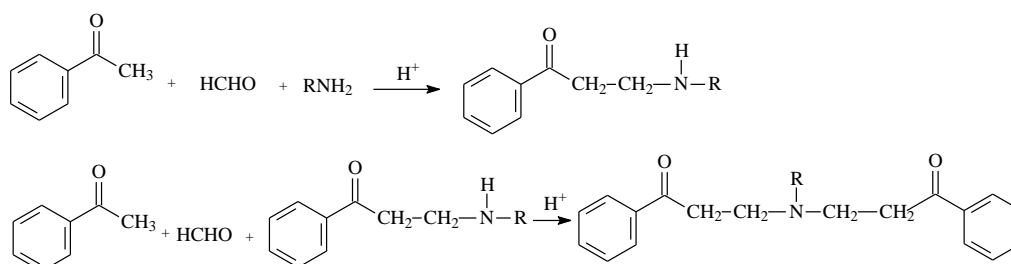
2. The enolizable carbonyl compound has active methylene group, stepwise condensation of two or more molecules of HCHO and amine with one molecule of the compound with active methylene group will take place.
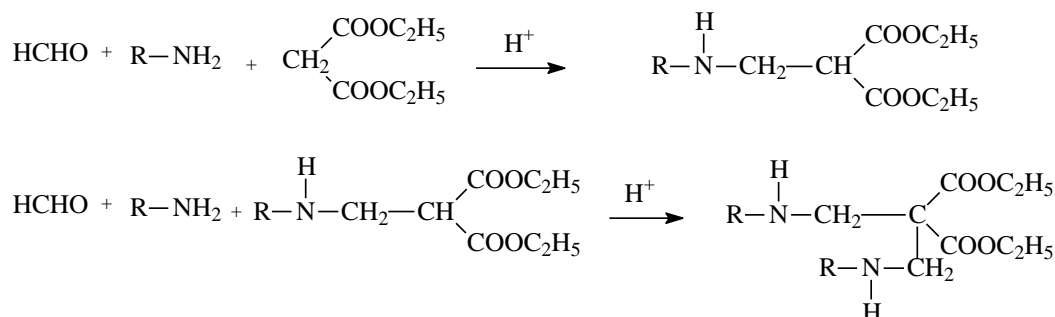
1. The Mannich base obtained may condense with excess HCHO
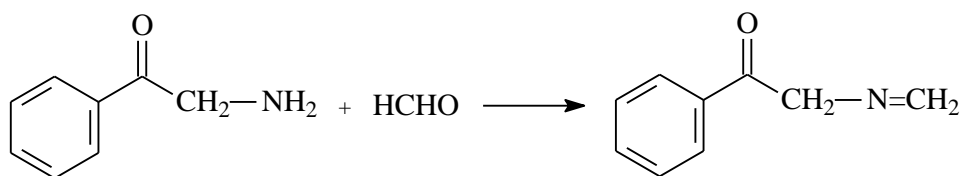
Mannich reaction is very important reaction for the synthesis of reaction intermediate imine salt. The mannich product can be converted to enones which can be used in Mannich addition. Phenols, furan, pyrrole, indole also give this reaction because intermediate of the reaction is iminium salt which is a strong electrophile and these compounds give aromatic electrophilic substitution (ArSE) reaction.
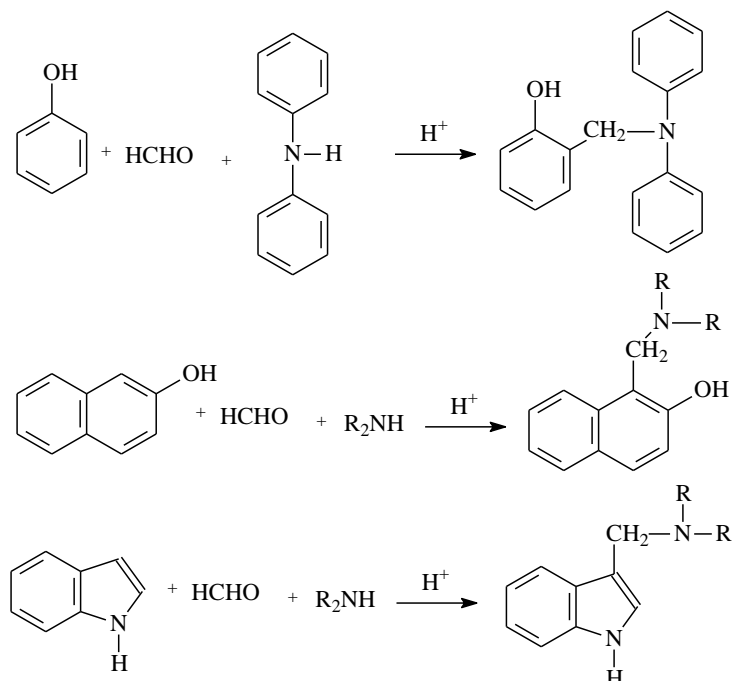
22. Knoevenagel reaction: It is a modified aldol condensation. In is simply a nucleophilic addition of active hydrogen to the carbonyl group which finally undero dehydration with the formation of α, β- unsaturated product. This reaction is catalysed by amines generally piperidine/buffer system containing an amine and acid. A base is required to generate carbanion while acid is for activation carbonyl group.
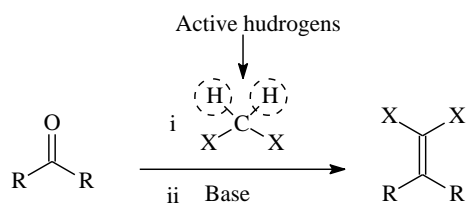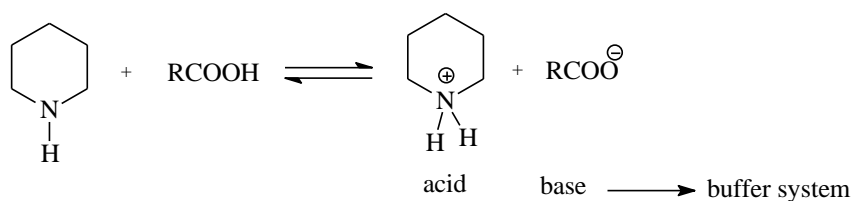
X = electron withdrawing group, XCH₂X may be

diethyl malonate   ethyl acetoacetate (EAA)   malonic acid   cynoacetic acid
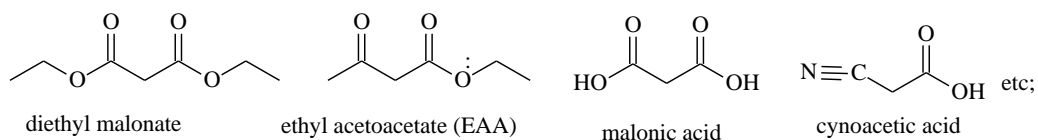
Mechanism of the reaction:

The sequencewise mechanism of Knoevenagel reaction is as follow:-

Step-I The weak base $RCOO^-$ abstract the hydrogen from active methylene group and provide aresonance stabilized enolate/ crabanion
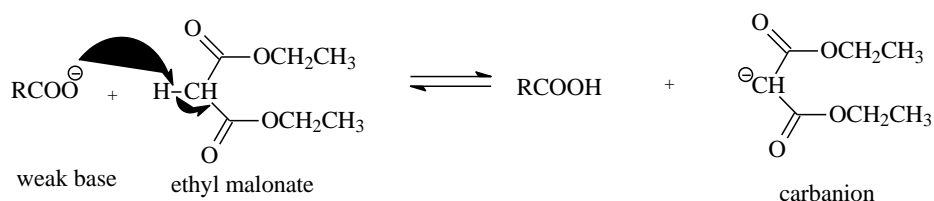
Step II. This step involve the formation of reactive electrophile from pyridine by reaction with aldehyde viz; benzaldehyde to form iminium ion. This intermediate is more reactive than carbonyl group
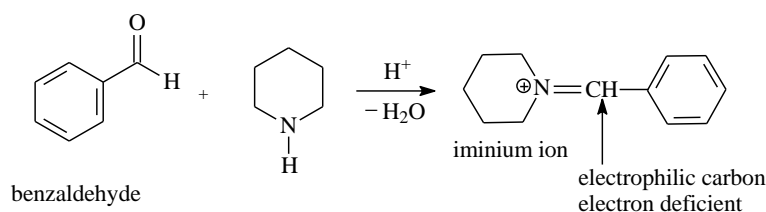
Step III In this step the electron-deficient carbon of iminium ion is attacked by carbanion
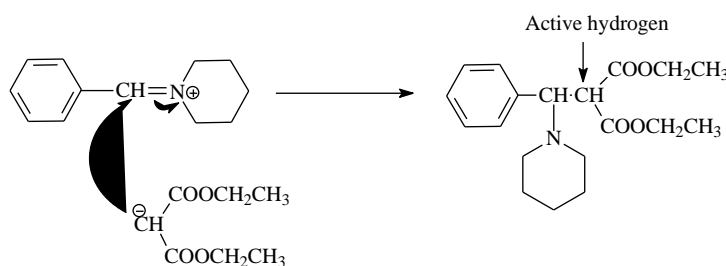
Step IV The weak base depronates acidic hydrogen followed by elimination of NR_2 group to give α, β- unsaturated derivative of the adduct
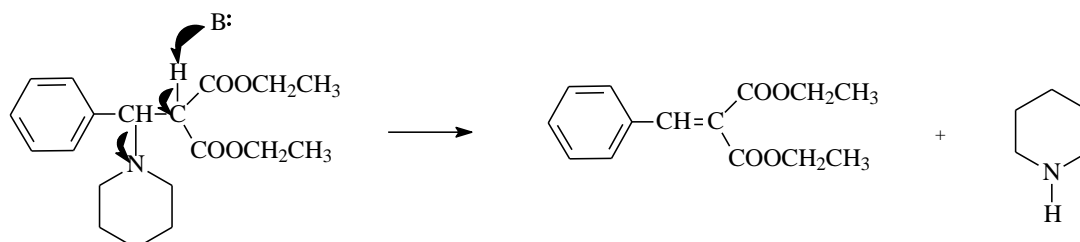
With malonic acid or cynoacetic acid as reactant, the products usually undergo decarboxylation, which occurs as a concerted decomposition.
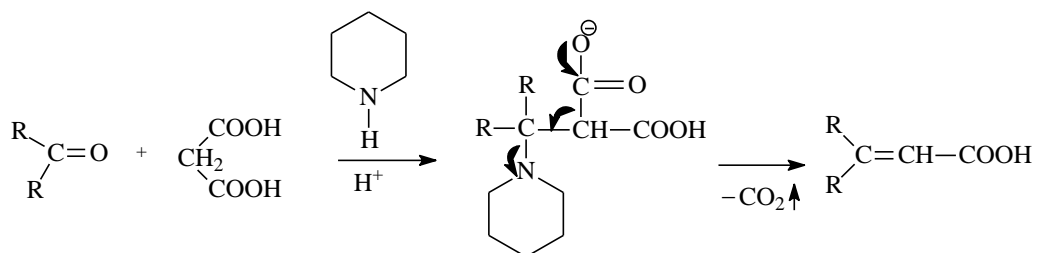
Decarboxylation is also carried out in   presence of pyridine.

benzaldehyde

cinnamic acid
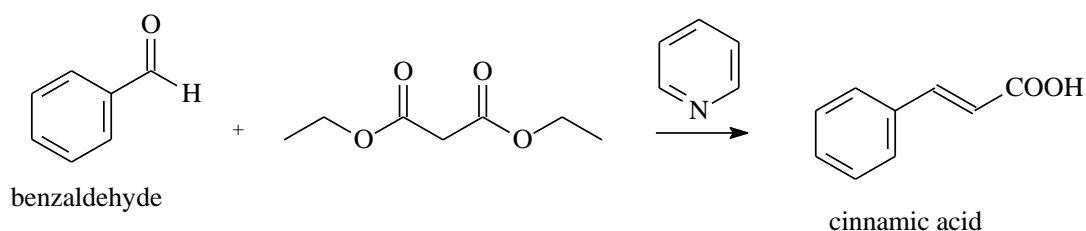
23. Benzoin

condensation reaction: The benzoin condensation is a reaction (often called a condensation reaction, for historical reasons) between two aromatic aldehydes, particularly benzaldehyde. The reaction is catalyzed by a nucleophile such as the cyanide anion or an N-heterocyclic carbene. The reaction product is a benzoin. In this umpolung reaction CN⁻ play key role as catalyst the well known example:

cynohydrin benzoin

benzoin

Mechanism
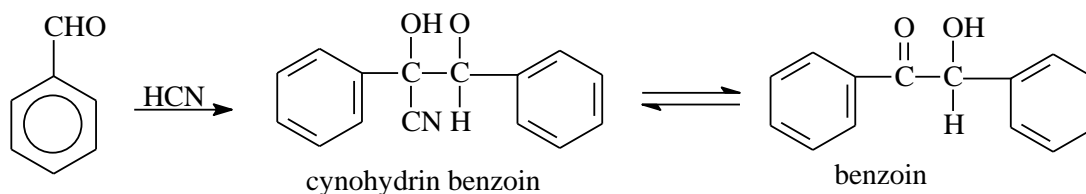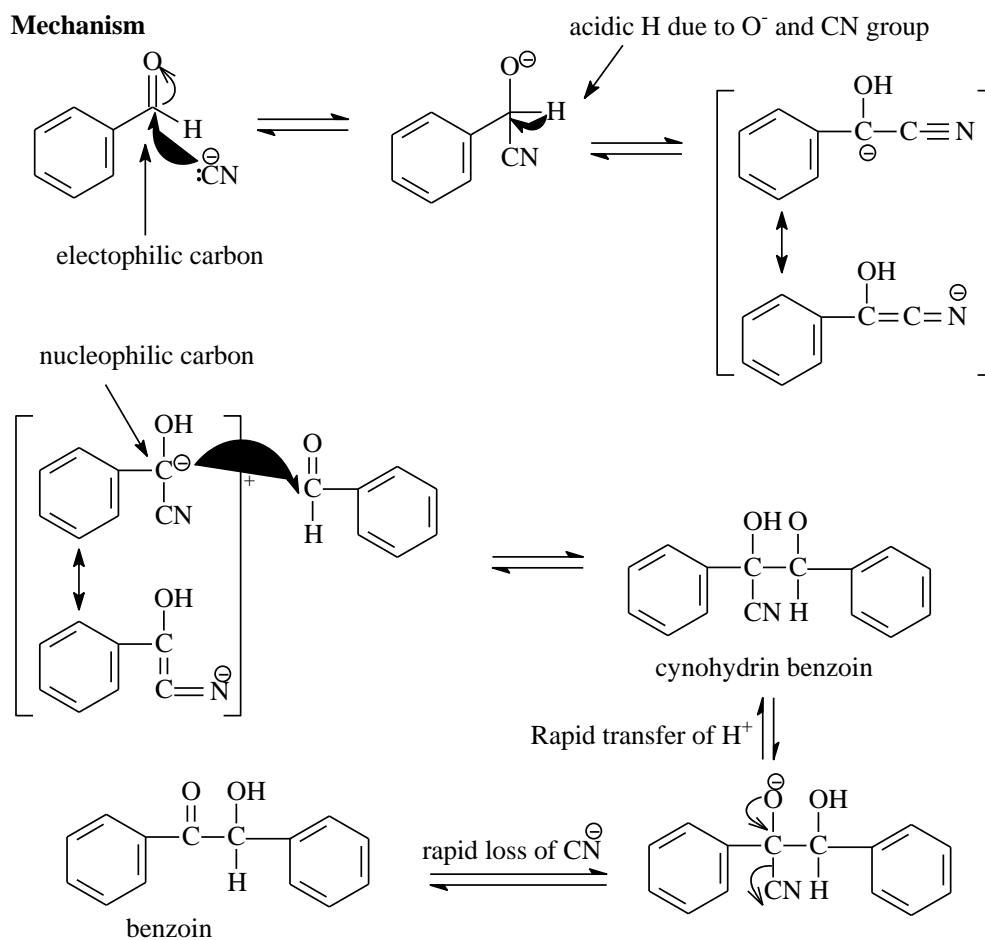
In this reaction CN⁻ act as catalyst which is due to its good nucleophilicity, stablizing nature to carbanion and good leaving group.

24. Perkin reaction: The Perkin was developed by English chemist William Henry Perkin to synthesize cinnamic acids in which an α,β-unsaturated aromatic acid is formrd by the aldol condensation of an aromatic aldehyde and an acid anhydride, in the presence of an alkali salt of the acid. The alkali salt acts as a base catalyst.

Mchanism: $CH_3COONa \rightleftharpoons CH_3COO^{\ominus} + Na^+$

cinnamic acid
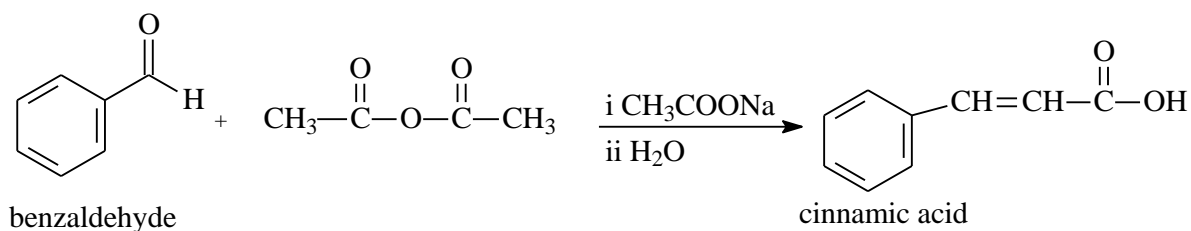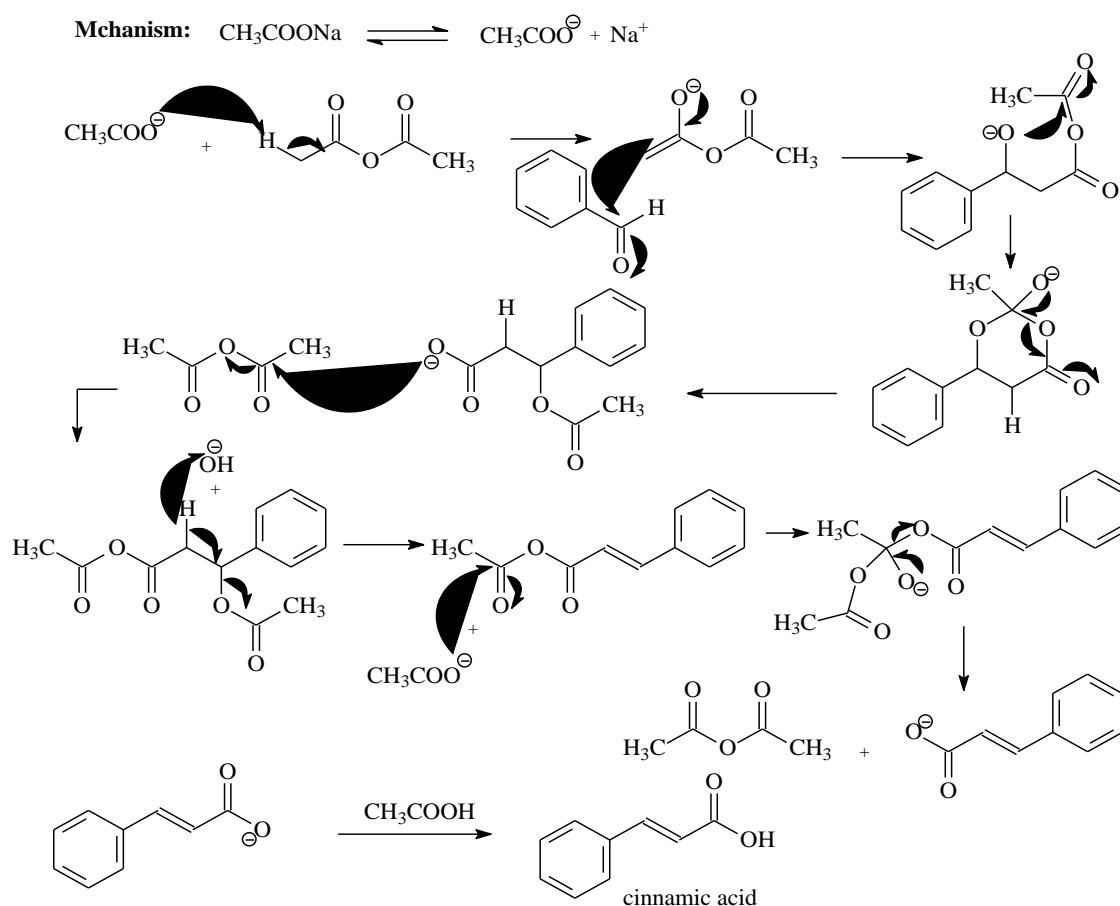
7.7 SUMMARY

- **Aldehydes** are compounds having general formula $C_nH_{2n}O$ and contain Oxo (Carbonyl) group $>C=O$. Here functional group –CHO occurs at the end of a chain. Primary alcohols are oxidized to aldehydes only by Collins reagent $(CrO_3.2C_5H_5N)$ and Corey's reagent $(CrO_3.C_5H_5N, PCC)$.

- Aldehydes undergo nucleophillic addition reactions due to polarity of carbonyl group. Reactivity of aldehydes towards nucleophillic addition reactions decreases as steric hindrance and +I effect of attached alkyl group increases. Aldehydes are easily oxidized, so they work as powerful reducing agents (reduce Fehling solution and Tollen's reagent).

- Aldehydes give a series of condensation reactions and alpha hydrogen substitution reactions as per their structural constitution. Aldehydes can be used as starting materials for the synthesis of other synthetically important compounds.

7.8 SELF ASSESSMENT

A. FILL IN THE BLANKS:

(1) The carbon of carbonyl carbon is _____ hybridised.

    (a) sp^3 (b) sp^2 (c) sp   (d) sp^3d

    Ans. :- (b)

(2) Boiling points of primary alcohols are _____ than the boiling points of corresponding aldehydes.

    (a) higher   (b) lower

    Ans :- (a)

(3) Aldehydes are prepared by the oxidation of _____

    (a) Primary alcohol   (b) Secondary alcohol   (c) Tertiary alcohol

    Ans :- (a)

(4) Melting points of aldehydes tend to _____ with increasing molecular weight.

    (a) decrease   (b) increase   (c) remain unchanged

    Ans :- (b)

(5) Aldehydes have _____ boiling points compared with those of alcohols.

    (a) low   (b) high

    Ans. :- (a) low

(6) Catalytic hydrogenation readily converts aldehydes to _____ alcohols.

    (a) Primary   (b) Secondary   (c) Tertiary

    Ans. :- (a)

(7) Aldehydes having α-hydrogen atoms usually do not undergo _____ reaction under its reaction condition.

    (a) Cannizaro   (b) Aldol   (c) Haloform

Ans. :- (a)

(8)   Appearance of silver mirror in Tollen's test indicates the presence of

(a) Alcohol   (b) Aldehyde   (c) Alkene   (d) alkane

Ans. :- (b)

(9)   Acetaldehyde on treatment with Fehling solution gives a precipitate of -

(a) Cu   (b) Cu_2O (c) CuO   (d) $CuCl_2$

Ans : - (b)

(10) Acetaldehyde on boiling with chlorine gas gives –

(a) $CH_3 - \underset{\underset{O}{\|}}{C} - Cl$ (b) $CCl_3 - \underset{\underset{O}{\|}}{C} - H$ (c) $CH_3\,CHCl_2$ (d) $CHCl_3$

Ans. :- (b)

B. TRUE/FALSE

1.   Both carbon and oxygen of ………group is sp^2 hybridised.

2.   IUPAC names of aldehydes are obtained by replacing the ending –e of the corresponding alkane with –al.

3.   Controlled oxidation of secondary alcohols using an acidified solution of $K_2Cr_2O_7$ produces aldehydes.

4.   Hydration of acetylene yields acetaldehyde.

5.   Density of aldehydes is less than water.

6.   Lower aldehydes are insoluble in water.

7.   As hydrocarbon part of aldehyde "compound increases solubility also increases.

8.   Carbon atom next to carbonyl group is called α-carbon.

9.   Wolf kishner reduction of aldehydes involves use of basic solution of Hydrazine as reducing agent.

10. Aldehydes react with PCl_5 to form gem – dihalides.

Ans. :- 1. T,   2. T,   3. F,   4. T,   5. T,   6. F,   7. F,   8. T,   9. T,   10. T

C. SHORT ANSWER QUESTIONS

1. Writing the structures arrange the following compounds in increasing order of their reactivity in nucleophillic addition reaction.

(a) Benzaldehyde,   p-Tolualdehyde,   p-Nitrobenzaldehyde

Ans :- p tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde

2. What is the structure of carbonyl group? How does it react with (i) HCN (ii) $NaHSO_3$

3. What happens when formaldehyde is treated with NaOH ?

4. Explain the reaction mechanism when acetaldehyde is treated with NaOH ?

5. Carbonyl compounds undergo nucleophillic addition reactions, why?

6. Write note on :-

(a) Witting reaction,   (b) Reformatsky reaction,   (d) MPV reaction.   (e) Perkin reaction

7. What happens when Aldehydes combine with alcohols in the presence of dry HCl ?

8. Aldehydes are powerful reducing agents. Explain.

9. α hydrogen of aldehydes is acidic. Discuss.

10. Different reagents give different products on reduction of carbonyl compounds. Elaborate it.

D. QUESTIONS RELATED TO IMPORTANT REACTIONS

Complete the following reaction with mechanism wherever applicable:-

5. C_6H_6 + HCN + HCl $\xrightarrow{\text{AlCl}_3}$

6. $R-CO\,Cl$ + H_2 $\xrightarrow{\text{Pd/BaSO}_4}$

7. (toluene) $\xrightarrow[\text{CrO}_3]{(CH_3CO)_2O}$? $\xrightarrow{\text{HOH}}$? $\xrightarrow{-H_2O}$

8. $R-CH_2OH$ $\xrightarrow{K_2Cr_2O_7/H^{\oplus}}$?

9. C_6H_5CHO + NaOH $\xrightarrow{\triangle}$

10. $\begin{matrix} CH_3 \\ H \end{matrix}C=O$ + $R_2C-P(C_6H_5)_3$ $\longrightarrow$

11. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$ + PCl_5 $\longrightarrow$

12. $6H-\overset{\overset{\displaystyle }{\|}}{\underset{\underset{\displaystyle O}{}}{C}}-H$ + $4\,NH_3$ $\longrightarrow$

13. $CH_3CH=O$ + H_2N-OH $\longrightarrow$

14. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$ + NH_3 $\longrightarrow$

15. $CH_3-\overset{\overset{\displaystyle Cl}{|}}{CH}-Cl$ $\xrightarrow[\text{NaOH}]{HOH}$? $\xrightarrow{-H_2O}$?
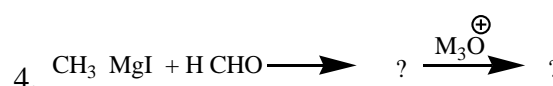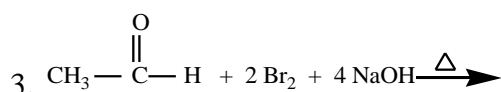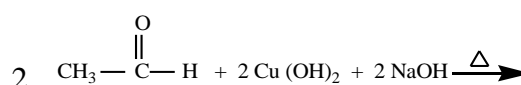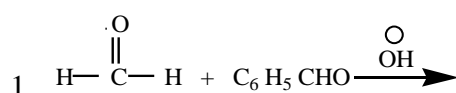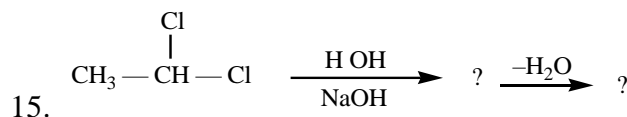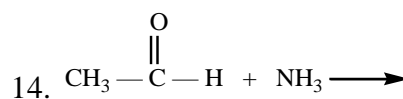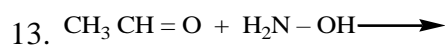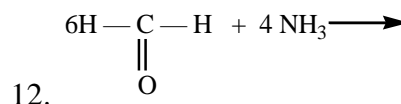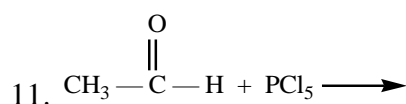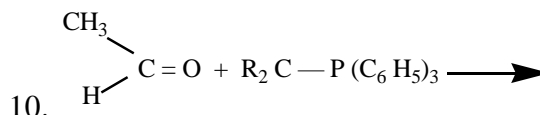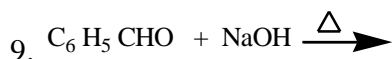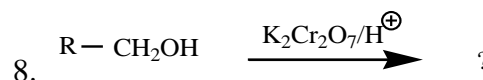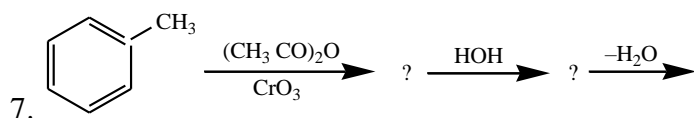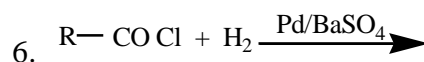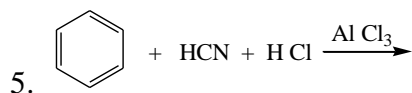
7.9 REFERENCES

1. I.L Finar, Organic Chemistry Vol. II., 5th edition, ELBS & Longman group Ltd., 1974.

2. R.T. Morrison and R.N. Boyd Organic Chemistry, 6th edition, Prentice Hall Private Ltd, 1997.

3. F.A. Carey and R.J. Sundberg Advanced Organic Chemistry, Plenum. 5th edition, 2007.

4. Jagdamba Singh and L.D.S. Yadav, Organic Chemistry vol. I, 8th edition-2013 Pragati Prakashan Pub.

5. S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry, Trinity Press 2016.

6. B.S. Bahal, A. Bahal. Advanced Organic Chemistry. S. Chand & Company Ltd. Ram Nagar, New Delhi 1993.

UNIT -8 KETONS

CONTENTS:

8.1 INTRODUCTION

In chemistry, a ketones (alkanone) are an organic compound with the structure RC (=O) R', where R and R' can be a variety of carbon-containing substituents. Structurally the ketone carbon is often described as "sp^2 hybridized", a description that includes both their electronic and molecular structure. Ketones are trigonal planar around the ketonic carbon, with C−C−O and C−C−C bond angles of approximately 120°
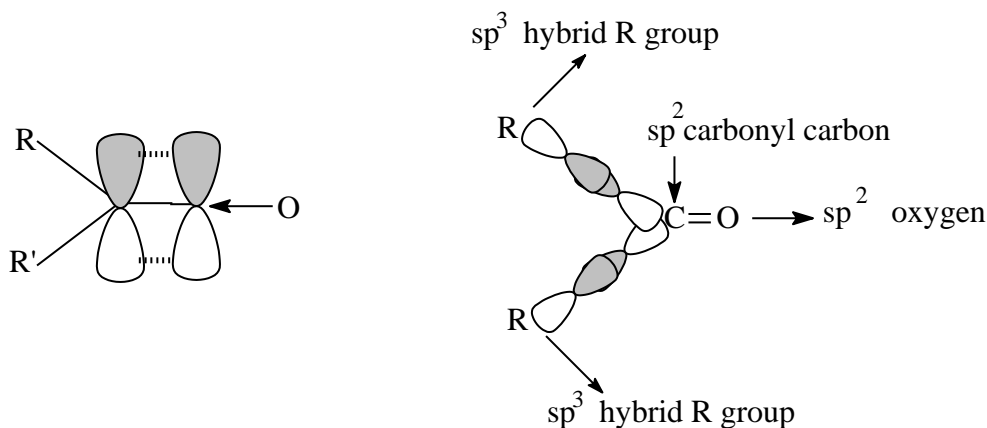
Basic skeletal structure of carbonyl group in ketone is same (Planer) as in aldehydes.

8.2 OJECTIVES

The objectives of this unit are to study about: -

- Functional group carbony, Molecular orbital structure of functional group, reactivity of carbonyl group, nucleophilicity of carbonyl group.
- To study types of reactions carbonyl group, undergo, mechanism of name reactions, effect of conjugation on carbonyl group reactivity. Although we already have discussed above factors in aldehydes unit.
- Now we will discuss the changes because of replacement of group H by an alkyl group.

8.3 NOMENCLATURE

Common names of ketones are named on the basis of the alkyl group attached to the carbonyl group. In IUPAC nomenclature ketones are designated by suffix – one. Prefix is the name of hydrocarbon (Alkanones). Here longest hydrocarbon chain containing carbonyl carbon is selected and named it by substituting 'e' of Alkane with 'one'. While numbering

the chain lowest number is given to carbonyl carbon. Other substituents are numbered named and placed as prefixes in alphabetic order. If there are two carbonyl groups in a molecule, it is named as Alkanedione.

$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 \qquad \text{dimethyl ketone \quad acetone}$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \qquad \text{ethyl methyl ketone}$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3 \qquad \text{methyl propyl ketone}$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3 \qquad \text{IUPAC} \qquad \text{2 pentanone}$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{||}}{C}}-CH_3 \qquad \text{5 methy 2 hexanone}$$

$$CH_3-\underset{\underset{O}{||}}{C}-CH_2-\underset{\underset{O}{||}}{C}-CH_2-CH_3 \qquad \text{2, 4 hexadienone}$$
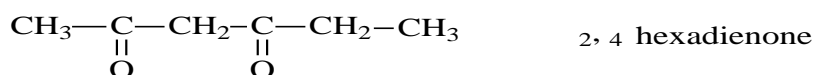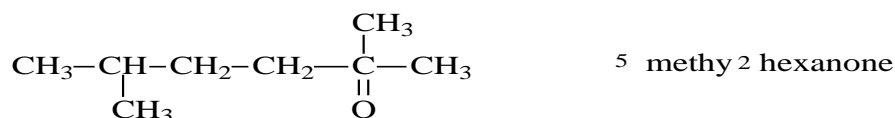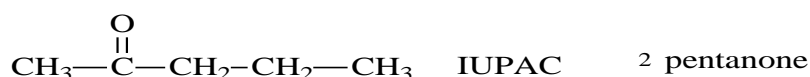
Polarised C = O bond (electronegativity C - 2.5, O - 3.5) makes carbon partially positively charged which attracts negatively charged nucleophiles (Here electrons from HOMO of nucleophile move to LUMO of electrophile i.e. C of C = O group).

Newly formed sigma bond converts trigonal sp^2 hybridized carbon atom of carbonyl group to tetrahedral SP^3 hybridized state attack of nucleophile is at approx. 107^0 to the C = O bond. And any part of molecule that causes steric hindrance to this will reduce rate of addition (nucleophillic addition). Acid and Base catalysis of carbonyl carbon in Nucleophilic addition reactions has been discussed in aldehyde unit.

8.4 SYNTHESIS OF KETONES

Like aldehydes ketones are prepared/synthesized by number of methods some are being discussed as follow.

1. Oxidation of secondary alcohols: - Oxidation of secondary alcohols with $K_2 Cr_2 O_7$, MnO_2, or chromic anhydride in acidic medium yield ketones. Firstly sec. alcohol gives

ketone with same number of carbon atoms as the original alcohol. However, prolonged treatment with oxidizing agents produces a mixture of acids, containing fewer number of carbon atoms than the original alcohol.

$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3 \quad \xrightarrow[\text{[O]}]{K_2Cr_2O_7} \quad CH_3-\underset{\overset{\displaystyle O}{||}}{C}-CH_3$$

$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CH_2-CH_3 \quad \xrightarrow[\text{[O]}]{K_2Cr_2O_7} \quad CH_3-\underset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_2-CH_3$$
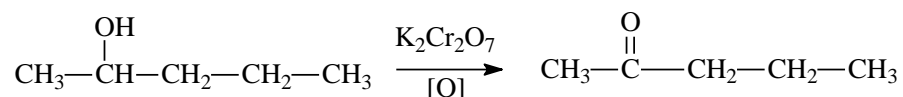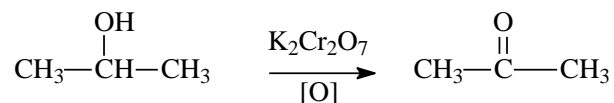
Tertiary alcohols are resistant to oxidation in neutral or alkaline medium but they are oxidized in acidic medium resulting in formation of mixture of acid and ketone and each contains fewer number of carbon atoms than the original alcohol.

Alkaline $KMnO_4$ is also oxidizing agents.

2. **By Oppenauer oxidation: -** It involves a special reagent alluminium-t-butoxide $[(CH_3)_3CO]_3$ Al, which is refluxed with secondary alcohol and acetone cyclohexanone is used as solvent. Here $[(CH_3)_3CO]_3Al$ acts as oxidizing agent and acetone accepts hydrogen as hydride ion from sec. alcohol.

$$R_1-\underset{\underset{\displaystyle OH}{|}}{CH}-R_2 \quad \xrightarrow[\underset{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}{}]{(CH_3CO)_3Al} \quad R_1-\underset{R_2}{\overset{\overset{\displaystyle O}{||}}{C}} \quad + \quad CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

Mechanism: -

Step-I

$$\left(CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O\right)_3 Al \quad + \quad R_1-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R_2 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \quad + \quad \left[\begin{array}{c} R_1 \quad\quad H \\ C \\ R_2 \quad\quad O \end{array}\right]_3 Al$$
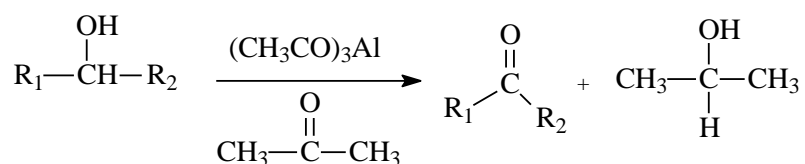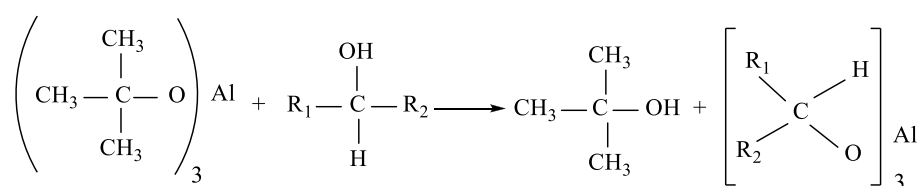
        Here exchange reaction takes place

Step-II

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 + Al\left[\overset{H}{\underset{O}{\overset{|}{C}}}\overset{R_1}{\underset{R_2}{}}\right]_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 \quad \overset{\oplus}{\underset{O}{}} - Al\left(O - \overset{R_1}{\underset{\underset{H}{|}}{C}}\overset{R_1}{\underset{R_2}{}}\right)_3^{\ominus}$$

New complex is formed.

Step-III

$$\begin{array}{c} \text{(reaction scheme)} \end{array}$$

Similarly, two more moles of acetone will react with above (one mole) formed complex and give two more moles of ketone product.

$$3\ CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 + Al\left(O - \overset{R_2}{\underset{\underset{H}{|}}{C}}\overset{R_2}{\underset{R_1}{}}\right)_3 \longrightarrow 3\ R_1 - \overset{}{\underset{\overset{\|}{O}}{C}} - R_2 + 3\left[\overset{CH_3}{\underset{H_3C}{}}C\overset{H}{\underset{O}{}}\right]_3 Al$$

This reaction is useful as for oxidation of polyfunctional compounds as this reaction conditions are mild. For e.g. in unsaturated alcohols as it (reagent) does not affect double bond.

Primary alcohols can also be oxidized by $[(CH_3)_3\ CO]_3\ Al$ if in acetone is replaced by p benzoquinone as it is better hydrogen acceptor than acetone.

3. By heating calcium salt of any monocarboxylic acid other than formic acid, ketones are obtained.

$$\left(R-\overset{\overset{\textstyle O}{\|}}{C}-O \right)_2 Ca \longrightarrow R-\overset{\overset{\textstyle O}{\|}}{C}-R + CaCO_3$$

4. When vapours of any monocarboxylic acid except formic acid are passed over Manganous oxide at 300^0C then ketone is obtained.

$$R\ COOH \xrightarrow{\ MnO\ } R-\underset{\underset{\textstyle O}{\|}}{C}-R + CO + H_2O$$
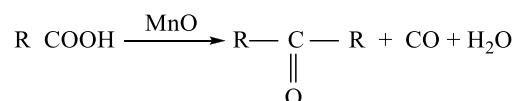
Mixture of monocarboxylic acids yield mixed ketones

$$R^1\ COOH + R^2\ COOH \longrightarrow R^1-\underset{\underset{\textstyle O}{\|}}{C}-R^2 + CO_2 + H_2O$$
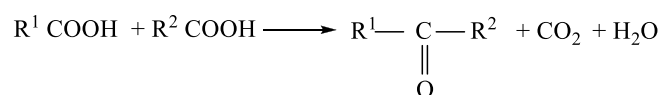
Besides this $R'COR'$ and $R^2\ COR^2$ are also obtained.

5. From Alkenes: Ketones can be prepared from alkenes as follow.

  (a) Ozonolysis: - Alkenes of following types when treated with ozone, yield ozonides and this on subsequent treatment with H_2O and zinc dust yield ketones
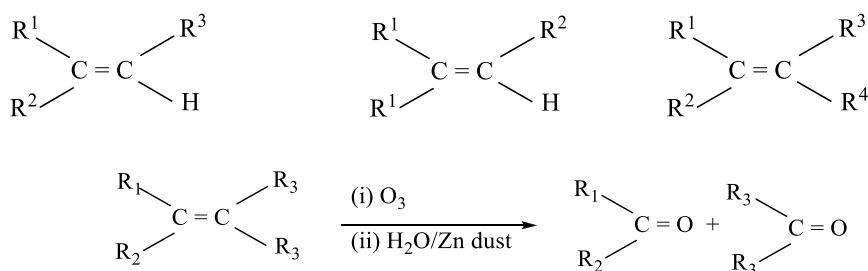
  (b) Lemieux Reagent: - An aqueous solution of $NaIO_4$ and trace of $KMnO_4$, lemieux reagent cleaves alkene to is diol and then to aldehydes or ketones.
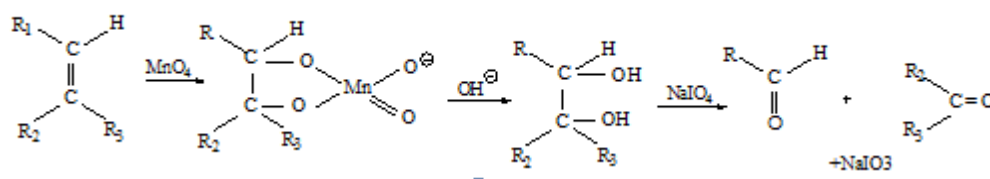
In place of $KMnO_4$, trace of OsO_4 can also be used and it prevents further oxidation to acids.

