

# GENERAL CHEMISTRY – IV

## d and f – Block Elements

### Introduction :

Periodic table is the systematic arrangement of elements in the order of increasing atomic numbers of the elements. On the basis of electronic configuration the periodic table has been divided into four blocks known as s , p, d and f block

### d – Block Elements

**Defination** : The elements in which last electrons enters the ‘ d ’ orbital of the penultimate shell i.e. (n-1) d orbital are cleed as d-block elements.

The d –block elements are called transition elements and consist of elements lying between s and p –blocks starting from fourth period onwards. These elements have properties which are transitional between those of s and p block elements. All these elements are metal.

The transition elements may be defined as elements whose atoms or simple ions in their common oxidation state contain partially filled d- subshell. The geneal electronic configuration of these metals is  $(n-1)d^{1-10} ns^{1-2}$

**Classification of d –block elements** : These are divided into three transition series.

- i) The first transition series. (3d-series) involves the filling of 3d- orbitals and has 10 elements from scandium ( Z = 21 ) to zinc ( Z = 30 ) in the fourth period.
- ii) The second transition series ( 4d-series) involves the filling of 4d orbitals and has 10 elements from ytterium ( Z= 39) to cadmium ( Z= 48 ) in the fifth period.
- iii) The third transition series ( 5d-series) involves the filling of 5d-orbitals and has 10 elements. The first element of this series is lanthanum( Z= 57 ) . it is followed by 14 elements ( lanthanides or lanthanons involving filling of 4f- orbitals). The next nine elements are from hafnium ( Z =72)to mercury ( Z = 80).
- iv) The fourth transition series ( 6d-series) involves the filling of 6d- orbitals and is incomplete starting from Actinium ( Z= 89 ) and extenedupto element with atomic number 104

### General Characteristics Of Transition Elements :

The members of given transition series do not differ so much from one another as those of non-transition elements ( representative elements) of the same period. The reason is that the electronic configuration of transition elements differ only in the number of electrons in ( n-1) d- subshell i.e., the number of electrons in the outermost shell ( n) remains the same. The outermost configuration is  $ns^2$  where n is the number of the period to which the given transition elements belong some important properties of transition elements are as follows.

1. **Metallic Character.** : d- Block elements have low ionisation energy and hence easily lose electrons to form cations. Further more these elements have only one or two

electrons in their outermost energy shell i.e., they have a large number of vacant orbitals in the outermost shell which make them form metallic bond. Because of this all the transition elements are metal.

They are generally (i) malleable and ductile (ii) forms alloys with several other metals. (iii) they are good conductors of heat and electricity. However, they differ from non-transition metals in being hard and brittle in certain cases. (Mercury has an exceptional behaviour. It is a liquid at room temperature). It is due to the presence of unpaired electrons in d-orbitals of their atoms which has a tendency for covalent bonding involving d-d overlappings. In a particular series the hardness increases upto the middle with increasing number of unpaired d- electrons. Thus, Cr, Mn and W having maximum number of unpaired d- electrons are very hard metals, while Zn, Cd and Hg are not hard metals due to the absence of unpaired electrons.

2. **Melting and Boiling Points:** The melting and boiling points of the transition elements are generally very high. This is due to the presence of covalent bonding by the unpaired d- orbital electrons.
3. **Atomic Radii:** The Variation in atomic radii across each transition series is not as simple as that observed in s and p- block elements. However, following overall trends in the variation of atomic radii across the period, are observed.
  - i) The atomic radii of the d-block elements of a given series generally decrease with increases in the atomic number. This is due to the fact that with an increase in atomic number the nuclear charge increases which in turn increasingly tends to attract the electron cloud inward resulting in decrease in size. However, the decrease in the radii across a period is not uniform. The decrease in radii of transition metals is small as compared to the decrease in the radii of s and p block elements for the same periods. For ex. The radii of the elements from Cr. To Cu are very close to one another. This may be explained on the basis of screening effect. In d- block elements electrons are added to an (n-1) d- subshell which adds to the primary screening effect. The additional electrons effectively screen the outer ns- electrons from the inward pull of the nucleus. As a result, the size of the atom does not change much from Cr to Cu.
  - ii) In a given series the atomic radius decreases from group 3 elements upto the group 10 elements and then increases again towards the end of the series. This anomalous increase in atomic radius towards the end of the series is because of the increased force of repulsion among the added electrons. Also the d- orbitals get completely filled in group 11 and 12 elements which also causes a decrease in force of attraction.
  - iii) Atomic radius increases on descending down the groups although the increase is not as significant as in case of s and p block elements. The very close similarity between the radii of the elements of second and third transition series, (Ex. Zr and Hf, Nb and Ta, Mo and W, Tc and Re etc.) is the consequence of the filling of 4f subshell.