6. Oxidation of 1, 2 glycols: - The following types 1, 2 glycols are oxidised (by lead tetracetate $(CH_3 COO)_4$ Pb or periodic acid HIO_4 or H_5IO_6) and form aldehydes and ketones respectively according to structure of glycols

$$R^1 CH - CH - R^2$$
$$\quad | \quad \quad |$$
$$\quad OH \quad OH$$

$$R - \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - \overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - R_1$$

$$H_3C \quad \quad CH_3 \qquad \qquad H_3C \quad \quad CH_3$$
$$\quad \overset{|}{C} - OH \qquad \xrightarrow[HIO_4]{[O]} \qquad \quad C \qquad \quad + \; HCHO$$
$$\quad \overset{|}{C} - OH \qquad \qquad \qquad \quad \overset{\|}{O}$$
$$H \quad \quad H$$
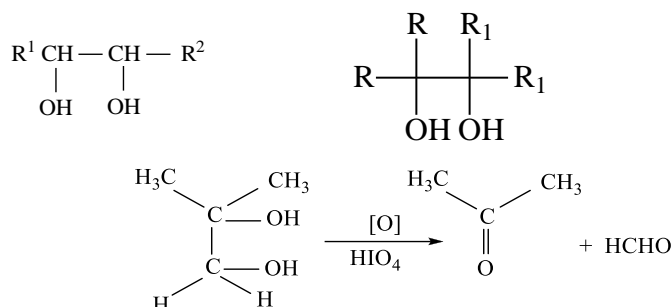
7. Alkynes: - Proper alkyl substituted on treatment with water in the presence of dil H_2SO_4 and $HgSO_4$ gives ketones

$$R \; C \equiv CH + HOH \xrightarrow[HgSO_4]{H_2SO_4}$$

$$R - C = CH_2 \; \rightleftharpoons \; R - \underset{\underset{\displaystyle O}{\|}}{C} - CH_3$$
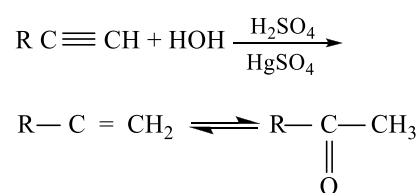
Similarly other homologues of acetylene on treatment with disiamyl borone followed by oxidation with H_2O_2 give ketones

$$R - C \equiv C - R \longrightarrow RCH = \underset{\underset{\displaystyle B \; Sia_2}{|}}{CR} \qquad \left((CH_3)_2 \; CH - \underset{\underset{\displaystyle CH_3}{|}}{CH} {-} BH \right)_2$$

Disiamyl borone Sia_2BH

$$\xrightarrow[OH^-]{H_2O_2} \quad R \; CH = CR \, (OH) \longrightarrow R - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - R$$
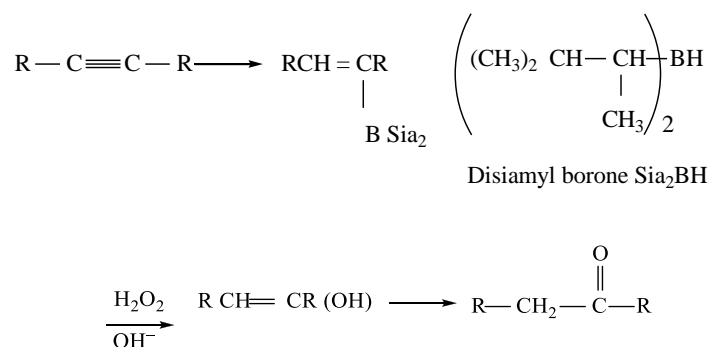
8. Lithium alkyls on treatment with CO_2 give good yield of ketone.

$$R \; Li + CO_2 \longrightarrow R - C \overset{\displaystyle O}{\underset{\displaystyle OLi}{\diagup}} \xrightarrow{RLi} R - \underset{\underset{\displaystyle R}{|}}{C} \overset{\displaystyle OLi}{\underset{\displaystyle OLi}{\diagup}} \xrightarrow{H_2O} R_2CO$$
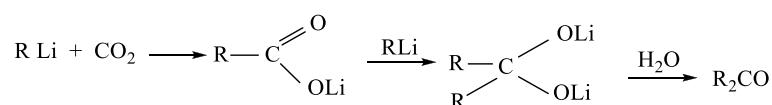
Similarly with acids also we get ketone
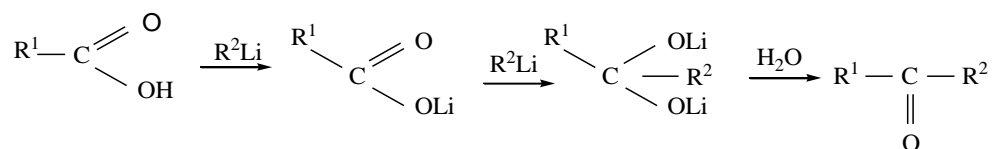
9. Addition of Grignard reagent to nitrile: - Reaction of Grignard reagents with nitriles forms ketones.

$$CH_3-C\equiv N + CH_3MgBr \longrightarrow CH_3-C=CNMgBr \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$
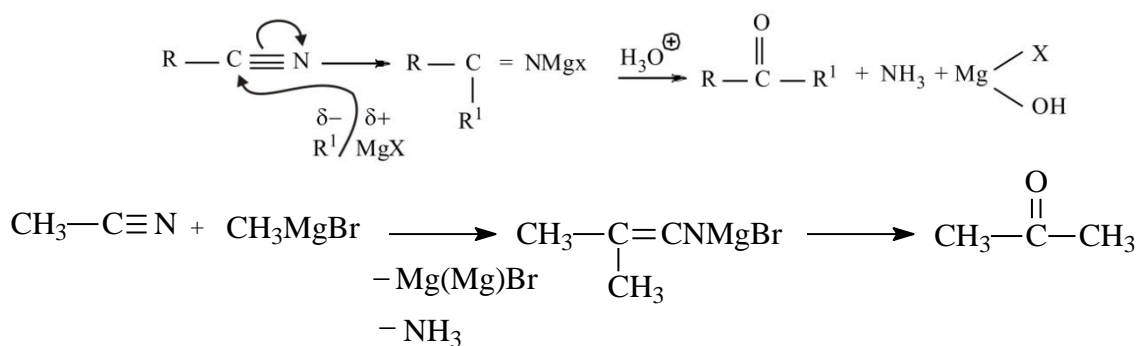
10.Wacker's Process: - Alkenes on treatment with $PdCl_2$ and $Cu\ Cl_2$ give ketone

$$CH_3CH=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Pd + 2HCl$$
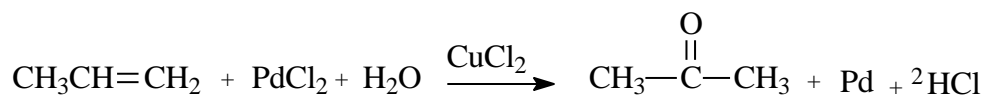
8.5 PREPARATIVE METHODS OF AROMATIC KETONES

The aromatic ketones are those compounds having a carbonyl appendage on the aromaticstructure to the other side of which one finds an alkyl or aryl group. Like aliphatic ketones aromatic ketones can be prepared by various methods

(1) Distillation of mixture of calcium benzoate and acetate yields acetophenone
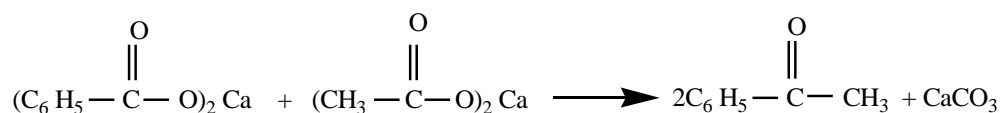
Heating of Calcium benzoate yields Benzophenone
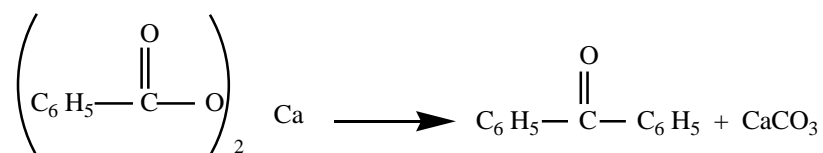
(2) Friedel Crafts acylation: - Treatment of benzene with acetyl chloride or acetic anhydride in the presence of $AlCl_3$ yields acetophenone
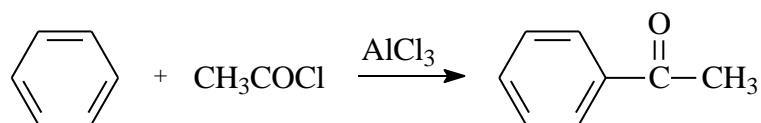
Use of benzoyl chloride gives benzophenone
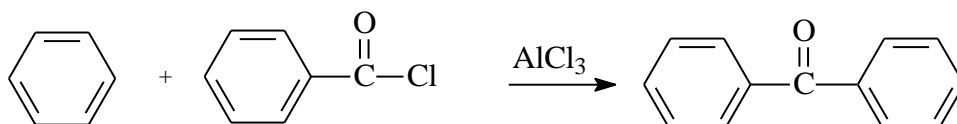
3) Benzene with carbonyl chloride in the presence of $Al Cl_3$ gives benzophenone.
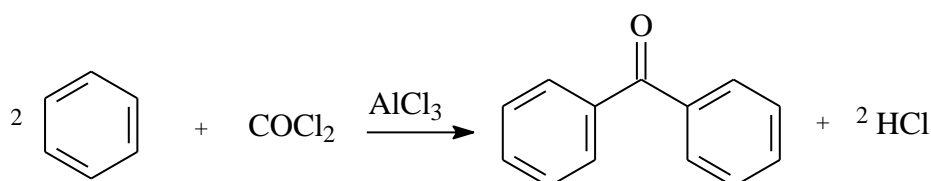
(4) Benzene with $C Cl_4$ in the presence of $AlCl_3$ yields dichloro compound, which on further steam distillation gives Benzophenone
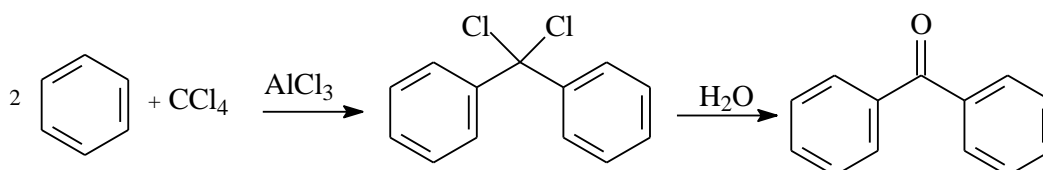
(5) Catalytic air oxidation – It is a commercial method to prepare acetophenone where ethyl benzene is treated with oxygen at 126^0C under pressure in the presence of Manganese acetate.
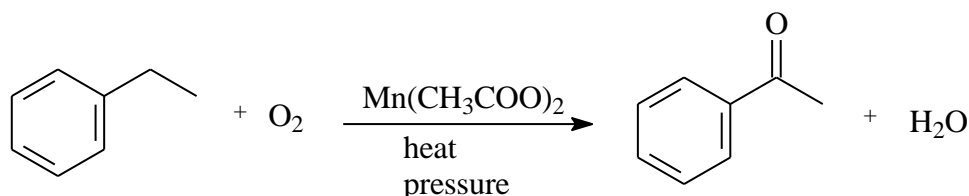
(6) Houben Hoesch reaction: - This reaction involves condensation reaction of cyanides with polyhydric phenols in the presence of $ZnCl_2$ and HCl resulting in formation of phenolic ketones.
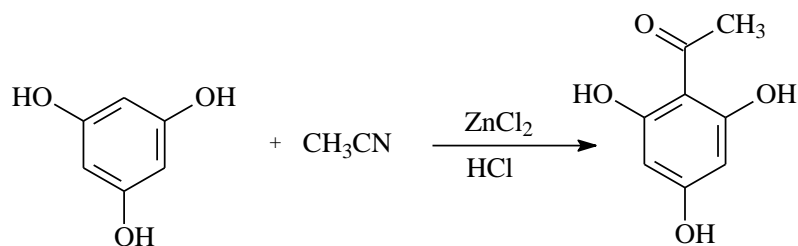
Mechanism: This reaction is extension of Gattermann's synthesis and follows the following sequential mechanism.
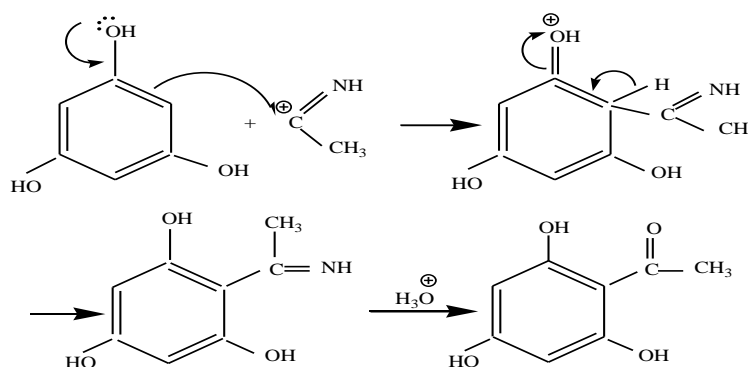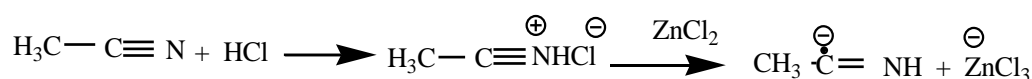
(7) Fries rearrangement – When aryl esters are treated with anhydrous $AlCl_3$ at 0C, results in the formation of o-and p- acyl derivative of phenols.
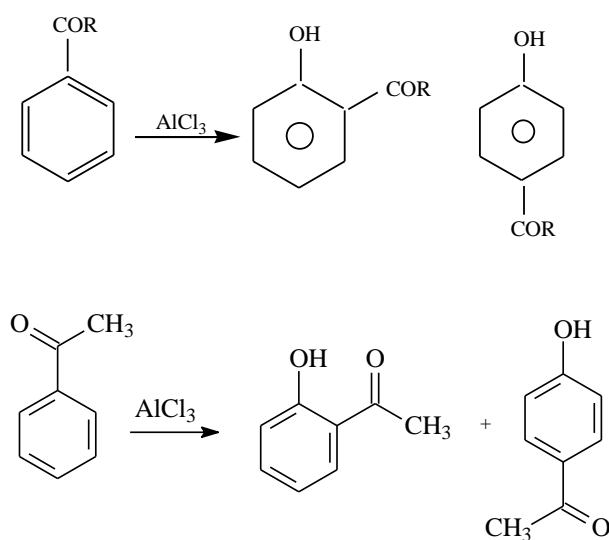
(8) From Grignard Reagent: - Aryl magnesium bromide with alkyl cyanides undergo nucleophillic addition reaction at carbon of cyanide, which on further hydrolysis with H_3O^+ gives aromatic ketone.
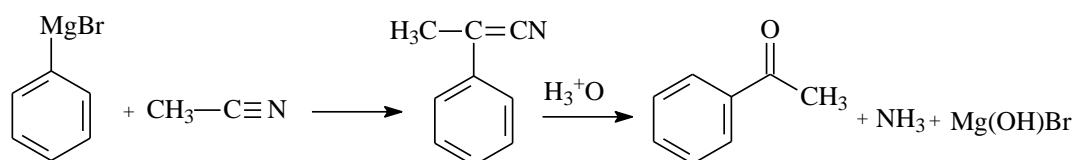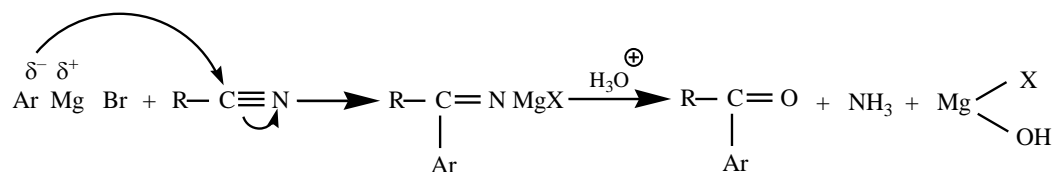
(9) From carboxyllic acids: - By passing vapours of any carboxylic acid except formic acid over MnO, We get a ketone.
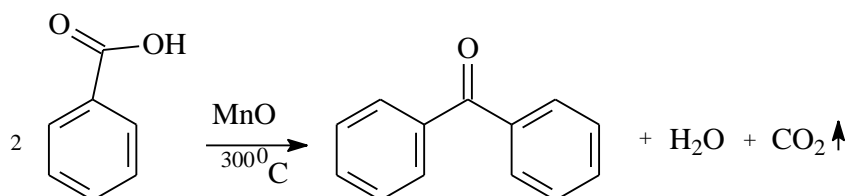
(10) Organo Cadmium compounds on reaction with acid chloride form ketones.

Reaction of cadmium chloride with Grignard reagent gives Organo Cadmium compounds.

$$2\,R - Mg - X \ + \ Cd\,Cl_2 \longrightarrow R_2\,Cd \ + 2\,Mg\,X\,Cl$$

Here R is primary alkyl group or aryl group.

8.6 PHYSIICAL PROPERTIES

1. Lower ketones are colourless liquids.

2. Lower ketones possess pleasant, sweet odours.

3. Density of ketones is less than water.

4. As discussed in aldehyde unit ketones have higher boiling points than corresponding alkanes but lower boiling points compared with those of alcohols of comparable molecular weights.

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} - CH_3 \qquad CH_3 - \underset{}{\overset{\overset{O}{||}}{C}} - CH_3 \qquad CH_3 - \underset{}{\overset{\overset{OH}{|}}{CH}} - CH_3$$

mol. wt.   58   58   60

boiling Point–12^{0}C   56^{0}C   82.5^{0}C

isobutane   acetone   isopropyl alcohol
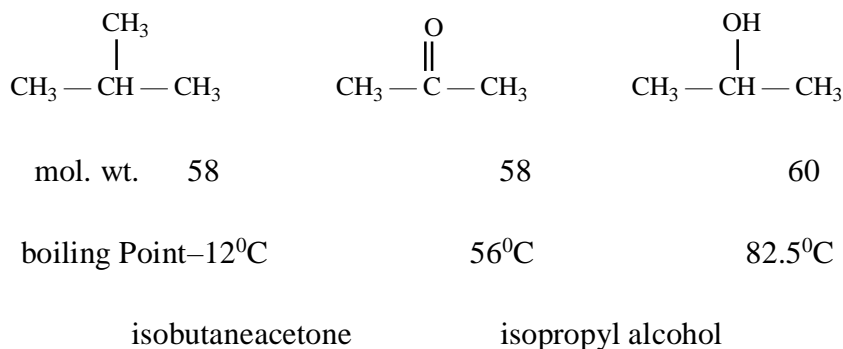
5. Lower ketones are soluble in water as they form hydrogen bonding with water. As alkyl chain of molecule increases, solubility in water decreases.

$$\underset{R}{\overset{R}{\diagdown}}C= \overset{\delta-}{O} ..... \overset{\delta+}{H} \underset{\underset{O}{\diagdown}}{} \overset{\delta+}{H} ...... \overset{\delta-}{O} = C\underset{R}{\overset{R}{\diagup}}$$
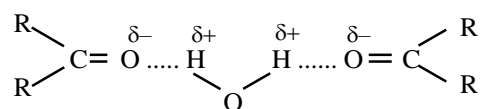
In infrared spectrum strong C = O Stretching band is observed in 1700 – 1740 cm^{-1} region.

Relative Reactivity: As discussed in detail in aldehyde unit it is to be noted that relative reactivity of ketones is less than aldehydes towards nucleophillic addition reaction. Here electron releasing alkyl group reduce positive charge of carbonyl carbon and thereby decrease reactivity of carbonyl group. Moreover, as compare to H atom alkyl group increases steric hindrance for attacking reagent (nucleophile) to reach at carbonyl carbon. Secondly after attack sp^2 hybridised carbonyl carbon becomes sp^3 hybridised in resultant adduct. Here bond angles are reduced from appr.120$^°$ to around 109$^°$. This adducts also gets steric strain due to increase of bulky groups. This strain is higher in ketones as compared to aldehydes.
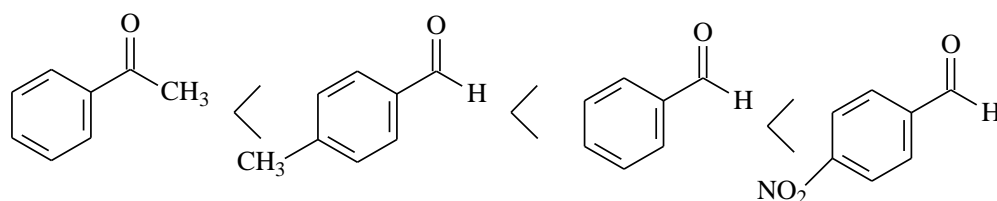
Acetophenone is ketone while other three are aldehyde. So, acetophenone is least reactive. *p*-toulaldehyde has electron donating methyl group at para position of benzene ring whereas *p*-nitrobenzaldehyde has an electron withdrawing nitro group at the para position and we

---

know that reactivity of carbonyl group is inversely proportional to electron density at carbonyl carbon so *p*-toulaldehyde is less reactive than benzaldehyde while *p*-nitrobenzaldehyde is more reactive than benzaldehyde. α-hydrogen of ketones are acidic and removable by strong bases.

8.7 CHEMICAL PROPERTIES

Ketones are reactive organic compounds and undergo many reactions like aldehydes.

8.7.1 ADDITION REACTIONS:

Like aldehydes the reactive carbony group of ketones gives addition reactions.

(1) Addition of sodium bisulphate (NaHSO₃) :- Ketones add on sodium hydrogen sulphite and form adducts called bisulphite addition compounds which are water soluble salts.
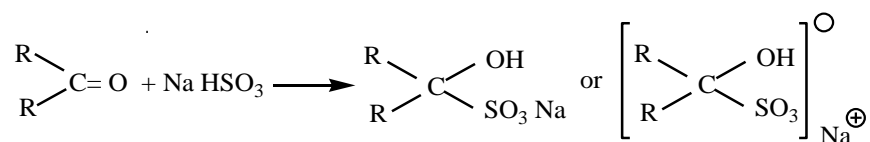
Thus formed adduct when treated with acid, base gives corresponding carbonyl compound.
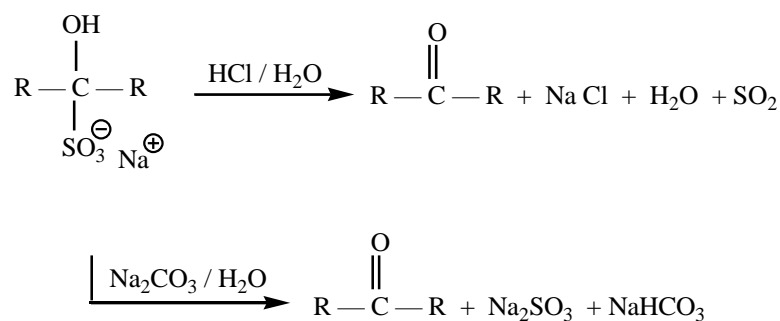
Mechanism: - In this reaction Na₂SO₃ acts as nucleophile through sulphur and attacks at carbonyl carbon which is followed by protonation of carbonyl anionic oxygen by bisulphite ion.
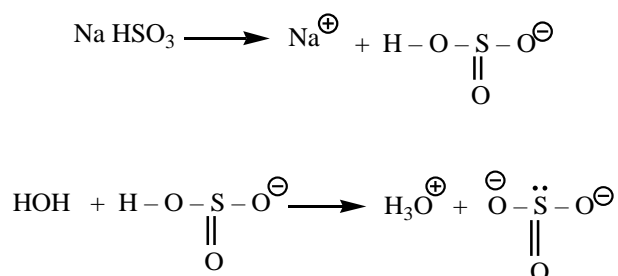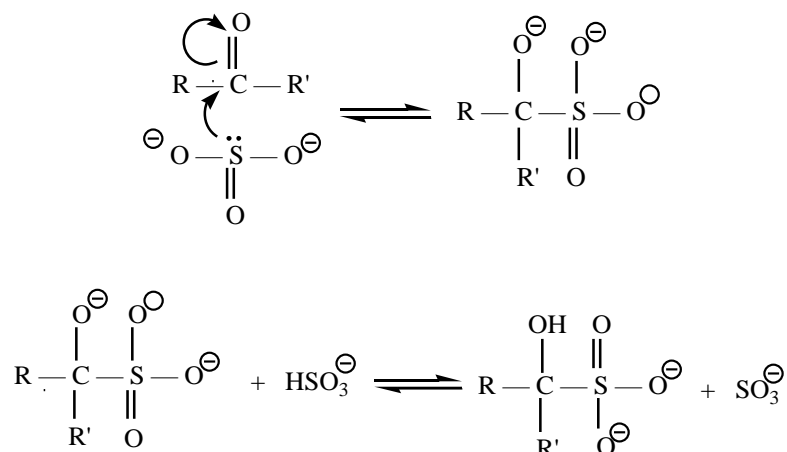
(2) **Addition of hydrogen cyanide (HCN) :-** Ketones add HCN in the presence of base catalyst to form cyanohydrins, which can further be hydrolysed to –COOH group
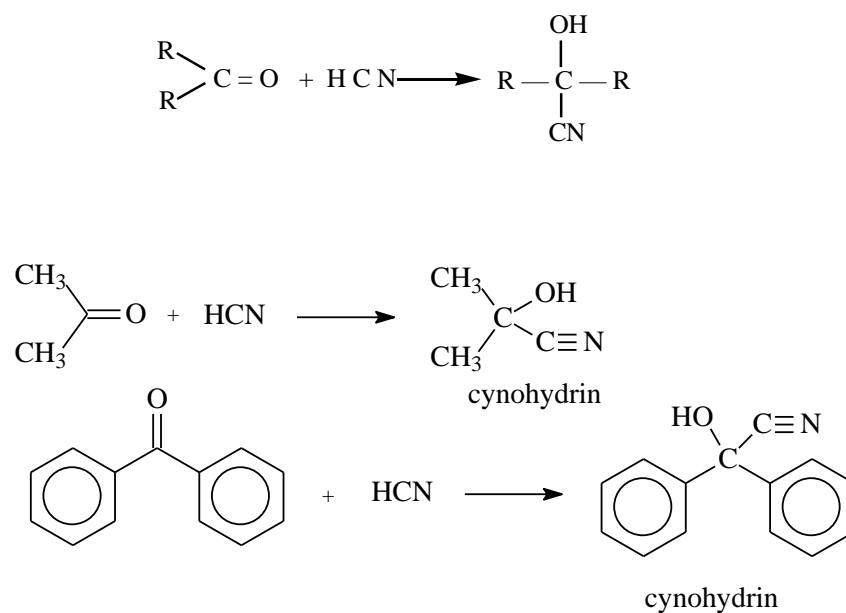
The mechanism of formation of cynohydrin is similar as discussed in aldehyde unit, hence can be persuied from aldehyde unit.

(3) Addition of Grignard reagents (RMgX): - ketones react with Grignard reagent to form complex which on hydrolysis with dilute acids gives tertiary alcohol.
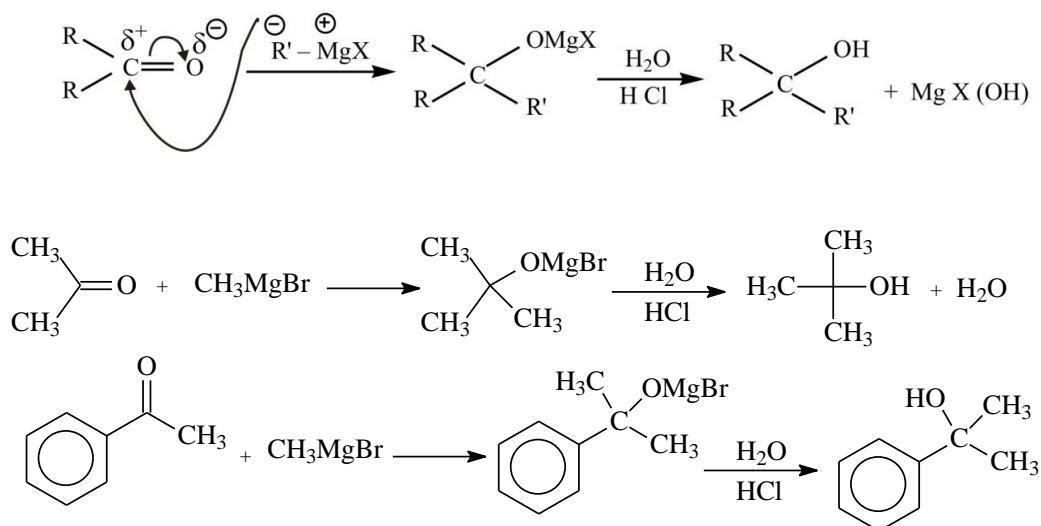
(4) Addition of ammonia (NH₃):- Ketones react with NH_3 and form complex condensation products.
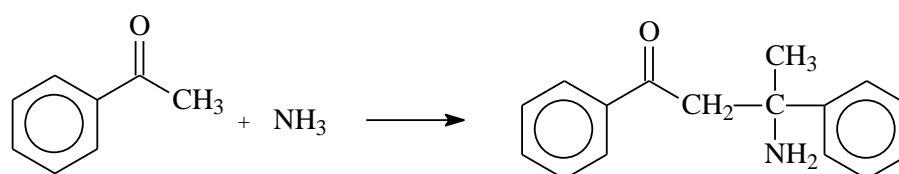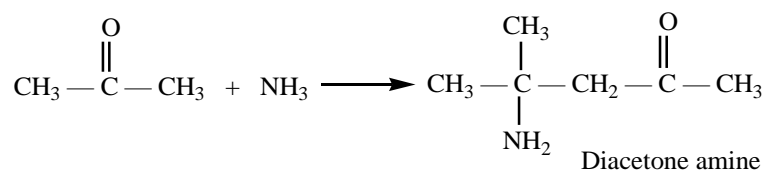
(5) Addition of terminal alkynes: - Ketones react with sodium salt of terminal alkynes to give alkynol.
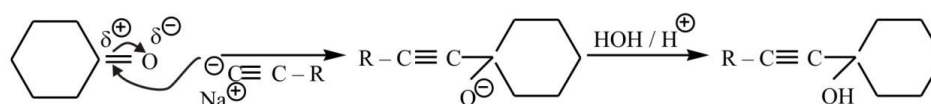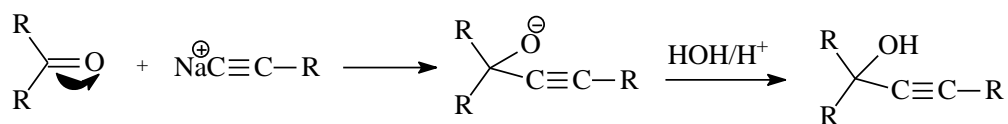
(6) Addition of alcohols (ROH): - Ketones react with alcohol in the presence of acids or base catalyst form hemiketals. Hemiketals are less stable than hemiacetals.
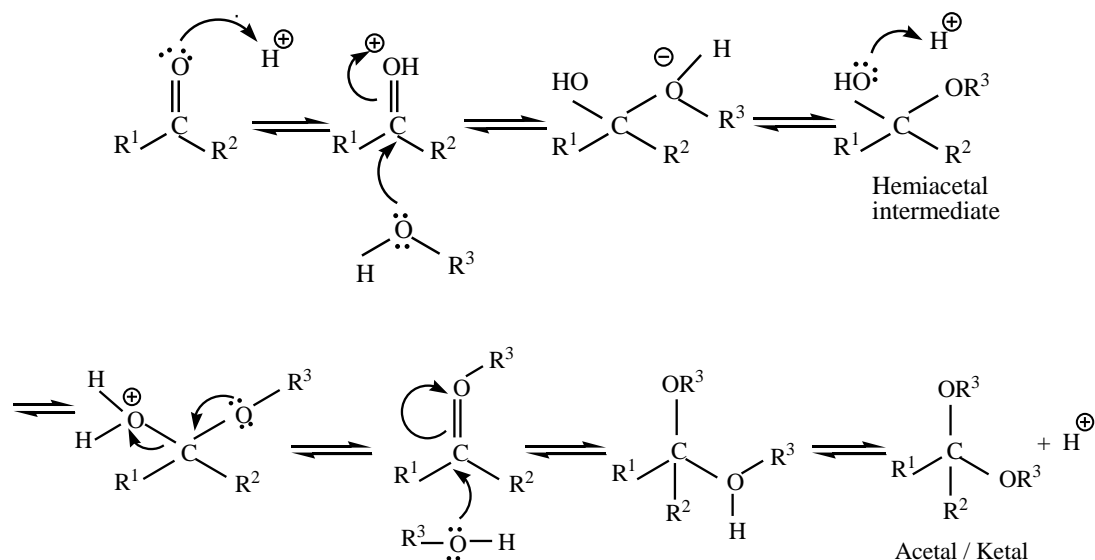
Hemiacetals of ketones are sometimes called hemiketals. In the above reaction excess of alcohol and removal of water leads reaction forward and excess of water favours backward reaction. Ketones don't form ketals readily as formed by aqueous dioxin. Solution of dioxolan on treatment with periodic acid regenerates ketone. Aldehydes, ketals may however be prepared by treating the ketone with ethyl orthoformate.
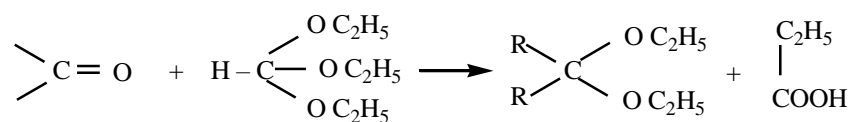
Ketones readily react with 1, 2 glycols to form dioxolans/cyclic ketal

hemiacetal

acetal/ketal
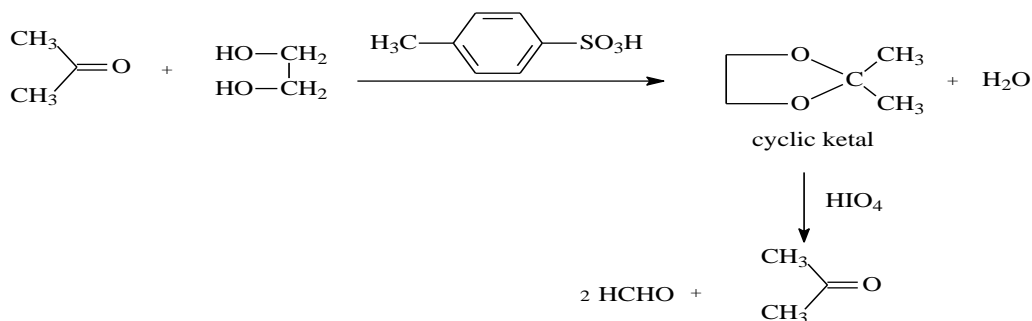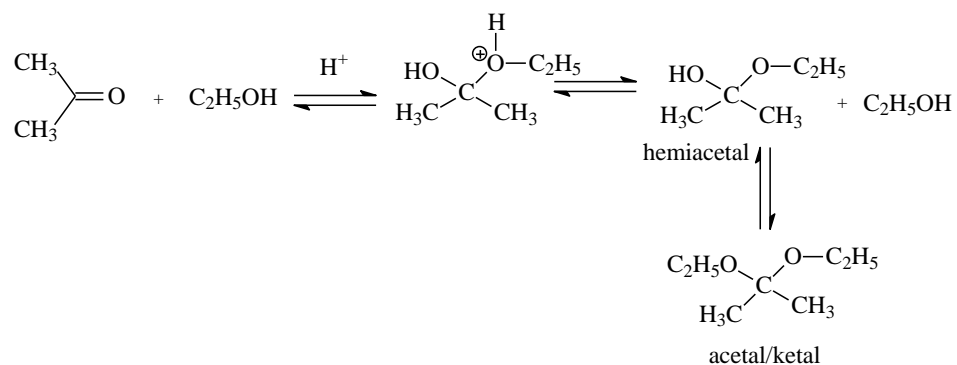
(7) Addition of mercaptans: - Thiols react more rapidly than alcohols to more rapidly to give thioketals.
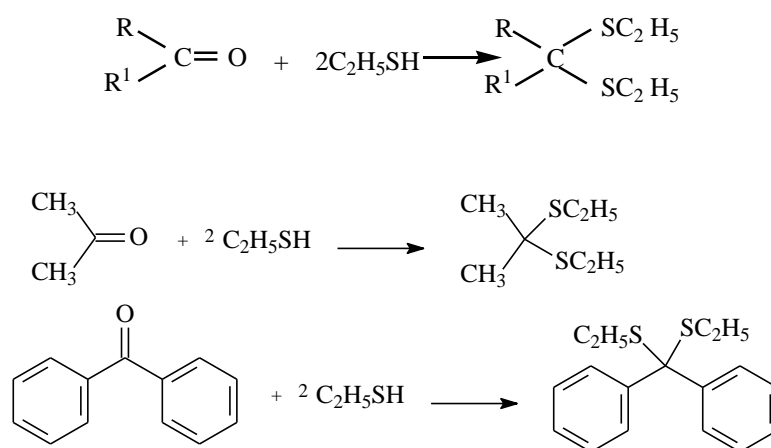
8.7.2 Addition reactions followed by elimination:

Ketones like aldehydes combine with nucleophile and eliminate neutral molecule like H_2O.The addition reaction of ketones followed by eliminations are being described as follow.

(8)   Addition of ammonia derivatives: - Nucleophiles of type $Y – NH_2$ ($Y = NH_2$, OH, C_6H_5NH, etc) combine with ketones and form carbon nitrogen double bonds, followed by elimination of water molecule.

$$H_3C-\underset{\text{(C=O)}}{C}-CH_3 \quad + \quad Y-:NH_2 \longrightarrow$$

$$\underset{H_3C}{\overset{O^{\ominus}}{C}}\underset{N\overset{\oplus}{}-Y}{CH_3} \quad \xrightarrow{H^+ \text{ transfer}} \quad H_3C-\underset{\underset{H}{N-Y}}{\overset{OH}{C}}-CH_3$$

$$\downarrow$$

$$H_2O \quad + \quad \underset{H_3C}{\overset{H_3C}{C}}=N-Y$$

$$\underset{\text{(phenyl)}}{C}-CH_3 \quad + \quad Y-NH_2 \longrightarrow \underset{\text{(phenyl)}}{C}\underset{CH_3}{\overset{N-Y}{}} \quad + \quad H_2O$$
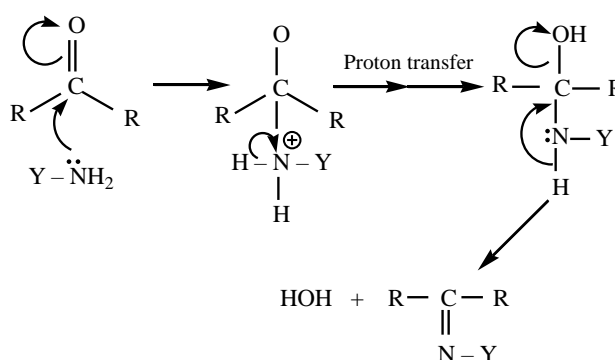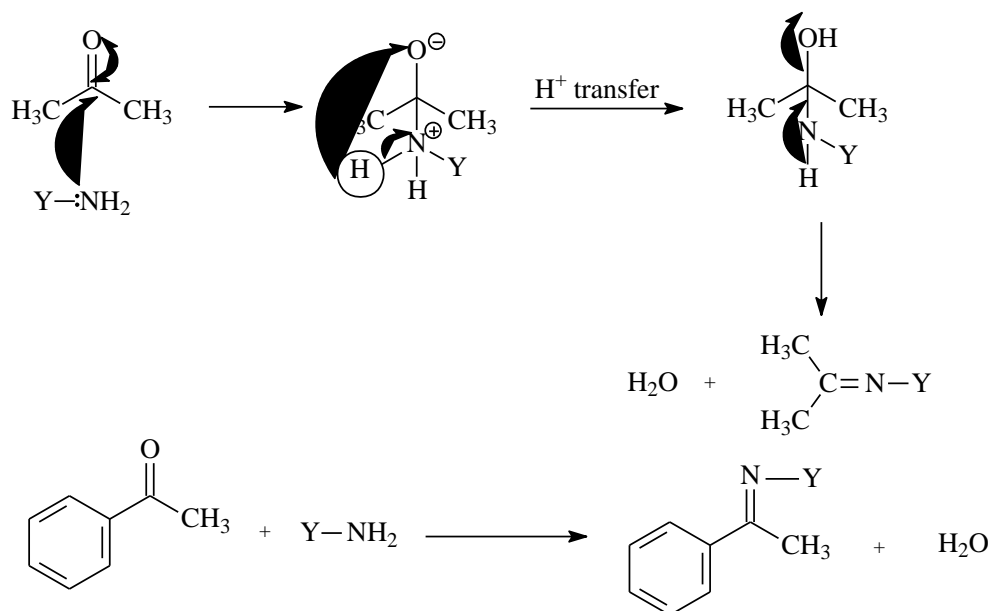
Above reaction is acid catalysed.

$R_2C=O$ reacting with:

- NH_2OH (Hydroxylamine) $\longrightarrow R-\underset{R}{\overset{R}{C}}=NOH + H_2O$ (Aldoxime)

- $RNHOH$ (N substituted hydioxylamines) $\longrightarrow R-\underset{}{\overset{R}{C}}=N\underset{O^{\ominus}}{\overset{R}{}}$ Nitrones (1, 3 addition)

- $NH_2 NH_2$ (Hydrazine) $\longrightarrow \underset{R}{\overset{R}{C}}=N-NH_2$ (Hydrazone)

- $H_2NNHC_6H_5$ (Phenyl hydrazine) $\longrightarrow \underset{R}{\overset{R}{C}}=N-\underset{H}{N}-C_6H_5$ (Phenyl hydrazone)

- $H_2N NH-$ (2, 4 dinitrophenyl hydrazine with NO_2) $\longrightarrow \underset{R}{\overset{R}{C}}=N-\underset{H}{N}-$ (2, 4, dinitrophenyl hydrazone)

- $H_2N-NH-\overset{O}{\overset{\|}{C}}-NH_2$ (Semicarbazide) $\longrightarrow \underset{R}{\overset{R}{C}}=N-N-\overset{}{C}-NH_2$ (Semicarbazone)
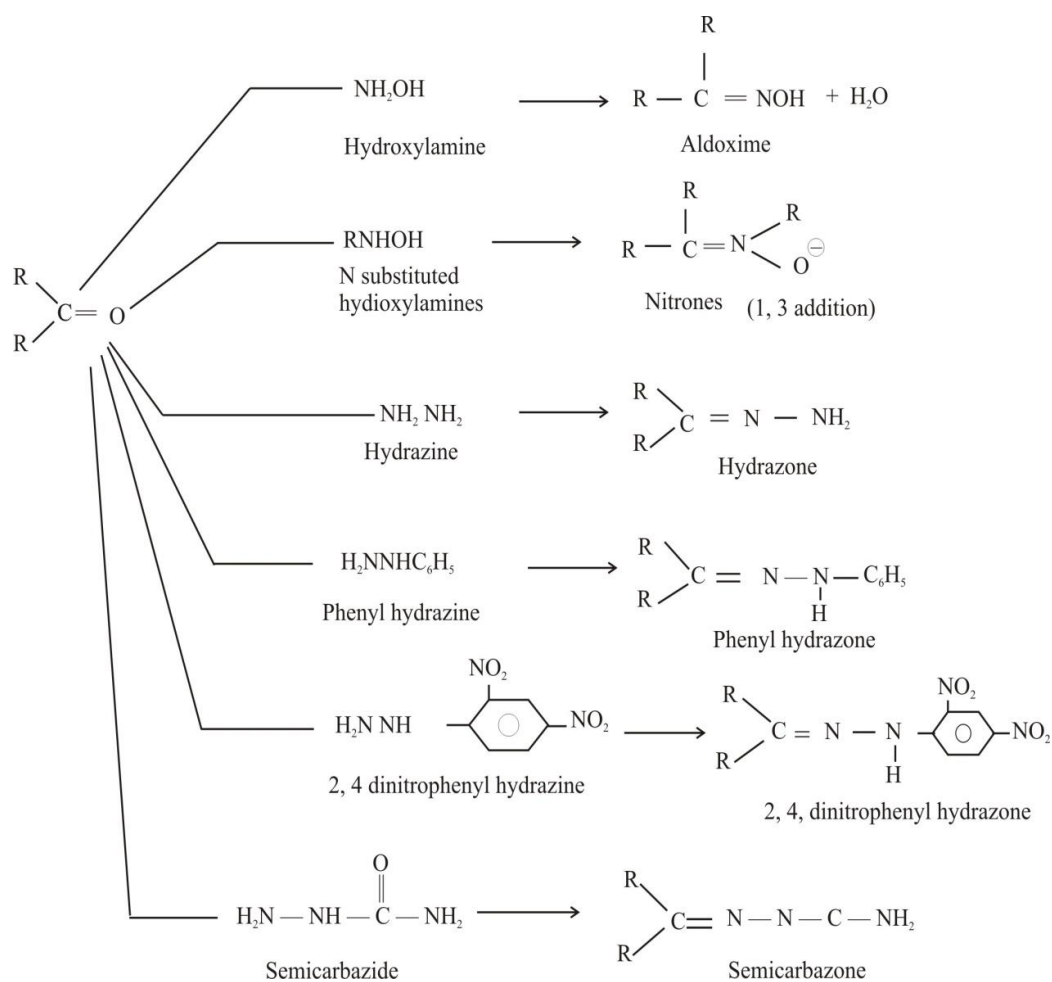
(9) Phosphorus pentachloride reacts with carbonyl compounds (simple).

$$\underset{H_3C}{\overset{H_3C}{>}}C=O \ + \ PCl_5 \longrightarrow \underset{H_3C}{\overset{H_3C}{>}}\underset{Cl}{\overset{Cl}{C}} \ + \ POCl_3$$
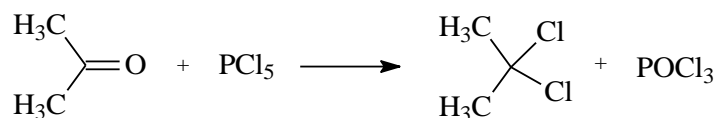
(10) Ketones react with aliphatic primary amines to form ketimines.

$$\underset{R^1}{\overset{R}{>}}C=O + \ R''NH_2 \rightleftharpoons \underset{R^1}{\overset{R}{>}}C=N\underset{R''}{\overset{H}{<}} \rightleftharpoons \underset{R^1}{\overset{R}{>}}C=N\underset{R''}{\overset{+H \oplus}{<}}$$

Mechanism :

$$\underset{R^1}{\overset{R}{>}}C=O + H^\oplus \longrightarrow \underset{R^1}{\overset{R}{>}}\overset{\oplus OH}{C} \longleftrightarrow R-\underset{\ominus}{\overset{OH}{C}}-R^1$$
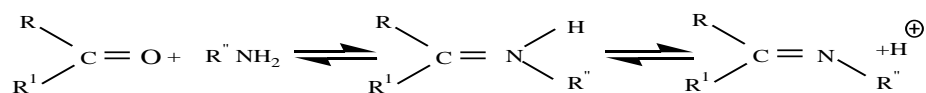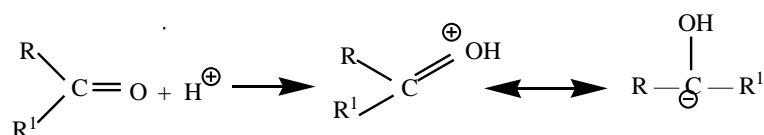
I

Acid catalyses above reaction and makes carbonyl carbon more electrophillic.

$$R-\underset{\overset{\oplus}{NH_2-R}}{\overset{OH}{C}}-R' \rightleftharpoons R-\underset{\underset{\oplus}{NH_2-R}}{\overset{OH}{C}}-R' \rightleftharpoons R-\underset{\underset{H}{\overset{\oplus}{N}}R}{\overset{\overset{\oplus}{OH_2}}{C}}-R' \longrightarrow R-\underset{N-R}{\overset{\|}{C}}-R'$$

$$\underset{H_3C}{\overset{H_3C}{>}}C=O \ + \ CH_3CH_2NH_2 \overset{H^+}{\longrightarrow} \underset{H_3C}{\overset{H_3C}{>}}C=N-CH_2CH_3$$
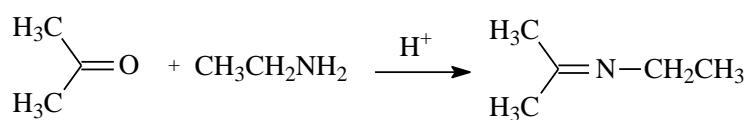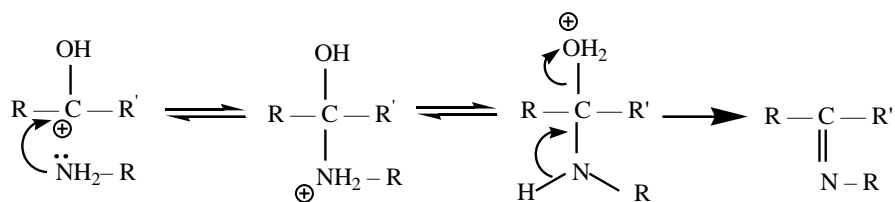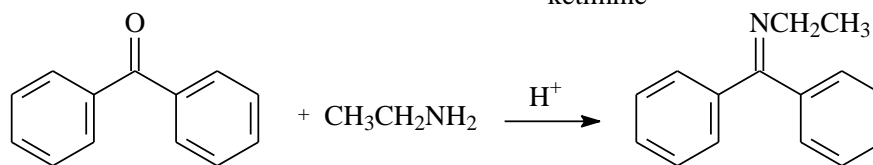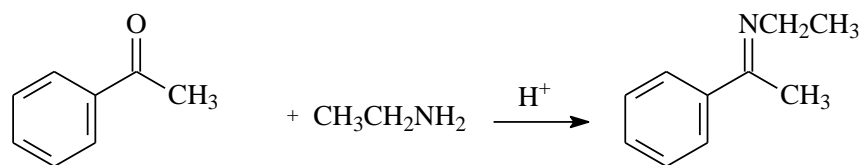
ketimine

ketimine

ketimine

At pH_7 formation of I is fast and as acidity increases dehydration also increases. However, if acidity increases further then I^{st} step addition of nucleophillic nitrogen of RNH_2 group decreases as acidity forms non nucleophillic nitrogen conjugate acid.

$$R - \overset{..}{N}H_2 \ + \ H_3O^{\oplus} \longrightarrow \ R - \overset{\oplus}{N}H_3 \ + \ H_2O$$

$$\text{Non nucleophillic}$$
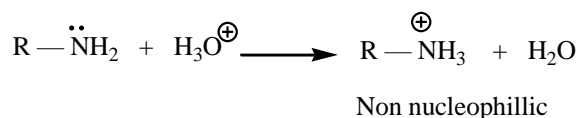
8.7.3 REDUCTION REACTIONS:

The carbonyl group of ketones can be reduced to $-CH_2-$ or $-CH$ by using reducing reagents. In continuation to other reactions the reductions are as follow.