#### 4. Atomic Volume and Densities:

- i) The atomic volume of the transition elements are much lower than those of their neighbouring s and p block elements. This is due to the fact that in d- block elements, the inner orbitals i. e. (n-1) d- orbitals are filled this leads to more nuclear pull resulting in decrease in volume.
- ii) Due to the decrease in atomic volume, the density of these elements increases. Therefore, the transition elements have quite have high density. Following trends are observed among the densities of the transition elements.
  - a) In a given transition series, the density increases across the series and reaches a maximum value at the middle of the series.
  - b) The density increases down the group because the atomic size of the elements of second and third transition series is nearly the same , their atomic masses increases nearly two fold and the densities of the elements of the third series are generally twice those of the corresponding elements of the second transition series

#### 5. Ionisational potential:

- i) Since atoms of transition elements are small in size, their ionisation energies are fairly high
- ii) The ionization potentials of the most of the d-block elements lie in between those of s and p –block elements. These are higher than those of s- block elements and are lower than those of p – block elements. This indicates that the d- block elements are less electropositive than the s- block elements.( alkali and alkaline earth metals).
- iii) The ionisation potential of d- block elements increases as we move across the series from left to right . However, the increase in the value is not as pronounced as in case of s and p – block elements of the same period. This is because in the transition elements , the effect of increasing nuclear charge is almost compensated by the extra screening effect provided by the increasing number of (n-1)d electrons

#### 6. Variable oxidation state.:

All transition elements, except the first and the last members of each series exhibit variable oxidation state. The cause of showing different oxidation states is due to the fact that there is only a small difference between the energies of the electrons in the ns orbitals and (n-1)d –orbitals with the result that both ns as well as (n-1)d –electron may be used for compound formation. Therefore , the variable oxidation state of transition elements are related to their electronic configuration. This is clear from the following table of oxidation state of elements of first transition series.

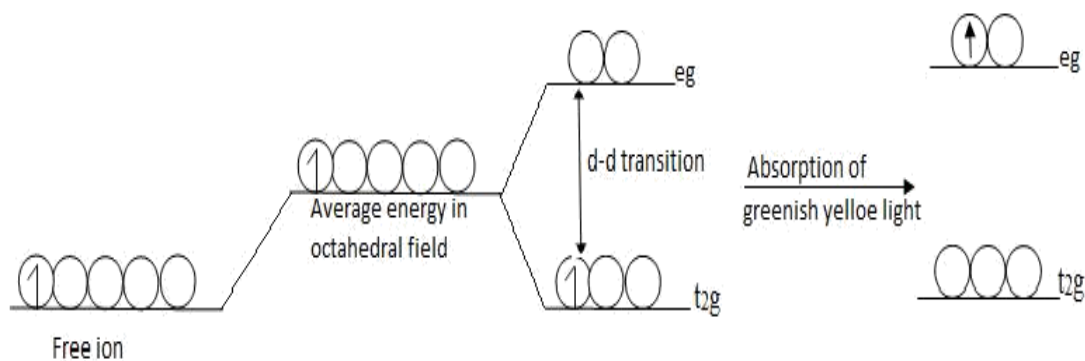
Elements	Outer electronic configuration	Oxidation
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^4 4s^2$	+2, +3, +4, +5, +6,
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

It must be noted that in some transition elements all of the (n-1)d –electrons are not involved during bond formation, e.g. iron ( $3d^6 4s^2$ ) should have +8 as its highest oxidation state, but actually it is only +6 which is also very rare( +2 and +3 are the common oxidation state of iron). The +6 ( and not +8) as the highest oxidation state is explained on the basis that during bond formation only the unpaired electrons of the 3d-subshell take part in bond formation. In iron there are 4 unpaired and 2 paired 3d-electrons and hence the effective electrons for bond formation in 3d-orbitals are only four which may give +6 as the highest oxidation state.