(11) Ketones are reduced to secondary alcohol, when treated with H_2 and Ni, H_2 and Pt, $LiAlH_4$ (lithium aluminium hydride) in THF (tetrahydro furan), $NaBH_4$ (sodium borohydride) in water or alcohol.
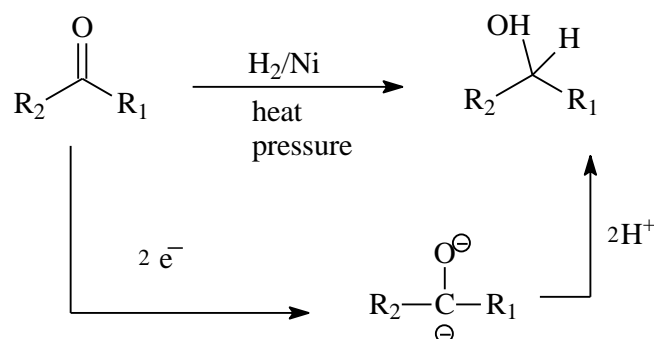
When reduction of unsaturated ketone with Ni and H_2 is carried out then preferentially double bond is hydrogenated or both double bond and carbonyl group are hydrogenated. But here only carbonyl group cannot be hydrogenated. $LiAlH_4$ and $NaBH_4$ type metal hydrides reduce carbonyl group but not isolated carbon-carbon double bond. C = C in conjugation with carbonyl group is sometimes reduced. $NaBH_4$ is milder reducing agent than $LiAlH_4$. So $NaBH_4$ is selective for carbonyl group if carbonyl and ester groups are present in same molecule.

Metal hydrides ($LiAlH_4$ and $NaBH_4$) transfer hydride ion to positive carbon of carbonyl group and then treatment with water or aqueous acid sets free alcohol from its salt.
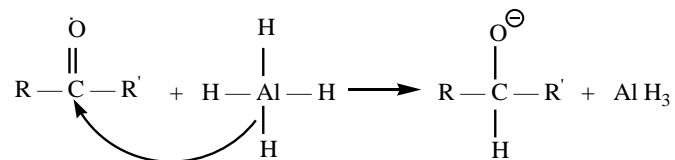
(12) Meerwein-Ponndorf-Verely reduction: - As discussed in aldehyde unit, ketones are also reduced to corresponding alcohol when ketones are dissolved in solution of isopropyl alcohol containing aluminium isopropoxide.
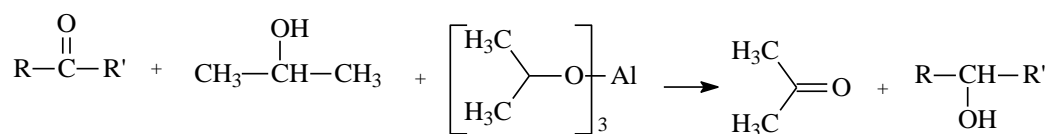
If aldehydes or ketones are unsaturated then it attacks only carbonyl group. Mechanism of MPV reduction of ketones is same as of aldehydes (discussed in aldehyde unit).

(13) Reduction to hydrocarbon: Ketones are reduced to $-CH_2-$ groups:

(a) Clemmensen reduction: - Carbonyl group of ketones is reduced to methylene group by using zinc amalgam and hydrochloric acid.
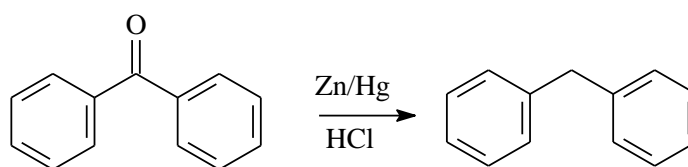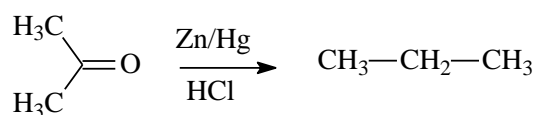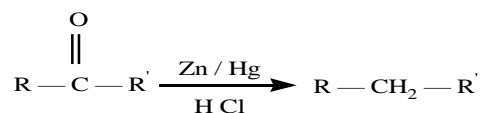
Mechanism of clemmensen reduction is already discussed in aldehyde unit.

(b) Wolf Kishner Reduction :- It involves conversion of carbonyl group to methylene group by heating ketones in the presence of excess hydrazine and a strong base (sodium ethoxide) at 180^0C.

$$R-\underset{\underset{O}{\|}}{C}-R' \ + \ NH_2\,NH_2 \ \xrightarrow{\text{NaOH}} \ \underset{R'}{\overset{R}{\diagdown}}C= NNH_2 \ \xrightarrow[180^0C]{OH} \ \underset{R'}{\overset{R}{\diagdown}}C\underset{H}{\overset{H}{\diagdown}} \ + \ N_2$$

<p align="center">Hydrazone</p>
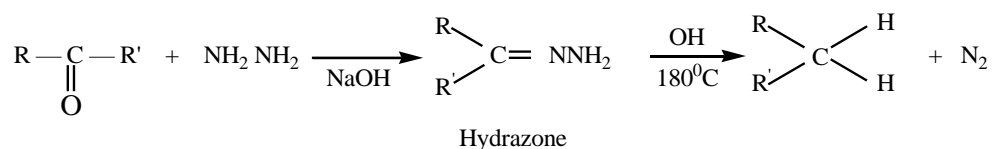
Reaction can be carried out room temperature in the presence of polar solvents like DMSO. In α, β- unsaturated carbonyl compounds, the Wolf Kishner reduction lead to double bond migration.

$$\underset{H_3C}{\overset{H_3C}{\diagdown}}C=O \ + \ NH_2-NH_2 \ \xrightarrow{H^+} \ \underset{H_3C}{\overset{H_3C}{\diagdown}}C=N-NH_2 \ \xrightarrow{\ominus OH} \ \underset{H_3C}{\overset{H_3C}{\diagdown}}CH-H \ + \ N_2$$
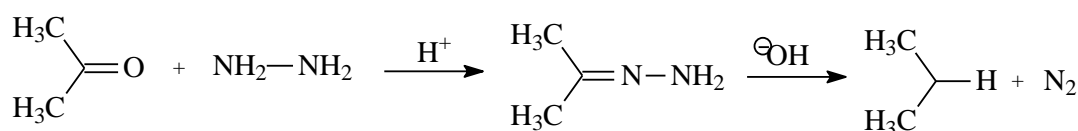
(14) Ketones when reduced by metals eg. magnesium in neutral or acidic medium forms pinacols (1, 2 glycols)

$$CH_3-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}}=O \ \xrightarrow[H_2O,\ H^+]{Mg\ /\ Hg} \ H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

<p align="center">Acetone</p>
<p align="center">2, 3 Dimethyl butane –2, 3-diol</p>
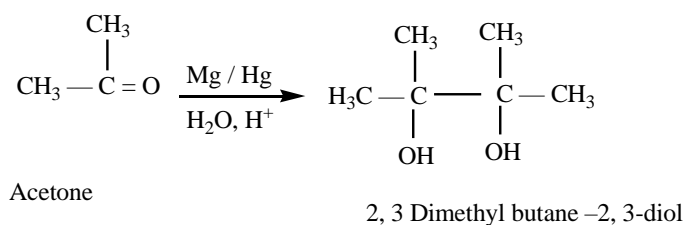
Pinacol under acidic condition undergo rearrangement to form pinacolone. This rearrangement is known as Pinacole-Pinacolone rearrangemenat.

This reaction is given by only ketones (not aldehydes).
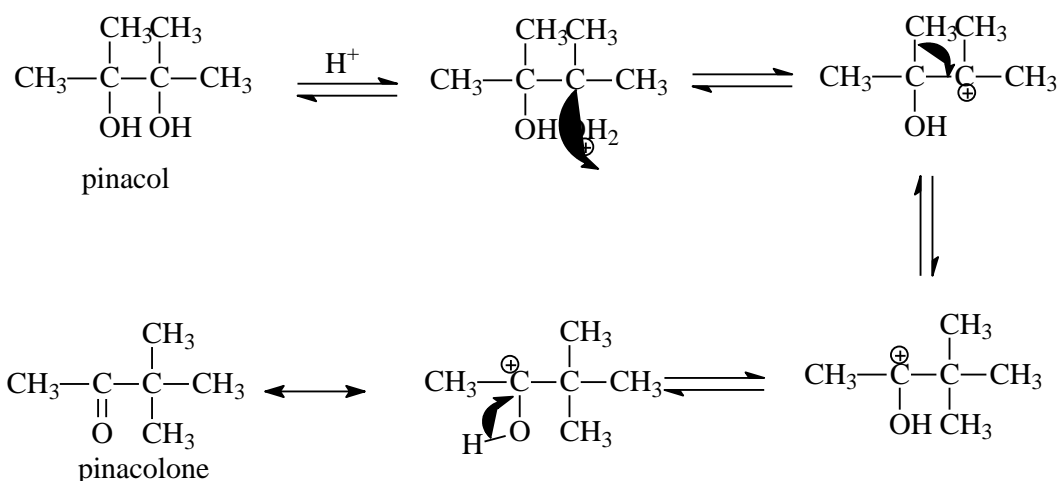
8.7.4 OXIDATION REACTIONS:

Ketones like aldehydes are oxidized to carboxylic acids. The oxid. Reactions of ketones in continuation are as under.

(15) Ketones can be oxidized by strong oxidizing agents such as alkaline $KMnO_4$ or hot concentrated HNO_3 etc. Here carbon atoms adjacent to carbonyl group are attacked and carbon atom joined to the smaller number of hydrogen atoms is oxidized preferably.

$$CH_3\ CO\ CH_2\ CH_3 \xrightarrow{\text{[O]}} 2CH_3\ COOH$$
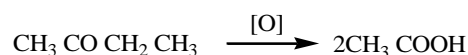
If adjacent carbon atoms have same number of hydrogen atoms, then smaller alkyl group retains carbonyl group.

Ketones donot reduce Fehling's solution, Benedict's solution or ammoniacal silver nitrate.

(a)   Baeyer Villiger Oxidation: - Aliphatic ketones on treatment with perbenzoic, peracetic, and monoperphthalic acid or permonoculphuric acid H_2SO_5 forms esters called Baeyer Villiger Oxidation.
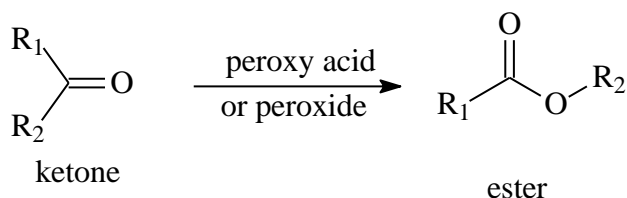
Mechanism: The sequential mechanism of Baeyer-Villiger reaction is as follow
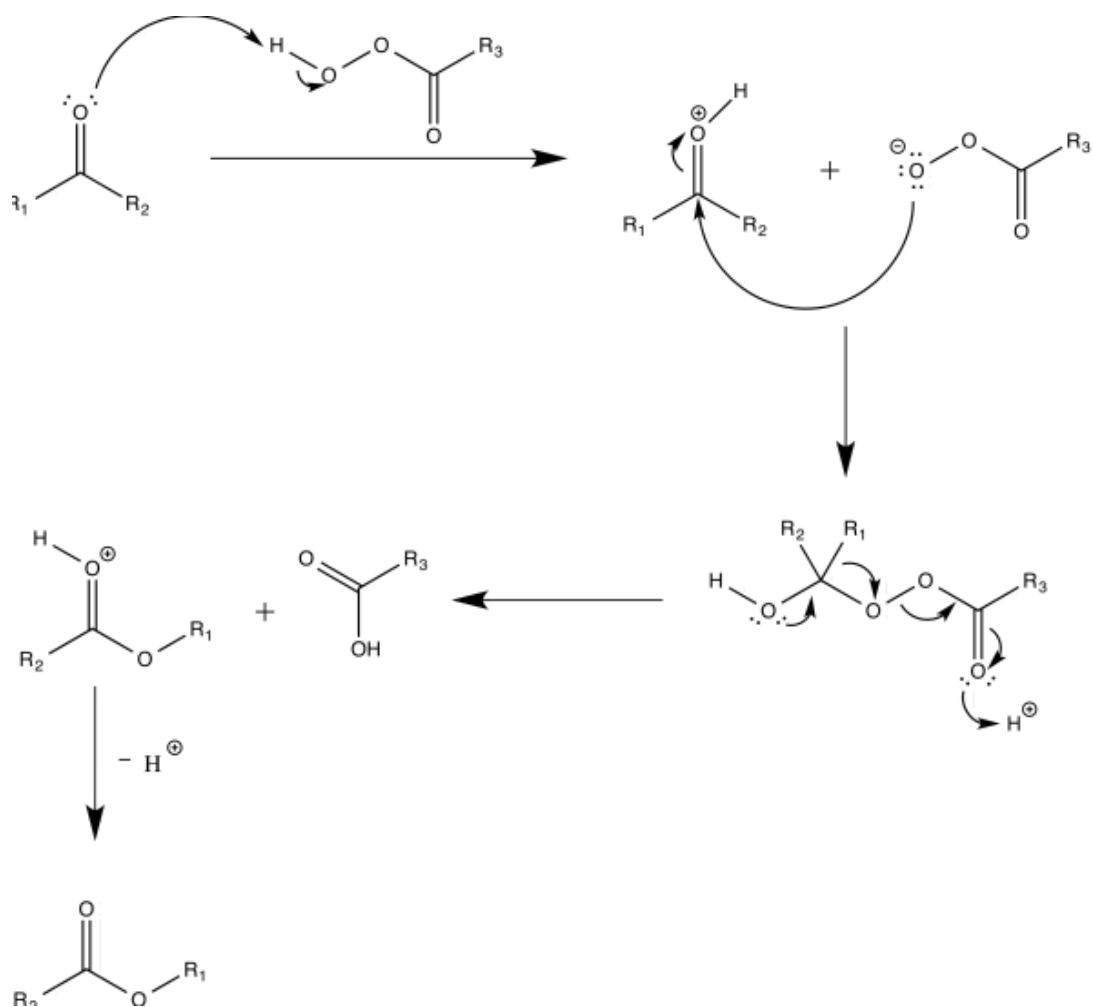
This rearrangement is intramolecular and migratory aptitude of an alkyl group is $3^0 > 2^0 > 1^0$.

(b) Oxidation with SeO₂:- SeO_2 oxidises methylene group adjacent to the carbonyl group of aldehydes and ketones.
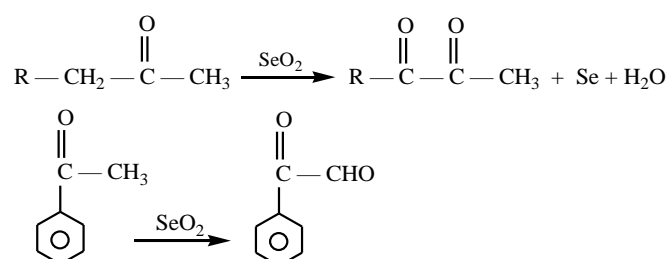
8.7.5 OTHER REACTIONS:

Earlier it has been discussed the acidity of α- hydrogens in carbonyl compounds which leads to different types of reactions in ketones eg. halogenation, condensation etc. In continuity some of the reactions of ketones are being discussed as follow

(16) Haloform Reaction: - Methyl ketones react rapidly with halogens (Cl_2, Br_2, I_2) in the presence of alkali to form mono, di and tri haloderivatives.
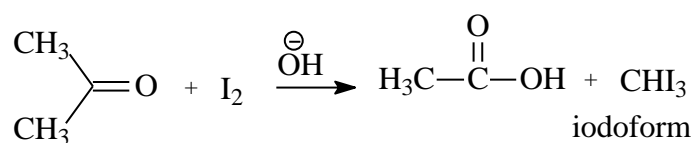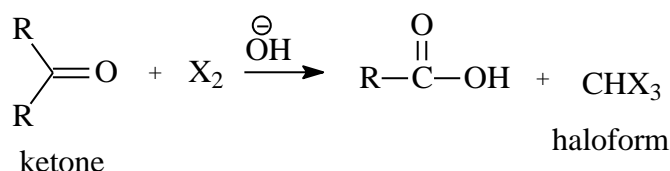
Mechanism
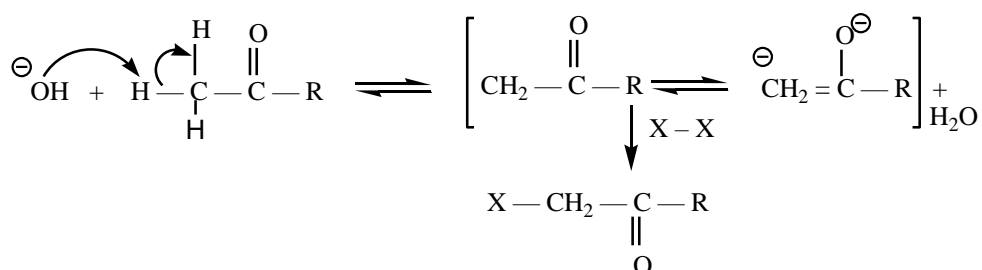
It involves abstraction of hydrogen by alkali and then resonance stabilization of conjugate base.Then carbanion displaces a halide from a halogen molecule.Introduction of halogen to methyl ketone enhances electronegativity of remaining α- hydrogens and they again undergo above process repeatedly forming trichalogenated ketones.
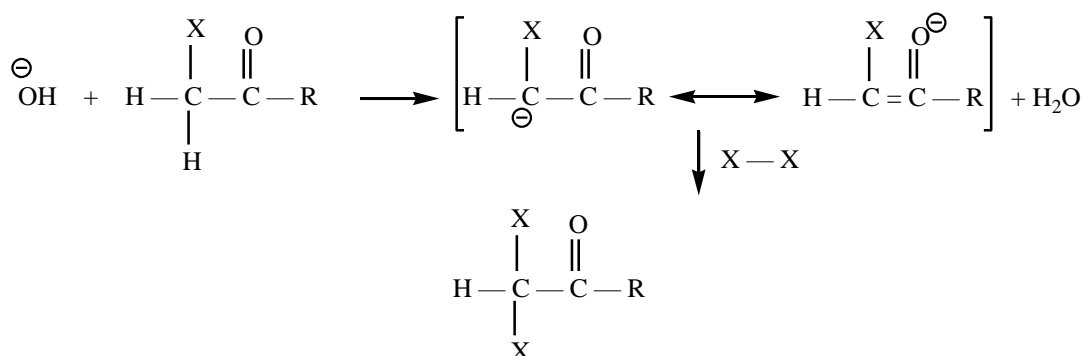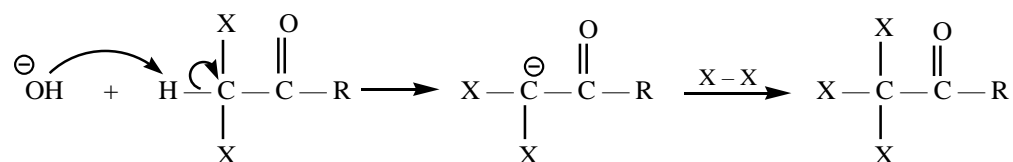
The trihalogenated ketones are unstable to base.
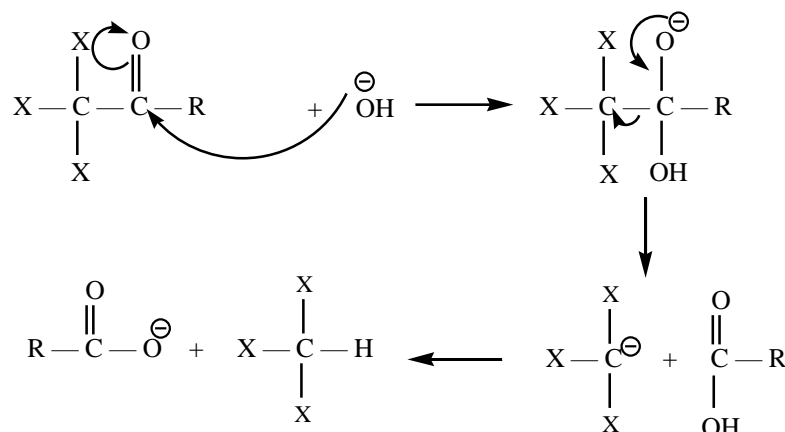
(17) Reformatsky Reaction: - Like aldehydes ketones also react with ☐ bromoester in the presence of Zinc which subsequently on acid hydrolysis result in ☐-hydroxy ester.

Acetone   Ethyl 3-hydroxy-3-methyl butanoate
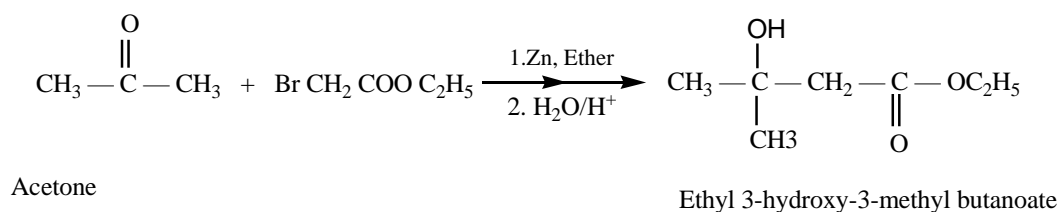
β- hydroxyl ester dehydrate to give unsaturated ester.

$$\left(CH_3 - CH = CH - \underset{\underset{O}{\|}}{C} - OC_2H_5 \right)$$
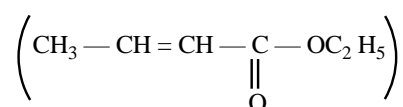
18) Wittig reaction: - Ketones react with alkylidene-phosphoranes (phosphorus ylides) in an atmosphere of nitrogen leads to alkene synthesis.

$$CH_3 \diagdown C=O \quad + \quad H_2\overset{\ominus}{C}-\overset{\oplus}{P}(C_6H_5)_3 \longrightarrow CH_3-\underset{}{\overset{CH_3}{C}}=CH_2 \quad + \quad (C_6H_5)_3P=O$$

ketone

$$\overset{CH_3}{\diagdown}C=O \quad + \quad H_2\overset{\ominus}{C}-\overset{\oplus}{P}(C_6H_5)_3 \longrightarrow CH_3-\overset{}{C}=CH_2 \quad + \quad (C_6H_5)_3P=O$$

acetophenone   isopropenyl benzene
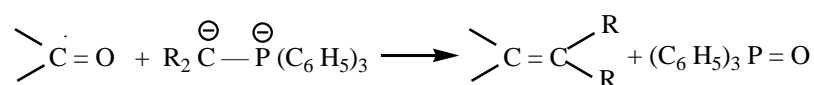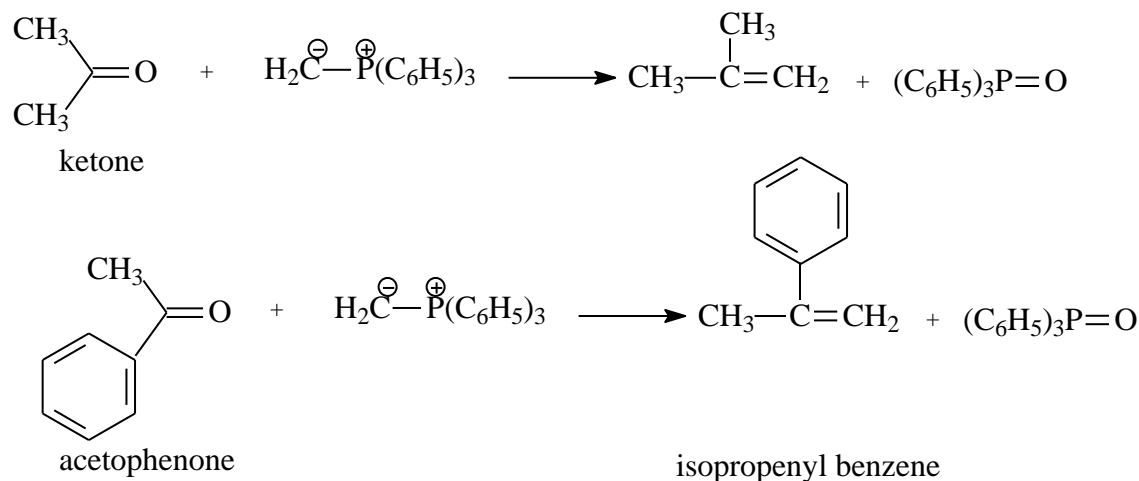
Mechanism of formation of phosphorus ylides and Witting reaction has been discussed in the previous unit pertaining to aldehydes. Reaction of ylides with ketones is slow as compared to aldehydes.

(19)   Aldol condensation: - Analogues to aldehydes, ketones having a hydrogen undergo self condensation in the presence of Ba(OH)$_2$ to form ketols.

$$CH_3-\underset{O}{\overset{O}{C}}-CH_3 \quad + \quad \underset{}{\overset{H}{C}}H_2-\underset{O}{\overset{O}{C}}-CH_3 \xrightarrow{Ba\,(OH)_2} H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2-\underset{}{\overset{O}{C}}-CH_3$$

Acetone   Diacetone alcohol
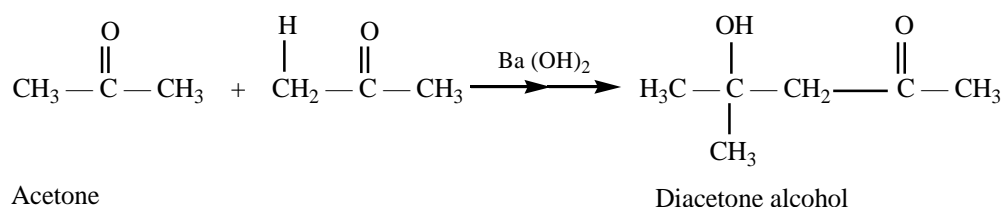
Ketols are easily dehydrated by heating or by dilute acids to form unsaturated ketones.

$$H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2-\underset{}{\overset{O}{C}}-CH_3 \xrightarrow{\triangle} H_3C-\underset{CH_3}{\overset{}{C}}=CH-\underset{}{\overset{O}{C}}-CH_3 \quad + \quad H_2O$$

4-Methyl – 3 – penten – 2 – one
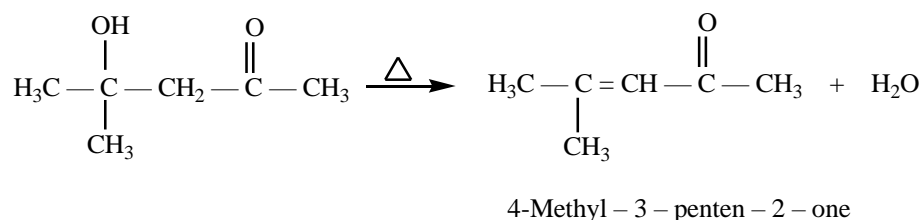
Mechanism of aldol condensation is similar to that of aldehyde which has already been discussed in aldehyde unit. However in mixed aldol condensation, when aldehydes condense with ketones in the presence of dil. alkali, it is the α- carbon (having hydrogen) atom of the ketone which is the attacking nucleophile.

$$CH_3\,CHO \;+\; CH_3\,CO\,CH_3 \xrightarrow{\;NaOH\;}$$

CH₃ — C(OH)(H) — CH₂ — C(=O) — CH₃

Acetaldehyde   Acetone   4 hydroxypentan – 2 one

CH₃ — C(=O) — CH₃ ⇌ ⁻CH₂ — C(=O) — CH₃ + H₂O

$$CH_3 - \overset{\delta\oplus}{C}(H) + \ ^{\ominus}CH_2 - C(=O) - CH_3 \rightleftharpoons CH_3 - C - C - C - CH_3$$

⇅ H₂O

H₃C — C(H)(OH) — C(H) — C(=O) — CH₃

8.7.6 SOME REACTIONS OF AROMATIC KETONES:

Aromatic ketones show nucleophillic addition reactions. Positive part of adding reagent always goes to carbonyl oxygen while negative part to carbonyl carbon. Though the reactions have aready been discussed here agin we discuss some important reactions with reference to aromatic ketones only.

(1) Addition of HCN:

⬡—C(=O)—CH₃ + HCN ⟶ ⬡—C(OH)(CN)—CH₃

cynohydrin

⬡—C(=O)—⬡ + HCN ⟶ ⬡—C(HO)(CN)—⬡

(2) Addition of Grignard Reagent: Like aliphatic ketones aromatic ketones give secondary alcohols while treated with Grignard reagent followed by hydrolysis.

Benzaldehyde   1-Phenyl-1-ethanol

Dimethyl phenyl
carbinol
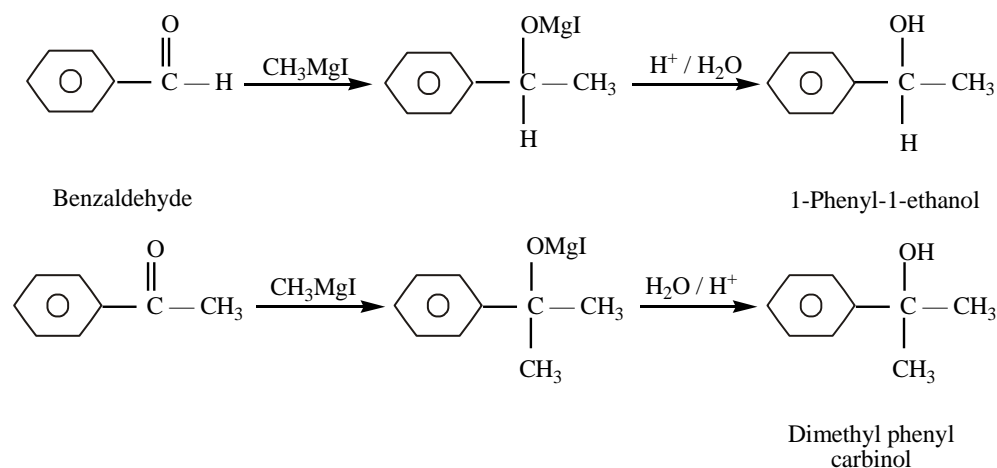
(3) Addition of sodium bisulphite:

Acetophenone does not give bisulphite addition reaction due to steric hindrance.

(4) Acetophenone reacts with hydroxylamine to form and methyl phenyl ketoxime in the presence of reagents as PCl_5, H_2SO_4, H_3PO_4 etc. This reaction is known as **Beckmann rearrangement**

ketoxime syn and anti
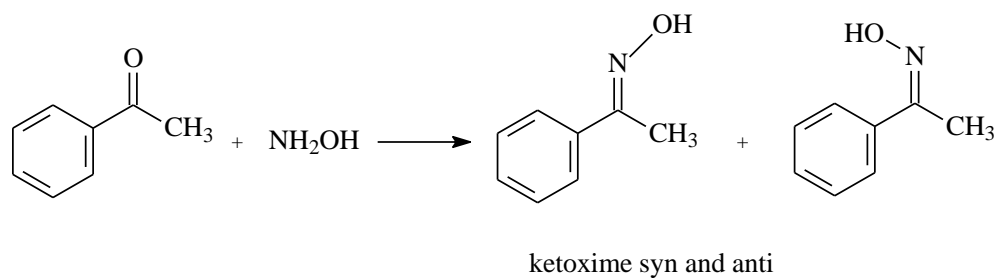
Mechanism:
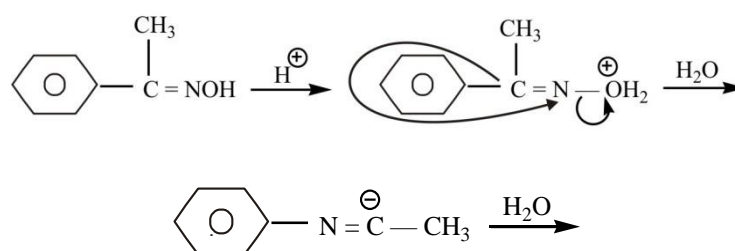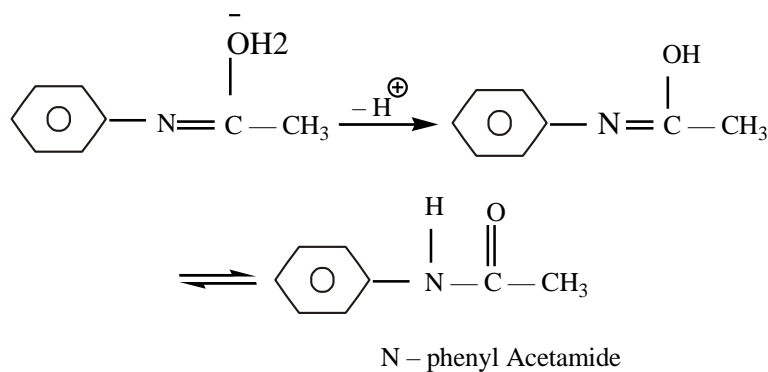
N – phenyl Acetamide

During Beckmann rearrangement it is methyl/phenyl group present in trans position migrate to the carbocation. Based on this we can distinguish syn or anti ketoxime. If phenyl group migrates, we get N-pheny- actamide and if methy group migrate, the product is actanilide.

(5) Acetophenone reacts with phenylhydrazine to give respective phenylhydrazones and eliminate water.
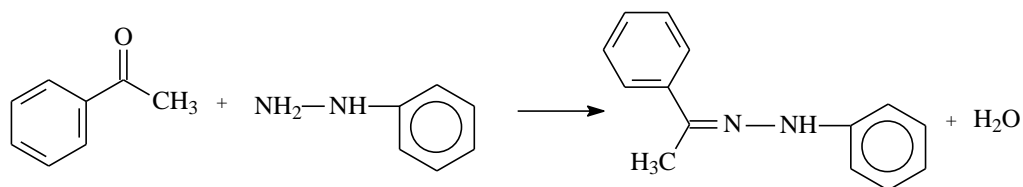
(6) Oxidation: Acetophenone is oxidized by acidic $K_2Cr_2O_7$ or $KMnO_4$ to give benzoic acid.
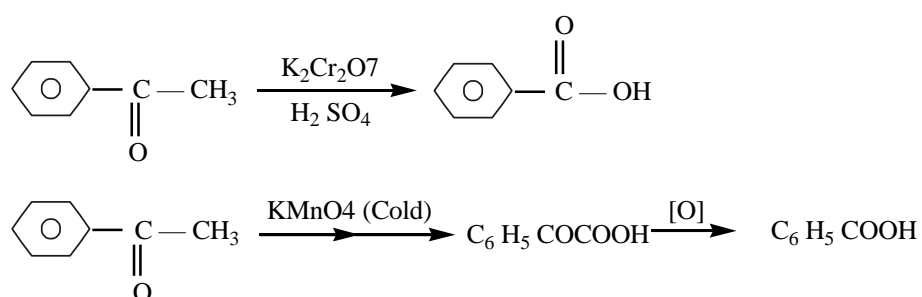
(7) Reduction: Acetophenone undergo reduction to form ethyl benzene
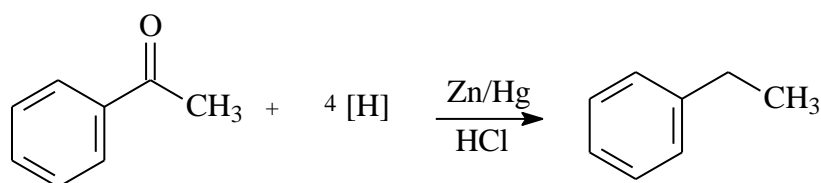
(8) Condensation Reactions: (a) Mixed Aldol condensation: - Acetophenone (has α-hydrogen) condenses with benzaldehyde to form phenyl styayl ketone.
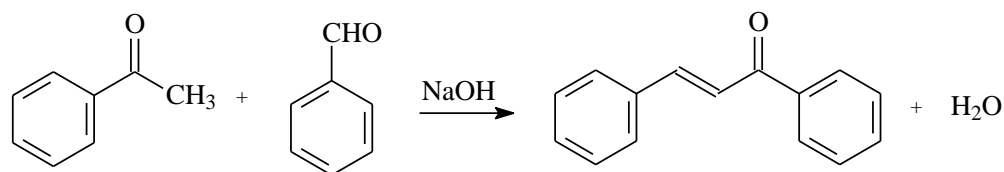
Condensation between aromatic aldehyde and aliphatic ketone (or mixed ketone) is also known as Claisen Schmidt reaction.

(b) Aldol type condensation: - Acetophenone undergoes self addition in the presence of aluminium t-butoxide to form dypnone.
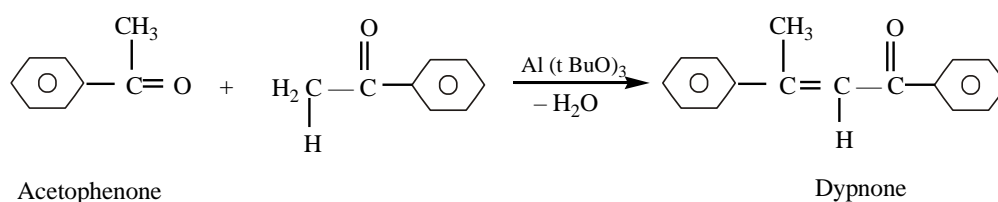
(9) Mannich reaction: - Acetophenone reacts with formaldehyde and ammonia or a primary amine or a secondary amine to form β--aminoketones.
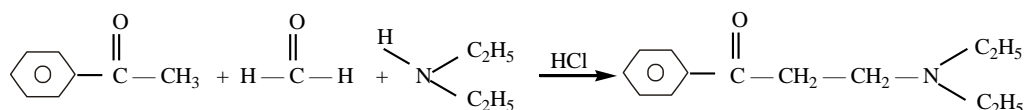
Mechanism:

(i) Mannich intermediate is formed by condensation of amine and formaldehyde in acidic medium

$$2 (CH_3 - CH_2)_2 NH + H - \underset{O}{\overset{}{C}} - H \rightleftharpoons H_2O + Et_2 N - CH_2 - N Et_2$$
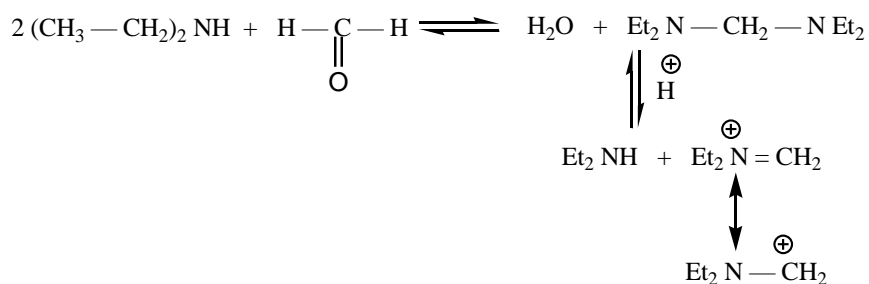
(ii) Mannich intermediate attacks acetophenone (enolic form)
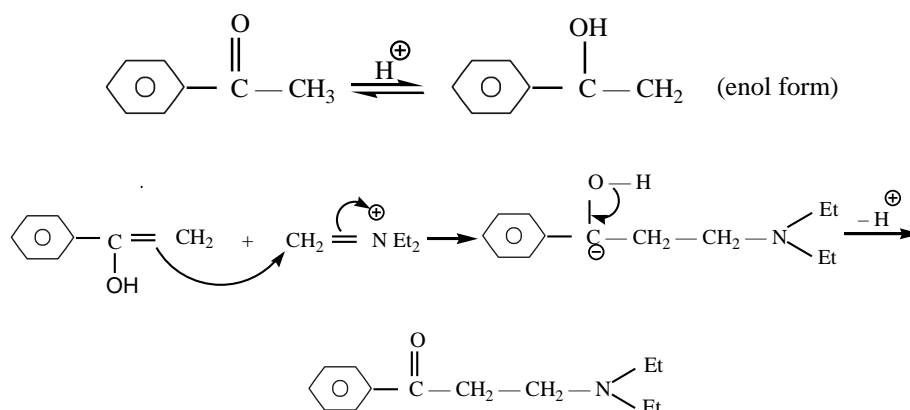
(10) Iodoform reaction: - Acetophenone reacts with Iodine in the presence of NaOH to form Iodoform (Reaction analogous to aliphatic aldehyde and ketones having methyl group showing haloform reaction).
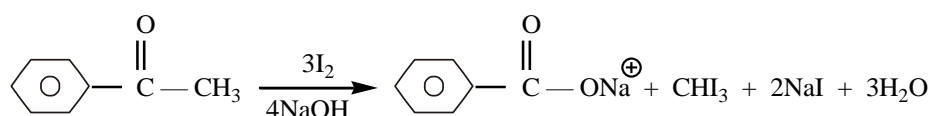
(11) Electrophillic substitution reaction: - Acetophenone undergo electrophillic substitution reaction– $COCH_3$ group are meta directing and deactivating.
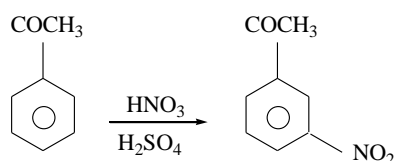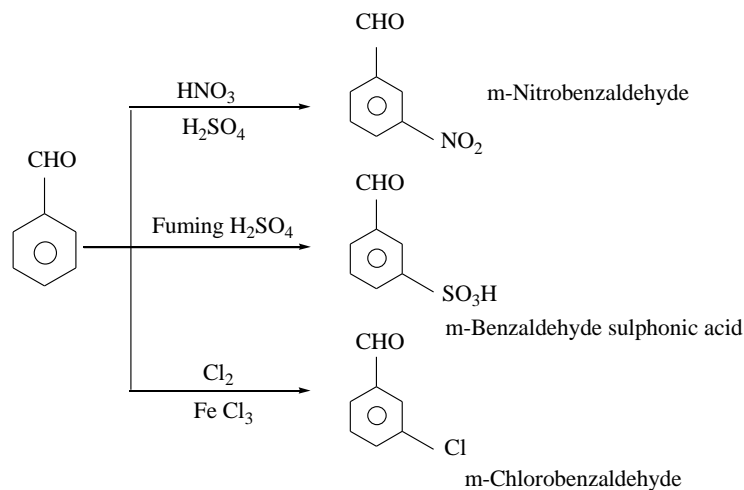
8.8 SUMMARY

- Ketones are the compounds which have general formula of C_nH_{2n} contain oxo (carbonyl) group and its functional keto group $>C=O$ lies within the chain. Secondary alcohols on Oppenauer oxidation (aluminium isopropoxide in presence of excess of acetone) give ketones.

- Ketones also show nucleophillic addition reactions but ketones are less reactive than corresponding aliphatic aldehydes as it involves change of carbon's hybridization from sp^2 to sp^3 and increased crowding at carbonyl carbon is sterically hindered. Also +I effect of alkyl group at carbonyl carbon reduces its nucleophilicity.

- Mild oxidizing agents like Tollen's reagent or Fehling's solution do not oxidize ketones. Strong oxidizing agents oxidize ketones as Conc. HNO_3, $KMnO_4/H_2SO_4$.

- They give condensation reactions and alpha hydrogen substitution reactions. Reagents like $LiAlH_4$, $NaBH_4$ etc, can reduce ketones.

8.9 TERMINAL QUESTIONS

Q.1 Tick out the correct option in following multiple choice questions.

1. Acetone is treated with excess of ethanol in the presence of HCl. The product obtained is

    a. $(CH_3)_2C\begin{smallmatrix}OH\\OC_2H_5\end{smallmatrix}$ b. $(CH_3)_2C\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$

    c. $CH_3CH_2CH_2COCH_3$ d. $CH_3CH_2CH_2COCH_2CH_2CH_3$
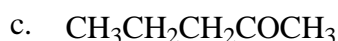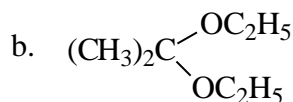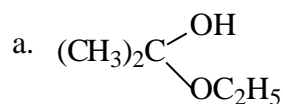
Ans. :- (b)

2. Clemmensen reduction of ketone is carried out in the presence of which of the following:-

    (a) H_2 and Pt as catalyst   (b) Glycol with KON   (c) Zn – Hg with HCl

    (d) Li Al H_4

     Ans. :- (c)

3. Identify the product in reaction:-

$$\langle O \rangle - C \equiv C - CH_3 \xrightarrow{H3O+,\ Hg^{2+}}$$
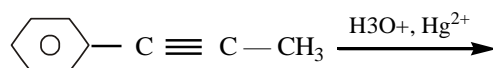
(a) $C_6H_5CH_2CH_2CHO$ (b) $C_6H_5COCH_2CH_3$ (c) $C_6H_5CH_2COCH_3$

(d) $C_6H_5COCOCH_3$

Ans. :- (b)

4. Compound A react with HCN and forms cyanohydrin which on hydrolysis gives carboxylic acid acid. So compound A is –

 (a) CH_3NH_2 (b) CH_3COCH_3 (c) $CH_3CO_6CH_5$ (d) C_6H_5OH

 Ans :- (b)

5. The compound which forms acetaldehyde when heated with dilute NaOH.

 (a) 1, Chloroethane   (b) 1, 1 dichloro ethane   (c) 1, 2 dichloro ethane

(d) 1, 1, 1 trichloro ethane

Ans. :- (a)

6. An organic compound X is oxidized by using acidified $K_2Cr_2O_7$. Resultant product reacts with phenyl hydrazine but does not answer silver mirror test. So the possible compound X is

(a) $(CH_3)_2CHON$ (b) CH_3CHO (c) CH_3CH_2OH (d) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Ans. :- (a)

7. To distinct 2-pentanone from 3-pentanone _____ reagent should be employed.

(a) $K_2Cr_2O_7 / H_2SO_4$ (b) Zn – Hg / HCl   (c) SeO_2

(d) Iodine / NaOH

Ans. :- (d)

(WB JEE 2009)

8. In which of the following reactions new carbon – carbon bond is not formed-

(a) Cannizaro reaction   (b) Wurtz reaction   (c) Aldol condensation

(d) Benzoin condensation

Ans. :- (a) (WB Jee 2009)

9. A strong base can abstract an a hydrogen from –

(a) Amine (b) Alkane (c) Alkene (d) Ketone

(CBSE AIPMT 2008)

Ans. :- (d)

10.
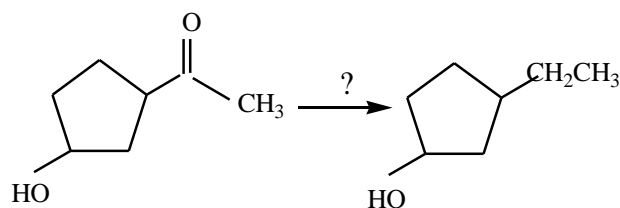
(a) Zn (Hg), HCl (b) $NH_2\ NH_2$, OH (c) H_2, Ni

(d) $NaBH_4$

Ans.:- (b)

11. What is the correct structure for 2-hydroxy acetophenone?
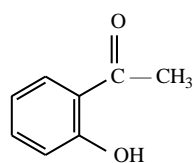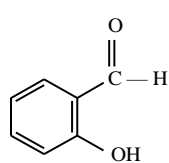
(a) (b) (c)
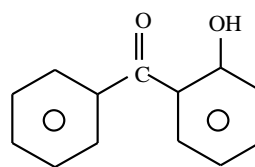
(d)
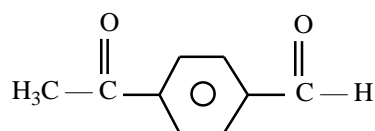
Ans. :- (a)

12. What is the major product of the following reaction?
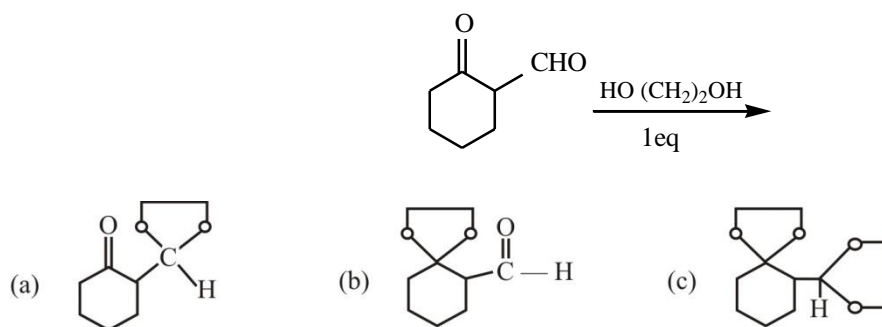
Ans. :- (a)

13. Cyclopentanol undergoes oxidation to give –

(a) Cyclopentene   (b) Cyclophentanone   (c) Cyclopentanal

Ans. :- (b)

14. Which of the following compounds gives positive iodoform test ?

(a) 3-Hexanone   (b) 1-Pentanol   (c) Acetone

(d) 3-Pentanone

Ans. :- (c)

Q.2 Short answer type questions

1.   Write IU PAC names of following compounds: -
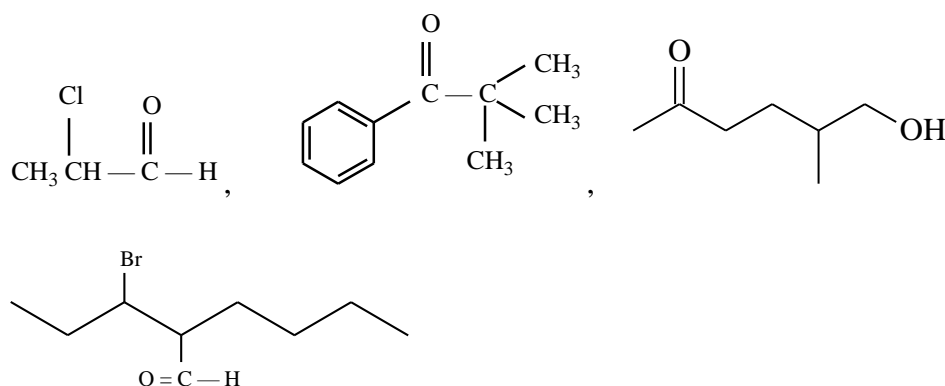
Ans: - 2-chloropropanal, 2, 2-dimethyl-1-phenyl propanone, 6-hydroxy -5 methyl -2-hexanone, 2-[1-bromoprophyl] hexanal.

2.   Why boiling points of aldehydes and ketones are higher than those of corresponding alkanes?

3. Why lower aldehydes are soluble in water?

4. How will you synthesize acetaldehyde from formaldehyde?

$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{(i) CH}_3\text{Mg Br}} H-\overset{\overset{OMg\ Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \xrightarrow{H_2O/H^{\oplus}} H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-H$$
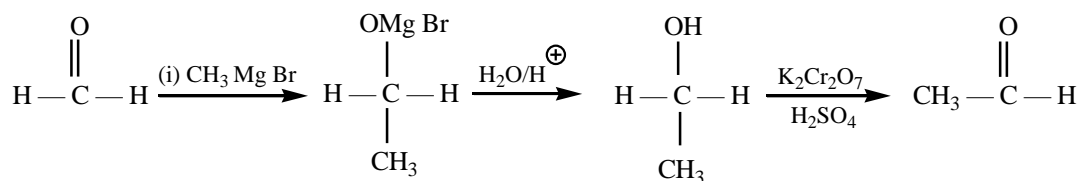
5. How will you synthesize lactic acid from acetylene?

$$CH\equiv CH \xrightarrow{H_2O/H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{HCN} CH_3-\overset{\overset{CN}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow{H_2O/H^{\oplus}} CH_3-\overset{\overset{COOH}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

6. Identify (A), (B) and (C)

$$CH_3-\overset{\underset{\underset{O}{\|}}{C}}{}-CH_3 \xrightarrow{Li\ Al\ H_4} (A) \xrightarrow{SOCl2} (B) \xrightarrow{Alco.KOH} (C)$$

(A) $CH_3-\overset{\overset{}{\underset{\underset{OH}{|}}{CH}}}{}-CH_3$ (B) $CH_3-\overset{\underset{\underset{Cl}{|}}{CH}}{}-CH_3$ (C) $CH_3-CH=CH_2$
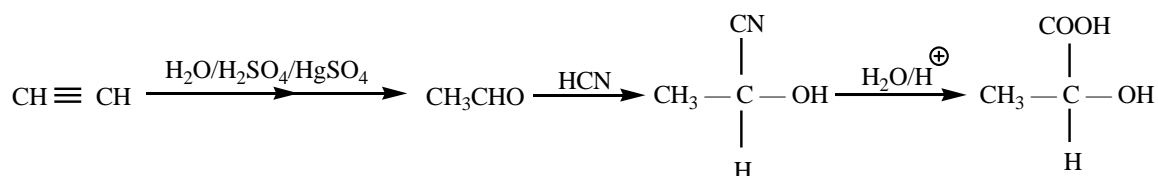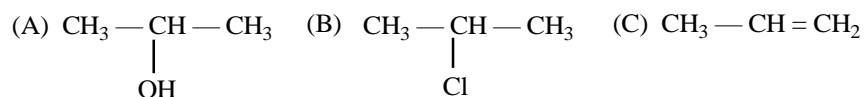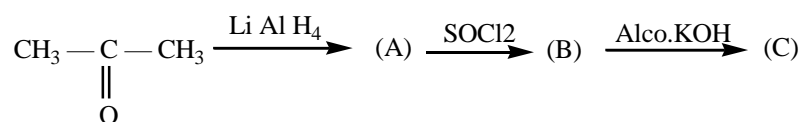
7. How did you distinguish formaldehyde from acetaldehyde?

Q.3. Complete the following reactions.

1. Identify A, B and C In the following: -

(A)   (B)   (C)
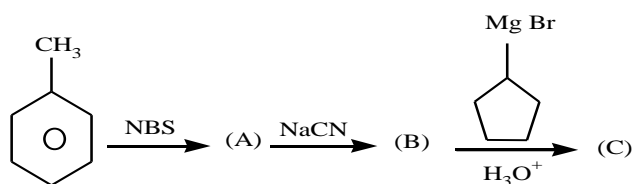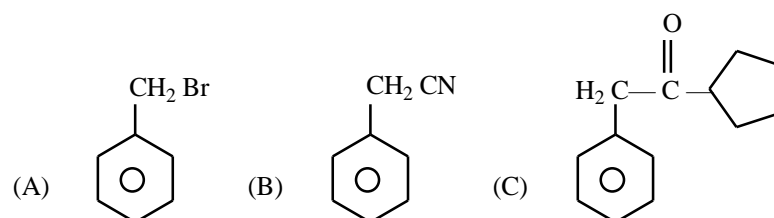
2. Arrange the following in increasing extent of hydration.
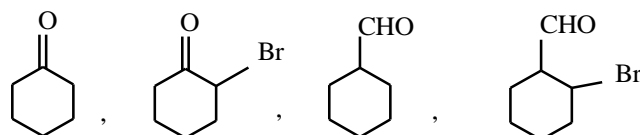
Ans – hydration increases with increasing H-bonding.
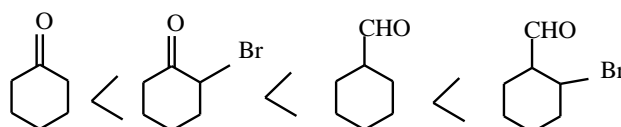
3.
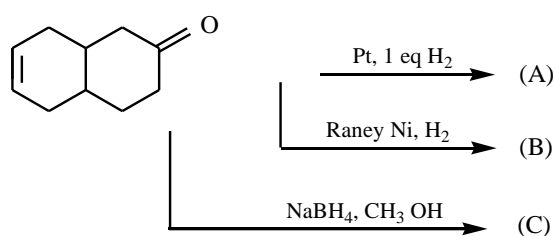
    Identify (A), (B) and (C)

Ans –

(A) is

(B) is

(C) is
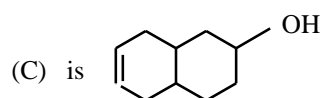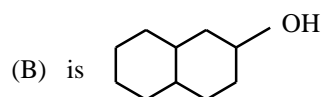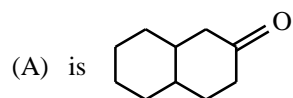
4.   Compound A, having the empirical formula C_7H_8 is chlorinated in sunlight to give a product which is hydrolysed to produce B. B after oxidation reacts with acetic anhydride in the Perkin reaction to produce an acid C which has an equivalent weight of 148. Give the name and structure of A, B and C.

Ans –

Toluene   Benzyl chloride   Benzyl alcohol

Benzaldehyde   Cinnamic acid
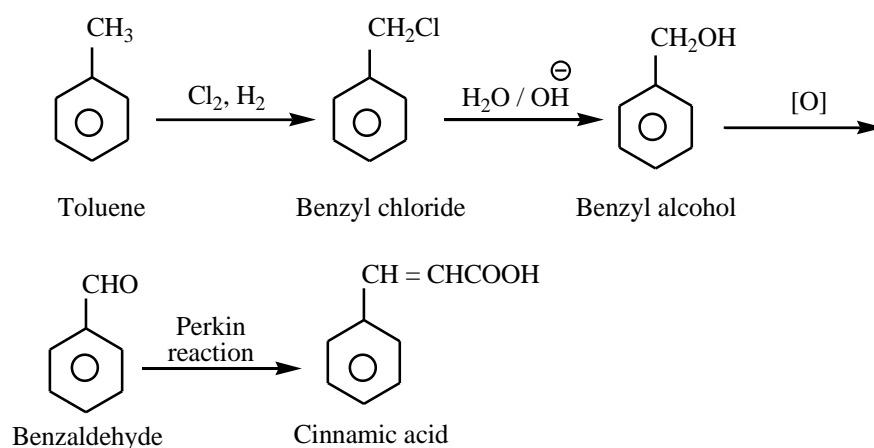
8.10 REFERENCES

1.   I.L Finar Organic Chemistry. Vol. 2., 5th edition, ELBS & Longman group Ltd., 1974.

2.   R.T. Morrison and R.N. Boyd Organic Chemistry, 6th edition, Prentice Hall Private Ltd, 1997.

3.   Organic Chemistry by Clayden, Greeves, Warren and Wothers 2nd edition 2012, Oxford University Press

4.   Jagdamba Singh and L.D.S. Yadav, Organic Chemistry vol. I, 8th edition-2013 Pragati Prakashan Pub.

5.   F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry, Plenum Pub. 5th Edition, 2007

6.   S.M. Mukherji and S.P. Singh, Reaction Mechanism in Organic Chemistry Trinity Press, 2016.

7.   B.S. Bahal, A. Bahal. Advanced Organic Chemistry. S. Chand & Company Ltd. Ram Nagar, New Delhi 1993

BLOCK-III

UNIT -9 THERMODYNAMICS-II

CONTENTS:

1.1   INTRODUCTION

The first law summarizes our experience regarding the transformation of energy. It states that (i) the different form of energy is inter convertible and (ii) when one form of energy disappears, an equivalent amount of energy of another kind must appear. But there some limitations of the first law. The first law does not indicate whether the change would at all occur and, if it occurs, to what extent. It also does not indicate the direction in which the change would take place.

Few examples are listed below:

1.   Suppose two bodies A and B are brought in contact of each other. Then according to first law, according to first law q amount of heat is lost by A, exactly q amount of heat will be gain by B or vice versa. First law does not indicate which body A or B will lose the heat. For this to know the direction of flow of heat we need another information, namely temperature of A and B.

2.   The dissociation of PCl_5 takes place in the following equilibrium

$$PCl_5 = PCl_3 + Cl_2:$$

The first law tells us only that if q amount of heat be evolved in the direct process in the dissociation of pentachloride, then in the opposite reaction of combination of trichloride and chlorine exactly q amount of heat would be absorbed. If we have an arbitrary mixture of PCl_5, PCl_3 and Cl_2, we cannot ascertain from the first law alone there would be dissociation of pentachloride or not. To determine the direction in which the chemical change would occur, we require the knowledge of the equilibrium constant of the reaction.

3.   The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, the second law of thermodynamics.

These examples illustrate the insufficiency of the first law. To ascertain the direction of a chemical or physical process we need something more beyond first law; before we can state second law of thermodynamics in a usable form, we must define some terms.

9.2 OBJECTIVES

After reading this unit you will able to the; -

- As we know thermodynamics concern itself with the flow of heat and it deals with relation between heat and work.

- The science of thermodynamics governs not only the transformation of heat or any other form of energy into work but also all types of interconversions of one kind of energy into another.

9.3 IRREVERSIBLE OR SPONTANEOUS PROCESSES

Changes taking place in a system without the aid of any external agency is termed as spontaneous processes several examples of such processes can be given. Some of these are follows.

(i) Water flows downhill spontaneously. We cannot reverse the direction of flow without some external aid

(ii) Suppose a vessel containing a gas at higher pressure P_1 be connected by a tube to another vessel where the pressure is less say P_2; $(P_1 > P_2)$. Now the gas would spontaneously move from the higher pressure to lower pressure. The process will continue until the two pressures are equalized. The process is unidirectional i.e., irreversible. When equilibrium is attained, the gas, by itself, will not rush back to the first vessel to increase the pressure to its original higher value.

(iii) If a bar of metal is hot at one end and cold at the other and, heat flows spontaneously from the hot end to the cold end until the temperature of the rod become uniform throughout. The process cannot be reversed. Our experience does not show that a metal bar having uniform temperature can become hot at one end and cold at another end spontaneously.

(iv) Electricity flows spontaneously flows from a point at higher potential to a point at a lower potential. The direction of flow of current can be reversed only by applying an external field to the opposite direction.

(v) Metallic copper is deposited with evolution of heat when copper sulphate solution is brought in contact with zinc, and the reaction continues until the chemical equilibrium is attained.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

The above reaction can be reversed only by passing electrical current between a copper rod and a zinc rod immersed in aqueous zinc sulphate. But electrical energy is required to do so will be more than the heat energy in the direct reaction.

9.4 CRITERIA OF SPONTANEITY

Some important criteria of spontaneous physical and chemical changes are given below.

(i)　　A spontaneous reaction is one way or unidirectional, for reverse change to occur, work has to be done.

(ii)　　For a spontaneous change to occur time is no factor. A spontaneous reaction may take place rapidly or very slowly.

(iii)　　If the system is not in equilibrium state, a spontaneous change is inevitable. The change will continue till the system attains the state of equilibrium.

(iv)　　Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed. To take the system away from equilibrium, some work must be done on the system.

(v)　　A spontaneous change accrues by decrease of internal energy or enthalpy. In addition to enthalpy an additional factor, entropy is also responsible for spontaneity.

The second law of thermodynamics which is formulated to record our experience about the direction of change may be therefore be stated as;

"All spontaneous processes are irreversible." Or we may also say **"All spontaneous processes tend to equilibrium."**

We may continue our attention to a specific case, namely the flow of heat as in our illustration 1.3(iii) we can express our experience by the statement given by Clausius.

"Heat itself will not flow from a lower to a higher temperature."

Or　　more elegantly stated; by Kelvin-Plank

"It is impossible for a self-acting machine unaided by any external agency, to convey heat from a body at a low temperature to one at a higher temperature."

9.5 SECOND LAW OF THERMODYNAMICS

We have studied in the previous unit (1.4) the basis of the second law for the guidance of a process in a definite direction. It is also a human experience that when every form of energy, including mechanical work, has a natural tendency to be transformed into thermal energy. The thermal energy shows no natural indication to be transformed into any other form. Only through the introduction of some mechanism, or machine, we can convert heat into other forms. Even then this conversion occurs to a limited extent and not completely.

Since heat is readily available, a good deal of human ingenuity is employed to find out the conditions and circumstances under which it would be possible to change heat into work.

The guidance as to the conditions under which heat changes into the direction of work would obviously come under the second law. For this reason, in enunciating second law we often find statements refer to the conversion of heat into work. It is now known that two conditions must be fulfilled to utilize heat into useful work.

1.   A mechanism commonly called the thermodynamic engine, is essential. Without the aid of an engine the conversion of heat into work is impossible. Further the engine must work in a reversible cyclic process.

2.   The engine must operate between two temperatures. It will take up heat at a higher temperature, convert a portion of it into work and give up the rest of the heat to a body at lower temperature.

Now suppose we have an engine, a cylinder with piston containing $\mathcal{X}$ gm moles of an ideal gas, at temperature T same as that of surroundings. Let the gas expands isothermally from a volume V_1 to volume V_2. There will be no change in internal energy, as the gas is ideal. The heat absorbed from the surroundings will be completely converted into work dw(=$\mathcal{X}$RTlnV_2/V_1) in accordance with the first law. Here in this case q quantity of heat from the surroundings is completely converted into work w. but when this has been achieved, the external agency (the engine), has suffered a change in volume from V_1 to V_2.

It is thus an experience that complete conversion of heat into work is impossible without leaving a permanent change elsewhere.

If we want to repeat the performance, the gas must be made to come back to its original volume and pickup heat a gain from the surroundings during expansion. To bring the gas to its original volume V_1 from V_2, we must perform isothermal work of compression equal to $\mathcal{X}$ RTln $\frac{V_2}{V_1}$, the same work that we obtained before. The net result is that the engine, working in a cycle at a temperature same as that of source of supplier of heat, would produce no work. Thus under isothermal conditions no engine can convert heat into work. That is why we cannot run our tramcars or motorcars with the heat of surrounding air, or we cannot utilize vast amount of ocean-heat to move our ships.

If we could produce a machine which could continuously take up heat from the reservoir and convert it partially or fully into work, we could achieve what is called the perpetual motion of second kind. Suppose we install a machine in our drawing room, which

would take up heat from the air of the room and do mechanical work (say, run a fan). The air will automatically cool from the loss of heat. Hence no supply of electric energy from the electric supply company would be needed. All attempts to produce such a perpetual motion machine of second kind have failed.

Ostwald said "It is impossible to construct a perpetual motion machine of the second kind."

"It is impossible to construct a machine operating in cycles that will convert heat into work without producing any other changes in the surroundings." This is Plank's statement of second law.

According to Clausius: "It is impossible to construct a heat engine which will continuously abstract heat from a single body and convert the whole of it to work without leaving changes in the working system."

Some statements of second law have been given in 1.4.

9.6 HEAT ENGINES

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of suitable device.

A machine which can do work by using heat that flows out spontaneously from a higher temperature source to a low-temperature sink, is called an engine.

A heat engine takes heat energy from a body of high temperature (reservoir) and converts some of it into work, returning the unconverted heat to a body of a low-temperature (sink). A basic heat engine is illustrated in Fig 9.1. A steam engine is a typical heat engine.
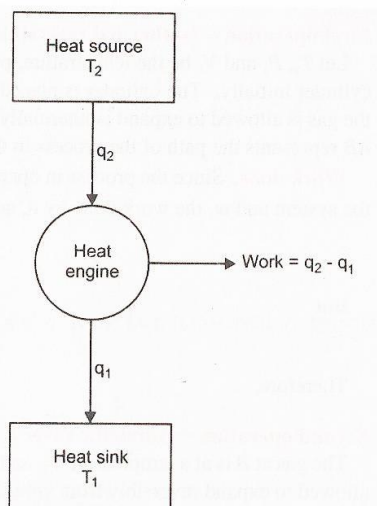
It takes heat from the boiler (high-temperature source) convert some heat to work and return the unused heat to the surroundings (low temp sink).

A heat engine running on a periodic cyclic process can yield work continuously.

9.7 CARNOT CYCLE

The brilliant French engineer Sadi Carnot in 1824 explained clearly how and to what extent work is obtainable from heat. Carnot started with two essential pre-requisites. Firstly, to estimate the work obtained from heat during its passage from higher to a lower temperature, the external agency (the engine) must come back to its original state so as to exclude any work involved in its change. That is, the engine must operate is complete cycles. Secondly, to obtain maximum work in a cycle of operation, every step should be carried out reversibly.

The typical Carnot's cycle consists of four hypothetical successive operations using one gm mole of a perfect gas as the working substance. We take gas enclosed in a cylinder fitted with a frictionless piston. To start with, the cylinder containing the gas is kept in a large thermostat at a higher temperature T_1 (source) and suppose volume of the gas be V_1. Then we proceed with the following operations.

  1. Isothermal reversible expansion
  2. Adiabatic reversible expansion
3. Isothermal reversible compression
4. Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle fig 9.2
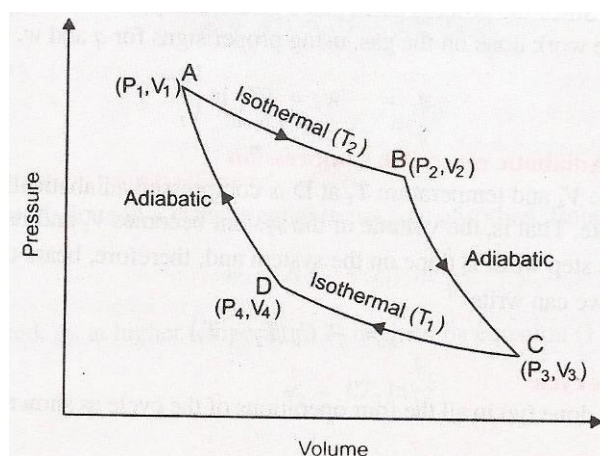
Fig 9.2 Indicator diagram of Carnot cycle

9.7.1   First operation-Isothermal reversible expansion:

Let T_2, P1 and V_1 be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature (T_2). Now the gas is allowed to expand isothermal and reversibly so that volume increases from V_1 to V_2. A B represents the path of the process in the diagram.

Being isothermal process $\Delta E=0$. If q_2 be heat absorbed by the system and w_1 the work done by it, according to first law of thermodynamics   ($\Delta E = q-w$).

$$q_2 = w_1$$

$$\text{but } w_1 = RT_2 \ln \frac{V_2}{V_1}$$

hence $q_2 = RT_2 \ln V_2/V_1$ ………..9.1

9.7.2   Second Operation-Adiabatic reversible expansion:

The gas at B is at a temperature T_2 and volume V_2 under the new pressure P_2. The gas now is allowed to expand adiabatically and reversibly from volume V_2 to V_3 when the temperature drops from T_2 to T_1 (along BC).

The process is adiabatic q=0. If w_2 be the work done, according to the first law equation ($\Delta E=q-w$),

$$\Delta E = - w_2$$

$$\text{or } w_2 = - \Delta E$$

But $\Delta E = -C_V (T_1-T_2)$

Therefore $w_2 = C_V (T_2-T_1)$ ..…9.2

9.7.3 Third operation- isothermal reversible compression:

Now the cylinder is placed in contact with a heat reservoir at a lower temperature T_1, the volume of the gas is compressed isothermally and reversibly from V_3 to V_4 (respectively by CD in diagram).

Now during compression, the gas produces heat, which is transferred to the low temperature reservoir. Since the process takes place isothermally, $\Delta E=0$, if q_2 is the heat

given to the reservoir and w_3, the work done on the gas, using proper sign for w and q, we have

$$-q = -w_3 = RT_1 \ln V_4/V_3 \qquad \dots\dots\dots 9.3$$

9.7.4 Fourth operation- Adiabatic reversible compression:

The gas with volume V_4 and temperature T_1 at D compressed adiabatically along DA until it regains the original state. That is volume of the system becomes V_1 and temperature T_2.

In this process the work is done on the system and, therefore, bears negative (-ve) sign.

It is denoted by w_4, we can write

$$-w_4 = -w(T_2-T_1) \qquad \dots\dots\dots 9.4$$

Adding up the work done(w) in all the four operations of the cycle as shown in equation (9.1), (9.2), (9.3) and (9.4) we have

$$W = w_1 + w_2 + (-w_3) + (-w_4)$$

$$= RT_2 \ln V_2/V_1 + C_V(T_2-T_1) + RT_1 \ln V_4/V_3 - C_V(T_2-T_1)$$

$$= RT_2 \ln V_2/V_1 + RT_1 \ln V_4/V_3 \qquad \dots\dots 9.5$$

If q is the net heat absorbed in the whole cycle

$$q = q_2-q_1$$

$$= RT_2 \ln V_2/V_1 - RT_1 \ln V_4/V_3 \qquad \dots\dots 9.6$$

For adiabatic changes for points B and C

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1} \qquad \dots\dots 9.7$$

For points A and D

$$T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1} \qquad \dots\dots\dots 9.8$$

Dividing equation 9.7 by equation 9.8

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

or $\qquad \frac{V_3}{V_4} = \frac{V_2}{V_1}$

substituting the value in equation 9.6 we have

q $= RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$

$= R(T_2-T_1) \ln \frac{V_2}{V_1}$ ……9.9

9.7.5 Calculation of efficiency:

Since total work done in a cycle is equal to net heat absorbed, from equation 9.9 and 9.5 we can write

W= $R(T_2-T_1) \ln V_2/V_1$ …..9.10

The heat absorbed, q_2 at higher temperature T_2 is given by the equation 9.1,

$q_2 = RT_2 \ln V_2/V_1$ …..9.11

Dividing 1.10 by 1.11

$w/q_2 = R(T_2-T_1) \ln (V_2/V_1)/ RT_2 \ln (V_2/V_1)$

$= (T_2-T_1)/T_2$ ..…. 9.12

The term w/q_2 is called thermodynamic efficiency of engine. It is denoted by η and gives the fraction of the heat taken from the high-temperature reservoir which it is possible to convert into work by a heat engine. The larger the temperature difference (T_2-T_1) between the high and low temperature reservoirs, the more the heat converted to work by the heat engine.

Now $w/q_2 = (T_2-T_1)/T_2 = \Delta T/T_2$

or w= $q_2\Delta T/T_2$ …………..9.13

This relation expresses the maximum amount of work obtainable from the heat flowing from T_2 to T_1, this is then the mathematical form of the second law.

The following points are to be noted.

(i)   Between two given temperatures, only $\Delta T/T_2$ fraction of the total heat supplied at T_2 is obtainable as work.

(ii)   W=q_2, only when T_1=0. That is if the engine works between absolute zero and a higher temperature, complete conversion of heat into work would be possible. Since working at 0^0K cannot be realized in practice, the complete transformation of heat into work is impracticable; the efficiency is thus always less than unity.

(iii) The efficiency of the engine depends only on the temperature of the source and sink (eqn 1.12). For a given source, the lower the temperature of the sink the greater will be the yield of work. Very often the sink is at the room temperature. In such a case, for greater output of work, the temperature of source should be high. This is the reason for using high pressure steam in boilers for production of power.

(iv) When $T_2 = T_1$, work w becomes zero. No work is available by operating an engine under isothermal conditions.

Example:

A Carnot engine working between 0^0C and 100^0C takes up 840 joules from high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

(a) Work done: $w = q_2 \, \Delta T/T$

$$= 840 \times 10^7 \frac{100}{373} = 2.25 \times 10^9 \text{ ergs}$$

(b) Heat rejected: $q_1 = q_2 \, T_2/T_1$

$$= 840 \times 273/373 = 6.14 \times 10^9 \text{erg}$$

(c)   Efficiency η: $= \frac{T_2 - T_1}{T_2} = \frac{100}{373} = 0.268$ or

η = work done/Total amount of heat absorbed from source

$$= 2.25 10^9 / 8.14 \times 10^9 = 0.268$$

9.8 THE CARNOT THEOREM

According to equation 9.12 the efficiency of an engine working reversibly depends only on the temperature of the source and the sink. It is independent of that nature of the substance or substances used for operations.

Two important deductions are easily arrived at on the assumptions of the validity of the second law. These deductions comprise Carnot theorem. The theorem states working between the same temperature limits.

(i) a reversible engine is more efficient than an irreversible one and

(ii) all reversible engines are equally efficient.

We can establish them in the following way.

To establish them we proceed in the following way.

(i)   Suppose we have an irreversible engine I and a reversible engine R. Let us assume that efficiency of I is greater than that of R, i.e., $\eta_I > \eta_R$. This means that if a source supplies same quantity of heat to both the engines, greater amount of work will be obtained from I than R. suppose the engines operate between the source at temperature T and sink at temperature T'. Now the energy changes with the two engines would be as follows as shown in Fig 9.3
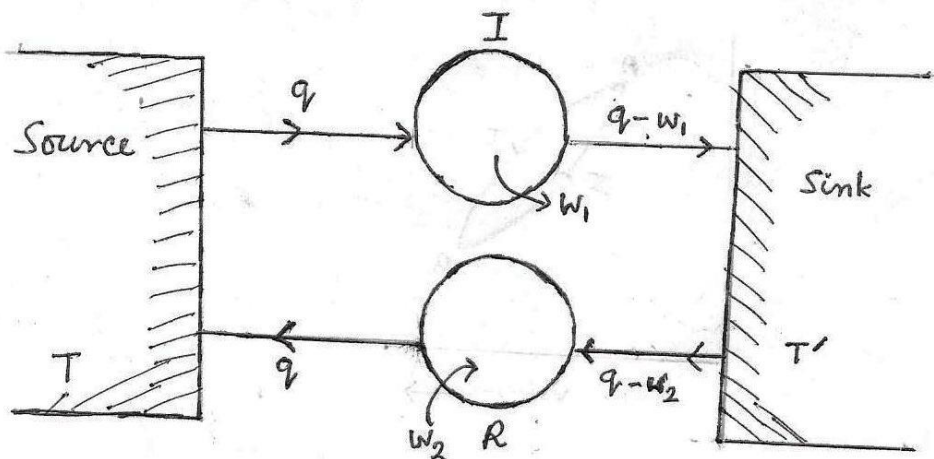
Fig 9.3 Comparison of efficiency of two engines.

Engine I		**Engine R**	
Heat supplied by source	q	Heat supplied by source	q
Work performed	w_1	work performed	w_2
Heat rejected to sink	$q-w_1$	Heat rejected to sink	$q-w_2$
We know $w_1 > w_2$ hence		$q-w_1 < q-w_2$	

Now let us carry out a cyclic process in which engine I would perform the forward process. It will be supplied with heat q from the source it will yield w_1 work and reject the rest of the heat to the sink. The reverse process will be done by the engine R which taking up heat $q-w_2$ from the sink and having w_2 units of work done on it, would return heat q to the source. In this cyclic process, the source has not ultimately lost any heat. The sink has suffered a heat loss. $(q-w_2) - (q-w_1)$. The coupled engine has yielded work= w_1-w_2, which is equal to heat lost by the sink. That means we have been able to convert completely the heat taken from the sink at the lower temperature fig 9.4. This is contrary to the second law and is improbable.

Hence efficiency of the reversible engine cannot be less than the efficiency of the irreversible one.

(ii)   Second part of the theorem can also be proved in a similar way. Suppose two reversible engines R_1 and R_2 work between the source (T) and sink (T`) let us assume one of the engines, say R_1 is more efficient than R_2. As before, let us couple the two engines to carry out a cyclic process. The engine R_1 takes up heat q from the source, yields work w_1 and rejects ($q-w_1$) heat to the sink, while the engine R_2 perform the opposite process taking ($q-w_2$) units of heat from the sink, with w_2 units of work done on it, and returning heat a back to the source. Since $\eta_{R1} > \eta_{R2}$, therefore $w_1 > w_2$. At the completion of the cyclic process the source has not lost any heat. The net result is that w_1-w_2 units of work has been produced. There is a loss of ($q-w_2$) – ($q-w_1$) = w_1-w_2 units of heat from the sink. The heat of the lower temperature sink is thus completely converted into work, which is against the second law. Thus, engine R_1 cannot be more efficient than R_2. Similarly, R_2 also cannot have greater efficiency than R_2. That is, both engines are equally efficient. Hence, all reversible engines working between the same temperatures must be equally efficient.

9.9 THERMODYNAMIC SCALE OF TEMPERATURE

Ordinarily the measurement of temperature is based on some property of the thermometric substance, such as linear or volumetric expansion, electrical resistance etc. There is one difficulty in such measurements. The variation in the property studied is not the same for different substances nor is it regular in different ranges of temperature. Thus, a constant-volume nitrogen thermometer will record a somewhat different value from that of the constant-volume helium thermometer for measuring T_1/T_2, the ratio of temperatures of two given reservoirs.

We have seen that the efficiency of the reversible engine is dependent only on the temperature of the source and the sink and is in dependent of the materials used. Hence

$$\eta = w/q$$

$$= (T_2-T_1)/T_2$$

$$\text{or} \quad (q_2-q_1)/q_1 = (T_2-T_1)/T_2$$

$$\text{or} \quad q_2/q_1 = T_1/T_2$$

Where q_2 and q_1 are the heat received from the source at T_2 and rejected to the sink at temperature T_1 respectively, T_2 and T_1 being expressed in ideal gas scale.

Kalvin proposed that a knowledge of heat (q_2) absorbed from the source and heat (q_1) rejected to the sink in a Carnot's engine would enable us to define the ratio of the temperature of the two reservoirs. Thus, we would be able to define a scale of temperature independent of any property of substance as q_2 and q_1 are independent of the materials used in the engine. It would then be a thermodynamical scale of measurement in which the principle of thermometry is being really replaced by that of calorimetry.

Let us take three reservoirs A, B and C in decreasing order of temperatures. Let us also denote by the symbol, τ, a quantity which is measure of the temperature or degrees of hotness of reservoirs fig 9.4
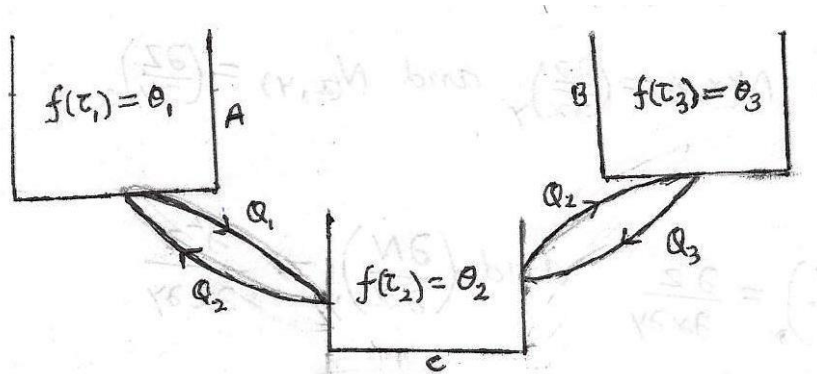
Fig 9.4 Thermodynamic scale of temperature

Now suppose a reversible Carnot's engine works between the boths A and B, receiving q_1 heat from A and rejecting q_2 heat to B then the ratio q_1/q_2 will be function of temperature of A and B, i.e., function of τ_1 and τ_2.

So, $q_1/q_2 = F(\tau_1.\tau_2)$ ……9.14

If we have now second Carnot's engine working between B and C taking heat q_2 from B and rejecting q_3 heat to C, then, as before,

$q_2/q_3 = F(\tau_2.\tau_3)$ 9.15

When these two engines are coupled together to work between A and C, naturally we have

$q_1/q_3 = F(\tau_1.\tau_3)$.… 9.16

dividing 12.16 by 12.15 we get

$$q_1/q_2 = F(\tau_1,\tau_3)/F(\tau_2,\tau_3) \qquad\qquad \text{.....9.17}$$

comparing 9.14 and 9.17

$$F(\tau_1,\tau_2) = F(\tau_1,\tau_3)/F(\tau_2,\tau_3) \qquad\qquad \text{......9.18}$$

The left-hand side of this equation does not contain τ_3 which occurs on the right-hand side. This is possible only when the function F is a ratio having identical forms in both the numerator and denominator.

i.e., $\qquad\qquad F(\tau_1,\tau_3) = f(\tau_1)/f(\tau_3) \qquad$ and $F(\tau_2,\tau_3) = f(\tau_2)/f(\tau_3)$

then we have $F(\tau_1,\tau_2) = F(\tau_1,\tau_3)/F(\tau_2,\tau_3)$

$$= \frac{f(\tau 1)}{f(\tau 3)} \cdot \frac{f(\tau 3)}{f(\tau 2)} = f(\tau_1)/f(\tau_2)$$

Hence from 1.14 $\qquad \dfrac{q1}{q2} = \dfrac{f(\tau_1)}{f(\tau_2)}$

Let this undermined function $\int(\tau)$ represent the temperature in these new thermodynamics scale and let it be denoted by θ then $q_1/q_2 = \theta_1/\theta_2$, where are the temperature in the thermodynamic scale of reservoirs A and B respectively and these do not depend on any property of the working substance of the engine.

Since $q_1/q_2 = \theta_1/\theta_2$ then, $(q_1-q_2)/q_1 = (\theta_1-\theta_2)/\theta_1$

or $\eta = (\theta_1-\theta_2)/\theta_1$, i.e., if $\theta_2=0, \eta = 1$

the ratio of the thermodynamic scale has been defined to be the temperature of the sink working down to which the engine would completely convert heat into work. Similarly, in Carnot cycle also

$$\eta = (T_1-T_2)/T_1, \text{ i.e.,} \qquad \text{if } T_2=0, \eta = 1$$

Hence the zero in the two scales are also identical. To honour this fundamental contribution of Lord Kelvin, the thermodynamic scale is called Kelvin Scale, with symbol ^0K. It relates the centigrade scale as, $0^0K=-273.16C$ and $273.16\ ^0K= 0^0C$.

9.10 SUMMARY

In this unit we have studied the:-

- Limitations of first law of thermodynamics and hence the need of second law. In nature all processes are spontaneous and all spontaneous processes tend to equilibrium.

- Flow of heat from high temperature to low temperature region is a spontaneous process. If we stall a device say an engine to obtain work when heat flows from high temperature to low temperature comes under second law of thermodynamics.

- Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work.

- Although the reversible cyclic processes are merely theoretical and imaginary, but the concept is highly useful in deriving certain important relationships.

9.11 TERMINAL QUESTIONS

A. Objective type questions:

1. For an adiabatic process:

(a) T=constant   (b) q =0   (c) q =constant   (d) w=0

2. The tendency of a process to occur naturally is called

(a) Momentum of the reaction   (b) spontaneity of the reaction

   (b) Equilibrium of the reaction   (d) capacity of a reaction

3. The efficiency of a heat engine operation between 400K and 300K is:

   (a) 0.25   (b) 1.0 (c) 0.75   (d) 0.50

B. Short answers type questions:

4.   What is a cyclic process? Explain.

5.   Write a note on Carnot Theorem.

6.   Give two statements of second law of thermodynamics.

C. Long answer type questions:

7. What is meant by efficiency of an engine? Derive expression for the same.

8. (a) What do you understand by the term enthalpy?

(b) "It is not profitable to carry out a process reversibly though maximum work can be obtained by doing so". Comment on the statement.

9.   (a) Derive a relation between pressure and volume for an adiabatic reversible expansion of an ideal gas.

        (c) Write a note on spontaneous reactions.

9.12. ANSWER

1. (b) 2. (b) 3. (a)

Source of study material

1. Principles of Physical Chemistry. By Puri, Sharma, Pathania

2. Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl G.D. Tuli

3. Physical Chemistry by P.C. Rakshit

Books recommend for further study

1. Physical Chemistry By Adkins

2. Thermodynamics By P.C. Rakshit

3. Thermodynamics for chemists By S Glasstone

UNIT -10 CONCEPT OF ENTROPY

CONTENTS:

10.1 INTRODUCTION

In unit-1 you have studied spontaneous processes. All natural processes are spontaneous and irreversible. In spontaneous processes there is decrease of internal energy or enthalpy. It implies that only such reaction will occur which are exothermic. But the melting of ice and evaporation of water are endothermic processes which proceed spontaneously (in exothermic processes heat is released and in endothermic processes heat is absorbed.) Clearly, there is some other factor in addition to ΔH which governs spontaneity. If is the second law of thermodynamics which introduces this new factor called entropy.

10.2 OBJECTIVES

After dealing with this unit learners will be able to: -

* In this unit learners will understand the basic concepts of the spontaneity and randomness, Concept of entropy, Definition of entropy.
* After that they will be able to the entropy change in isothermal expansion of an ideal gas, Entropy changes in reversible and irreversible processes, Physical significance of entropy
* In the middle part of this unit, they will be able to the entropy of mixture of ideal gases, Entropy of mixing, Entropy as a measure of the disorder of the system, Entropy as a measure of probability, Clausius inequality and Work function and free energy function
* And end of this unit learnes will be able to the, Gibb's Helmholtz equation, Clausius Clapeyron equation and Application of clausius-Clapeyron's equation

10.3 SPONTANEITY AND RANDOMNESS

Careful examination shows that in processes like melting of ice and evapouration of water, there is an increase of randomness or disorder of the system. The water molecule in ice is arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganized and can move more freely. The movement of molecules becomes freer still when the water evaporates into space and now, they can roam about throughout the entire atmosphere. In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

The efficiency of an engine is given by the relation

$$\eta = (q_1 - q_2)/q_1 = (T_1 - T_2)/T_1 \qquad \dots\dots 10.1$$

q_1 is the amount of heat absorbed at temperature T_1 from the source and q2 is the amount of heat rejected at temperature T_2 to the sink.