7. **Complex Formation** : The cations of transition metals have a great tendency to form complexes with several molecules or ions called ligands. The tendency of formation of complexes is due to the following two factors.
  - i) The cations of these metals are very small in size and have a high effective nuclear charge. Thus they have a very high positive charge density which facilitates the acceptance of lone pairs of electrons from other molecules or ions.
  - ii) The transition metal cations have vacant inner d-orbitals which are of appropriate energy to accept lone pair of electrons from the ligands. The bond involved in the formation of complexes are coordinate hence the complexes are termed as coordinate complexes.
8. **Formation of Coloured Compound:** the transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one d-orbital to another i.e., intra d-d transition takes place. Thus , when light falls certain visible wavelength are absorbed. The transmitted ( unabsorbed) or reflected light ( or colour) appears coloured and gives the colour of compounds. The ions having no d-d transition are colourless.

To understand the cause of colour in transition metal complexes, consider complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  , In this case, titanium is in +3 oxidation state.

The electronic configuration of  $\text{Ti}^{+3}$  :  $[\text{Ar}]3d^1$



During the formation of complex, as the six water molecules approach  $\text{Ti}^{+3}$  ion from different side these develop a negative field around it, as they donate lone pair present on oxygen to metal ion. There occurs repulsion between electrons of metal ion and ligand and energy of degenerate orbitals of metal ions increase and ultimately they split into two set of orbitals. The electron present in  $\text{Ti}^{+3}$ , prefers lower set of d-orbitals. The energy gap between two set of d-orbitals is very less and the energy available in the visible light is sufficient to cause excitation of electron from lower set of d-orbitals to higher set of d-orbitals, called a d-d transitions.  $\text{Ti}^{+3}$  absorbs greenish yellow component of white light during excitation of electrons, hence its aqueous solution appears as purple. This is because purple is the complimentary colour of greenish yellow in white light.

9. **Magnetic Properties:** Most of the transition elements show paramagnetism.

Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules. The magnetic character is comparable in terms of magnetic moment given by the expression  $= \sqrt{n(n+2)}$  Bohr Magneton, where  $n$  = the number of unpaired electrons. In general, greater the number of unpaired electrons, greater is the magnetic character. The maximum paramagnetism is noticed in  $d^5$  case which has maximum number of unpaired electrons.

10. **Formation of alloys :** due to their almost equal atomic sizes, they can mutually substitute one another in the crystal lattice to form alloys.

11. **Formation of non-stoichiometric compounds and interstitial compounds. :** transition metal can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen etc., in the vacant spaces between the crystal lattice forming inter-orbital compounds. For example,  $\text{FeC}$ ,  $\text{Fe}_8\text{N}$ ,  $\text{TiH}_2$ . This property differentiates these metals from non-transition elements. The products obtained are hard and rigid. Non – stoichiometric compounds like i.e.  $\text{Fe}_{0.98}\text{O}$ ,  $\text{Fe}_{0.86}\text{S}$ ,  $\text{VH}_{0.56}$ ,  $\text{TiH}_{1.7}$  are often classified as interstitial compounds.

12. **Catalytic properties:** Many transition metals and their compounds show catalytic properties, the most common being Fe, Pt, Ni,  $\text{V}_2\text{O}_5$  etc. This property may be either due to their variable valency (incomplete d-orbitals) which enables them to form unstable intermediate compounds or due to the fact that they can provide a suitable reaction surface.

13. **Reactivity** : The *d*- block elements are unreactive due to the following factors:

- i) **High ionisation energies** : on account of small size of their atoms, ionisation energies of *d*- block elements are fairly high
- ii) **High heats of sublimation**: Due to presence of covalent bonding, these have high heats of sublimation.

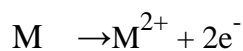
The tendency to remain unreactive is more pronounced in platinum and gold in the third transition series.

14. **Standard Electrode Potential** : The standard reduction potential of all the transition elements (except Cu and Hg in 3d-series etc.) is lower ( negative ) than that of hydrogen(taken as Zero ) . thus all the transition elements, with negative reduction potential, liberate hydrogen from dilute acids



However, some metals evolve hydrogen very slowly because they are protected from the attack of acids by the formation of an impervious layer of an inert oxide. For example, chromium is so unreactive that it can be used as a protective non-oxidising metal.

15. **Reducing Properties**: Transition metals with sufficiently negative standard reduction potential should be good reducing agents i.e, they should be oxidised easily to their ions.