This equation can be rearranged in the following form.

$$1-q_2/q_1 = 1-T_2/T_1 \qquad ……..10.2$$

Equation 2.2 may also be written in general form.

$$q_{rev}/T = constant \qquad ………10.3$$

Where q_{rev} is the quantity of heat exchanged in a process carried out reversibly at a temperature T. It may be noted that each step in the Carnot cycle is considered to be carried out reversibly. This is an important generalization since the quantity q_{rev}/T represents a definite quantity, which is state function, is the entropy change of the system.

10.3.1 Concept of entropy

The equation 10.2 has been derived by assigning positive sign to heat absorbed (q_2) and negative sign to the heat given out (q_1) by the system. Describing q_1 and q_2 merely as heats exchanged (may be evolved or absorbed). Then equation 10.2 can be written as

$$q_1/T_1 + q_2/T_2 = 0 \qquad …………10.4$$

Thus, when the isothermal and adiabatic processes in a Carnot cycle are carried out, reversibly, the summation of q/T terms is equal to zero.

Let there is a cyclic process carried out reversibly which consists of a series of Carnot cycles. In this cyclic process the change from the state A to state B and back to A is carried out reversibly as shown in Fig 10.1
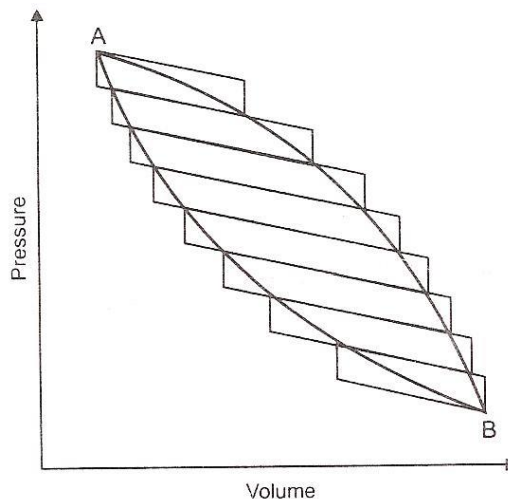
Fig 10.1 Reversible cycle

The path ABA may be considered to comprise of a number of small Carnot cycles, i.e., of a series of isothermals and adiabatic as shown in the figure. If each isothermal and adiabatic change is made extremely minute, i.e., each Carnot cycle is made extremely small by increasing their number, the path inside the loop cancel one another and the cycle corresponds to continuous curve ABC. Thus, any reversible cycle can be regarded as being made up of infinite number of small Carnot cycles.

For each Carnot cycle $\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$, it follows that in the case of the reversible cycle ABA, comprising of series of Carnot cycles, the summation term takes the form.

$$\sum \frac{q}{T} \qquad\qquad \text{……10.5}$$

When the changes are infinitesimal, the above equation can be put as,

$$\sum dq/T = 0 \qquad\qquad \text{……10.6}$$

Since the cycle is performed in two steps, viz., from a A to B and back from B to A, it follows that

$$\sum dq/T = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \qquad\qquad \text{…….10.7}$$

The integral $\int_A^B \frac{dq}{T}$ is the summation of all the dq/T terms when the system changes from A to B along the path I and $\int_B^A \frac{dq}{T}$ is the summation when the system returns from state B to the original state A along path II.

From equation 2.7

$$\int_A^B dq/_T = - \int_B^A dq/_T$$

or $\qquad\qquad \int_A^B dq/_T \ (path\ I) = \int_A^B \frac{dq}{T} \ (path\ II) \qquad \text{……10.8}$

It follows from equation 2.8 that $\int_A^B dq/_T$ is a definite quantity independent of the path followed for the change and depends only upon the initial and final states of the system. This quantity, therefore like ΔE and ΔH, should represent the change in some single-valued function of the states A and B of the system. This function is called entropy and is denoted by the symbol S. if S_A is the entropy of the system in state A and S_B entropy in the final state B, then the change in entropy, ΔS is given by the equation.

$$\Delta S = S_B - S_A = \int_A^B dq/_T \qquad \text{......10.9}$$

For each infinitesimal change,

$$dS = dq/T \qquad \text{.....10.10}$$

At constant temperature, for a finite change dS becomes ΔS and dq becomes q

$$\text{Hence } \Delta S = q/T \qquad \text{.....10.11}$$

It may be emphasized that since entropy is a state function, the change of entropy (ΔS) for the change of state from A to B will invariably be the same whether change is reversible or not. However, mathematically, it can be given by the equation

$$\Delta S = \int_A^B dq/_T \qquad \text{........10.11}$$

Only when the change has been brought reversibly. This is because the above equation has been derived from Carnot cycle in which all the changes are brought about reversibly.

10.3.2 Definition of entropy

In the above discussion gives only the physical definition of entropy. But classical thermodynamics does not require a physical explanation of the concept of entropy. All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.

In 1850 Clausius introduced a numerical definition of entropy. According to him entropy of a system (not undergoing physical or chemical changes), is a constant quantity when there is no communication of heat. When heat (q) flows into a system at temperature T, the entropy increases by q/T. Heat flowing out of a system produces a corresponding decrease. The entropy could be precisely defined as:

For a reversible change taking place at fix temperature T, the entropy change ΔS is equal to heat energy absorbed or evolved divided by the temperature T.

$$\text{That is,} \qquad \Delta S = q/T \qquad \text{............10.12}$$

If heat is absorbed than ΔS will be positive and there will be increase in entropy. If heat is evolved, ΔS will be negative and there is decrease in entropy. From second law in transfer of heat certain portion of energy (available energy) is used for work. The remaining energy is called unavailable energy which is related with the entropy.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

10.3.3 Unit of entropy

Since entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of calories per degree per mole i.e., cal mole^{-1}K^{-1} in entropy units eu. In the SI system, the units are joules per mole per degree, i.e., J mole^{-1}K^{-1}. These are represented by EU.

$$1 \text{ eu} = 4.184 \text{ EU}$$

10.3.4 Standard entropy

We know that the entropy of a pure crystal is zero at absolute zero because there is most orderly arrangement of particles (or least disorder). Therefore, it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above K^0. It is often referred to as standard entropy.

Substance	Entropy, $S°$		Substance	Entropy, $S°$	
	cal mol^{-1} K^{-1}	J mol^{-1} K^{-1}		cal mol^{-1} K^{-1}	J mol^{-1} K$^-$
Ag (s)	41.32	172.9	H$_2$ (g)	31.21	130.6
AgCl (s)	58.5	24.5	H$_2$O (g)	45.11	188.7
Al (s)	6.77	28.3	H$_2$O (l)	16.72	69.96
Al$_2$O$_3$ (s)	12.19	51.0	HCl (g)	44.62	186.7
C (s, graphite)	0.58	2.4	HNO$_3$ (l)	37.19	155.6
CO (g)	47.30	197.9	H$_2$SO$_4$ (l)	37.5	157.0
CO$_2$ (g)	51.06	213.6	Hg (l)	18.2	76.1
CH$_4$ (g)	44.50	186.2	K (s)	38.30	160.2
CH$_3$OH (l)	30.3	126.8	KCl (s)	57.24	239.5
CO(NH$_2$)$_2$ (s)	25.0	104.6	K$_2$SO$_4$ (s)	42.0	176.0
C$_2$H$_2$ (g)	48.0	200.8	N$_2$ (g)	45.77	191.5
C$_2$H$_6$ (g)	54.85	229.5	NH$_3$ (g)	46.01	192.5
Ca (s)	36.99	154.8	Na (s)	36.72	153.6
CaCO$_3$ (s)	22.2	92.9	NaCl (s)	17.30	72.88
Cl$_2$ (g)	53.29	223.0	O$_2$ (g)	49.0	205.0
Fe (s)	6.5	27.0	S (s)	7.62	31.9
Fe$_2$O$_3$ (s)	21.5	90.0	SO$_2$ (g)	59.40	248.5

Table 10.1 Standard entropies of some substances (25^{0}C, 1 atm)

The absolute entropy of a substance at 25^{0}C (278K) and one atmosphere pressure, is called the standard entropy; S^0

The absolute entropy of elements is zero only at 0K in a perfect crystal, and standard entropies of all substances at any temperature above 0K always have positive values Table 2.1 shows standard entropies of some elements and compounds. Entropy is an extensive

property. Its value therefore, depends upon the amount of the substance involved. it is necessary, therefore, to make a mention of the quantity of the substance taken. This quantity usually taken as one mole.

10.4 ENTROPY CHANGE IN ISOTHERMAL EXPANSION OF AN IDEAL GAS

In isothermal expansion of an ideal gas carried out reversibly, there will be no change in the internal energy, i.e., $\Delta E=0$ and hence from first law equation $\Delta E=q-w$

$$q_{rev} = w \qquad \dots 10.13$$

In such a case, the work done in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T, is given by

$$q_{rev} = nRT\ln V_2/V_1 \qquad \dots 10.14$$

now, $\Delta S = q_{rev}/T$

hence, $\Delta S = \frac{1}{T} nRT\ln V_2/V_1$

$$= nR\ln V_2/V_1 = nR\ln P_1/P_2$$

$$= 2.303nR\log V_2/V_1 = 2.303nR\log P_1/P_2 \qquad \dots 10.15$$

Solved problems

Question 1:

Calculate the entropy change involved in thermodynamic expansion of two moles of an ideal gas from a volume 5 litres to a volume 50 litres isothermally at 303K

Solution: Formula $\Delta S_T = 2.303$ nlog V_2/V_1

$$= 2.303 \times 2 \times 8.314 \log 50/5$$

$$= 2.303 \times 2 \times 8.314 \log_{10}$$

$$= 38.22 JK^{-1}$$

Question 2:

Calculate the entropy change involved in the evaporation of one mole of water at 100^0C. latent heat of evaporation of water is 9650 cals per mole.

Solution:

Formula $\Delta S = H_v/T$

$H_v = 9650$ cals

$T = 273+100^0 = 373K$

Hence ΔS $= 9650/378$

$= 25.87$ cal K^{-1} mole^{-1}

10.5 ENTROPY CHANGES IN REVERSIBLE AND IRREVERSIBLE PROCESSES

Consider isothermal expansion of an ideal gas at constant temperature into vacuum. This will, evidently proceed spontaneously, i.e., irreversibly. Since there is no opposing force, the work done (w) by the system will be zero. Further, since there is no change in temperature during the process, there will be no change in the internal energy of the system, i.e., $\Delta E=0$ hence from first law equation q=0, i.e., no heat absorbed or evolved in the process. In other words no heat is supplied to or removed from the surroundings. The entropy of the surroundings, therefore, remains unchanged.

Now entropy of a system is a function only of the state of the system, i.e., its temperature and pressure (or volume) and is independent of previous history of the system. In the process under consideration, the volume of the gas increases, say, from V_1 to V_2 at constant temperature T. hence, entropy increase of the system considering that one mole of the gas is involved, would be given by

$\Delta S= Rln(V_2/V_1)$ ……………10.16

The total increase in entropy of the system and its surroundings during the spontaneous process of expansion considered above is, thus, Rln V_2/V_1. Since $V_2>V_1$ it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surrounding considered together.

Now let us consider isothermal expansion of the ideal gas from V_1 to V_2 carried out reversibly at the same temperature T. the expansion is carried out infinitesimally slowly, i.e., the pressure on the frictionless piston is so adjusted that is remains always less than that of the gas by an infinitesimal small amount. In this case, the gas does some external work given

by $w = -P\Delta V$. consequently, an equivalent amount of heat (q_{rev}) is absorbed reversibly by the system from the surroundings at temperature T, hence increase in the entropy of the system is q_{rev}/T.

The heat lost reversibly at temperature T given by surroundings is also q_{rev}. hence decrease in the entropy of the surroundings is q_{rev}/T.

Giving proper sign, giving positive for increase and negative for decrease of entropy, the net entropy change of the system and its surroundings is

$$q_{rev}/T - q_{rev}/T = 0 \qquad \text{.......10.17}$$

Thus, in the reversible isothermal expansion of the gas, the total entropy changes of the system and surroundings considered together is zero.

Hence net conclusion is that:

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together while in the thermodynamically reversible process; entropy of the system and its surroundings taken together remains unchanged.

Thus mathematically we can express

$$(\Delta S_{sys} + \Delta S_{sur}) = 0 \qquad \text{for reversible processes}$$

$$\Delta S_{sys} + \Delta S_{sur}) > 0 \qquad \text{for irreversible processes}$$

Combining these two, we have

$$\Delta S_{sys} + \Delta S_{sur} \gtreqless 0 \qquad \text{.........10.18}$$

Where equal to sign refers to a reversible process and greater than sign refers to an irreversible process.

We can state equation 10.18 as follows:

In a reversible process, the entropy of the system and the surroundings taken together remains constant while in an irreversible process, the entropy of the system and the surroundings taken together increases.

This statement is of great importance as it helps us to predict whether a given process can take place spontaneously or not, i.e., whether it is thermodynamically feasible or not.

Since all processes in nature occur spontaneously, i.e., irreversibly, it follows that the entropy of the universe is increasing continuously. This is another statement of second law of thermodynamics.

The essentials of the first law and second law of thermodynamics were thus summed up by Clausius as follows:

The energy of universe remains constant and the entropy of the universe tends to maximum.

10.6 *PHYSICAL SIGNIFICANCE OF ENTROPY*

Entropy is a measure of disorder or randomness of a system. The entropy of the system increases if it goes from orderly state to disorderly state. This concept of entropy has led to the conclusion that all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy. At this state, all motions ceases. In case of a perfect crystal the entropy is zero. This is third law of thermodynamics.

10.6.1 Entropy changes of an ideal gas with change in P, V and T

Since entropy of a system varies with the state of a system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. since T is taken generally as one of the variables, the second variable to be considered may be V or P. thus the two variables to be considered are either T and V or T and P.

10.6.2 Variation of entropy with temperature and volume

Let us consider one mole of an ideal gas occupying volume V, pressure P and temperature T. the increase in entropy of the gas in absorbing dq amount of heat reversibly at temperature T is given by

$$ds = dq_{rev}/T \qquad \ldots\ldots\ldots\ldots 10.19$$

According to the equation of first law of thermodynamics

$$dq_{rev} = dE + PdV$$

putting the value of dq_{rev} in equation 10.19 we get

$$ds = \frac{dE + PdV}{T} \qquad \ldots\ldots 10.20$$

we know PV=RT   (for one mole of the gas)

$$P = RT/V$$

and $\quad C_V = \dfrac{dE}{dT} \quad$ or $\qquad dE = C_V dT$

C_V is molar heat capacity at constant volume.

$$ds = [C_V dT + (RT/V)\, dv]/T$$

$$ds = C_V dT/T + R\, dV/V \qquad\qquad …10.21$$

Integrating the above equation from initial state when temperature is T_1 and volume is V_1 to final state when temperature is T_2 and volume is V_2 assuming C_v to be constant with in temperature range T_1 and T_2 we have

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{c_V\; dT}{T} + R \int_{V_1}^{V_2} dV/V \qquad …..10.22$$

Thus $\Delta S = S_2 - S_1 = C_V \ln T_2/T_1 + R\ln V_2/V_1 \qquad …..10.23$

For n moles of an ideal gas the above equation can be written as

$$\Delta S \qquad = nC_V \ln T_2/T_1 + nR \ln V_2/V_1 \qquad …..10.24$$

$$= 2.303 C_V \log T_2/T_1 + 2.303 nR \log V_2/V_1 \qquad …..10.25$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperature.

Case I:

At constant temperature for an isothermal process $T_1 = T_2$ then from equation 10.23

$$\Delta S_T \qquad = R\ln V_2/V_1$$

$$= 2.303 R \log V_2/V_1$$

$$= 2.303 \log P_1/P_2 \qquad \text{(As } P_1 V_1 = P_2 V_2\text{)}$$

In an isothermal expansion $V_2 > V_1$ or $P_1 > P_2$ hence ΔS_T is positive whereas in isothermal contraction $V_2 < V_1$ and $P_1 < P_2$ then ΔS_T will be negative.

and for n moles

$$\Delta S_T \qquad = nR\ln V_2/V_1$$

$$= 2.303 nR \log V_2/V_1$$

Thus subscript T in ΔS_T indicates that temperature remains constant during the process.

Case II:

At constant volume (i.e., isochoric process) the equation 2.23 reduces to:

$$\Delta S_V = C_V \ln T_2/T_1$$

$$= 2.303 \, C_V \log T_2/T_1$$

for n moles:

$$\Delta S_V = nC_V \ln T_2/T_1$$

$$= 2.303 \, n \, C_V \log T_2/T_1$$

The subscript V in ΔS_V indicates that volume remains constant during the process. It follows that increase in temperature of an ideal gas at constant volume is accompanied by increase of entropy.

10.6.3 Variation of entropy with temperature and pressure

We have from equation 2.23

$$\Delta S = C_V \ln T_2/T_1 + R \ln V_2/V_1 \qquad \ldots 10.23$$

If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$$P_1 V_1 = RT_1 \quad \text{for one mole of the gas in the initial state}$$

$$P_2 V_2 = RT_2 \quad \text{for one mole of the gas in the final state}$$

Then $V_2/V_1 = P_1 T_2/P_2/T_1$

Substituting this value of V_2/V_1 in equation 10.23 we get

$$\Delta S = C_V \ln T_2/T_1 + R\ln (P_1 T_2)/(P_2 T_1)$$

$$= C_V \ln T_2/T_1 + R \ln P_1/P_2 + R \ln T_2/T_1$$

$$= (C_V + R) \ln T_2/T_1 - R \ln P_2/P_1$$

$$= C_P \ln T_2/T_1 - R \ln P_2/P_1 \qquad \ldots\ldots 10.26$$

for n moles we have

$$\Delta S = nC_P \ln T_2/T_1 - nR \ln P_2/P_1 \qquad \ldots\ldots 10.27$$

$$= 2.303 \text{ n } C_P \log T_2/T_1 - 2.303 \text{ nR } \ln P_2/P_1 \quad \ldots 10.28$$

It is evident from the above equation that the entropy change for the change of state of an ideal gas depends upon the initial and final pressure as well as on the initial and the final temperature.

Case I:

At constant pressure, i.e., when process is isobaric $P_1=P_2$ then equation 2.26 reduces to,

$$\Delta S_P = C_P \ln T_2/T_1$$

$$= 2.303 \text{ } C_P \log T_2/T_1$$

and for n moles

$$\Delta S_P = nC_P \ln T_2/T_1$$

$$= 2.303 \text{ n } C_P \log T_2/T_1$$

Evidently increase in temperature of an ideal gas at constant pressure is accompanied by increase in entropy.

Case II:

When temperature remains constant then,

$$\Delta S_T = -R \ln P_2/P_1 = R \ln P_1/P_2$$

$$= 2.303 \text{ R } \log P_1/P_2$$

$$= 2.303 \text{ R } \log V_2/V_1$$

and for n moles

$$\Delta S_T = 2.303 \text{ n R } \log P_1/P_2$$

$$= 2.303 \text{ n R } \log V_2/V_1$$

$$\text{as } P_1V_1 = P_2P_2 \text{ so } P_1/P_2 = V_2/V_1$$

10.6.4 Entropy changes accompanying change of phase

From solid phase to liquid phase:

Let us consider a case when a solid changes into liquid state at its fusion point. The process requires heat for this purpose, known as heat of fusion.

Consider melting of one mole of a substance reversibly at the fusion point T_f, at constant pressure. Let ΔS_f be the molar heat of fusion. The entropy changes of the process, ΔH_f, will then be given by

$$\Delta S_f = \Delta H_f/T \qquad \text{……..} \quad 10.29$$

10.6.5.   From liquid phase to vapour phase:

Suppose one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b, under a constant pressure. Let ΔH_V be the molar heat of vapourisation. The entropy change accompanying the process will then be given by

$$\Delta S_V = \Delta H_V/T \qquad \text{…..} 10.30$$

Since ΔH_f and ΔH_V are both positive, the processes of fusion and vapourisation are both accompanied by increase of entropy?

If we consider the change of state from vapour to liquid or from liquid to solid, then ΔH_V and ΔH_f will both be negative and hence the process of condensation of vapour or freezing of a liquid would be accompanied by decrease of entropy.

Example 1:

Calculate the entropy change when one mole of ethanol is evaporated at 351 K. the molar heat of vaporization of ethanol is 39.84 K J mole^{-1}.

Solution: we know $\Delta S_V = \Delta H_V/T_b$

Hence $\Delta H_V = 39.84$ KJ mole^{-1}

$= 39840$ J mole^{-1}

and $T_b = 351$ K

then $\Delta S_V = 398.40/351$ C

$= 113.5$ J K^{-1} mole^{-1}

Example 2:

Calculate the entropy change in the melting of 1 Kg of ice at 0^0C. Heat of fusion of ice is 334.72 Jg^{-1}

Solution:

$$\Delta S_f \quad = \Delta H_f/T$$

$$= 334.72/273$$

$$= 1.226 \text{ J } K^{-1}g^{-1}$$

For one Kg change of entropy will be   1.226x1000

$$= 1226 \text{ } JK^{-1} \text{ } Kg^{-1}$$

10.6.6 Change of entropy from one crystalline form to another

The change in entropy when one mole of a solid substance undergoes change of state from one crystalline form (say, rhombic form) to another crystalline form (say, monoclinic form) at the transition temperature T_t, is given by

$$\Delta S_t = \Delta H_t/T_t$$

Where ΔH_t is the molar heat of transition of substance. Molar heat of transition is the amount of heat absorbed or evolved by one mole of a substance when it undergoes change to state from one crystalline form to another at the transition temperature.

10.7 ENTROPY OF MIXTURE OF IDEAL GAS

From equation 10.21 we have the reaction for entropy change for one mole of an ideal gas

$$dS = C_V dT/T + RdV/V$$

integrating this equation assuming that C_V remains constant for an ideal gas,

$$S = C_V \ln T + R \ln V + S_o \qquad\qquad ....10.31$$

where S_o is constant of integration

now $C_P - C_V = R$

so $C_V = C_P - R$

and $V = RT/P$

we have

$$S = (C_P - R) \ln T + R \ln(RT)/P + S_o$$

$$S = C_P \ln T - R \ln T + R \ln R \ln T - R \ln P + S_o \qquad \dots 10.32$$

$$= C_P \ln T - R \ln P + S`_o \qquad \text{where } R \ln R + S_o = S`_0, \text{ another constant.}$$

Entropy of a system consisting of a mixture of gases would evidently be given by the sum of the individual entropies of the constituents at pressure (or concentrations) existing in the mixture. If n_1 and n_2 are the number of moles of two gases present in the mixture and p_1 and p_2 are their partial pressure, then entropy of the mixture is given by

$$S = n_1 (C_P \ln T - R \ln p_1 - S`_o) + n_2 (C_P \ln T - R \ln p_2 + S`_o) \qquad \dots 10.33$$

The partial pressure of p_1 of an ideal gas is given by the expression

$$p_1 = x_1 P \qquad \dots 10.34$$

Where x_1 is mole fraction of that particular gas in the mixture and P is total pressure.

Substituting for p_1 and p_2 in equation 10.33 we get

$$S = n_1 (C_P \ln T - R \ln x_1 P + S`_o) + n_2 (C_P \ln T - R \ln x_2 P + S`_o)$$

$$= n_1 (C_P \ln T - R \ln x_1 - R \ln P + S`_o) + n_2 (C_P \ln T - R \ln P + S`_o) \qquad \dots 10.35$$

This equation given entropy of mixture of two ideal gases.

Entropy of mixing:

Entropy of mixing is defined as the difference between the entropy of the mixture of gases and the sum of the entropies of the separate gases, each at a pressure P. Thus

$$\Delta S_{mix} = n_1 (C_P \ln T - R \ln x_1 P - R \ln P + S`_o) + n_2 (C_P \ln T - R \ln x_2 - R \ln P + S`_o)$$

$$- [n_1 (C_P \ln T - R \ln P + S`_o) + n_2 (C_P \ln T - R \ln P + S`_o)]$$

$$= -n_1 R \ln x_1 - n_2 R \ln x_2 \qquad \dots 10.36$$

$$\text{Now} \quad x_1 = n_1 / (n_1 + n_2) \qquad \text{(mole fraction of first gas)}$$

$$\text{and} \quad x_2 = n_2 / (n_1 + n_2) \qquad \text{(mole fraction of second gas)}$$

for a total of one mole of the gaseous mixture the entropy of mixing is given by

$$\Delta S_{mix} = -n_1/n_1 + n_2 \, R \ln x_1 - n_2/n_1 + n_2 \, R \ln x_2 \qquad \dots 10.37$$

$$\text{Hence} \quad \Delta S_{mix} = -x_1 R \ln x_1 - x_2 R \ln x_2$$

Since mole fraction x_1 or x_2 is a fraction, hence entropy of mixing is always positive. Hence entropy of mixing is always positive. Hence mixing of two or more gases is spontaneous process.

Example:

Calculate entropy of mixing of one mole of oxygen gas and one mole of hydrogen gas, assuming that no chemical reaction occurs and the gas mixture behaves ideally (R=8.3145 K^{-1}mole^{-1}).

Solution:

Here n_1= 1 mole and n_2=1 mole

Mole fraction of oxygen = 1/(1+1)=1/2=.50

and mole fraction of hydrogen = 1/(1+1)=1/2=.50

ΔS_{mix} = -R($n_1 \ln x_1 + n_2 \ln x_2$)

= -8.314(ln.50+ln.50)

= -8.314x2ln.50

= -8.314x2x2.303log ½

=-8.314x2x2.303 (-.3010)

= 11.523 JK^{-1}

10.8 ENTROPY AS A MEASURE OF THE DISORDER OF THE SYSTEM

We have already studied in the above discussion that all spontaneous processes, such as flow of heat from hot end to a cold end of a conductor, expansion of a gas in vacuum, diffusion of solute from a concentrated to a dilute solution, are accompanied by increase in the disorder of the system. Spontaneous processes are accompanied by increase in the entropy a well as increase in the disorder of the system.

We have also studied that melting of a solid or evaporation of liquid is accompanied by increase of entropy. At the same time, it is known that a solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in liquids and least in gases. Thus, increase of entropy implies increase in disorder.

Thus entropy is regarded as a measure of the disorder of a system.

10.9 ENTROPY AS A MEASURE OF PROBABILITY

The thermodynamic probability is the number of ways in which a given system in a specified thermodynamic state can be realized w is the probability of the system. S = f(w).

All spontaneous processes lead to increase in entropy and also increase in disorder. A little consideration will show that when a process is spontaneous it means that it is proceeding from a less probable to more probable state. It appears, therefore, that there is a close relation between entropy S and the thermodynamic probability W of the state of the system, both of which increase at the same time. This relationship was expressed by Boltsman as

$$S = k \ln W + \text{constant} \qquad \ldots\ldots.10.38$$

Where k is Boltzmann constant (=R/N)

According to Planck the constant in the above equation is zero. Hence

$$S = k \ln W \qquad \ldots\ldots.10.39$$

This equation is called Boltzmann entropy equation

A solid at absolute zero temperature is considered to be in most ordered state. In this case, evidently, W is unity and hence $S_o = 0$. The entropy of crystalline solids at absolute zero is, therefore, taken as zero.

10.10 CLAUSIUS INEQUALITY

Entropy changes in an irreversible cyclic process

Consider a cyclic process, similar to that of Carnot cycle in which one or more of its stages are performed irreversible. Let ABCD denote the cycle in figure 2.2 in which AB and CD are isothermal stages. Let us further suppose, the absorption of heat δq_1^* by the system at temperature T_1 from the source along AB is irreversible. The rest of the stages are carried out reversibly. The asterisk (*) would indicate the irreversibility, otherwise transformation is reversible. The heat δq_2 is given to the sink at temperature T_2 along CD.
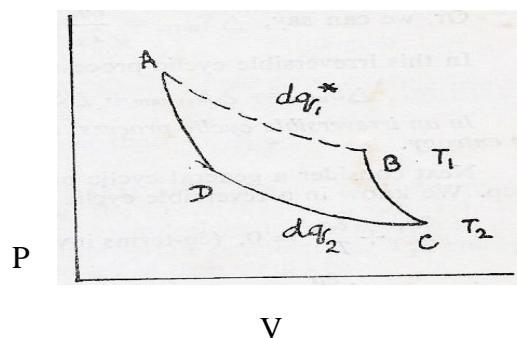
Fig 10.2 entropy change in irreversible cycle.

This is an irreversible cycle and hence the efficiency of the engine is less than that of the Carnot cycle, or,

$$(\delta^* q_1 - \delta^* q_2)/\delta^* q_1 < (T_1 - T_2)/T_1$$

$$or \ \delta q_2/T_2 < \delta^* q_1/T_1$$

When the cycle is completed, the engine has returned to its initial state

$$\Delta S_{system} = 0$$

Now consider the surroundings and find out the q/T terms. It is $- \delta^* q_1/T_1$ for the source and $\delta q_2/T_2$ for the sink.

Hence for the surroundings

$\sum q/T = \delta q_2/T_2 - \delta^* q_1/T_1$ which is from equation 10.5 is greater than zero, i.e., positive.

The heat change of sink is reversible. The heat $\delta^* q_1$ from the source was taken by the system irreversibly. The source has lost $\delta^* q_1$ and its entropy has decreased. The entropy-change of the source from A to B would be evaluated as stated earlier by supposing the loss of heat δq_1 occurred reversibly and consequently

$$\Delta S_{source} = - \delta^* q_1/T_1$$

Or we can say,

$$\Delta S_{surr} = \delta q_2/T_2 - \delta^* q_1/T_1 > 0$$

In this irreversible cyclic process, therefore

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = 0 + \Delta S_{surr} > 0$$

In an irreversible cycle process, there would occur a net increase in entropy.

Next consider a general cyclic process involving an irreversible step.

We know in a reversible cyclic process

$$= \delta q_1/T_1 + \delta q_2/T_2 = 0 \quad (\delta q\text{- terms involve their own signs})$$

i.e., $\qquad \oint \frac{\delta q}{T} = 0 \quad \text{(revesible)}$

in an irreversible cycle

$$(\delta q_1 - \delta q_2)/\delta q_1 < (T_1 - T_2)/T_1$$

Hence $\qquad\qquad\qquad q_1/T_1 + \delta q_2/T_2 < 0$

This is often referred as Clausius enequality.

10.11   WORK FUNCTION AND FREE ENERGY FUNCTION

The sum of the entropy changes of the system and surroundings ($\Delta S_{sys} + \Delta S_{surr}$) serves as a criterion of spontaneity or feasibility of a process. If total entropy change is positive, the process is feasible. If it is zero the system remains in a state of equilibrium. However, in order to decide about the feasibility of a process, we shall have to know the entropy change of the system as well as that of the surroundings. This is not always convenient. We may, therefore, consider entropy change in terms of other state functions which may be determined more conveniently. Two such functions are the work function A and free energy function or Gibbs free energy G. These two functions are such that they utilize entropy in their derivation. These are defined by the equations.

$$A = E-TS \qquad\qquad \text{….. 10.40}$$

$$G = H- TS \qquad\qquad \text{…..10.41}$$

As E, H and S are state functions hence A and G are also state functions. The exact nature of these functions will be clear from the following

10.11.1 Work function (A)

The work function A is defined as

$$A = E- TS$$

Let us consider a system which undergoes a change of state from (1) to (2) at constant temperature. As already discussed above A is a state function depends only on initial and final states.

$$A_1 = E_1 - TS_1 \qquad \text{......10.42}$$

and
$$A_2 = E_2 - TS_2 \qquad \text{.....10.43}$$

substracting 2.42 from 2.43 we get

$$A_2 - A_1 = E_2 - E_1 - T(S_2 - S_1)$$

or
$$\Delta A = \Delta E - T\Delta S \qquad \text{...….10.44}$$

10.11.2 Free energy function

By definition free energy function is given by the equation

$$G = H - TS$$

If the system change from initial state (1) to final state (2) then free equations can be written as

$$G_1 = H_1 - TS_1 \qquad \text{….10.45}$$

and
$$G_2 = H_2 - TS_2 \qquad \text{….10.46}$$

substracting equation 2.45 from 2.46 we get

$$G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$$

$$\Delta G = \Delta H = T\Delta S \qquad \text{…..…10.47}$$

10.11.3 Variation of work function with temperature and volume

We know work function is represented as

$$A = E - TS$$

Differentiation of this equation gives

$$dA = dE - TdS - SdT$$

but
$$dE = TdS - PdV \qquad \text{from final and second law of thermodynamics.}$$

$$dA = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT \qquad \text{.….10.48}$$

At constant temperature

$$dA_T = -PdV$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

And at constant volume

$$dA_V = -SdT$$

hence

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \dots..10.49$$

This relation is utilized for establishing Gibbs-Helmholtz relation.

10.11.4 Variation of free energy with temperature and pressure

By definition

$$G= H-TS$$

Since

$$H= E+PV$$

hence

$$G= E+PV – TS$$

upon differentiating

$$dG= dE+PdV+VdP-TdS-SdT \qquad \dots\dots10.50$$

For an infinitesimal stage of reversible process,

$$dq= dE+PdV \quad \text{(from first law of thermodynamics)}$$

Also

$$dq= TdS \qquad \text{(from second law of thermodynamics)}$$

Hence

$$TdS = dE+PdV \qquad \text{or} \qquad dE= TdS-PdV \qquad \dots.10.51$$

This equation is also known as combined equation of first and second law of thermodynamics as both the laws are included in it. Substituting the value of dE in equation 2.50 we get

$$dG \quad = TdS- PdV+PdV+VdP-TdS-SdT$$

$$= VdP-SdT \qquad \dots.10.52$$

At constant temperature

$$dG_T = VdP$$

or

$$\left(\frac{\partial G}{\partial T}\right)_T = V \qquad \dots..10.53$$

and at constant pressure

$$dG_P = -SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{......10.54}$$

This expression is useful in establishing Gibbs Helmholtz relation.

From equation 2.54

$$dG = VdP$$

Let the free energy of the system be G_1 at pressure P_1 and G_2 at pressure P_2 then integrating the above equation we get;

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \int_{P_1}^{P_2} dP/P$$

$G_2-G_1 = RT\ln P_2/P_1 = 2.303RT \log \frac{P_2}{P_1} = 2.303\ln \frac{V1}{V2}$ 10.55

Where V_1 and V_2 are the initial and final volumes respectively.

10.12 GIBB'S HELMHOLTZ EQUATION

These are the two equations derived by Gibbs and Helmholtz and are known as Gibbs-Helmholtz equations. One equation can be expressed in terms of changes in free energy (ΔG) and enthalpy (ΔH), while the other can be expressed in terms of changes in work function(ΔA) and internal energy (ΔE). The former is generally employed and is applicable to all processes, chemical or physical, but in a closed system. From equation 10.52

We know $dG = VdP - SdT$

At constant pressure

$$dG = -SdT$$

Let G_1 represent free energy of a system in its initial state at temperature T. suppose the temperature rises to T +dT where dT is infinitesimally small. Let the free energy at the new temperature be G_1+dG, then

$$dG_1 = -S_1 dT \qquad \text{.....10.56}$$

where S_1 is entropy in the initial state. Now suppose free energy of the system in the final state be G_2 at temperature T, and G_2+dG_2 is the free energy at temperature T+dT in the final state; then

$$dG_2 = -S_2 dT \qquad \text{.....10.57}$$

where S_2 is the entropy of the system is the final state.

Substracting 2.56 from 2.57 we get

$$dG_2 - dG_1 = - (S_2 - S_1)\ dT$$

$$d\ (\Delta G)\ = -\Delta SdT$$

as the pressure is constant, therefore,

$$\left(\frac{\partial}{\partial T}(\Delta G)\right)_P = -\Delta S \qquad \qquad ……10.58$$

We know $\qquad\qquad \Delta G = \Delta H - T\Delta S$

Hence $\qquad\qquad \Delta G = \Delta H + T\left(\frac{\partial}{\partial T}(\Delta G)\right)_P \qquad\qquad …….10.59$

This equation is known as Gibbs-Helmholtz equation. It is applicable to all processes occurring at constant pressure. It has been used for calculating the heat change ΔH for a process or a reaction taking place at constant pressure provided the values of free energy at two different temperatures are known.

10.13 CLAUSIUS CLAPEYRON EQUATION

An equation of fundamental importance which finds extensive application in one-component two-phase system was derived by Claucius and Clapeyron, from the second law of thermodynamics is known as Clausius Clapeyron equation.

The two phases in equilibrium may be any of the following types:

(i)   Solid and liquid   S $\rightleftharpoons$ L at the melting point of solid

(ii)   Liquid and vapour L $\rightleftharpoons$ V at the boiling point of liquid

(iii)   Solid and vapour S $\rightleftharpoons$ V at the sublimation temperature of solid

(iv)   One crystalline form to another crystalline form as rhombic sulphur to monoclinic sulphur.

$S_R \rightleftharpoons S_M$ at the transition temperature of the two allotropic forms.

In deriving the Clausius-Clapeyron equation we must keep in our mind that, when the system is in equilibrium there is no change in free energy. If water is in equilibrium with its vapour the free energy in water phase is equal to free energy in vapour pahse. In general,

equal amounts of a given substance must have exactly the same free energy in two phases at equilibrium with each other.

Consider the change of a pure substance from phase A to phase B in equilibrium with it at a given temperature and pressure. If G_A is free energy per mole of the substance in the initial phase A and G_B is the free energy per mole in the phase B, then since $G_B = G_A$, there will be no free energy change, i.e.,

$$\Delta G = G_B - G_A = 0 \qquad \text{.....10.60}$$

If temperature of such a system is raised, say from T to T+dT, the pressure will also have to change, say form P to P+dP, in order to maintain equilibrium.

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $G_A + dG_A$ and that in phase B, $G_B + dG_B$. since two phases are still in equilibrium, hence

$$G_A + dG_A = G_B + dG_B \qquad \text{......10.61}$$

From equation 2.60 and 2.61 we have

$$dG_A = dG_B \qquad \text{........10.62}$$

we know $dG = VdP - SdT$

then $dG_A = V_A dP - S_A dT$

and $dG_B = V_B dP - S_B dT$

From equation 2.62 we have

$$V_A dP - S_A dT = V_B dP - S_B dT \qquad \text{......10.63}$$

$$dP(V_B - V_A) = dT(S_B - S_A)$$

or $\frac{dP}{dT} = (S_B - S_A)/(V_B - V_A) \qquad \text{......10.64}$

It may be noted that V_A and V_B are molar volumes of the pure substance in the two phases A and B respectively.

From definition of entropy $T\Delta S = q$

or $S_B - S_A = \Delta S = q/T$

So   equation 2.64 becomes:

$$dP/dT = \frac{q}{T(V_B - V_A)} \qquad \text{.....10.65}$$

this equation is known as Clapeyron's equation

this equation gives change in pressure dP which must accompany the change in temperature dT or vice versa, in the case of a system containing two phases of a pure substance in equilibrium with each other. Suppose the system consists of water in two phases, viz., liquid and vapour in equilibrium with each other at temperature T, i.e.,

water (liquid) $\longleftrightarrow$ water (vapour)
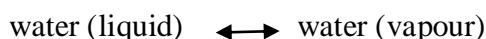
Then q= molar heat of 298aporization ΔH_V

V_B = volume of one mole of water in the vapour phase, say, V_g

V_A = volume of one mole of water in the liquid phase, say V_l

and T will be boiling point of water say T_b

then equation 2.65, will take the form

$$dP/dT = \frac{\Delta H_V}{(V_g - V_l)} \qquad \text{....10.66}$$

The molar volume of a substance in the vapour state is considerably greater than in the liquid state. In the case of water, for example, the value of V_g at 100^0C is 18x1670=30060 ml while that of V_l is only a little more than 18 ml. Thus V_g-V_l can be taken as V_g without introducing any serious error. The Clapeyron's equation can be written as

$$dP/dT = \Delta H_V/T_g \qquad \text{....10.67}$$

Assuming that gas law is applicable, i.e., PV=RT or P=RT/P

Hence $\qquad\qquad$ $dP/dT = P\Delta H_V/RT^2 \qquad$ 10.68

$\qquad$ or $\qquad\qquad$ $dP/P = \Delta H_V/RT^2 \, dT$

$\qquad$ or $\qquad\qquad$ $d(\ln P) = (\Delta H_v/RT^2)/dT$

Assuming that ΔH_V, remains constant over a small range of temperature, we have

$$\int d\ln P = \frac{\Delta H_V}{R} \int \frac{dT}{T^2} \qquad \text{....10.69}$$

On integrating between limits of pressure P_1 and P_2 corresponding to temperature T_1 and T_2, we get

$$\int_{P_1}^{P_2} d\ln P = \frac{\Delta H_V}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln P_2/P_1 = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \qquad \dots\dots 10.70$$

This integrated form of Clapeyron's equation is known as Clausius Clapeyron's equation.

10.13.1 Application of Clausius-Clapeyron's equation

(i)   Calculation of molar heat of vaporization

(ii)   Effect of temperature on vapour pressure of a liquid

(iii)   Effect of pressure on boiling point

(iv)   Calculation of molar elevation constant

(v)   Calculation of molar depression constant

10.14 SUMMARY

* As you have studied that first law of thermodynamics is law of conservation of energy. It does not tell us about the direction of the reaction.

* In second law you have studied the direction of a particular process by defining reversible (equilibrium) and irreversible (spontaneous) processes.

* A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together, while in a thermodynamically reversible process the entropy of the system and its surroundings taken together remains unchanged.

* By making use of entropy, we have introduced free energy function and work function. The free energy function is an important function as it gives an idea about feasibility of a reaction. If free energy remains constant the system will be in equilibrium, and if it is negative the process is feasible.

* Study of Gibbs-Helmholtz equation and Clausius-Clapeyron's equation are of importance for various calculations.

10.15 TERMINAL QUESTIONS

A. Objective type questions

1. An adiabatic process is an:

(a) isobaric process   (b) isochoric process

(c) isoenthalpic process   (d) isoentropic process

2. Mixing of two or more gases is a:

(a) spontaneous process   (b) non-spontaneous process

(c) reversible process   (d) none of these

3. The change in entropy of a reaction is given by:

(a) $\Delta S = \sum S_{reactants} + \sum S_{products}$ (b) $\Delta S = \sum S_{products} - \sum S_{reactants}$

(c) $I = \sum S_{reactants} - \sum S_{products}$ (d) none of these

4. The free energy function G is defined as :

(a) G=H+TS   (b) G=H-TS   (c) G=TS-H   (d) None of these

5. The change in free energy is measure of

(a) Net work done   (b) Net change in entropy   (c) Net change in enthalpy

(d) Net change in internal energy

A. Short answers type questions

1. Define entropy

2. Write a note on physical significance of entropy

3. Define expression for the entropy change accompanying variation of temperature   and
volume.

4. Show that entropy is a state function.

C. Long answer type questions

1. Discuss entropy change in reversible and irreversible processes. Comment on the statement
"entropy of the universe is always increasing".

2. Derive an expression for the entropy of a mixture of two ideal gases. Define from it an
expression for the entropy of mixing of two ideal gases.

3. Derive two important forms of Gibbs-Helmholtz relation. What are its important
applications.

4. (a) Write a note on Clasius-Clapeyron's relation.

   (b) Discuss the variation of Gibbs free energy function with temperature.

10.16 ANSWERS

1. (d)   2. (a)   3. (b)   4. (b)   5. (a)

Source of study material

1.   Principles of Physical Chemistry. By Puri, Sharma, Pathania

2.   Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl G.D. Tuli

3.   Physical Chemistry by P.C. Rakshit.

Books recommend for further study

1.   Physical Chemistry by Adkins.

2.   Thermodynamics by P.C. Rakshit

3.   Thermodynamics for chemists by S. Glasstone

UNIT: 11 PHASE EQUILIBRIUM-I

CONTENTS:

11.1 INTRODUCTION

Phase Equilibrium is an important tool of the quantitative treatment of heterogeneous system inequilibrium. The No. of phase that can exist in equilibrium depends upon the condition of temp,pressure and concentration of different phases.The phase rule can't be express in words. In a hetero generous system at equilibrium, the sum ofthe number of degrees of freedom and the number of phases is equal to the number of componentsplus two. Mathematically it defined as,F=C-P+2 Where C = Component, P= No. of Phases, F= No. of degree of Freedom.

11.2 OBJECTIVES

A system consists of parts which have different physical properties (sometime differentchemical properties) and which are separated by boundaries, the system is said to be heterogeneous. The equilibrium between different parts or phases usually explained by fourprinciples.

i. Nerest distribution law.

ii. Law of mass action.

iii. Clapyron equation

iv. Phase Rule

11.3 STATEMENT AND MEANING OF THE TERM

11.3.1 Phases

It is defined as a homogeneous part of a system which is physically and chemically different fromanother part also it is mechanically separable from other part of the system.Completely misciblegas and liquids form a singles phase while immiscible system give different phases i.e., solid +Liquid, solid +gas, have two components. Phases are denoted by P.

11.3.2 Components

The number of components of a system at equilibrium, the minimum number of independentvariable constitutions (chemical species) which are required to express quantitively

thecomposition of each and every phase either directly or in terms of chemical equation is calledcomponents or denoted by C. In the chemical equation negative and zero signs being permitted.

Example: (i) Water system consist of the equilibrium.

<div align="center">

Ice= Water = Vapour

(Solid) (Liquid)(Gasecus)

</div>
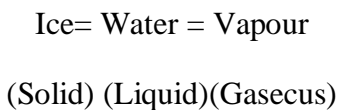
This system consists of one component only, i.e., it is a one component system because thecomposition of each of the three phases present can be directly expressed as H_2O

(ii) Sulphur system consisting of four phases- Monoclinic (s), Rhombic(s), Liquid (L) andvapors(g) is also one component system because the composition of each phase can be expressed

in term of one constituent sulphur.

The no. of component is calculated by

<div align="center">

C=S-E-R

</div>

Where S= Total No. of constituents or species

E= No. of equation representing equilibrium between the constituents

R= No. of restrictions for electrical neutrality.

Example:

<div align="center">

Na_2SO_4-H_2O

</div>

(a) Assuming no dissociation

S=2, E=0(No chemical reaction/equilibrium), R=0(No. restriction of electrical neutrality or material balance, C=S-E-R=2-0-0=2

Thus no. of components =2

(b) Assuming complete dissociation of the salt.

<div align="center">

S=3(Na^+, $SO_4^{2-}$and H_2O)

</div>

E=0, R=1(For electrical neutrality, $2Na^+= SO_4^{2-}$),   C=S-E-R=3-0-1=2, Thus no. of components=2

(c) Assuming dissociation of H_2O also.

S=6(Na_2SO_4, Na^+, SO_4^{--}, H_2O, H^+, OH^-)

E=2($Na_2SO_4 \rightarrow 2Na^+ + SO4^{--}$ and $H_2O \Rightarrow H^+ + OH^-$)

R=2($2Na^+ = SO_4^{2-}$ i.e. number of moles of Na^+ 2 X No. of moles of SO_4^{2-} and $H^+ = OH^-$)

C=S-E-R=6-2-2=2,   Thus no. of components=2

11.3.3 Degree of Freedom

It is defined as the no. of independent variables such as temperature, pressure and concentration which must be specified in order to define the system completely. It is denoted by F Greater the no. of component C, greater the degree of freedom F.

Greater the No. of phases P, smaller the number of degree of freedom F. Degree of freedom as also known as variance.

11.4 DERIVATION OF GIBBS PHASE RULE

Consider a heterogeneous system in equilibrium consisting of C "components distributed in Pphase, The Degree of freedom of the system are equal to the number of independent variableswhich must be fixed arbitrarily to define the system completely. The number of such variable isequal to the total number of variables minus the number of variables which are definedautomatically by virtue of the system being in equilibrium.At equilibrium, each phase has the same temperature and pressure, so there is one temperature variable and one pressure variable for the whole system. So, these variables totaltwo only. The number of composition (or concentration) variables, however, is much more. To define the composition of each phase, it is necessary to mention(C-I) compositionvariables, because the composition of the remaining component may be obtained by difference.For P phases, thus, the total number of concentration or composition variables will be P(C-1).

Total number of variables

= P(C-1) for composition + 1 for temperature + 1 for pressure

According to thermodynamics as derived in equation (3) (cf. 12.5), when a heterogeneous systemis in equilibrium, at constant pressure and temperature, the chemical potential (μ.) of any givencomponent must be the same in every phase. Therefore, if there is one component in three phasesx, y and z and one of these phases, say x is referred to as the standard phase, then this fact may berepresented in the form of two equations:So, for each component in equilibrium in three phases, two equations are known. Therefore, for each component in P phases, (P-1) equations are known. For C components, thusthe number of equations or variables that are known from the conditions of equilibrium are C (P-1).Since chemical potential is a function of pressure, temperature and concentration, each equation represents one variable.

Therefore, the number of unknown variables (which should be fixed) or degree of freedom,

F= number of variable- number of equations

$$F=[P(C-1+2]-[C(P-I)] \text{ or } F=C-P+2,\dots\dots\dots\dots ..11.1$$

This equation is the phase rule of Gibbs.

11.5 PHASE EQUILIBRIUM

A System is in equilibrium is the properties like temperature, composition etc. of the variousphases do not undergo any change with time.

It is of two types.

(i) True equilibrium (ii) metastable equilibrium

(i) True Equilibrium: It is defined as, If the same state can be achieved by approach from either direction. For example, theequilibrium between ice and water at I atm. Pressure and 0 0C is a true equilibrium, because itcan be attained by melting of ice or by freezing of water.

(ii) Metastable equilibrium: If the state of a system can be attained only from one direction and that too by very carefulchange of conditions. it is called a state of metastable equilibrium. For

example, water at 2 ^{0}Ccan be obtained only by very careful cooling of liquid water but not by melting of ice. Hence

water at -2 ^{0}C is said to be in a state of metastable equilibrium.

11.5.1 Criteria for phase equilibrium

Three equlibria exist in phase equilibria is a multi-component system.

(i) Thermal Equilibria: The temperature is every part of the system must be the same as otherwise heat may flow from one part of the system to another.Suppose a system consists of two phases A and B with temperature T_A and $T_B$respectively.

At equilibrium, let a small amount of heat dq. flows from phase A to phase B.

Then, Entropy change of phase A $(dS_A)= -\dfrac{dq}{TA}$

Entropy change of Phase B $(dS_B) =\dfrac{dq}{TB}$

So, Total entropy change of system

$$dS \;=\; \frac{dq}{T\,A} \;+\; \frac{dq}{TB}$$

The condition for equilibrium is terms of entropy change is (dS)E.V.=0

$$\text{i.e.} \quad -\frac{dq}{TA} \;+\; = \; \frac{dq}{TB} \;= 0, \text{or} = \; \frac{dq}{TA} \;+\frac{dq}{TB} \quad \text{or, } T_A = T_B$$

(ii) Mechanic Equilibrium:

The equilibrium is where the pressure in every part of the system must be the same otherwise, matter may flow form one part of the system to another. In an isolated systemcontaining two phases in equilibrium at constant volume and temperature.A small amount of matter flows from phase A to B so, that volume phase A decrease by smallvolume dV and volume of phase B increase by small volume dV.The pressures of the two phases are PA and PB respectively. So, change in Helmoltz free energy ofphase A(dA$_A$) = PA dv, Change in Helmoltz free energy of phase B(dA$_B$)= PBdV

But at equilibrium (dA)V.=0

$$dA = dA_A + dA_B = -P_A dV + P_B dV = 0 \text{ or } P_A = P_B$$

(iii) Chemical Equilibrium: At equilibrium, the chemical potential of any component in all thephases must be the same. This is called Thermodynamic criteria for phase equilibrium. For asolution (or phases containing several constituents, the chemical potential of any component is the increase of decrease of free energy that takes place, at constant temperature andpressure, for the addition or removal of one mole of that component, keeping the amount of all other components constant it is usually represented by 'μ')

11.6 PHASE EQUILIBRIUM OF ONE COMPONENT SYSTEM

Some of the one component system and their phase diagrams can be given as:

11.6.1 a. Phase diagram of water system

The system consists of three phases.

Ice (solid)⇌Water (liquid) + Vapour (gas)

(s)   (l) (g)
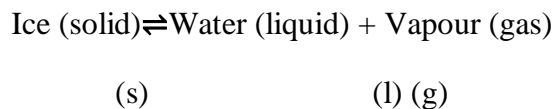
These three single phases may occur in four possible combinations in equilibrium as

(i) Liquid ⇌Vapour

(ii) Solid ⇌Vapour

(iii)Solid ⇌Liquid

(iv)Solid ⇌ Liquid ⇌Vapour
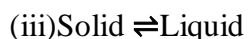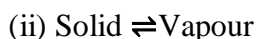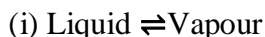
The number of phases that can exist in equilibrium at any point depends upon the conditionsof temperature and pressure. These conditions have been determined experimentally and aphase diagram is constructed by plotting pressure against temperature (Fig 11.1). The phasediagram consists of:

(i) Three stable curves OA, OB, OC and one metastable curve OA'

(ii) Three areas and

(iii)Definite point, O.

These are separately discussed as under:
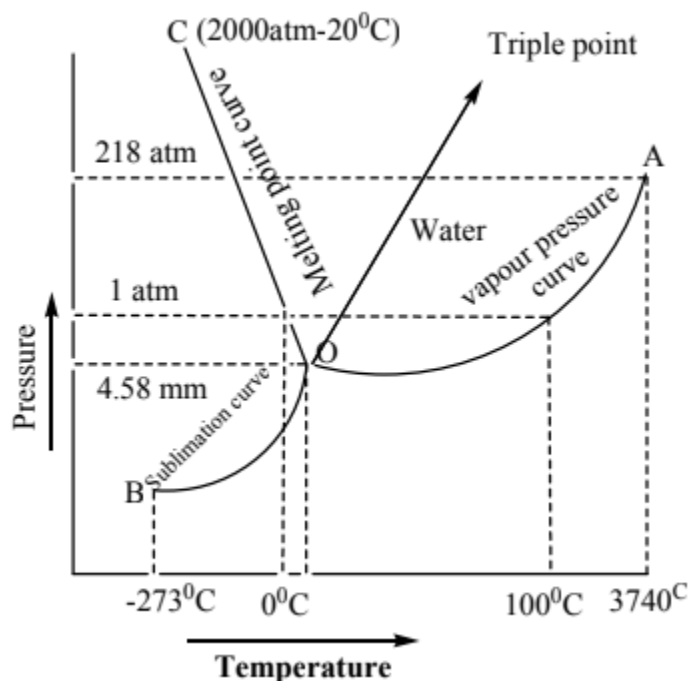
Fig. 11.1 Water System

(i) Cureves (i) OA. This is the vapour pressure curve of water. It represents the equilibrium betweenliquid water and vapour at different temperatures. At any point on the curve, the two phases arepresent. The curve starts from point O, the freezing point of water and ends at A, thecritical temperature (3740 °C) beyond which the two phases merge into each other. Considerany point on the curve. For a fixed value of pressure, the temperature has also a fixed value. if bykeeping the pressure constant, an attempt is made to raise the temperature then the liquidphase will disappear and if the temperature is lowered then the vapour phase will disappear, Thus,to define the system completely at any time, it is necessary to mention either temperature or

pressure. In other words, pressure being fixed. Therefore, water-vapour system is univariant,or it has one degree of freedom. It also follows from the phase rule equation.

$$F=C-P+2$$

$$F=1-2+2=1$$

(ii) OA. The dotted curve OA: a continuation of curve OA represents the vapour pressure curveof super-cooled water. It is a metastable curve. On being disturbed, the supercooled phase atonce changes to solid ice and the curve merges into OB.

(**iii) OB.** It is the sublimation curve or the vapour pressure curve of ice. It gives values oftemperature and pressure at which ice and vapours can exist together. It is obtained bystudying the effect of pressure on the freezing point of water. The curve starts from pointO, the freezing point of water and ends at B (-273^0C). As temperature decreases, the vapourpressure of ice tends to become negligible. We find that for a particular temperature, therecan be one and only one pressure value and vice versa. In other words, ice- vapour system isunivariant, or has one degree of freedom.

(iv)OC. It is melting point curve and represents the equilibrium between ice and liquid water atvarious pressures. In other words, It shows the effect of pressure on the melting point of ice.It should be noted that the line OC is inclined towards the pressure axis. The slope of thecurve OC indicates that melting point of ice is lowered by increase of pressure. Thereis, however, no limit for the curve OC. It goes up to a point corresponding to 2000atmospheresand -20^0C. At this point, one type of ice changes into another solid modificationbut the solid-liquid equilibrium remains.At any point on the curve OC, two phases (ice and liquid water) are present in equilibrium.

Hence the system is univariant, or the degree of freedom is one.

(**II) Areas:** The areas, i.e., the regions bounded by two lines give the conditions of temperatureand pressure under which the single-phase i.e., ice or liquid water or vapour is capable ofstable existence. Area below AOB has water vapour, BOC has ice and the area COA hasliquid water. These areas are bivariant because to locate any point in the area, temperature aswell as pressure must be fixed, thus indicating two degrees of freedom. This also followsfrom phase rule equation.

$$F=C-P+2$$

$$F=1-1+2=2$$

(III) Triple point: It is a point where the three curves OA, OB, OC meet. At this point, the threephases-ices, water and vapour are in equilibrium. It should be noted that it is only a pointindicating that there is only one set of conditions under which it is possible for the threephases to exist together. The point O is a self-defined point corresponding to the definitetemperature of 0.0098^0C and a definite pressure of 4.58 mm. If either pressure ortemperature is changed, then one of the three phases will disappear. Since on changingeither pressure or temperature one of the phases disappears, therefore, the system at point O has no degree of freedom, that is, it is invariant or nonvariant. The same result

follows from the phase rule equation.

$$F = C-P+2$$

$$F = 1-3+2 = 0$$

11.6.2. Phase diagram of carbon dioxide system

Phase diagram of carbon dioxide system resembles that of water system with some differences.The phase diagram for carbon dioxide system is shown in Fig.11.2. It has three distinct areas inwhich carbon dioxide can exist either as solid, liquid or gas.

Areas

The area on the R.H.S. of the curve ABD consists of the vapor phase. The area above the curve CBDconsists of the liquid phase while the area on the L.H.S. of the curve ABC consists of the solidphase.
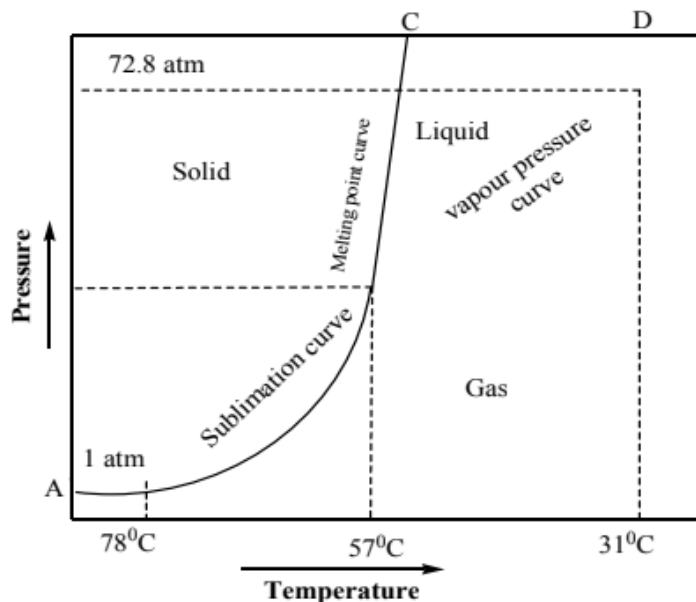
Fig 11.2 The phase diagram for the carbon dioxide system.

Curves:

AB is the sublimation curve along which solid carbon dioxide is in equilibrium with the gas. BDis the vaporization curve along which liquid carbon dioxide is in equilibrium with the gas. These curvesend at 31.1^0C, the critical temperature of CO2 and corresponding to a pressure of 72.8atmospheres. The curve BC is the fusion curve along which solid and liquid carbon dioxide arein equilibrium with each other.

Point:

B is the triple point at which all the three phases of carbon dioxide co-exist in equilibrium withone another. The temperature of the system at this point is -57^0C while the pressure is 5.2 atm. Aslight variation in temperature or pressure at this point may result in the disappearance of one ofthe two phase. For example, a slight increase in temperature will result in the disappearance ofthe solid phase and the equilibrium will shift along the curve BD while a slight decrease intemperature will result in the disappearance of the liquid phase and the equilibrium will shiftalong the curve BA. Keeping the temperature constant, if the pressure is increased, the gaseousphase will disappear and the equilibrium will shift along the curve BC.The phase diagram of carbon dioxide resembles that of water in showing three distinctareas for solid, liquid and gaseous phases. But it differs from the latter in several respects. In thefirst place, the melting

point slopes away from the pressure axis. This indicates that increase ofpressure raises the melting point of solid carbon dioxide.The second difference is that solid carbon dioxide can exist in equilibrium with its liquidonly at a very high pressure equal to 5.2 atm. This is unlike the water system in which ice andwater can exist in equilibrium even at a very low pressure equal to 4.58 mm of Hg (Refer tophase diagram of water).

The third difference is that the vapour pressure of solid carbon dioxide even at extremelylow temperature is very high and many times higher than that of ice.

11.6.3. Sulphur system

We can describe the sulphur system into following steps:Sublimation curve of rhombic sulphur, represented by AB curve. This curve AB gives the vapourpressure of rhombic sulphur at different temperature. Here, the two phases in equilibrium are (S_R - S_M) rhombic sulphur and its vapour, is monovarietal. Therefore, at one temperature, there can beone vapor pressure only. Point B is the transition temperature (95.6^0C) at which rhombicsulphur changes into monoclinic sulphur. B is thus a triple point at which three phase, two solidsand the vapour ($S_R - S_M - S_V$) coexist in equilibrium.Sublimation curve of monoclinic sulphur, represented by BC curve. The curve BC is thesublimation curve of monoclinic sulphur. It gives vapour pressure of monoclinic sulphur atdifferent temperatures. As the number of phase is 2, the system is monovarient. The point C isthe melting point (120^0C) of monoclinic sulphur. This is another triple point at which threephases, viz., monoclinic sulphur, liquid and vapour ($S_M - S_L - S_V$) are in equilibrium. This is anon – variant point.Vapour pressure curve of liquid sulphur, represented by CD curve. Here, the two phase ($S_L - S_V$)equilibrium is also monovarient.

Transition curve of rhombic sulphur to monoclinic sulphur, represented by BE curve. The BEcurve gives the effect of pressure on the transition temperature of rhombic sulphur intomonoclinic sulphur. The equilibrium involved along the curve is (S_R - S_M). Both the phases aresolid. The system is monovarient. Since transformation of rhombic into monoclinic sulphur isaccompanied by increase of volume, the increase of pressure causes a rise in the transitiontemperature.
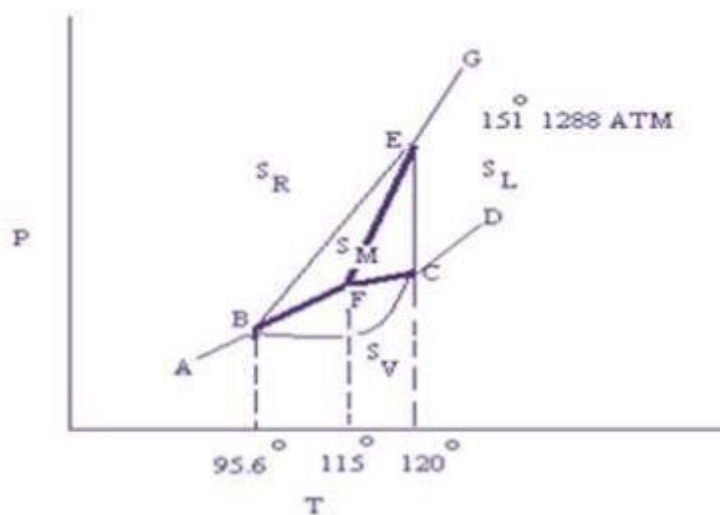
Figure 11.3 Sulphur System

Fusion curve of monoclinic sulphur, represented by CE curve. This gives the effect of pressureon the melting point of monoclinic sulphur. The two – phase equilibrium ($S_M – S_L$) along thecurve CE is univarient. As the melting point of monoclinic sulphur is accompanied by a slightincrease of volume, it follows from Clausius – Clapeyron equation that the melting point will riseslightly by the increase of pressure. The curve CE, therefore, slops slightly away from thepressure axis. As the slop of this curve is much less than that of the curve BE. The two curvesmeet at the point E. Thus, E is another triple point where three phases, viz., rhombic sulphurmonoclinic sulphur and liquid sulphur ($S_R – S_M – S_L$) are in equilibrium and the system is non– variant. At E, the temperature is 151^0C and the pressure is 1290atm.Fusion curve of rhombic sulphur, represented by EG curve. Here, the two phase (SR – SL)equilibrium is also monovarient as the number of phases is 2.Metastable equilibria indicated by solid line BF, EF, CF are metastable curve thus, here Frepresents melting point of the metastable rhombic sulphur. F, is another triple point wherethe three phases viz. $S_R – S_L – S_V$, coexist in metastable equilibrium with liquid.It should be noted that the variation of vapour pressure of all phases of sulphur with temperaturealways can be studied with the help of Clausius – Clapeyron equation. The BE curve, slopsaway from the pressure axis because, dp/dt have positive sign in Clausius – Clapeyron equationdue to lesser density (1.95 g/cm^3) of monoclinic sulphur than rhombic sulphur (2.05 g/cm^3)and V_B is larger than V_A

$$\frac{d\,p}{dT} = \frac{\Delta xH}{T(VB-VA)}$$

11.7 PHASE EQUILIBRIUM OF TWO COMPONENT SYSTEM

Broadly, there are three types of two-component system involving solid-liquid equilibria.

Type I. Those in which the two components do not react with each other but simply mix intoeach other in the molten slate or in the solution. Examples of such system are lead-silver systemand KI-H_2O system.

Type II. Those in which the components react to form a compound with congruent meltingpoint. These are those system in which the two pure components react to form a compoundwhich is stable up to its melting point at the melting point, it melts to give a liquid of the samecomposition as that of the solid compound. The compound formed is then said to have acongruent melting point.

For example, in $FeCl_3$-H_2O system, each hydrate formed is stable up to the melting point and

possesses a congruent melting point.

Type III. Those in which the components react to form a compound with incongruent meltingpoint. These are those two-compound formed does not remain stable up to the melting point. Onheating, it starts decomposing before the melting point to give a new solid phase and a solutionwith composition different from that of the solid phase. When this happens, the compound is saidto undergo a transition or peritectic(reaction and is said to have incongruent melting point. Ingeneral, a peritectic reaction may be represented by the equation$C_2 = C_1+$ solution, molten),C_2 represents is the compound formed as a result of reaction between the two pure components'and (C_1 is the new compound (or a pure consitituent) formed as a result of decomposition ofcompound (C_2 below its melting point. An example of this type of system is Na_2SO_4-H_2Osystem in which the hydrates formed undergo peritectic reaction.

11.7.1 Phase diagram of Bismuth-Cadmium (Bi-Cd) system

This is an example of a two-component system which forms a simple eutectic. The variousphases that may be present are (I) solid bismuth (ii) solid cadmium (iii) solution of bismuth incadmium or vice versa in the molten stale (iv) vapour.
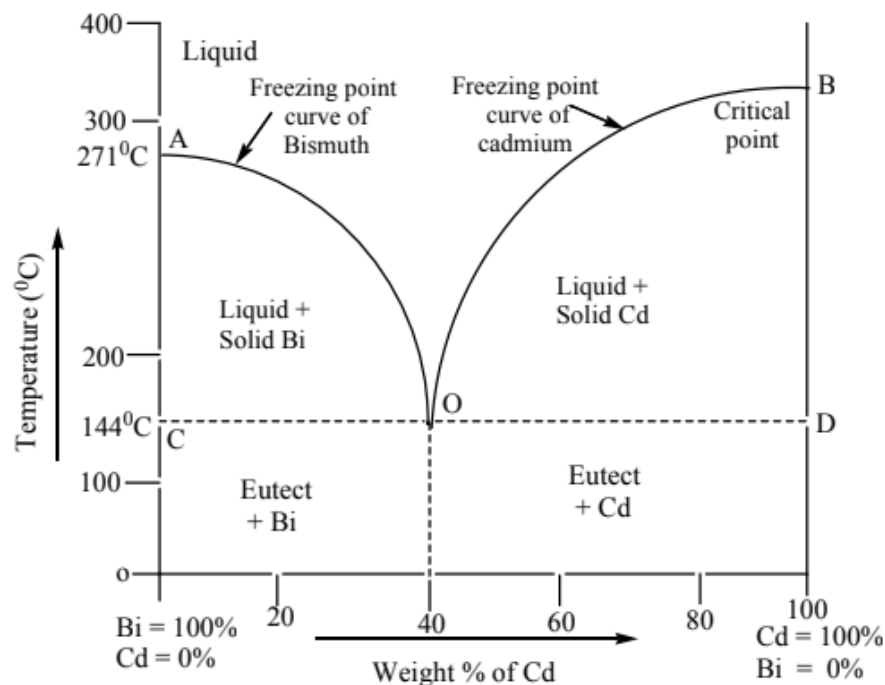
Fig 11.4

Curve AO. It represents the freezing point curve of bismuth to which different amounts ofcadmium are added. The point A represents the melting point, or freezing point of pure bismuth(271^0C). We find that the melting point (or) free/mi point) of bismuth is lowered gradually byaddition of cadmium into it. The added cadmium goes into the solution and the separation ofbismuth occurs till the point) is reach. At this point, no more cadmium goes into the solution asthe solution becomes saturated with cadmium and hence the melting point of bismuth does notfall further. Thus, the point O represents the composition with lowest melting (point 144^0C).

Point O represents the eutectic po9int. Along the curve AO, two phases in equilibrium are solidbismuth and liquid melt (neglecting the vapour phase). Therefore, the system is univariant asshown below.

Curve BO. This is the freezing point curve of cadmium to which different amounts of bismuthare added. The point B represent the melting point or freezing point of pure cadmium (32 1 V)We find that melting point of cadmium decreases as more and more of bismuth is added into itthe added bismuth goes into the solution and the separation of solid cadmium takes place. This continues till the point O is reached. At this point no more bismuth goes into the solution and thesolution is said to have become saturated with bismuth.Hence, the melting point does not fall any longer.Along the curve two Phases solid cadmium and liquid melt are in equilibrium

Therefore,

$$F=C-P+1=2+1=1 \text{ i.e., the system is invariant.}$$

It may be noted that the point -, on me curves AO and BO represent the initial freezing pointswhile the points on the line CD represent the final freezing points. It may also be noted that thecurve AO is not only freezing point curve of bismuth but may also be considered as solubilitycurve of bismuth because the points on this curve represent the solubilities of bismuth in themolten cadmium at various temperatures Similarly, the curve BO may also be considered as thesolubility curve of cadmium.Eutectic Point O. This is the point where the two curves AO and BO meet. At this point solidbismuth and solid cadmium are in equilibrium with the melt, i.e, three phases are present Degreeof freedom at the point O is zero.

$$F=C-P+1=2-3+1=0$$

The point O represents the lowest possible temperature (144^0C) below a liquid phase cannot existand above which the liquid phase cannot be enriched in either component by freezing out theother component. Such a liquid mixture of two components which has the lowest freezing pointcompared to all other liquid mixtures is called emetic mixture. This mixture freezes out completely at constant as solid phases in the same proportion in which they were present in theliquid phase. The temperature corresponding point O is called I he cutectic temperature. This isalways lower than the melting points of the either component. In this system, eutectic mixture(containing about 40% Cd and 60% Bi by mass) melts at 144^0C, which is lower than the meltingpoint of bismuth (271^0C of cadmium (321^0C).

11.7.2 Pb-Ag System

Pb-Ag system is a four phase and two component systems for which a complete phase diagramcan be represented as:
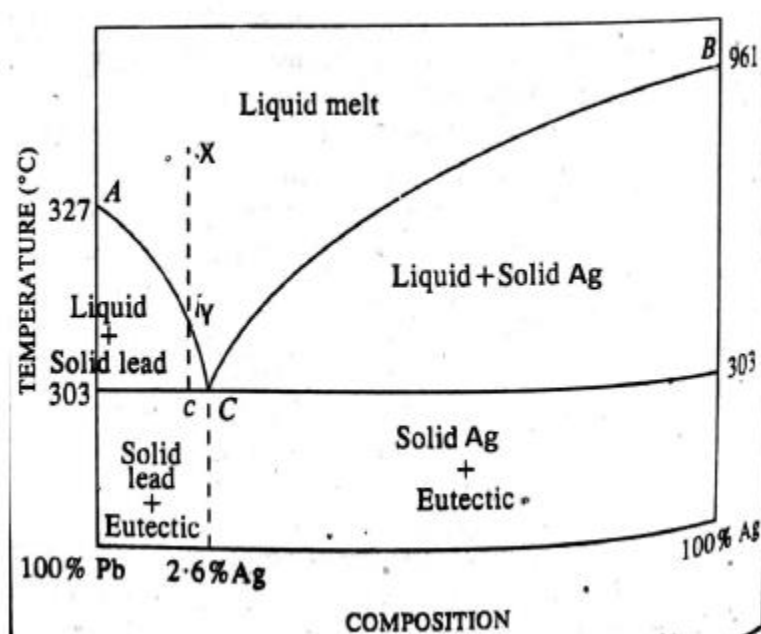
Fig.11.5 Phase diagram of Pb-Ag system

According to the above phase diagram the various regions, curves, eutectic point, eutectic T andeutectic composition in the phase diagrams of Pb-Ag system can be define d as:Various regions: Different types of the regions present in the two component PB-Ag system aregiven as.

a) Region above the ACB: Liquid solution of Pb and Ag

b) Region within the ACD: Solid Pb and Solution of Ag in Pb

c) Region within the BCD': solid Ag and the solution of Pb in Ag

Various curves

1. Curve AC indicates the freezing curve of Pb with the addition of Ag in which point Aindicates the freezing point of pure Pb.In the curve Ac; C = 2, P = 2, So according to reduced phase rule;

$$F = C - P + 1$$

$$F = 2 - 2 + 1 = 1$$

i.e. System in the curve AC will be univariant.

2. Curve BC indicates the freezing curve of Ag with the addition of Pb, in which point Bindicates the freezing point of pure Ag.

Eutactic point, Eutactic temperature and Eutactic composition: In the phase diagram ofPb-Ag system the melting point of AC and BCcurve is known as eutectic point. Temperature andcomposition corresponding to this eutectic point are known as eutectic temperature (303^{0}C) andeutectic composition (97.4% Pb + 2.6% Ag) for Pb-Ag system.

11.7.2.1 Pattinson's process for desilverisation of lead

Galena (PbS. an ore of lead) is usually associated with silver. When galena is processedfor the extraction of lead, some traces of silver pass into it, because silver is soluble in lead tosome extent. The lead thus obtained is known as argentiferous lead the desilverisation of lead iscarried out which can be easily understood from the phase diagram of lead-silver system, shownin Fig. 11.4.

The argentiferous lead containing small percentage of silver is first of all heated to atemperaturewell above its melting point so that the system consists only of liquid phaserepresentedby the point x in Fig. 11.4. It is then allowed to cool gradually along the line xywithout any change inconcentration till the point y is reached. When this point is reached, leadstarts separating and solution will contain progressively increasing amounts of silver. Furthercooling shifts the system along the line yC. Lead continues to separate out. (Which can beremoved with the help of ladles' perforated spoons) and the melt continues to be richer andricher in silver, till the point O is reached where an alloy containing about 2.4% of silver isobtained.

The above principle is employed in Pattinson's process which is used for increasing therelative proportions of silver in the alloy. The relative increase in the amount of solid lead thatseparates out and in the proportion of silver in the melt on cooling as shown in Figure.

11.8 SUMMARY

- With the help of phase rule, it is possible to predict qualitatively the effect of change ofpressure, temperature and concentration on a heterogeneous system in equilibrium. In the phasediagram the various phases can be represented by area.

- One phase, by line two phases and bypoint three phases in equilibrium. Metastable equilibrium, allotropy, enantiotropy, monotropy hasbeen explained for equilibrium conditions of state of matter.

11.9 TERMINAL QUESTIONS:

A. Objective types questions:

1. The degree of freedom at a triple point unary diagram for water _____

(a) 0 (b) 1 (c) 2 (c) 3

2. Following is wrong about the phase diagram

(a) It gives information on transformation rate.

(b) Relative amount of different phases can be found under given equilibrium conditions.

(c) It indicates the temperature at which the different phases start to melt.

(d) Solid solubility limits are depicted by it.

3. Pick the odd one of the following:

(a) Isomorphous alloy (b) Terminal Solid Solution

(c) Intermediate Solid Solution (d) Compound

4. The boundary line between (Liquid + Solid) and (Solid) regions must be part of _____

(a) Solvus (b) Solidus (c) Liquidus (d) Tie- Line

5. An invariant reaction that produces a solid up on cooling two liquids:

(a) Eutectic (b) Peritectic (c) Monotechtic (d) Syntectic

6. A Liquid Phase produces two solid phases during _____ reaction up on cooling.

(a) Eutectic (b) Eutectoid (c) Peritectic (d) Peritectoid

7. On heating one solid phase results in another solid phase plus one liquid phase during

----------- Reaction.

(a)Eutectic (b) Peritectic (c) Monotechtic (d) Syntectic

8. In a one component system the maximum number of phases that can co-exists in

Equilibrium is:

(a) 1 (b) 2 (c) 3 (d) 4

9. In terms of number of phases (P), components (C) and degrees of Freedom (F), the

Phase rule is expressed as:

(a) $P + C = F + 2$ (b) $F = P + C - 2$

(c) $P + F = C + 2$ (d) $P - F = C + 2$

10. In the phase diagram of the benzene- naphthalene system, the point C is called the:

(a) Eutectic Point (b) Congruent Point (c) Triple Point (d) Critical Point.

11. Lowest temperature is reached by using:

(a) $CaCl_2 2H_2O$ (b) Acetone with dry ice (c) NH_4Cl (d) Ether + Dry Ice

12. A compound with an incongruent melting point decomposes on heating into:

(a) A liquid of the same composition as the solid.

(b) A new solid phase and a solution with a composition different from that of the solid Phase.

(c) A new and a solution with the same composition as that of the solid Phase.

(d) A solution of fixed composition.

B. Short Answer Questions:

1. Define the terms :- Phase, Components and degree of freedom

2. What do you understand by desilverization. (Pattinson's Process)

C. Long Answer Questions:

1. Discuss the phase diagram of water system

2. Discuss the phase diagram of sulphur system.

3. State the Phase rule and give its derivations.

11.10 ANSWERS

1. (a) 2. (a) 3. (a)4.(b) 5. (d) 6. (a) 7. (b) 8. (c) 9. (c) 10. (a) 11. (d) 12. (b)

11.11REFERENCES AND FURTHER STUDIES

1. Essential of physical chemistry by Bahl, Bahl and Tuli.

2. Principles of physical chemistry By Puri, Sharma and Pathania.

3. Physical chemistry By P.C. Rakshit.

4. Physical chemistry By Atkins.

UNIT 12: PHASE EQUILIBRIUM - II

CONTENTS:

12.1 INTRODUCTION

Phase as we know is the homogenous part of a system which has same physical and chemicalproperties throughout the system. For example, mixture of gas consists of one phase. System onthe other hand is the part of universe which is under consideration.The present unit deals with the study of phase equilibrium that includes different topics likephase rule, congruent melting point, incongruent melting point, freezing mixture, liquid- liquidmixture, ideal liquid mixture, Henry's law, azeotropes, partially miscible liquids, lower consolutetemperature, upper consulate temperature, immiscible liquids, steam distillation.

In order to understand the unit properly we will go through the above topic in detail along withsuitable examples.

12.1 OBJECTIVES

After reading this unit you will be able to:

• Define Phase rule.

• Know congruent and incongruent melting point.

• Classify liquid- liquid mixture.

• Define the lower and upper consolute temperature.

• Explain the process of steam distillation.

• Define freezing mixture.

12.3 SOLID SOLUTION

Solid solution consists of a solute dissolved in a particular solvent forming a homogeneous

solution. Here the crystal structure of the solvent does not change by the addition of the solute.

For example metal alloys, moist solids. These solutions are used in industries. When these

solutions attain unstability, the two phases (solute and solvent) separate out.

12.4 COMPOUND FORMATION WITH CONGRUENT MELTINGPOINT (Mg-Zn)

For two component system A and B, a compound AB is formed chemically. There are three phases, solid component A, solid component B and solid compound AB formed by combining A and B. As a result of melting, fourth phase i.e. liquid phase is formed. Congruent melting point is defined as a temperature when the composition of the liquid formed by melting of solid compound is same as the composition of the solid compound. At congruent melting point, system having two components gets reduced to one component as both the liquid and solid form of the compound AB have same composition. As the system is two components, we apply reduced phase rule for calculating the number of degrees of freedom.

At congruent melting point: $F = C - P + 1 = 1 - 2 + 1 = 0$ (Non- variant)

Keeping magnesium (Mg) in place of A, Zinc (Zn) in place of B and compound $MgZn_2$ in placeof AB, we obtain Mg- Zn system. Therefore, the system consists of four phases: solid Mg, solidZn, solid $MgZn_2$ and liquid phase of $MgZn_2$. Figure 12.1 shows the phase diagram of Mg-Znsystem which consists of area, curves and points.
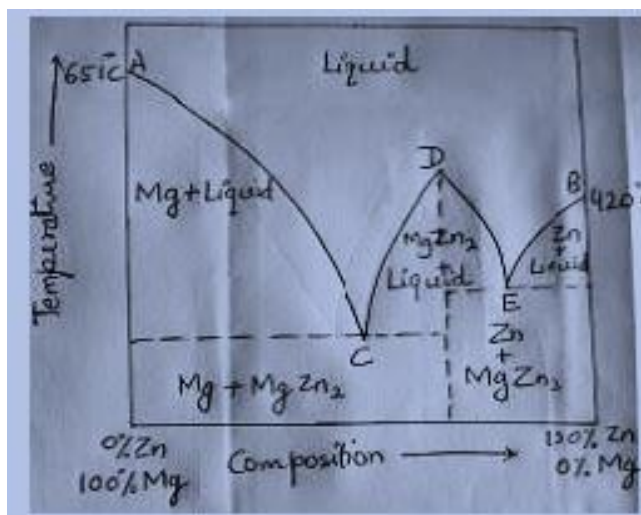
Figure 12.1. Phase diagram of Mg-Zn system

The figure shows that there are four curves: AC, CD, DE and EB. The curve AC represents thefreezing point of Mg, curve CD represents the freezing point of intermetallic compound

$MgZn_2$,curve DE represents the lowering of the melting point and curve EB represent the freezing pointcurve of Zn. Along the curve, two phases exist in equilibrium. Therefore, applying reduced phaserule, we have: $F = C – P + 1 = 2 – 2 + 1 = 1$ (Monovariant). The area above the four curvesrepresents only one phase i.e. liquid phase which consist of solution of Mg and Zn. Here thdegree of freedom is two which is obtained by using reduced phase rule. There are three points inthe phase diagram of Mg- Zn system i.e. point C, D and E. At point C, there are three phases inequilibrium: solid Mg, solid $MgZn_2$ and a liquid. Thus, according to reduced phase rule, thenumber of degrees of freedom is zero at the points. At point E, there are also three phases: solidZn, solid $MgZn_2$ and a liquid phase. Here also the number of degree of freedom is zero. Point Drepresents a congruent melting point of the compound having two phases: one solid phase$MgZn_2$ and another liquid $MgZn_2$ having same composition.

12.5 INCONGURENT MELTING POINT (NaCl-H₂O), (FeCl₃- H₂O) AND (CuSO₄- H₂O) SYSTEM)

There are some compounds which on heating get decompose without melting. Therefore,such compounds have different composition from that of the solid phase. Incongruent meltingpoint also known as transition temperature of a compound is defined as the temperature at whichthe composition of a solid compound is different from the components formed by thedecomposition of this solid compound. This decomposition results in the formation of anothersolid and a liquid which shows that there are three phases. The number of degrees of freedom atincongruent melting point is equal to zero (non- variant). Now we will discuss two componentsystem: NaCl – H_2O system, $FeCl_3$- H_2O system and $CuSO_4$- H_2O system one by one.

12.5.1 NaCl – H2O system

This is a two-component system having four phases: solid NaCl, solid H_2O, $NaCl.2H_2O$ and aliquid phase (solution). The phase diagram of NaCl – H_2O system is given in Figure 12.2. Thecompound formed is $NaCl.2H_2O$ which dissociates to form another solid and a liquid.
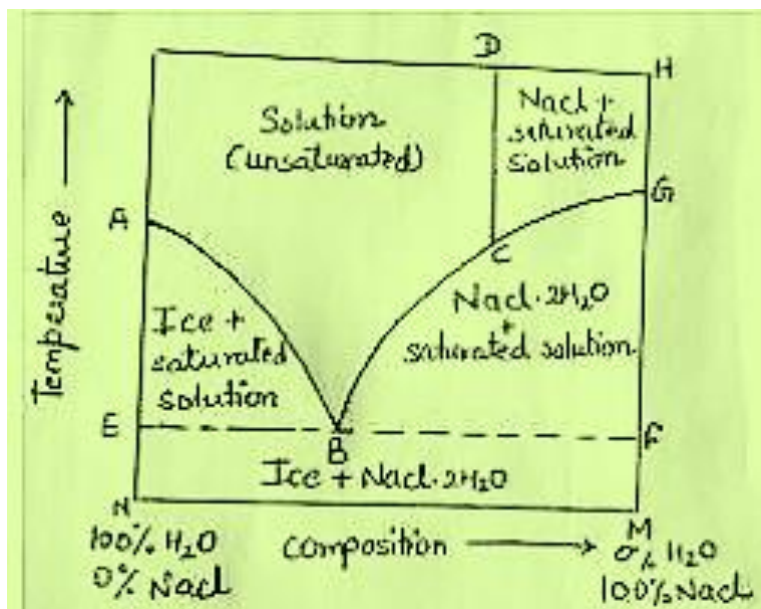
Figure 12.2. Phase diagram of NaCl – H₂O system

The phase diagram consists of curves, points and area. There are three curves represented by AB,BC and CD in the phase diagram. The curve AB represents the depression in freezing point ofwater which is due to the addition of sodium chloride (NaCl). As two phase are in equilibrium(ice + solution) along the curve, therefore number of degree of freedom is equal to one ascalculated by using reduced rule ($F = C - P + 1 = 2 - 2 + 1 = 1$ (monovariant). The curve BCrepresents the solubility curve of hydrated NaCl i.e. $NaCl.2H_2O$. Along this curve, $NaCl.2H_2O$and solution phase are in equilibrium. Therefore, the number of degree of freedom is one(monovariant). The third curve CD represents the equilibrium between solid NaCl and solution.Here also the degree of freedom is one. There are five area in the phase diagram A_1, A_2, A_3, $A_4$and A5. Figure 2 also shows that there are two points in the diagram, one point B and other pointC. At point B, three phase exist in equilibrium (solution, ice and solid $NaCl.2H_2O$). Usingreduced phase rule, the number of degrees of freedom calculated is zero (non-variant). Point B isalso known as eutectic point and the corresponding temperature is known as eutectictemperature.Point C represents incongruent meting point in which compound $NaCl.2H_2O$decomposes to form NaCl and a liquid (saturated solution).

12.5.2 FeCl₃- H₂O system

$FeCl_3$- H_2O system consists of two components FeCl3 and H2O which exist in vapour phase, ice,$Fe_2Cl_6.4H_2O$, $Fe_2Cl_6.5H_2O$, $Fe_2C_{16}.7H_2O$, $Fe_2Cl_6.12H_2O$. The phase diagram of $FeCl_3$-H_2Osystem consists of curves, points and areas as shown in Figure12.3.
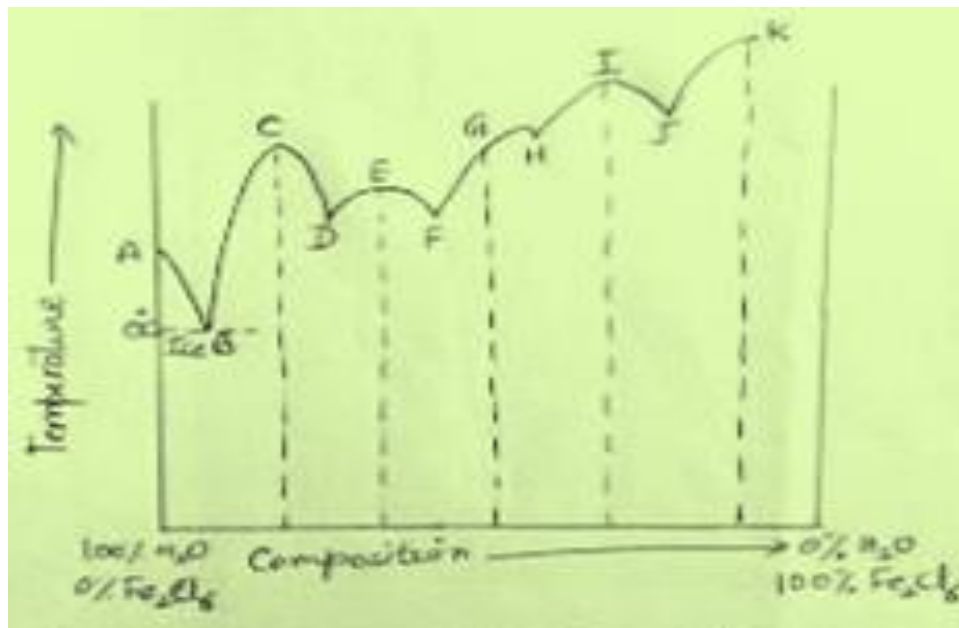
Figure 12.3. Phase diagram of FeCl₃- H₂O system

It is clear from phase diagram that $FeCl_3$- H_2O system consist of ten curves which are AB, BC,CD, DE, EF, FG, GH, HI, IJ and JK. Curve AB represents depression in freezing point of wateron addition of $FeCl_3$. There are three phases (ice, vapour and solution) which are at equilibriumalong the curve AB. The curve BC represents the solubility curve of $Fe_2Cl_6.12H_2O$ along whichthree phases exist in equilibrium (vapour, saturated solution phase and $Fe_2Cl_6.12H_2O$). The curveCD represents the melting point curve of Fe2Cl6.12H₂O. The curve DE represents the solubilitycurve of $Fe_2Cl_6.7H_2O$ while the curve EF represents the melting point curve of $Fe_2Cl_6.7H_2O$. Thecurve FG represents the solubility curve of Fe2Cl6.5H2O while the curve GH represents themelting point curve of $Fe_2Cl_6.5H_2O$. The curve HI represents the solubility curve of $Fe_2C_{16}.4H_2O$while the curve IJ represents the melting point curve of $Fe_2Cl_6.4H_2O$. The last curve i.e. JKrepresents the solubility curve of anhydrous ferric chloride (Fe_2Cl_6).There are nine points in the phase diagram of $FeCl_3$- H_2O system. These are points B, C, D, E, F,G, H, I and J. Point B, D, F, H and J are called eutectic points while the points C, E, G and I arecalled congruent melting point. At point B: ice, $Fe_2Cl_6.12H_2O$ and solution phase exist

inequilibrium. At point D: $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$ and solution phase are in equilibrium. Atpoint F: $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$ and solution phase exist in equilibrium. At point H:$Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.4H_2O$ and solution phase exist in equilibrium while at point J: $Fe_2Cl_6.4H_2O$,Fe_2Cl_6 and solution exist in equilibrium. It is clear that at all the eutectic points, the degree offreedom is zero as the number of phases are three and the component is two. At the congruent meltingpoint, the solid phase (hydrate) and the liquid phase are in equilibrium having the samecomposition. The degree of freedom obtained by using the reduced phase rule is zero.