However they are not good reducing agents as compared to elements of Group 1 , 2 and 13 . this is because the transition metals have less tendency to form ions due to their low reactivity.

**IRON** :Fe , At. No. 26, [Ar] 3d<sup>6</sup> 4s<sup>2</sup>

It is a reactive metal and do not occur in free state. In combined state it occurs in the ores

**Some important ores are :**

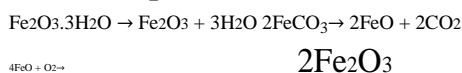
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| i) Haematite Fe <sub>2</sub> O <sub>3</sub>                    | iv) Magnetite Fe <sub>3</sub> O <sub>4</sub> |
| ii) Limonite Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O | v) Iron pyrites FeS <sub>2</sub>             |
| iii) Copper pyrites CuFeS <sub>2</sub>                         |  |

### Extraction.

Cast iron is extracted from its oxides by reduction with carbon and carbon monoxide in a blast furnace to give pig iron. The extraction of iron from the oxide ores involves the following steps :

1. **Ore dressing**. The large lumps of the ore are broken into small pieces. Most of the ores are rich enough and do not require further concentration. However, if clay is present, it is removed by washing with water.

2. **Roasting.** The ores are usually roasted to remove most of the moisture, to burn the organic matter and some of sulphur and arsenic; and to convert ferrous oxide to ferric oxide.



- (i) The ore becomes sintered (porous) and this facilitates its reduction to metallic iron later on.
- (ii) Ferric oxide does not form a slag at so low a temperature as ferrous oxide. Therefore, the early formation of a fusible slag (which would attack the lining of the furnace) is checked.

3. **Smelting.** The reduction of the roasted ore of ferric oxide is carried out in a blast furnace.

**Reactions in blast furnace.** The temperature of the internal portions vary between 200<sup>0</sup>C at the top to about 1600<sup>0</sup>C at the furnace bottom. The various reaction taking place at various parts of the furnace are described below.

- (i) The reduction of ferric oxide is done by carbon and carbon monoxide. The combustion of coke to carbon monoxide occurs at the hottest part of the furnace (between 1473K to 1873K).



The carbon monoxide is the essential reducing agent.

- (ii) Carbon monoxide reacts with ferric oxide in two ways as shown below



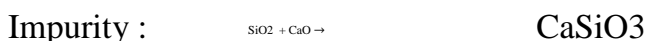
Reaction (a) begins at 673 K. It is exothermic and reversible. Hence according to Le-chatelier's principle more iron will be produced in the furnace at lower temperatures.

Reaction (b) is not reversible.

- (iii) Ferrous oxide formed is reduced by coke in the endothermic reaction occurring at about 1073 K.



- (iv) The lime stone decomposes at about 1073 K and the calcium oxide reacts with sandy (silica) impurities to form a slag of calcium silicate.



*slag*

- (v) The reduction of iron oxide is completed by coke at about 1473 K and cementite Fe<sub>3</sub>C and graphite enter the iron. Other reactions also occur at high temperatures e.g., silica is reduced to silicon and these enter iron as ferrosilicon.





A similar reaction occurs with any phosphate present and some  $\text{Fe}_3\text{P}$  is retained by the iron. Other impurities present in iron are  $\text{FeS}$  and  $\text{Mn}$ , which form an alloy.

- (vi) The slag,  $\text{CaSiO}_3$  being lighter than the molten iron, floats on the top of it (incidentally preventing it from being oxidized by the air blast) and is withdrawn at intervals.

The slag may be used in road making, in making foamed slag blocks for building, cement etc.

The gases leaving at the top of the furnace contain upto 28%  $\text{CO}$ , and are burnt in Cowper's stoves to pre-heat and air for blast.

The molten iron tapped off is run into boat shaped moulds, in which it solidifies into blocks known as pigs (hence the name pig iron) or more generally conveyed directly in the liquid form to steel making plants.

The three commercial varieties of iron differ in their carbon contents. These are:

1. **Cast iron or Pig-iron:** It is the most impure form of iron and contains highest proportion of carbon (2.5 – 4%).
2. **Wrought iron or Malleable-iron:** It is the purest form of iron and contains minimum amount of carbon (0.12 – 9.25%).
3. **Steel:** It is the most important form of iron and finds extensive applications. Its carbon content (impurity) is mid-way between cast iron and wrought iron. It contains 0.2 – 1.5% carbon. Steels containing 0.2 – 1.5% of carbon are known as mild steels, while those containing 0.5 – 1.5% carbon are known as hard steels.