12.5.3 CuSO4- H2O system

$CuSO_4$- H_2O system is a twocomponent system as it contains $CuSO_4$ and H_2O. The systemconsists of five phase: vapour, anhydrous $CuSO_4$, $CuSO_4.H_2O$, $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$.Anhydrous means without water. Figure12.4 represents the phase diagram of $CuSO_4$- H_2O system.
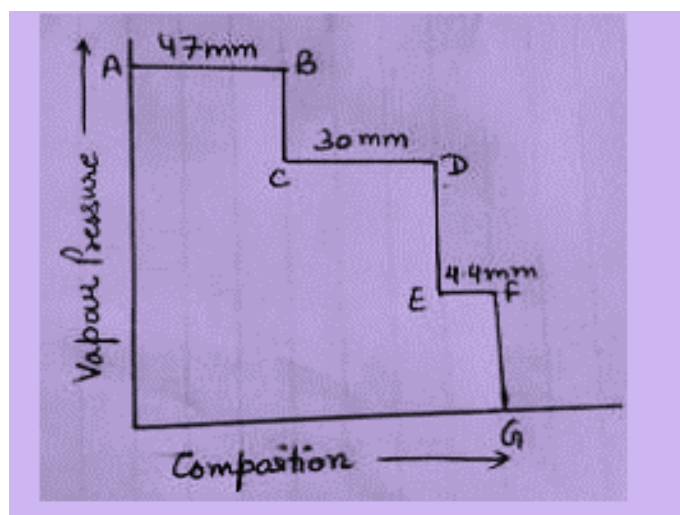
Figure 12.4 Phase diagram of CuSO₄- H₂O system

The phase diagram consists of curves: AB, BC, CD, DE, EF and FG. The curve AB representsthe dehydration curve of CuSO4.5H2O where it dissociates to form $CuSO_4.3H_2O$. Along thecurve AB, three phases are in the equilibrium: $CuSO_4.5H_2O$, $CuSO_4.3H_2O$ and vapour phase.The curve BC represents the decrease in vapour pressure from 47 mm to 30 mm which is due tothe conversion of $CuSO_4.5H_2O$ to $CuSO_4.3H_2O$. The curve CD represents the dehydration curveof CuSO4.3H2O which is due to the formation of $CuSO_4.H_2O$. Along the curve CD, there

arethree phases in equilibrium: $CuSO_4.3H_2O$, $CuSO_4.H_2O$ and vapour. The curve DE represents the

decrease in vapour pressure from 30 mm to 4.4 mm which is due to the conversion of$CuSO_4.3H_2O$ to $CuSO_4.H_2O$. The curve EF represents the dehydration curve of $CuSO_4.H_2O$which results in the formation of anhydrous CuSO4 at a particular pressure. Three phases exist inequilibrium along the curve EF: $CuSO_4.H_2O$, anhydrous CuSO4 and vapour phase. The curve FGrepresents the decrease in vapour pressure resulting in the formation of anhydrous $CuSO_4$.There are seven points in the phase diagram of $CuSO_4$- H_2O system: A, B, C, D, E, F and G. atpoint A, $CuSO_4.5H_2O$ is present in pure form. At point B, $CuSO_4.5H_2O$ get completelyconverted into $CuSO_4.3H_2O$. At point C, the dehydration of $CuSO_4.3H_2O$ starts. At point D,$CuSO_4.3H_2O$ get completely converted into $CuSO_4.H_2O$. At point E, the dehydration of$CuSO_4.H_2O$ starts. At point F, $CuSO_4.H_2O$ get completely converted into $CuSO_4$. At point G,anhydrous $CuSO_4$ is present.

12.6 FREEZING MIXTURES

Freezing mixtures are defined as a mixture of salt and ice which decreases the temperature of the system. For example, a mixture of sodium nitrate and ice, sodium chloride and ice, ammonium chloride and ice, ammonium nitrate and ice. Let us discuss how these mixtures lower the temperature of the system: When salt is added to ice, some of the salt get dissolved inwater (formed by melting of ice) resulting in the formation of three phases: ice, salt and solutionwhich are in contact with each other. At eutectic temperature, all three phases exist in equilibrium.The melting of ice and dissolution of salt require heat which results in the lowering oftemperature.

12.6.1 Acetone-dry ice

Acetone-dry ice constitutes a freezing mixture. Dry ice as we know is solid CO_2. Thismixture is commonly used in the laboratory for lowering the temperature of the system. In asealed container, when dry ice is added to the acetone, dry ice undergoes the process ofsublimation (conversion of solid into vapour) causing intense lowering of temperature by takingcan attain the freezing point of acetone. The cooling bath used in the laboratory also consist of amixture of acetone and dry ice.

12.6.2 Liquid- liquid mixtures

Liquid-liquid mixtures are also called by name solution of liquid in liquid. Solution as we knowconsist of a solute and a solvent. In liquid- liquid mixture, solute and solvent both are in liquidphase and are volatile in nature. The liquid- liquid mixture depends on the type of intermolecularforces and the nature of these forces between them. The properties of these mixtures dependupon the vapour pressure, viscosity, refractive index, surface tension etc. Depending upon themiscibility of two liquids, these mixtures are classified into three types:

12.6.2.1 Immiscible liquid-liquid mixture

In these mixtures, both the liquids are insoluble in each other forming a layer between them.These liquid mixtures do not interfere with the properties of the individual liquid. For example,benzene in water, kerosene in water, oil in water.

12.6.2.2 Partially miscible mixture

In these liquid mixtures, both the liquids are soluble to some extent or to a limited ratio resultingin the formation of two layers. With increase in temperature, the miscibility of these liquidmixture increases. For example, nicotine- water system, phenol- water system, triethylamine-water system.

12.6.2.3 Completely miscible mixture

In these liquid mixtures, two liquids are completely soluble in each other at all ratio. Forexample, ethanol- water system, benzene- acetone system. These mixtures are classified into twotypes: ideal liquid mixture or ideal solution and non-ideal liquid mixture or non- ideal solution.

12.7 IDEAL LIQUID MIXTURES

These mixtures are also known as ideal solutions. In ideal solution, each component obeysRaoult's law at all temperatures and concentration. For an ideal solution, enthalpy of mixing iszero ($\Delta H_{mix} = 0$) and volume of mixing is also zero ($\Delta V_{mix} = 0$). It means that final volume of thesolution is equal to the sum of the volume of two liquid being mixed. In ideal solution, theinteraction between A-B is same as the interaction between A-A and B-B which are theconstituent. The partial molar volume of a constituent in an ideal solution is equal to the

molarvolume of the constituent when present in the pure form. For example, n-hexane and n-heptane,benzene and toluene, carbon tetrachloride and chloroform, n-butyl chloride and n-butyl bromide.

12.8 RAOULT'S LAW

According to Raoult's law: At any temperature, the partial pressure of a component (volatile liquid) of a solution is equal to the vapour pressure of the pure component multiplied bythe mole fraction of that particular component present in the mixture. Consider a binary mixturecontaining two volatile liquid A and B. Let xA and xB are the mole fraction of two liquid A and Bwhile PA and PB are the partial pressure of two liquid A and B. Hence according to Raoult's law:

$$P_A = x_A P_A^0 \qquad\qquad \text{and } P_B = x_B P_B^0$$

Where P_A^0 and P_B^0 are the vapour pressure of the pure liquid A and B respectively. A solution issaid to be ideal, if all the constituent of a mixture obeys Raoult's law at all temperature andconcentration. Figure 12.5 represents the vapour pressure curve for an ideal solution.
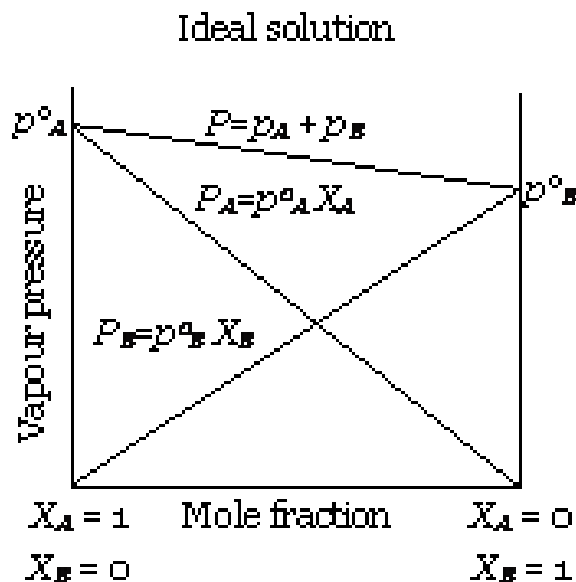
Figure 12.5 Vapour pressure curve for an ideal solution

When the constituent of a mixture affects the intermolecular forces or when there is a formationof a compound by the interaction of the components, Raoult's law is not applicable.

Vapourpressure of a liquid is defined as the pressure exerted by the vapour in equilibrium with a liquidin a closed container a particular temperature. Let us calculate the vapour pressure of an idealsolution. Total vapour pressure of a solution (P) is equal to the sum of the partial pressure of two

liquid A (P_A) and B (P_B) respectively.

$$P = P_A + P_B = x_A P_A^0 + x_B P_B^0$$

12.9 HENRY'S LAW

Henry's law is applicable for a solution of a gas in a liquid. This law is given by WilliamHenry. According to this law: At a particular temperature the mass of a gas (m) dissolved indefinite amount of a solvent is directly proportional to the pressure of the gas (P) which is inequilibrium with the solution. Accordingly:

$$m = k P$$

Where k is proportionality constant or Henry's law constant. The value of k depends upon thenature of the gas and the solvent. Figure 12.6 shows the validity of Henry's law.
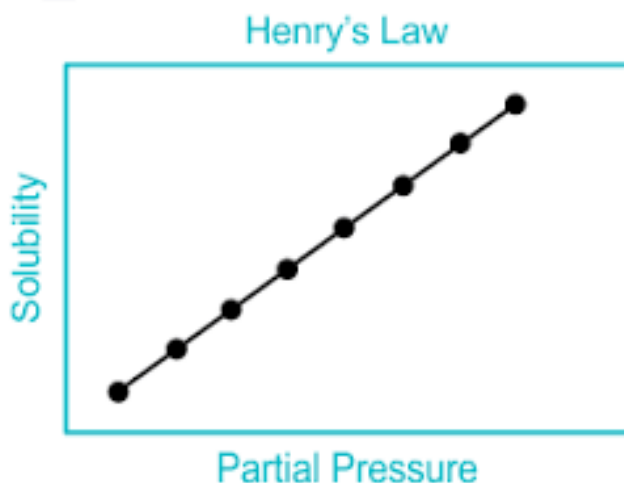
Figure 12.6 Validity of Henry's law

Henry's law is not applicable under the conditions given: Firstly, when the solubility of a gas in aparticular solvent is low. Secondly, when a gas undergoes association or dissociation in

thesolvent. Thirdly, when pressure is very large and fourthly when temperature is very low or veryhigh.

12.10 NON- IDEAL SOLUTION

Non- ideal solutions are also known as non- ideal liquid mixtures or real solutions. If asolution don not obey Raoult's law over the entire range of concentration and temperature, thesolution is said to be non- ideal solution. The vapour pressures of these solutions are higher orlower than the pressure obtained by using Raoult's law. Here the enthalpy of mixing and volumeof mixing is not equal to zero. In these solutions, the force between A-B is different from A-Aand B-B (individual components). Non- ideal solutions are classified into two types: Non- idealsolution showing positive deviation (vapour pressure obtained is higher than calculated usingRaoult's law) and non- ideal solution showing negative deviation (vapour pressure obtained islower than calculated using Raoult's law).

12.10.1 Non-ideal solution showing positive deviation

In the solution of component A and B, the interaction between A-B is weaker than the A-A and B-Binteraction. Hence the vapour pressure of the solution is higher than the pressure predicted by Raoult.The enthalpy of mixing is positive. For example, ethanol and hexane, acetone and carbon disulphide, carbon tetrachloride and benzene, and carbon tetrachloride and toluene. Figure12.7represents the curve showing positive deviation.

P-X graph for non-ideal solution
showing +ve deviation
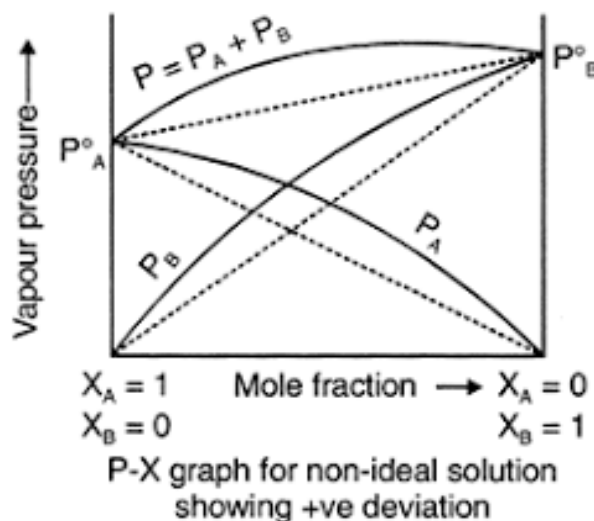
Figure 12.7 Non-ideal solutions showing positive deviation

12.10.2 non-ideal solution showing negative deviation

In the solution of components A and B, the interaction between A-B is stronger than A-A and B-Binteraction. Here the vapour pressure of a solution is lower than the pressure predicted by Raoult.The enthalpy of mixing is negative. For example, acetone and water, phenol and aniline,chloroform and benzene, acetic acid and pyridine. Figure 12. 8 represents the curve showingnegative deviation.
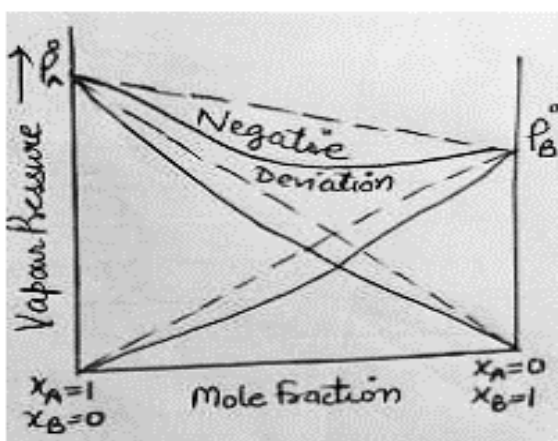
Figure 12.8 Non- ideal solutions showing positive deviation

12.11   AZEOTROPES   (HCl-H₂O)   (MAXIMUM BOILINGAZEOTROPES)

Azeotropes are also known as constant boiling mixtures. It is defined as mixtures which have same composition both in solution phase as well as in vapour phase. It is difficult to separate the components of these mixtures by fractional distillation. Azeotropes have a characteristic boiling point which is either lower (negative deviation) or higher (positive deviation) than any of its constituents. Azeotropes having positive deviation are called minimum boiling azeotropes. For example, nitric acid and water. Azeotropes having negative deviation are called maximum boiling azeotropes. For example, ethanol and water.Let us discuss HCl- H_2O system. It is a two-component mixture. It possessa maximum boiling point which shows that the system have low

volatility. Figure 12.9 represents the boiling temperature versus the composition curve of HCl-H_2O system.
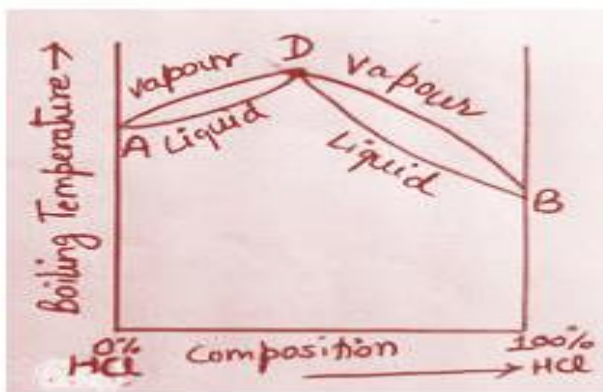
Figure 12.9 Boiling temperature versus composition curve of HCl- H_2O system

We know that pure water boils at 100^0C and the boiling point of HCl is -85^0C. The mixturethat constitutes the azeotrope boils at 108.5^0C and 1atm pressure contains 20.24% of HClshown by point D. If a solution contains less than 20.24% of HCl undergoes distillation, thewater constitutes the distillate. This is shown by AD in the Figure 12.9. In this case, we are unable torecover the pure HCl as the residue left contains a mixture of the same composition (20.24% ofHCl solution in water). If a solution contains more than 20.24% of HCl undergoes distillation asshown by BD, the pure HCl constitutes the filtrate. In this case, we can recover the pureHCl as the residue having the same composition.

12.12 ETHANOL- WATER SYSTEM (MINIMUM BOILING AZEOTROPES)

This is a two- component system in which one component is ethanol and other is water.The azeotropic mixture of ethanol and water boils at 78.13^0C and at one atmospheric pressure shown by point C. The mixture contains 95.6 % of ethanolic solution in water. Figure 12.10represents the boiling temperature versus composition curve of C_2H_5OH- H_2O system.
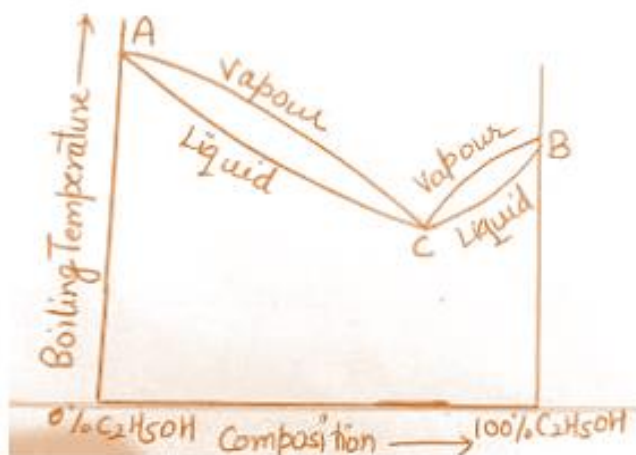
Figure 12.10 Boiling temperature versus composition curve of C_2H_5OH- H_2O system

If a solution having a composition between pure water and 95.6 % ethanol undergoes distillationas shown in Figure 10 by AC, ethanol (95.6 %) constitutes the distillate while the pure water constitutes the residue. In the second case, if the solution having a composition between pure ethanoland 95.6 % ethanol undergoes distillation as shown in Figure 10 by BC, ethanol (95.6 %) andpure ethanol get separated.

12.13 PARTIALLY MISCIBLE LIQUIDS

As discussed earlier, these are the liquid mixture forming two layers which are soluble ineach other to some extent. The miscibility of these liquid mixtures depends on temperature. At aparticular temperature, two partially miscible liquid mixtures become completely miscible. Thistemperature is known as critical solution temperature or convolute temperature. For example,phenol- water system, triethylamine- water system and nicotine-water system. Let us discussthese systems one by one:

12.13.1 Phenol –water system

When phenol mixed with water, there is a formation of two layers as these liquids are partiallymiscible. Figure 12. 11 shows the variation of temperature with phenol composition. It is clear thatwith increase in temperature, the miscibility of two liquids increases. At 65.8 ^{0}C, two liquids(phenol and water) get completely miscible and the corresponding temperature is known

ascritical solution temperature. Critical solution temperature is a characteristic property of aparticular system. This system possesses upper critical solution temperature.
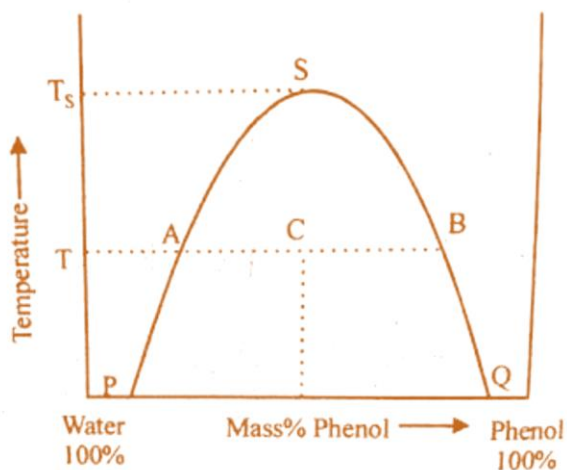
Figure 12.11 Phenol –water system

12.14.2 Triethylamine-water system

In this system, two liquids are taken trimethylamine and water. Both the liquids are allowed to mix resulting in the formation of two layers. The critical solution temperature is below 18.5 ^{0}C and above this temperature, these two liquids become partially miscible as shown in Figure 12.12 These systems possess lower critical solution temperatures.
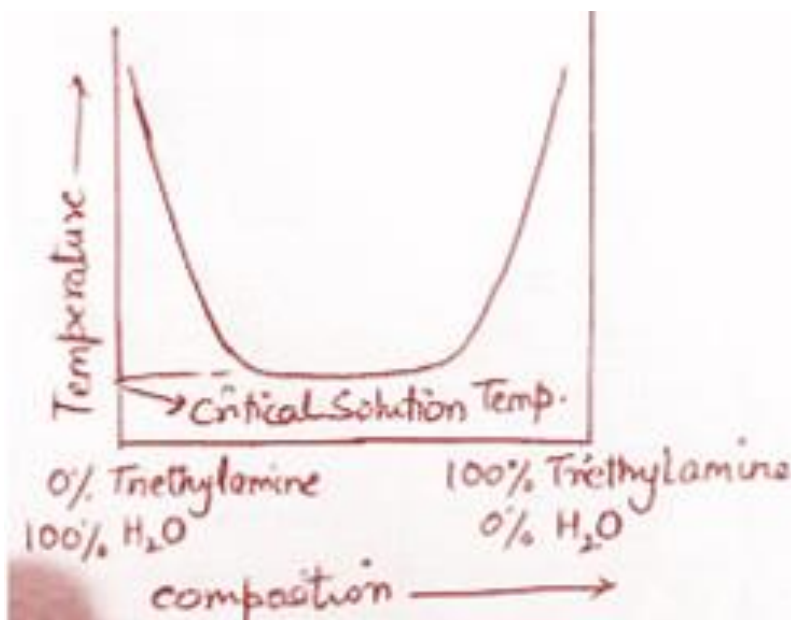
12.13.3 Nicotine- water system

Here the two liquids taken are nicotine and water which are partially soluble. For this system there are two temperatures at which these liquid mixtures get completely miscible. These twotemperatures are 60.8^0C (lower critical temperature) and 208^0 C (upper critical temperature). It isclear that when the temperature range is between 60.8 ^{0}C to 208 ^{0}C, the two liquids become partially miscible as shown in Figure 12.13.
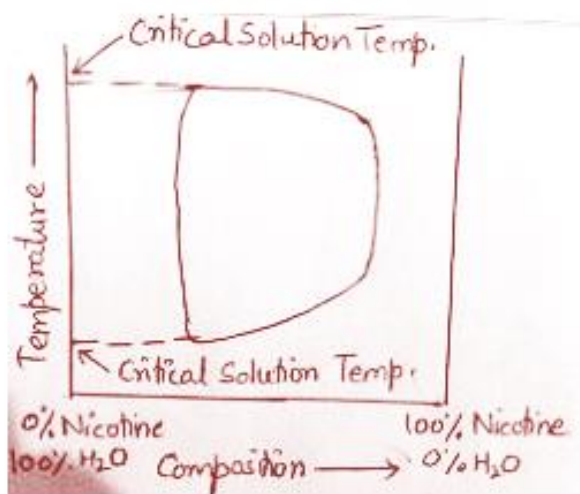
Figure 12.13 Nicotine- water system

12.14 LOWER AND UPPER CONSOLUTE TEMPERATUTE

As we have discussed earlier the consolute or critical solution temperature, isdefined as a temperature at which two partially miscible liquidsbecome completely miscible.There are two consolutetemperatures: one is lower consolute temperature and the other is upper consolute temperature. In case of phenol- water system, there is upper consolute temperaturewhich is 65.8 ^{0}C, above which two liquids becomes completely miscible. The lower consolute temperature is possessed by trimethylamine- water system.

12.15 EFFECT OF IMPURITY ON CONSOLUTE TEMPERATURE

We know that consolute temperature is one of the characteristic properties of a systemand is affected by the presence of a small number of impurities. In case first, if the impurity is solublein any one of the liquids, it will affect the miscibility (decreases) thereby raising the upper consolute temperature and decreasing the lower consolute temperature. For example, the presence of sodium chloride as impurity in phenol- water system raises the upper consolute temperature. In case second, if the impurity is soluble in both the liquid, the miscibility of two liquids increases thereby decreasing the upper consolute temperature and increasing the lower consolute temperature. For example, the presence of sodium salt (soap) in phenol- water system lowers the upper consolute temperature.

12.16 IMMISCIBLE LIQUIDS, STEAM DISTILLATION

Immiscible liquids as we have discussed earlier are not soluble in each other. Forexample, kerosene in water, oil in water. Distillation is a process that involves evaporation followed with condensation. In steam distillation, steam is passed into a round bottom flask containing the impure organic liquid. Through steam distillation, we purify the given organic liquid which is immiscible in water based on their volatility. Figure 12.14 shows the processof steam distillation.
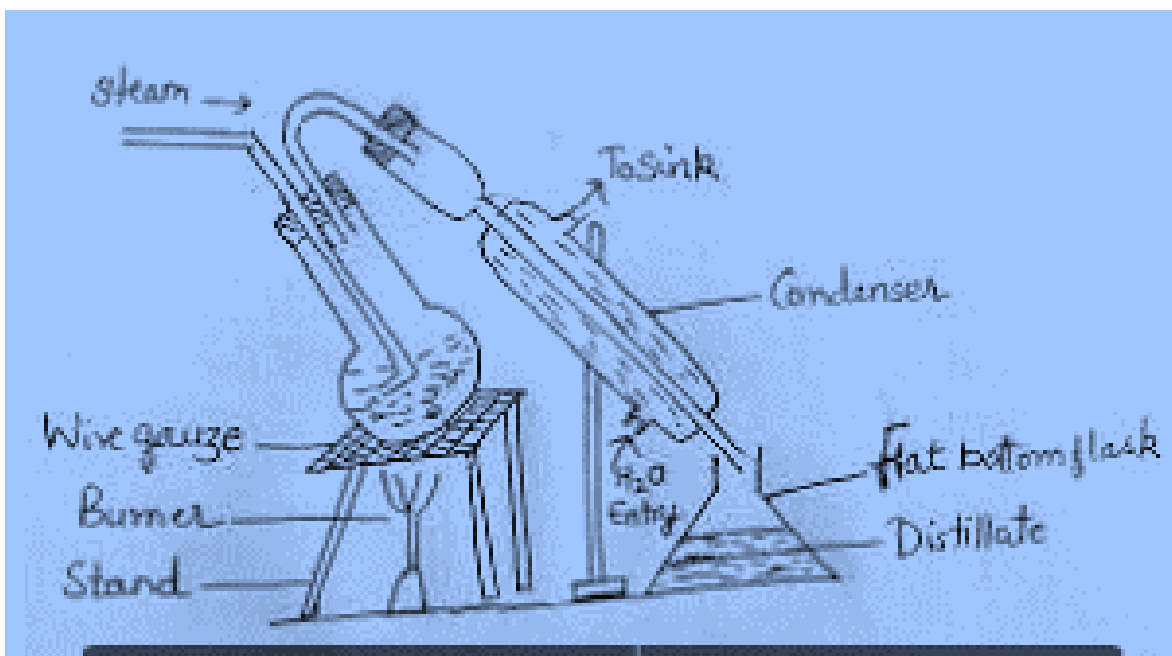
Figure 12.14 Steam distill

The Figure 12.14 consists of a condenser, adapter, flat bottom flask and round bottom flask. In a roundbottom flask, impure organic liquid containing water having non-volatile impurities is placed.Our aim is to remove the impurity and purify the organic liquid. Allow the steam to pass throughthe round bottom flask. Now using a burner, heat the flask which leads to the formation ofvapour. The vapour along with steam passes through the condenser. Condenser as we know is an apparatus used for converting vapor phase into liquid phase. The distillate (liquid producedafter the process of distillation) is collected in a flat bottom flask. In the flat bottom flask, theformation of two layers takes place. One layer is of pure organic liquid and another layer is ofwater. Then by using separating funnel, we can separate the two liquid. In this way, we purify the organic liquid. The process of steam distillation is used for the purification of phenylaminei.e. aniline and for calculating the approximate weight of an organic liquid.

12.17 SUMMARY

In this unit, we have discussed about the concept of phase, component, degree of freedom, congruent melting point, incongruent melting point, freezing mixtures, and miscibility. Weare able to know about the types of solution which are classified on the basis of miscibility and the process of steam distillation used for the purification of an impure organic liquid.

• **Congruent melting point** - Temperature when the composition of the liquid formed bymelting of solid compound is same as the composition of the solid compound.

• **Incongruent melting point** - Temperature at which the composition of a solid compoundis different from the components formed by the decomposition of this solid compound.

• **Azeotropes -** Mixture having same composition both in solution phase as well as in vapourphase.

• **Immiscible liquid mixture –** Liquid mixture not soluble in each other.

• **Consolute temperature -** Temperature at which two partially miscible liquid becomescompletely miscible.

• **Partially miscible liquids** – Liquid mixture soluble to some extent.

• **Distillation –** Process involving evaporation followed with condensation.

12.18 TERMINAL QUESTIONS

A. Objectives Type Questions:

1. Phenol- water system consist a liquid mixture which are .... miscible.

2. Consolute temperature is also known as .... temperature.

3. Triethylamine-water system contain .... consolute temperature.

4. Addition of NaCl in phenol- water system .... the upper consolute temperature.

5. Steam distillation is used for the purification of .... liquid.

6. Azeotropic mixture is also known as .... mixture.

7. .... law gives the relationship of solubility of a gas with pressure.

8. Ideal solution obeys .... law at all range of temperature and concentration.

9. Non- ideal solutions are also known as .... solution.

10. Kerosene in water consists of a system which is ....

11. Water consists of .... phases.

12. Phase rule for one –component system is given by ....

13. Phase rule for two-component system is given by ....

14. Chloroform and benzene constitute a system showing .... deviation.

15. Ethanol and hexane constitute a system showing .... deviation.

B. Short Answer Type Questions:

1. Explain in detail about the liquid- liquid mixture.

2. Explain the concept of congruent and incongruent melting point by giving suitable example of each.

3. What are Azetropes?

C. Long Answer Type Questions:

1. State and explain the Rault's & Henery Law and also discuss the importence of these laws.

2. Write an example of partialymiribleliquid mixture.

3. Draw & discuss the phase diagram of Mg-Zn system.

4. Discuss the NaCl-H2O System having incongruent melting point.

12.19 ANSWER

Fill in the blanks:

1. Partially; 2. Critical solution; 3. Lower; 4. Raises; 5. Organic; 6. Constant boiling; 7. Henry's;

8. Raoult's; 9. Real; 10. Immiscible; 11. Three; 12. $F = C - P + 2$; 13. $F = C - P + 1$; 14.

Negative; 15. Positive.

12.20 REFERENCES AND FURTHER STUDIES

1.Bahl, A., Bahl, B. S., Tuli, G. D. (2014), Essentials of Physical Chemistry, S. Chand &CompanyPvt. Ltd., New Delhi.

2.Puri, B. R., Sharma, L. R., Pathania, M. S (2012), Principles of Physical Chemistry, VishalPublishing Co., Jalandhar, India.

BLOCK–IV: LABORATORY WORK

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 OBJECTIVES

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 apply to all users of the laboratory.

- All learners are expected to adhere to safety guidelines and maintain safety standards 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 detail 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 burn 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 some pungent vapors in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still eating 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 the eye must be washed with a dilute solution of alkali sodium bicarbonate solution few timeand 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, and respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing, etc.

- If you feel any symptoms occur due to the inhalation of gases first go away from the working place (lab) in the open place. If still feel some problems consult with a 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 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 steps to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant step you can take to reduce the risk in any laboratory environment. While incidents can occur even in a 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.

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.

13.8 BIBLIOGRAPHY

1. Guidelines for Chemical Laboratory Safety in Secondary Schools. American Chemical Society 1155 Sixteenth Street, NW Washington, DC 20036, 2016.

2. Mobin Shaikh, Laboratory & Chemical Safety Guidelines, Indian Institute of Technology (IIT), Indore.

3. Sudha Goyel, Chemistry Practical-I, Krishna Publication Media (P) Ltd. Meerut, 2017.

UNIT 14: INORGANIC EXERCISE: INORGANIC MIXTUREANALYSIS

CONTENTS:

14.1   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. You will then perform confirmatory tests for the remaining anions in question to determine whether the anions are present or absent.

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 inorganic qualitative analysis involves the identification of ions present in a sample. 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

Qualitative analysis involves the identification of the substances in a mixture. When chemical methods are used in the identification of mixtures of metal cations, these ions are usually separated before identification can occur. After they have been separated, the 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.

14.2. OBJECTIVES

- To identify common anions 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.

- Identify different anions using a qualitative analysis technique.

- 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^-).

- To separate different cations in aqueous mixtures using selective precipitation and to confirm their identities using chemical tests.

- To classification of the cation into Analytical groups.

- Preliminary Investigation of the Sample.

- To preparation of solution for the analysis of Cations.

- Separation of cation into Analytical Groups.

- Analysis of the cations of Analytical Group I,II, III, IV, V VI and zero group.

- Classification of the cation into Analytical groups

- Solubility and solubility product: Relation between Solubility and Solubility products.

- The common ion effect; complex formation

- The separation of Cations in to analytical Groups: The precipitation of Group I cations, the separation of Group II cation from Group IV Cations, The Precipitation of Group III Cations, The Precipitation of Group V Cations.

- Preliminary Investigation of the Sample

- Preparation of solution for the analysis of Cations

- Separation of cation into Analytical Groups

- Analysis of the cations of Analytical Group I: Separation and Identificationof the cations of Analytical Group I

- Analysis of the cations of analytical Group II: Separation of Analytical Group II into group IIA and Group IIB, Separation of the Cations of group IIA, Separation of the Cations of group IIB, Identification of the cations of Group II

- Analysis of the cations of analytical Group III: Separation and Identification of the cations of analytical Group III.

- Analysis of the cations of analytical Group IV: Separation and identification of the cations of Analytical group IV.

- Analysis of the cations of analytical Group V: Separation and identification of the cations of Analytical group V.

- Analysis of the Cations of Analytical Group VI

- Chemical reactions involved in the test of basic radicals

14.3 *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 into 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 to 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	A white precipitate appears. A yellow precipitate appears.

		presence of conc. HNO_3.	

* Interfering radicals (or anions)

14.4 PRELIMINARY TEST FOR THE ANIONS

A preliminary test for the anions is done based on 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	NO_2^- may be present.

S. No.	Anion	Experiment	Observation	Inference
			evolved.	
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 with turbidity.	$(S_2O_3^{2-})$ is expected to be present.
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 (Br₂) is evolved and solution becomes orange.	Br⁻ is expected.
3.	Iodide anion(I⁻)	On conducting the above reaction.	Dark violet fumes (I₂) are observed	(I⁻) May be present.
4.	Nitrate anion (NO₃⁻)	In the above reaction.	* Pungent light brown gas (NO₂) is evolved.	(NO₃⁻) may be present.
5.	Oxalate anion (C₂O₄²⁻)	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	(C₂O₄²⁻) 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 (BO₃³⁻)	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.

14.5 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:

$XY + Na_2CO_3 \longrightarrow XCO_3 + Na_2Y$ (X and Y are bivalent radicals)**e.g.**

$SnCl_2 + Na_2CO_3 \longrightarrow SnCO_3 + 2NaCl$ (Soda extract)

$CaC_2O_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2C_2O_4$ (Soda extract)
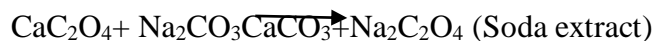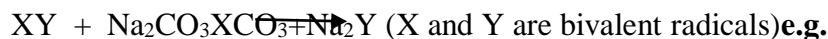
The filtrate so obtained after neutralization with suitable acid, can be used to detect certain anions. The acid is to be added in excess till bubbles cease to evolve. This indicates the complete neutralization of the solution (soda extract). The common anions which can be identified easily using soda 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	Brown ring of $FeSO_4$.

		FeSO$_4$ solution	NO compd. results.
SO$_4$$^{2-}$	dil. HCl	BaCl$_2$ soln.	BaSO$_4$: White ppt.
C$_2$O$_4$$^{2-}$	dil. CH$_3$COOH	CaCl$_2$ soln.	CaC$_2$O$_4$: White ppt.
CH$_3$COO$^-$	dil. HCl	Neutral FeCl$_3$ solution.	Basic ferric acetate: brownish red ppt.
PO$_4$$^{3-}$	dil. HNO$_3$	Conc.HNO$_3$+(NH$_4$)$_2$ MoO$_4$, 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$_2$CO$_3$ 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.

14.6 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 to the mouth of the 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-}, SO_3^{2-}, 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 $\rightarrow$ 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 an 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$\rightarrow$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.

(iii)

Reactions Involved:

Carbonate : $Na_2CO_3 + 2\ HCl \rightarrow 2NaCl + H_2O + CO_2 \uparrow$
anion (CO_3^{2-}) $Ca\ (OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$
                                                 White (milky)

$CaCO_3 + H_2O + CO_2 \rightarrow Ca\ (HCO_3)_2$ (Soluble)
                            excess

Salphite $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 \uparrow$
anion (SO_3^{2-}) $Ca(OH)_2 + SO_2 \rightarrow CaSO_3$ (Milky) + H_2O
                      $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)$ (Green) + H_2O

Sulphide $FeS + H_2SO_4 \rightarrow H_2S \uparrow + FeSO_4$
anion (S^{2-}) $(CH_3COO)_2\ Pb + H_2S \rightarrow PbS$ (black) $\downarrow + 2CH_3\ COOH$
 $Na_2S + Na_2\ [Fe(NO)(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$
                                              Sod. Nitroprusside
                                              (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)
                      $2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$
                   $I_2 + starch \rightarrow$ 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^-)

$3CH_3COOH + FeCl_3 \rightarrow (CH_3COO)_3 Fe$ (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)

$NaCl + Ag NO_3 \rightarrow AgCl \downarrow$ (ppt) + $NaNO_3$

$AgCl \downarrow + 2NH_4OH \rightarrow Ag (NH_3)_2 Cl$ (soluble) + $2H_2O$

Bromide   : $K Br + H_2SO_4 \rightarrow KHSO_4 + HBr$

anion (Br^-) $2HBr + H_2SO_4 \rightarrow Br_2 \uparrow$(reddish brown vapours)+ $SO_2 \uparrow$ + $2H_2O$

$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$

$Na Br + AgNO_3 \rightarrow Ag Br \downarrow$ (Light yellow ppt.)+$Na NO_3$

$2 NaBr + 4 HNO_3 \rightarrow Br_2 \uparrow + 2NaNO_3 + 2NO_2 \uparrow + 2H_2O$

$2HBr + Cl_2 \rightarrow$ $Br_2 \uparrow + 2HCl$

$Br_2 + CHCl_3$ or $CCl_4 \rightarrow$ Orange yellow colour (Br_2 dissolves)

Iodide $NaI + H_2 SO_4 \rightarrow NaHSO_4 + HI$

anion (I^-) $2HI + H_2SO_4 \rightarrow I_2 \uparrow$ (Violet vapours) + $SO_2 \uparrow$ + $2H_2O$

$2 NaI + MnO_2 + 3H_2SO_4 \rightarrow I_2 \uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$

$I_2 + starch \rightarrow$ 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: $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

Anion (NO^-_3) $4 HNO_3 \rightarrow 4 NO_2 \uparrow$ (Brown fumes)+ $O_2 \uparrow$ + $2H_2O$

$3Cu + 8HNO_3 \rightarrow 3 Cu (NO_3)_2 + 2NO \uparrow + 4 H_2O$

$$2 \, NO + O_2 \rightarrow 2 \, NO_2 \uparrow (\text{Brown})$$

Ring Test: $6 \, FeSO_4 + 2 \, HNO_3 + 2 \, H_2SO_4 \rightarrow 3 \, Fe_2(SO_4)_3 + 4 \, H_2O + 2NO\uparrow$

$FeSO_4 + NO \rightarrow FeSO_4 . NO \, (\text{Brown ring})$

Oxalate :	$Na_2C_2O_4 + 2H_2SO_4 \rightarrow 2NaHSO_4 + H_2O + CO_2 \uparrow + CO \uparrow$
anion ($C_2O_4{}^{2-}$):	$2CO + O_2 \rightarrow 2CO_2$
	$Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 \downarrow (\text{white ppt.}) + 2NaCl$
	$Ca \, C_2 \, O_4 + H_2 \, SO_4 \rightarrow Ca \, SO_4 + H_2 \, C_2O_4 \, (\text{oxalic acid})$

$2 \, KMnO_4 + 3 \, H_2SO_4 + 5 \, H_2C_2O_4 \rightarrow K_2SO_4 + 2 \, MnSO_4 + 10 \, CO_2 \uparrow + 8 \, H_2O \, Na_2C_2O_4 +$
$MnO_2 + 2 \, H_2SO_4 \rightarrow Na_2 \, SO_4 + MnSO_4 + 2 \, H_2O + 2 \, CO_2 \uparrow$

Fluoride:	$2 \, NaF + H_2 \, SO_4 \rightarrow Na_2 \, SO_4 + 2 \, HF \uparrow \rightarrow$
Anion (F-)	$Si \, O_2 + 4 \, HF \rightarrow Si \, F_4 + 2 \, H_2O \rightarrow$
	$3 \, Si \, F_4 + 3 \, H_2O \rightarrow 2 \, H_2 \, Si \, F_6 + H_2Si \, O_3 \, (\text{white deposit})$

Borate:	$Na_3BO_3 + 3 \, H_2SO_4 \rightarrow 3 \, NaHSO_4 + H_3 \, BO_3 \, (\text{Boric acid})$
Anion ($BO_3{}^{3-}$)	$H_3 \, BO_3 + C_2H_5OH \rightarrow (C_2H_5)_3 \, BO_3 \uparrow (\text{ethyl borate}) + 3 \, H_2O$
	$CaF_2 + H_2SO_4 \rightarrow Ca \, SO_4 + 2HF$
	$Na_3 \, BO_3 + 3 \, H_2 \, SO_4 \rightarrow 3 \, Na \, HSO_4 + H_3 \, BO_3$
	$2 \, H_3 \, BO_3 \rightarrow B_2 \, O_3 + 3 \, H_2O$
	$B_2 \, O_3 + 6 \, HF \rightarrow 2 \, BF_3 \, (\text{burns with green flame}) + 3 \, H_2O$

Sulphate **anion** ($SO_4{}^{2-}$)	$Na_2 \, SO_4 + BaCl_2 \rightarrow Ba \, SO_4 \, (\text{white ppt}) + 2 \, NaCl$

Phosphate	$Na_3 \, PO_4 + 3 \, HNO_3 \rightarrow H_3 \, PO_4 + 3 \, NaNO_3$
anion ($PO_4{}^{3-}$)	$H_3PO_4 + 12 \, (NH_4)_2 \, Mo \, O_4 + 21 \, HNO_3 \rightarrow$
	$(NH_4)_3 \, PO_4 \, 12 \, Mo \, O_3 \downarrow + 12 \, H_2O + 21 \, NH_4 \, NO_3.$
	(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:

   $NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$

   $(NH_2)_2\,CO + 2\,HNO_2 \rightarrow 2\,N_2 \uparrow + 3\,H_2O + CO_2 \uparrow$

   $NaNO_2 + NH_4Cl \rightarrow NaCl + N_2 \uparrow + 2\,H_2O$

   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.

14.7 CLASSIFICATION OF CATIONS INTO ANALYTICAL GROUPS

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.

14.8 SOLUBILITY AND SOLUBILITY PRODUCT

In the simple terms if a substance dissolves in a solvent, it is said to be soluble (more accurately solute) and the resulting mixture is known as solution (may be unsaturated or saturated). This tendency of a solute to get dissolved in a solvent is called, in a general sense, its solubility. The solubility depends on the nature of both the solute (substance) and the solvent. It is more accurately defined as "**the number of grams of the substance which is dissolved in 100 grams of the solvent in a saturated solution at a given temperature.**

The solubility of a solid substance in a given solvent depends mainly on the temperature and very slightly on the pressure. For most solid substances, it increases with increasing temperature, e.g., solubility of $AgNO_3$ increases rapidly but that of NaCl increases slowly. The change in solubility with changing temperature is usually expressed using solubility curves(plots of the number of grams of solute dissolved in 100 grams of solvent along ordinate

against the temperature along abscissa) There are also some substances whose solubility decreases with rising temperature, e.g. Li_2CO_3, NaOH, etc.