Steel is generally manufactured from cast iron by three processes, viz., (i) Bessemer process which involves the use of a large pear-shaped furnace (vessel) called Bessemer converter, (ii) L.D. process and (iii) open hearth process, Spiegeleisen (an alloy of  $\text{Fe}$ ,  $\text{Mn}$  and  $\text{C}$ ) is added during manufacture of steel.

**Heat treatment of steels.:** Heat treatment of steel may be defined as the process of carefully heating the steel to high temperature followed by cooling to the room temperature under controlled condition. Heat treatment of steel is done for the following two purposes.

- (a) To develop certain special properties like hardness, strength, ductility etc. without changing the chemical composition.
- (b) To remove some undesirable properties or gases like entrapped gases, internal stresses and strains. The various methods of heat treatment are :
  - (i) **Annealing:** It is a process of heating steel to redness followed by slow cooling.
  - (ii) **Quenching or hardening:** It is a process of heating steel to redness followed by sudden cooling by plunging the red hot steel into water or oil.
  - (iii) **Tempering:** It is a process of heating the hardened or quenched steel to a temperature much below redness (473 – 623 K) followed by slow cooling.
  - (iv) **Case-hardening:** It is a process of giving a thin coating of hardened steel to wrought iron or to a strong and flexible mild steel by heating it in contact with charcoal followed by quenching in oil.
  - (v) **Nitriding:** It is a process of heating steels at about  $700^\circ\text{C}$  in an atmosphere of ammonia. This process imparts a hard coating of iron nitride on the surface of steel.

## Properties of Steel:

The properties of steel depend upon its carbon contents. With the increase in carbon content, the hardness of steel increases while its ductility decreases.

- (i) Low carbon or soft steels contain carbon upon 0.25 percent.
- (ii) Medium carbon steels or mild steels contain 0.25 – 0.5 percent carbon.
- (iii) High carbon or hard steels contains 0.5 – 1.5 percent carbon.
- (iv) Alloy steels or special steels are alloys of steel with Ni, Cr, Co, W, Mn, V etc., For example, stainless steel is an alloy of Fe, Cr and Ni and it is used for making automobile parts and utensils. Tool steel is an alloy of Fe, W, V etc.

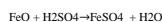
## Uses of steel:

In general, steels are used for making machinery parts, girders, tools, knives, razors, household utensils, etc. The specific use of steel depend upon the nature of metal added to iron.

## Compounds of Iron:

1. **Oxides of Iron.** Iron forms three oxides FeO, Fe<sub>2</sub>O<sub>3</sub>, (haematite), Fe<sub>3</sub>O<sub>4</sub> (magnetite also called magnetic oxide or load stone).

(i) **Ferrous oxide, FeO:** It is a black powder, basic in nature and reacts with dilute acids to give ferrous salts.



It is used in glass industry to impart green colour to glass.

(ii) **Ferric Oxide, Fe<sub>2</sub>O<sub>3</sub>:** It is a reddish brown powder, not affected by air or water; amphoteric in nature and reacts both with acids and alkalis giving salts. It can be reduced to iron by heating with C or CO.



It is used as red pigment to impart red colour to external walls and as a polishing powder by jewellers.

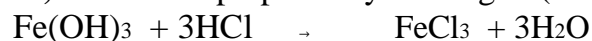
(iii) **Ferrosferric oxide, Fe<sub>3</sub>O<sub>4</sub> (FeO.Fe<sub>2</sub>O<sub>3</sub>):** It is more stable than FeO and Fe<sub>2</sub>O<sub>3</sub>, magnetic in nature and dissolves in acids giving a mixture of iron (II) and iron (III) salts.



2. **Ferrous sulphide, FeS.** It is prepared by heating iron filing with sulphur. With dilute H<sub>2</sub>SO<sub>4</sub>, it gives H<sub>2</sub>S.