Solubility Product and Precipitation

When a sparingly soluble substance, say AB, is kept in contact with water for some time at a definite temperature, the following equilibrium is established:

AB   ⇌   AB   ⇌ $\underline{A^+ + B^-}$ and $\underline{[A^+] [B^-]}$ = K (from law of mass action)

Solid   Dissolves   Ions   [AB]

The concentration of the unionised [AB] is constant at a given temperature if excess of AB is present. Hence, $[A^+] [B^-]$ = K [AB] = constant. Therefore, "**In equilibrium, the product of the ionic concentration is constant at a given temperature. This constant product, $[A^+] [B^-]$, is called the solubility product (Ks)**". When the ionic product exceeds the solubility product, the solution is super saturated and precipitation occurs but if the ionic product is less than the solubility product, the solution is unsaturated and precipitation does not occur. This is called theory of precipitation. This can also be represented as

Ionic product < solubility product, Ks, the salt dissolves.

Ionic product > solubility product, Ks precipitation takes place.

Relation between Solubility and Solubility Product

The solubility of a sparingly soluble substance (electrolyte) of 1:1 can be calculated using the principle of the solubility product. Let it be AB.

$$Ks (AB) = [A^+] [B^-]$$

$$If [A^+] = [B^-] = s \text{ moles per liter}$$

$$Ks (AB) = s.s = s^2$$

$$Or \ s = \sqrt{Ks}$$

Where s = solubility of AB in moles per liter and Ks (AB) is the solubility product of AB.

But for the substances (electrolytes) or 1:2 or 2:1 type, i.e., AB_2 or A_2B type

$$Ks = s \times (2s)^2 \text{ or } (2s)^2 \times s = 4s^2$$

$$\therefore s = \sqrt[3]{\frac{Ks}{4}} \text{ moles per liter}$$

14.9 THE COMMON ION EFFECT

The phenomenon of lowering the degree of ionisation of a weak electrolyte substance by adding to its solution a solution of strong electrolyte having a common ion and thus decreasing the concentration of the ion other than the common ion of the weak electrolyte is known as **Common ion effect.** For example, NH_4OH, a weak base (electrolyte) dissociates in solution as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

On applying the law of mass action $[NH_4^+]$ $[OH^-]$ =K $[NH_4OH]$ = constant, on adding strong electrolyte, NH_4 $Cl, NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$, NH_4^+ ions are added to the solution. Thus the concentration of NH_4^+ ions coming both from NH_4Cl and NH_4OH (common ion) increases but K remains constant at any given temperature. As a result, the value of $[NH_4OH]$ must increase thereby decreasing the value of $[OH^-]$. This indicates that the degree of ionisation of NH_4OH is decreased by the addition of NH_4Cl which furnishes the common ion, NH_4^+. Similarly the ionisation of H_2S, a weak electrolyte, is diminished in the presence of HCl, a strong electrolyte, giving common H^+ ions.

The principle of common ion effect is of immense importance in qualitative analysis because this provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte. The common examples are: precipitation of second group radicals as sulphides using H_2Sin presence of HCl and that of fourth group cations as sulphides in presence of NH_4OH. Similarly precipitation of third group cations as hydroxides using NH_4OH in presence of NH_4Cl. The detailed account will be given in the respective groups.

Complex Formation

Complex ion formation is of great importance in qualitative analysis (i) to dissolve a precipitate alone or from a mixture of two or more (ii) to check the precipitation of a particular cation by complex ion formation. For example,

(a) AgCl is soluble in ammonia solution due to the formation of the complex ion, $[Ag (NH_3)_2]^+$.

$$Ag^+ + 2\, NH_3 \rightarrow\ [Ag\,(NH_3)_2]^+.$$

This capacity of Ag^+ ion is utilized in its separation from Pb^{2+} and Hg_2^{2+} ion.

(b) Separation of Cu^{2+} and Cd^{2+} ions is also based on the complex formation tendency with CN^- ions from KCN solution: $K_3\,[Cu\,(CN)_4]$ and $K_2\,[Cd\,(CN)_4]$. Of the two complex ions $[Cu (CN)_4]^{3-}$ and $[Cd(CH_4)]^{2-}$, the value of instability constant for the copper complex ion is less than cadmium complex ion and hence more Cd^{2+} ions are available in the solution than Cu^{2+} ions. In the presence of H_2S gas, CdS (yellow ppt) is formed but the copper ion remains unaffected.

$$[Cd\,(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^- \text{ and } H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$Cd^{2+} + S^{2-} \rightleftharpoons CdS \text{ (yellow ppt.)}.$$

14.10 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 sulfides but in different media, group II cations are precipitated in acidic medium (HCl) and those of group IV in a 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,

$$\text{i.e. } [M^{2+}]\,[S^{2-}] > KS$$

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 the 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 the presence of NH_4OH when Mg remains in solution.

14.11PRELIMINARY 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:

$$Na_2B_4O_7\ 10H_2O \xrightarrow{-10H_2O} Na_2\ B_4O_7 \rightarrow B_2O_3 + 2NaBO_2 \text{ (glassy bead)}$$

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.

14.12 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.

14.13 SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

Based on 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⁺⁺, Hg₂ (ous)	Dil. HCl	(Chlorides) AgCl, AgCl, PbCl₂, HgCl₂	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_2Sboil the solution with V_2	(Hydroxides) Al(OH_3) Fe(OH_3) $Cr(OH_3)$	White ppt. Brown ppt. Green ppt.
4.	Fourth group	$Ni^{++,}Co^{++}, Zn^{++,}Mr$	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) BaCO₃, CaCO₃, SrCO₃	Black ppt. White ppt.
6.	Sixth Group	Mg^{++}	&(NH^4) ₂CO_3 and shake	(Phosphate) $MgNH_4PO_4$	White crystalline ppt.

		well. Fifth Group (Phosphate) Filtrate+ Na_2HPO_4 Solution		

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 (despite 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]groupradicals. 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.

14.14 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

Analysis of the 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. There doesn't need to be complete precipitation of metallic ions of a particular group using 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 ndA 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$_2$S 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$_2$S is passed in the rest of the solution. It is faltered and washed well with H$_2$S water. The filtrate is kept for III group. Different radicals give the following coloured precipitates.

Hgs	Black(so metimes red)	C ds	Yellow
Pbs	Black(or Brown)	As_2S_2	Yellow
Bi_2S_2	Brown	SnS_2	Yellow
Cu S	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)

14.15 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.

Black residue	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$_2$SO$_4$ to the whole filtrate and filter.		
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.	**White residue** It may contain Dissolve this residue in conc. Solution of CH$_3$COONH$_4$ and add K$_2$CrO$_4$ yellow ppt pb (Lead) confirmed.	**Filtrate:** It may contain Bi, Cu and Cd as nitrate. Add to it excess of NH$_4$OH and filter:	
		White residue: It may be Bi(OH)$_3$. Dissolve the residue in the least quantity of conc. HCl divide it in	**Filtrate:** It may contain Cu and Cd. If it is bule Cu is there if it iscolourless 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.

	two parts: (I) To first part add excess of water white ppt. (II) To second part add. Sod stannite soln. black ppt. (Bismuth confirmed)	Now pass H$_2$S yellow ppt. Cd++ (cadrnium) confirmed. Second method: Add. conc. HCl and pass H$_2$S and filter.	
		Black residue: Cu^{++}(Copper) confirmed.	**Filtrate:** Dilute it and pass H$_2$S again yellow ppt. (cadmium)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$_2$S gas yellow ppt. Cd^{++} (Cadmium) confirmed.

14.16 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 heatYellow 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 boil and pass H_2S gas. Filter if a ppt. is obtained.	
	Orange residue: 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.	**Filtrate:** 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 THE 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 IV^{th}group. Dissolve the ppt. in 2 c.c. of H_2O_2 or over 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 :	Filtrate :	
Brown ppt . it may contain $Fe(OH)_3$ or $MnO(OH)$.	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 colourMn^{++} (Manganese) confirmed. (ii) Dissolve the precipitate in dil. HNO_3 or dill. HCI and divide it in two parts: To first part add $K_4[Fe(CN)_6]$ deep blue colour or ppt. (b) To second part add ammoniumSulphocyanideBlood red colour Fe^{+++}(Ferric) Confirmed.	(a) First part CH_3COOH +$(CH_3COOH)_2Pb$ ↓ 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^{+++}(Aluminium) 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 to convert all ferrous salts into ferric salts.

(iv) Addition of NH_4Cl before NH_4OH is essential otherwise the basic radicals of IVth 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.

14.17 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^{++})
Sulphide	Black (NIS) Green- Green	Black(CoS) PinkPink	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 greencolour (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 solutionMn^{++}(Manganese) confirmed.	**Filtrate:** It may contain zinc.Pass H_2S in the filtrate. A white grey ppt.Zn^{++}(Zinc) confirmed.

14.18ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

After boiling off H_2S, concentrate the fourth group filtrate 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 soln. 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).

14.19 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.

14.20CHEMICAL REACTIONS INVOLVED IN THE TEST OF BASIC RADICALS

First Group: Lead(Pb^{++}),Silver(Ag^+)Mercurous (Hg_2^{++})andlead (Pb^{++}).

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl2 \downarrow + 2HNO3$$
$$\text{White ppt}$$

$$PbCl_2 + 2KI \longrightarrow PbI_2 \downarrow + 2HCl$$
$$\text{Yellow ppt.}$$

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_2 \downarrow + 2KCl$$
$$\text{Yellow ppt}$$

$$PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2KCl$$
$$\text{White ppt}$$

SILVER (Ag+) :

$$AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3$$
$$\text{White ppt}$$

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$
$$\text{Silver ammonichloride}$$

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl \downarrow + 2NH_4NO_3$$
$$\text{White ppt}$$

Mercurous (Hg^{++}):

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 \downarrow + 2HNO_3$$

White ppt

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow HgNH_2Cl + Hg + NH_4Cl + 2Cl$$

Ammino mercuric chloride
Black

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

White ppt

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg \downarrow + SnCl_4$$

Grey ppt

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.

$$2HNO_3 + 3H_2S \longrightarrow 4H2O + 2NO \uparrow + 3S \downarrow$$

$$2NaNO_2 + 2HCl + H_2S \longrightarrow 2NaCl + 2NO \uparrow + 2H_2O + S \downarrow$$

$$Na_2SO_3 + 2HCl + 2H_2S \longrightarrow 2NaCl + 3H_2O + 3S \downarrow$$

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S \downarrow$$

Mercuric (Hg^{++}) :

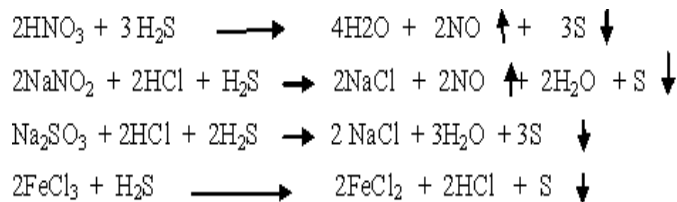$$HgCl_2 + H_2S \longrightarrow HgS \downarrow + 2HCl$$

Black ppt

$$3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 2NO \uparrow + 3S + 4H_2O$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

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.

$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO \uparrow + 3S + 4H_2O$

$Pb(NO3)2 + H2SO4 \longrightarrow PbSO_4 \downarrow + HNO_3$

                 White ppt

$PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2Pb(SO_4)_2 + (CH_3COO)_2Pb$

$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2CH_3COOK$

Bismuth (Bi^{+++})

$2BiCl_3 + 3H_2S \longrightarrow Bi_2S_3 \downarrow + 6HCl$

                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

$2BiCl_3 + 3Na_2SnO_2 + NaOH \longrightarrow 2Bi \rightarrow + 3Na_2SnO_3 + 6NaCl + 3H_2O$

Copper ($Cu++$) :

$CuCl_2 + H_2S \longrightarrow CuS \downarrow + 2HCl$

              Black ppt.

$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO \uparrow + 3S \downarrow + 4H2O$

$Cu(NO3)2 + 4NH4OH \longrightarrow Cu(NH_3)_4(NO_3)_2 + 4H_2O$

                 Tetraamine copper nitrate
                 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++):

$$CdCl_2 + H_2S \longrightarrow CdS \downarrow + HCl$$

<div align="center">Yellow ppt</div>

$$CdS + 2HCl \longrightarrow CdCl_2 + H_2S \downarrow$$

$$CdCl_2 + 2NH_4OH \longrightarrow Cd(OH)_2 \downarrow + 2NH_4Cl$$

$$Cd(OH)_2 + 2NH_4Cl + 2NH_4OH \longrightarrow [Cd(NH_3)_4]Cl_2 + 4H_2O$$

<div align="center">Tetramine cadmium chloride
Colourless</div>

Copper- Cadmium Separation :

$$CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2 \downarrow$$

$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 \downarrow + (CN)_2 \uparrow$$

<div align="center">White ppt.</div>

$$Cu_2(CN)_2 + 6CN \longrightarrow 2K_3[Cu(CN)_4]$$

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 : $[Cu(CN)] \rightleftharpoons Cu^+ + 4CN^-$

<div align="right">(Very small dissociation
due to to greater stability
of the complex ion)</div>

Primary : $K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)]^{2-}$

                 Pot. Cadmicyanide

Secondary : $[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{++} + 4CN^-$

<div align="right">(Considerable dissociation
due to lesser stability of the complex ion)</div>

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^{+++}):

$$AsCl_3 + 3H_2S \longrightarrow As_2S_3\downarrow + 6HCl$$
$$\text{Yello ppt.}$$

$$As_2S_3 + 3(NH_4)2S_2 \longrightarrow 3(NH_4)3AsS_3$$
$$\text{Ammonium thio arsenite}$$

$$3(NH_4)3AsS_3 + 6HCl \longrightarrow As_2S_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$$
$$\text{Ammonium thio arsenite} \qquad\qquad \text{Yello ppt}$$

As_2S_3 dissolves in nitric acid forming arenic acid(H_3AsO_4)

$$H_3AsO_4 + 12(NH_4)2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4.12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$$
$$\text{Yello ppt}$$

Antimony (Sb^{+++}):
$$\text{Ammonium arsenomolybdate}$$

$$3SbCl_3 + 3H_2S \longrightarrow SbS_3\downarrow + 6HCl$$
$$\text{Orange ppt.}$$

$$SbS_3 + 3(NH_4)2S_2 \longrightarrow 2(NH_4)3SbS_3$$

$$SbS_3 + 3(NH_4)2S_2 \longrightarrow 2(NH4)_3SbS_4 + S\downarrow$$
$$\text{Ammonium thio-antimonate}$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_5\downarrow + 6NH_4Cl + 3H_2S\uparrow$$

$$SbS_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow$$

$$SbS_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow + 2S\downarrow$$

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
$$\text{Milky(Antomony oxychloride)}$$

Tin (Sn^{++},Sn^{++++}):

$$SnCl_2 + H_2S \longrightarrow SnS\downarrow + 2HCl$$
$$\text{Brown ppt.}$$

$$SnCl_4 + 2H_2S \longrightarrow SnS_2\downarrow + 4HCl$$

SnS- Insoluble in ordinary amm. sulphide but soluble in yello amm. sulphide.

SnS$_2$- Soluble in ordinary amm. sulphide

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_2$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_2$$
$$\text{Amm. thio-stannate}$$

$$(NH_4)_2 SnS_3 + 2HCl \longrightarrow SnS_2\downarrow + 2NH_4Cl + H_2S\uparrow$$
$$SnS_2 + 4HCl \longrightarrow SnCl_4 + 2H_2S\downarrow$$

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4$$
$$\text{White ppt.}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_2$$

Third Group

IRON, ALLMINIUM, CHROMIUM

Fe^{+++}, Al^{+++}, Cr^{+++}

In the third group ferrous salts(Fe^{++}) areoxidized to ferric salts (Fe^{+++}) by boiling it with few drops of con. HNO_3.

$$2FeCl_2 + 8HNO_3 \longrightarrow 2Fe(NO_3)_3 + 4HCl + 2NO_2\uparrow + 2H_2O$$

Iron (Fe^{+++}):

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3NH_4Cl$$
Brown ppt.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$2FeCl_3 + 6NH_4CNS \longrightarrow Fe[Fe(CNS)_6]_3\downarrow + 12KCl$$
Ammo. thiocyanate   Ferric sulphocyanide
                                     Blood red colour

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe[Fe(CNS)_6]_3 + 12KCl$$
Pot. ferrocyanide   Ferric ferrocyanide
                                   Deep blue colour

Aluminium (Al^{+++}):

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + NH_4Cl$$
White ppt.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_3 + 2H_2O$$

$$NaAlO_3 + NH_4Cl + H_2O \longrightarrow Al(OH)_3\downarrow + NH_3 + NaCl$$

Chromium (Cr+++):

$$2CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3\downarrow + 3NH_4Cl$$
Green ppt.

$$Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

$$2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O$$

$$Cr(OH)_3 + 4NaOH \ 3H_2O_2 \longrightarrow Na_2CrO_4 \ 5H_2O \ 3NaBr$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4\downarrow + 2CH_3COONa$$
Yello ppt.

Fourth group

ZINC, MAGNASIUM, COBALT

Zinc (Zn^{++})

$$ZnCl2 + H2S \longrightarrow ZnS\downarrow + 2HCl$$
White grey ppt.

$$ZnS + 2HCl \longrightarrow ZnCl_2 \ 2H_2S\downarrow$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$
White ppt.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2HCl$$

MANGANESE (Mn^{++}) :

$$MnCl_2 + H_2S \rightarrow MnS \downarrow + 2HCl \uparrow$$
Buff coloured ppt.

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S \uparrow$$

$$MnCl_2 + 2NaOH \rightarrow Mn(OH)_2 \downarrow + 2NaCl$$

$$2Mn(OH)_2 + O \rightarrow 2MnO(OH) \downarrow + H_2O$$
Brown ppt.

$$MnO(OH) + 2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + HMnO_4$$
Pink colour
(Permanganic acid)

COBALT (Co^{++}) :

$$CoCl_2 + H_2S \rightarrow CoS \downarrow + 2HCl$$

$$3CoS + 2HNO_3 + 6HCl \rightarrow 3CoCl_2 + 2NO \uparrow + 3S \downarrow + 4H_2O$$
Aqua-regia

$$CoCl_2 + 2HNO_2 \rightarrow Co(NO_2)_2 + 2KCl$$

$$CO(NO_2)_3 + 4KNO_3 \rightarrow K_4[Co(NO_2)_6]$$
Pot. cobaltonitrite

$$2K_4[Co(NO_2)_6] + 2CH_3COOH + O \text{ (air)}$$
Pot. cobaltonitrite
$$\rightarrow 2K_3[Co(NO_2)_6] \downarrow + 2CH_3COOK + H_2O$$
Yellow ppt.
Pot. cobaltinitrite

NICKEL (Ni^{++}) :

$$NiCl_2 + H_2S \rightarrow NiS \downarrow + 2HCl$$
Black ppt.

$$3NiS + 2HNO_3 + 6HCl \rightarrow 3NiCl_2 + 2NO \uparrow + H_2O + 3S \downarrow$$
Aqua-regia

2.

CH₃—C = NOH
|
CH₃—C = NOH
Dimethyl glyoxime
+ 2NH₄OH + NiCl₂ ⟶

(Structure of Nickel dimethyl glyoxime complex)

+ 2NH₄Cl + 2H₂O
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

---

waterisoxidised 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.

$$CoCl_2 + 2NaHCO_3 \rightarrow (Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \rightarrow Na_4[Co(CO_3)_3] + 3H_2O + 3CO_2 \uparrow$$
Sod. cobalto carbonate

$$2Na_4[Co(CO_3)_3] + Br_2 \rightarrow 2Na_3[Co(CO_3)_3] + 2NaBr$$
Sod. cobalto carbonate   Sod. cobalti carbonate
(Green)

$$Br_2 + H_2O \rightarrow 2HBr + O$$

$$NiCl_2 + 2NaHCO_3 \rightarrow NiCO_3 + 2NaCl + H_2O + CO_2 \uparrow$$

$$2NiCO_3 + 3H_2O + O \rightarrow 2Ni(OH)_3 \downarrow + 2CO_2 \uparrow$$

$$2Ni(OH)_3 \rightarrow Ni_2O_3 \downarrow + 3H_2O$$
Nickelic hydroxide   Black ppt.

FIFTH GROUP
BARIUM, STRONTIUM, CALCIUM
$(Ba^{++}, Sr^{++}, Ca^{++})$

BARIUM (Ba^{++}) :

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3 \downarrow + 2NH_4Cl$$
White ppt.

$$BaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ba + H_2O + CO_2 \uparrow$$
Barium acetate

$$(CH_2COO)_2Ba + K_2CrO_4 \rightarrow BaCrO_4 \downarrow + 2CH_3COOK$$
Barium acetate   Yellow ppt.

STRONTIUM (Sr^{++}) :

$$SrCl_2 + (NH_4)_2CO_3 \rightarrow SrCO_3 \downarrow + 2NH_4Cl$$
White ppt.

$$SrCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Sr + H_2O + CO_2 \uparrow$$
Strontium acetate

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \rightarrow SrSO_4 \downarrow + 2CH_3COONH_4$$
Strontium acetate   White ppt.

CALCIUM (Ca^{++}) :

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + 2NH_4Cl$$
White ppt.

$$CaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + H_2O + CO_2 \uparrow$$
Calcium acetate

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 \downarrow + 2CH_3COONH_4$$
Calcium acetate   White ppt.

Sixth group

Magnesium (Mg^{2+}):

$Mg(NO_3)_2 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4 \downarrow + 2NaNO_3$ (white ppt.) $+ H_2O$

zero group:

Ammonium (NH_4^+)

$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3 \uparrow$

$NH_3 + HCl \rightarrow NH_4Cl$ (white fumes)

14.20 SUMMARY

- This unit gives the classification of anions (Acidic Radicals).
- 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. It is is obtained after boiling the salt or mixture with an excess of sodium carbonate solution.
- Na_2CO_3 used in the preparation of soda extract should be pure, free from chloride and sulphate which are generally present as impurities. 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.

14.21 REFERENCES

1.Practical Chemistry by D. N. Bajpai, O P Pandey & S Giri, S Chand publication.

2.Advanced Practical Organic Chemistry by N K Vishnoi Vikas Publication.

3.Comprehensive Practical Organic Chemistry by V.K Ahluwalia and sunita Dhingra.

4. 4.Text Book of Organic Practical Chemistry, A.I. Vogel.

14.22 TERMINAL QUESTIONS

1.What are group reagents? What are the advantages of using the group reagents in qualitative analysis?

2.What is water –extract and how is it prepared and used?

3.What is the purpose of preparing sodium extract for identification of anions?

4.Name the solutions that give;

a) A black ppt. on mixing.

b) A white ppt. on mixing , soluble in ammonia.

c) A red ppt . on mixing , soluble in excess of one of them.

5.What is aqua regia? Explain its functioning?

6.In third group , would it be permissible to use $NaCl + NaOH$ buffer instead of $NH_4Cl + NH_4OH$?

7.How can you confirm that a substance is partially soluble in water?

8. What is the basic difference between preliminary and confirmatory test.

9. Why do we prefer NH_4OH to other alkalis in III group precipitation?

UNIT-15: ORGANIC EXERCISE: CHEMICAL

PHYSICAL

AND FUNCTIONAL GROUP TEST

CONTENTS:

15.1 INTRODUCTION

Quantitative tests are involve to, study and dentification of various Organic compounds and then careful correlated the observed fact.Because functional groups influence the physical, chemical, and spectral properties of an organic compound, a chemist can identify a compound's functional groups by measuring certain physical properties, observing its chemical behavior with different classification reagents, and studying other spectral data.

15.2 OBJECTIVES

Inthischapter,Learnerslearnthefollowingobjectives.

- Systematic analysis and identified the organic compounds by physical and chemical tests.
- Different physical and chemical testswith special reference to alcohols, phenol, aldehyde and ketones.
- With physical and chemical test differences between alcohol - phenol and aldehyde–ketones.

15.3 TEST FOR FUNCTIONAL GROUPS

The general procedure, adopted for systematic analysis of Functional groups consists of followings steps:

15.3.1 Preliminary examination

Physical State, Colour and Odour: A careful observation of the physical state, colour and characteristic smell of the compound gives useful information regarding the nature of the compound. For example, the colour of a compound is related to its chemical constitution or else to some impurities in it. Similarly, there are certain groups of compounds which have similar smell. The following table is helpful to some extent in correlating the physical characteristics and the chemical nature.

Colourless solids	Carbohydrates, simple acids, some phenols, amides and anilides
Coloured solids	Nitro compounds, amines, phenols, quinines
Colourless liquids	Alcohols, aldehydes, ketones, simple hydrocarbons and simple acids.
Coloured liquids	Nitro compounds, phenols and amines

Carbolic smell	Phenols.
Smell of bitter almonds	Benzaldehyde and nitrobenzene
Fruity-pleasant smell	Esters.
Spirituous smell	Alcohols.
Pungent smell	Formic acid or formalin

15.3.2 Ignition test

Take a small portion of the given compound on a metallic spatula and ignite it over non-luminous flame and note the changes:

Observation	Inference
a)Burns with a sooty flame	May be an aromatic compound
b)Yellow and non-sooty flame	May be an aliphatic compound.
c) Chars	May be a carbohydrate, hydroxyl acid or Sulphanic acids
d)Smell of ammonia:	Nitrogenous compound like urea

.

Note: Some of the aliphatic compounds like $CHCl_3$, CCl_4 and C_2Cl_6, owing to high percentage of carbon, give sooty flame.

15.3.3 Solubility behaviour

The behaviour of the compound towards various solvents like water, dilute caustic soda, dil. HCl and conc. H_2SO_4 also reveals its nature. Take a small portion of the substance and note its solubility in above solvents:

Observation	Inference
(a) Soluble in hot water and solution is acidic to litmus	Salts of aromatic bases. Lower aliphatic acids, hydroxyl acids or polyhydroxy phenols.
(b) Soluble in hot water and solution is acidic	Higher acids or some phenols.
(c) Soluble in cold water and solution in neutral	Carbohydrates or alcohols.

(d)	Soluble in hot water and solution is neutral	Starch, quinones.
(e)	Soluble in cold dil. $NaHCO_3$ with effervescence	Carboxylic acids.
(f)	Soluble in cold dil. NaOH	Carboxylic acids or phenols.
(g)	Soluble in hot NaOH and give off ammonia	Amides, ammonium salts.
(h)	Soluble in cold conc. H_2SO_4	Aromatic hydrocarbons or phenols.
(i)	Soluble in hot conc. H_2SO_4 and charring occurs	Carbohydrates, Aldehyde, ketones or hydroxyl acids.
(j)	Soluble in dil. HCl	Amines

15.3.4 Test for Unsaturation

(a)   Test with Bromine: Take a solution or suspension of the compounds in water and add to it few drops of bromine water. You may also take a solution/suspension of the compound in carbon tetrachloride and add to it a solution of bromine, shake well and note the changes:

Observation	**Inference**
(i) *Decolourisation*	Unsaturated compounds containing Alkene(C=C).
(ii) *A precipitate is obtained*	Amines and phenols.

(b)   Test with alkaline KMnO₄ solution: Dissolve a small amount of the substance in water or acetone. Add to it 1 ml of dil. sodium carbonate solution and a few drops of potassium permanganate solution and shake well.

If the colour of the permanganate disappears, the given compound may be unsaturated. Heating is forbidden in this test.

15.3.5 Detection of functional group, Alcohols,Phenols, Aldehyde, Ketone

The determination of functional groups depends largely on the correct determination of elements. Once the functional group present in the organic compound is known, one can find out the name of the probable compound with the help of melting point or boiling point. Next procedure is to

study some specific reactions of the compound and then to confirm its name by preparing suitable derivatives. It may be noted that element carbon, hydrogen and oxygen are not tested for. This clearly means that if not other element is present, functional group containing carbon, hydrogen and oxygen are determined.

The test for functional groups should be performed according to the following way:

When only Carbon, Hydrogen and/or Oxygen are present.

S. No.	Class	Functional group	Tests
1.	Alcohols	-OH	**i)** In a dry test tube, take 2 mL of O.S, add 1 g of anhydrous sodium sulphate (to absorb water if already present) and filter. To the filtrate, add a small piece of sodium. Effervescence due to evolution of H_2 shows the presence of an alcohol. **(ii)** To 1 mL of O.S. or its aqueous solution, add a few drops of ceric ammonium nitrate. A pink or red colour shows the presence of an alcohol.
2.	Phenol	Phenolic-OH	(i) Blue litmus changes to red but no effervescence with $NaHCO_3$. (ii) **FeCl₃ test.** To 1 mL of aqueous or alcoholic solution of original substance (O.S) add 2-3 drops of neutral or very dilute solution (aqueous) of ferric chloric. A blue, green, red or violet colour indicates presence of phenolic group $(-OH)$. (iii) **Libermann's test.** All phenols in which para position is free respond to this test. Take 0.2 g of O.S. and a few crystals of $NaNO_2$ in a dry test tube and heat gently for a minute.

			Cool the mixture, add 1 mL of conc. H_2SO_4 and shake. A deep green or blue colour develops, upon dilution with water the solution turns red. To it, add excess of dil. NaOH solutions, the red solution again becomes deep green or blue. It indicates the presence of phenolic group. (iv) **Phthalein test.** Take 0.2 g each of O.S. and phthalic anhydride in a dry test tube, add 0.5 mL of conc. H_2SO_4 and heat for a minute. Cool, make it alkaline with dil. NaOH solution. Pour a few drops of this solution in 20 mL water taken in a beaker. Characteristic colour shows the presence of phenolic group, e.g. Pink colour – Phenol, *o*-Cresol Blue colour – Catechol, *m*-Cresol NO colouration – *p*-Cresol.
3.	Aldehydes	$$-C{\overset{\displaystyle O}{\underset{\displaystyle H}{\Big<}}}$$	**(i) Schiff Test.** To 1 mL aq. or alcoholic solution of O.S. and 2 mL of Schiff reagent and shake. A deep red or violet colour shows the presence of aldehydic group (never heat during this test). **(ii) Tollen's test.** To about 2 mL of Tollen's reagent add about 0.5 g of O.S. and heat the mixture on water bath. Formation of silver mirror or blackish precipitate indicates the presence of aldehydic group. (This test is also given by reducing sugars). **(iii) Fehling solution test.** Add Fehling solution B to A until a blue precipitate first formed is redissolved to give a deep blue solution. To it add a little of O.S. and heat for 2 minutes.

			Reddish brown precipitate shows the presence of aldehydic group. (This test is also given by reducing sugars).
4.	Ketones	$\diagup C = O$	**(i)** No colour with Schiff reagent. **(ii) 2, 4 Dinitrophenylhydrazine test.** Add 1-2 drops (0.5 g) of O.S. to 2 mL of 2, 4 dinitrophenylhydrazine solution (Brady's reagent). Shake vigorously. Heat and cool. A red, yellow or orange. Coloured precipitate indicates the presence of ketonic group.

15.4 CHEMICAL AND PHYSICAL TESTS

15.4.1   Difference between alcohols and phenols

Alcohols	Phenols
1.Alcohols does not react with bromine water.	1. Phenol react with bromine water to give white precipitated.
2**.** Alcohols does not react with NaOH.	2.Phenol react with NaOH produce sodium Phenoxide product.
3.Ferric chloride reacts with the aliphatic alcohol.	3.Ferric chloride reacts with the aromatic alcohol(Phenol) to form a purple solution due to the displacement of the chloride anions with the aromatic rings

15.4.2   Difference between Aldehyde and Ketone

Aldehydes	Ketones
1. Aldehydes reat with Schiff reagents produce deep red violet colour	1. Ketones do not respond this reaction.
2**.** When the aldehyde compound is treated	2.Ketones do not respond with Fehling's

with Fehling's solution Cu^{2+} is reduced to Cu^+ and the aldehyde is reduced to acids.Due to this the compound gives a reddish-brown precipitate. (Aromatic aldehydes do not respond to Fehling's test.)	reagents.
3. Aldehydes react with Tollens reagent giving a grey-black precipitate or a silver mirror.	3. Ketones do not respond to this test.
4. Aldehydes react with chromic acid and gives a green to blue precipitate	4.Ketones do not react with chromic acid.
5.Aldehydes do not respond to this test.	5.Ketones reacts with alkali and forms an anion which further reacts with sodium nitroprusside and forms a red coloured complex ion.

15.5 SUMMARY

- The present unit provide a detailed description of analysis and identifies the organic compounds by physical and chemical tests.

- Determination of various functional groups and their confirmatory tests are also included in the unit.

- The unit also comprises how to separate the alcohols -phenolic, and aldehyde –Ketones by chemical and physical tests.

15.6 REFERENCE AND FURTHER STUDIES

1.Practical Chemistry by D. N. Bajpai, O P Pandey & S Giri, S Chand publication.

2.Advanced Practical Organic Chemistry by N K Vishnoi Vikas Publication.

3.Comprehensive Practical Organic Chemistry by V.K Ahluwalia and Sunita Dhingra.

15.7 TERMINAL QUESTIONS

---

1. Write any two tests to identify of Aldehyde functional group.

2. Write any two tests to the identification of Ketone's functional group.

3. Define the test ,which is given by Ketones not by aldehydes.

4. Write the test in which phenols give red precipitate but alcohol is not.

5. What are the general procedure , adopted for systematic analysis of Functional groups?

6. Which reagent/test is used to differentiate between benzaldehyde and acetophenone?

7. What is the Tollens Test for Aldehyde?Do Ketones give Tollens Test?

UNIT 16: PHYSICAL EXCECISE: PARTITION COEFFICIENTAND TRANSITION TEMPERATURE

CONTENTS:

16.1 INTRODUCTION

Partition equilibrium is the phenomenon of a solute distributing itself between two distinct phases in contact with one another, Fig.1. The two phases could be gas and liquid or two immiscible liquids. According to Nernst distribution law, when a liquid or solid substance is added to a mixture of two immiscible liquids, the ratio of the concentration of solute distributed between two immiscible solvents at a given temperature is a constant and does not depend on the amount of the solute used i.e.

$$K_D = C_1 \text{(Phase 1)}/C_2 \text{(Phase 2)}$$

Where C_1 and C_2 are concentration of similar molecular species in the two immiscible liquids 1 and 2 at a constant temperature. K_D is called the partition coefficient or distribution coefficient.

Figure.16.1. Distribution of iodine between H$_2$O (X) and CCl$_4$ (Y)

If more of the solute is added to the system, the solute will distribute itself between the immiscible liquids so that the ratio of the solute concentration remains the same at constant temperature independent of the total quantity of solute in the same molecular state. The important condition for the above law to hold is that the solute is in the same molecular state in both the liquid phases.

Validity of the law

1. Temperature and pressure should remain constant throughout the experiment.

2. Equilibrium state should have been attained.

3. Neither solution should have reached the saturation state

4. The two liquids should be immiscible.

5. The molecular state of the solute should be the same in both the layers

The transition temperature is the temperature at which a material changes from one crystal state (allotrope) to another. More formally, it is the temperature at which two crystalline forms of a substance can co-exist in equilibrium.Like when rhombic sulfur is heated above 95.6 °C, it changes form into monoclinic sulfur; when cooled below 95.6 °C, it reverts to rhombic sulfur. At 95.6 °C the two forms can co-exist.It is clear that, 95.6°C is the transition temperature of sulphur.

16.2 OBJECTIVES

After studying this unit, you should be able to: -

1. Understand the concept of partition equilibrium of a solute between two phases.
2. Define Nernst distribution.
3. Calculation of the partition coefficient of a solute distributed between two phases.
4. Determine the distribution coefficient of iodine between water and CCl_4 at room temperature.
5. Determine the distribution coefficient of benzoic acid between water and toluene at room temperature.
6. Learners understood the basic facts of the transition temperature.

To Determine the transition temperature of salt hydrates.

16.3 DETERMINATION OF PARTITION COEFFICIENT OF IODINE IN WATER/ TETRACHLOROMETHANE

16.3.1 Chemicals and Apparatus Required

Potassium dichromate, sodium thiosulphate (0.1N and 0.01N), potassium iodide, starch indicator, iodine, CCl_4 and distilled water. Well-stoppered reagent bottles (150 cm^3), burette, pipettes, conical flasks and porcelain troughs.

16.3.2 Principle

This experiment is an example of a partition system involving the distribution of I_2 between an aqueous phase and a water immiscible organic phase namely carbon tetrachloride.

$$I_{2\,(aq)} \quad \rightleftharpoons \quad I_{2(CCl4)}$$

$$K= [I_{2\,(aq)}]/ [I_{2(CCl4)}] = 0.0116$$

Solvent CCl_4 remains in the lower layer as it is denser than water. The non-polar I_2 is more soluble in the nonpolar organic solvent than in the highly polar solvent, water. The amount of I_2 in both the layers is analysed by titrating aliquots pipetted out from each layer with standardized sodium thiosulphate using starch as indicator.

16.3.3 Procedure

1. Label three bottles I, II and III. Make the following mixtures in each bottle as given in Table 1 and shake the bottles in a mechanical shaker for about an hour. Place the bottles in a water trough for 20 minutes to attain equilibrium.

Table 1. List of Amount of iodine in CCl4 and water to make various mixtures

Bottle No.	Contents
I	20 cm^3 of saturated solution of iodine in CCl_4 + 200 cm^3 of distilled water
II	25 cm^3 of saturated solution of iodine in CCl_4 + 250 cm^3 of distilled water
III	30 cm^3 of saturated solution of iodine in CCl_4 + 300 cm^3 of distilled water

2. Standardize thiosulphate solution with the help of standard potassium dichromate solution and repeat the titrations for concordant readings as shown in Table 2.

3. Pipette out 5 cm^{3}of the CCl_4 layer from bottle I into a conical flask and add 20 cm^3 of distilled water. Add 2 cm^3 of 10% KI solution. Titrate this solution against a previously standardized 0.1N thiosulphate solution using starch as indicator. The end point is the disappearance of blue colour. Repeat the experiment to get concordant values. Record your readings as shown in Table 3.

4. Now pipette out 25 cm^3 of the aqueous layer from bottle I. Titrate this solution against a previously standardized 0.1N thiosulphate solution using starch as indicator. The end point is the disappearance of blue colour. Repeat the experiment to get concordant values. Record your readings as shown in Table 4.

5. Tabulate your readings as shown in Table 5 to determine K_D.

6. Repeat the above procedure for bottle II and III.

16.3.4 Observation

Table 2. Titre values for standardization of sodium thiosulphate

Volume of K$_2$Cr$_2$O$_7$ cm^3	Burette reading /cm^3		Volume of sodium thiosulphate/ cm^3
	Initial	Final	
20			
20			

Table 3. Titre values for titration of Iodine present in the organic layer with thiosulphate in bottle I

Bottle	Volume of CCl$_4$ layer/ cm^3	Burette Reading / cm^3		Volume of Thiosulphate cm^3
		Initial	Final	
I				
II				
III				

Table 4 Titre values for titration of Iodine present in aqueous layer with thiosulphate in bottle I

Bottle	Volume of aqueous layer cm^3	Burette Reading/ cm^3		Volume of Thiosulphate cm^3
		Initial	Final	
I				
II				
III				

Table 5. Determination of dissociation constant K_D

Bottle	Layer	Volume of Thio cm^3	Strength of I_2	$K_D = C_1/C_2$
I	CCl$_4$			
	Aqueous			
II	CCl$_4$			
	Aqueous			
III	CCl$_4$			
	Aqueous			

16.3.5 Calculations

A. Standardisation of sodium thiosulphate solution

$$N_1 \times V_1 = N_2 \times V_2$$

N_1= concentration of $K_2Cr_2O_7$

V_1= volume of $K_2Cr_2O_7$
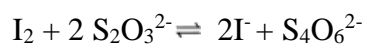
N_2= concentration of sodium thiosulphate

V_2= volume of sodium thiosulphate

$$N_2 = \frac{N_1 \times V_1}{V_2}$$

B. Aqueous Phase

$$I_2 + 2\,S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-}$$

$$N_1 \times V_1 = N_2 \times V_2$$

N_1= concentration of I_2 in the aqueous layer

V_1= volume of I_2 in the aqueous layer

N_2= concentration of thiosulphate solution

V$_2$= volume of thiosulphate solution used in titration of aqueous layer

The volume of sodium thiosulphate consumed in the titration is equivalent to the amount of iodine present.

Equivalent weight of iodine =

Concentration of iodine in aqueous layer, $[I_2]_{H2O}$ =   …. N

C. Organic Phase

$$N_1 \times V_1 = N_2 \times V_2$$

N$_1$= concentration of I$_2$ in the organic layer

V$_1$= volume of I$_2$ in the organic layer

N$_2$= concentration of thiosulphate solution

V$_2$= volume of thiosulphate solution used in titration of organic layer

Concentration of iodine in organic layer, $[I_2]_{CCl4}$ =   …. N

The volume of sodium thiosulphate consumed in the titration is equivalent to the amount of iodine present.

$$K_D = N [I_2]_{H2O}/N[I_2]_{CCl4}$$

16.3.6 Result

The distribution coefficient of iodine between CCl$_4$ and water is found to be………….

16.4 TO DETERMINE THE TRANSITION TEMPERATURE OF HYDRATED SALT

16.4.1 Chemicals and apparatus required

Beaker, Boiling tube, Tripod stand, Glass rod, wire gauze, stand and clamp, thermometer

with cork, burner, water and hydrated salt.

16.4.2 Theory of transition temperature

- The different crystalline forms of a polymorphous may not be equally stable at a given temperature. The temperature at which both the crystalline forms are stable and coexist is called the transition point or transition temperature.

- When a salt hydrate is heated, it loses water of crystallization at a particular temperature and above that temperature only the anhydrous form exits.

16.4.3 Principle

Salthydrates changes into the anhydrous form or less hydrated form at certain temperature known as the transition temperature.The transition and its accompanied by absorption or liberation of heat and it occurs at constant temperature.These are the best examples of 2-components of three-phase systems. According to theGibb's phase rule, degree of freedom,

$$F = C - P + 2$$
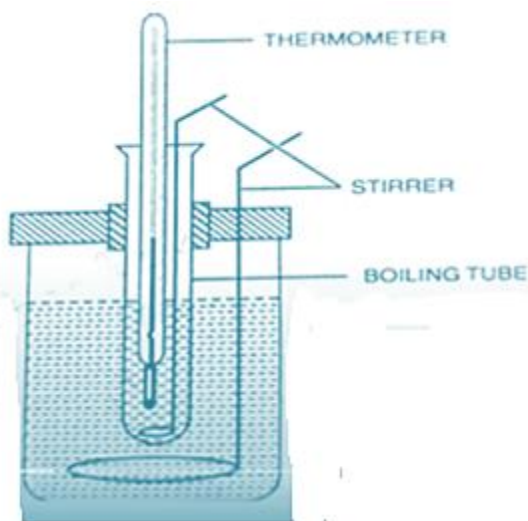
Where,   C = Number of components

P = Number of Phase

Therefore, F = 2 – 3 + 2 = 1

Therefore, the system is invariant at constant pressure. Hence the transition temperature is aconstant. The salt hydrate exists as a liquid solution above this transition temperature. If this liquid is cooled then the rate of cooling will be immediately changed at thetransition temperature, which can be directly noted.

16.4.4 Procedure

1.About7-8 g of the given salt hydrate is taken in a boiling tube, carrying a thermometer and stirrer.

2.The boiling tube keep inside a beaker containing water is heated till the solid melts and the temperature raises by about 5^0C more.

3. Then it is taken out of the tube, and time-temperature reading are noted for every 30 seconds.

4.The temperature remains constant for some time. If supercooling occurs, add one more crystal of the given salt hydrate.

5.A graph is also plotted with temperature against time. Thus the transition temperature of the given salt hydrate can be determined.

Apparatus used to determine the transition temperature

16.4.5 Observation

S. No.	Time (minut)	Temperature (^{0}C)	
		Heating (^{0}C) t_1	Cooling (^{0}C) t_2
1.	……..	……..	……….
2.	……..	………	………….
3.	………	……..	……….
4.	………	……….	………
5.	……..	……..	………
		Mean = X	Mean = Y

16.4.6 Calculation

The average of change points of the heating and cooling curve is:

$$t = \frac{t1+t2}{2} \quad = \quad ....^{0}C$$

16.4.7 Result

The transition temperature of hydrated salt is ……………. ^{0}C.

16.4.8. Precautions

1.The substance should be heated slowly with constant stirring.

2.The substance should be powdered form.

16.5 SUMMARY

- A number of varying mixtures of solute in two immiscible solvents were made in reagent bottles, shaken and left to attain equilibrium.
- The concentration of the solute in each layer was determined by titration with a suitable titrant using appropriate indicator.
- According to Nernst distribution law, the partition coefficient of the solute is the ratio of concentration of solute in solvent 1 to solvent 2 at constant temperature.
- Two cases were studied. In the first case i.e. distribution of iodine between water and CCl_4, the molecular species in both solvents is similar.
- In the second case (distribution of benzoic acid in water and toluene) the solute associates to form dimer in the organic solvent.

16.6 REFERENCE AND FURTHER STUDIES

1.Practical Chemistry by D. N. Bajpai, O P Pandey & S Giri, S Chand publication.

2.Advanced Practical Organic Chemistry by N K Vishnoi Vikas Publication.

3.Mendham,J.;Denny,R.C.;Barnes,J.D.;ThomasM.and SivasankarB.,Textbook

OfQuantitativeChemicalAnalysis,Pearson