3. **Ferric chloride, FeCl<sub>3</sub>:** It is prepared by treating Fe(OH)<sub>3</sub> with HCl



The solution on evaporation give yellow crystals of FeCl<sub>3</sub>.6H<sub>2</sub>O

## Properties.:

- (i) Anhydrous FeCl<sub>3</sub> forms reddish-black deliquescent crystals.
- (ii) FeCl<sub>3</sub> is hygroscopic and dissolves in H<sub>2</sub>O giving brown acidic solution due to formation of HCl



- (iii) Due to oxidizing nature of Fe<sup>3+</sup> ions FeCl<sub>2</sub> is used in etching metals such as copper.
- $$2\text{Fe}^{3+} + \text{Cu} \rightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}(\text{aq})$$
- (iv) In vapour state FeCl<sub>3</sub> exists as a dimer, Fe<sub>2</sub>Cl<sub>6</sub>

4. **Ferrous sulphate, FeSO<sub>4</sub>, 7H<sub>2</sub>O (Green vitriol):** It is prepared as follow.



- (i) On exposure to moist air crystals become brownish due to oxidation by air.
- $$4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)SO}_4$$
- (ii) On heating, crystals become anhydrous and on strong heating it decomposes to Fe<sub>2</sub>O<sub>3</sub>, SO<sub>2</sub> and SO<sub>3</sub>.



- (iii) It can reduce acidic solution of KMnO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  - (iv) It is generally used in double salt with ammonium sulphate.
- $$(\text{NH}_4)_2\text{SO}_4 + \text{FeSO}_4 + 6\text{H}_2\text{O} \rightarrow \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$
- Mohr's salt is resistant to atmospheric oxidation.
- (v) It is used in the ring test for nitrate ions where it gives brown coloured ring of compound FeSO<sub>4</sub>.NO.



**Mohr's salt**, FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O. It is also known as ferrous ammonium sulphate and is a light green coloured double salt.

## COPPER:

Important **ores** of copper are :

- (i) Copper pyrites (chalcopyrite) CuFeS<sub>2</sub> : Cu<sub>2</sub>S.Fe<sub>2</sub>S
- (ii) Cuprite (Ruby copper) : Cu<sub>2</sub>O
- (iii) Copper glance : Cu<sub>2</sub>S
- (iv) Malachite : Cu(OH)<sub>2</sub>.CuCO<sub>3</sub>

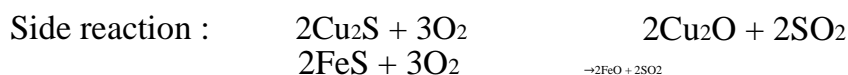
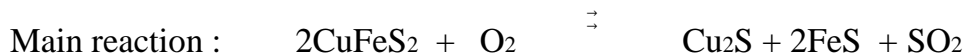
(v) Azurite :  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$

### Extraction of copper.

Most of copper (about 75%) is extracted from its sulphide ore, copper pyrites, which contains varying amounts of copper and iron sulphides.

The extraction of copper from its sulphide ores involves the following steps:

1. **Concentration of ore:** The ore is concentrated by the froth floatation process.
2. **Roasting:** The concentrated ore is roasted by hot blast of air when volatile impurities are removed.



3. **Smelting:** The roasted ore is mixed with silica and heated in the furnace. The ferrous oxide formed is converted into slag.



Some oxide of copper which is formed in the charge is converted into sulphide by FeS.  $\text{Cu}_2\text{O} + \text{FeS} \rightarrow \text{FeO} + \text{Cu}_2\text{S}$

The mixture of copper and iron sulphides melt together to form 'matte' and the slag floats on its surface. Molten matte is collected after removing the slag.

4. **Conversion of matte into Blister copper – (Bessemerisation):** Molten matte is introduced into a Bessemer converter. Silica is added to it and a hot blast of air is passed. The volatile oxides are driven off and the iron oxides combine with silica to form slag.



Slag is removed. By this time most of iron sulphide is removed.

Some of the cuprous sulphide is oxidized to cuprous oxide and the blowing is continued until cuprous sulphide and oxide are present in right proportions to bring about auto reduction.



When the matte is completely converted into copper, the blast of air is stopped and copper poured off in sand moulds. As the copper cools any sulphur dioxide dissolved by the metal is expelled and blisters are produced on the surface. The copper thus obtained is called the blister copper which contains about 98% pure copper and 2% impurities (Ag, Au, Ni, Zn etc.)

5. **Electrolytic refining:** This method is used for obtaining copper used in electrical industry. The electrolytic bath contains an acidified solution of copper sulphate, impure copper (blister copper) acts as anode while cathode is of pure copper strip. When electric current is passed, there is transfer of pure copper from anode to cathode which gradually grows in size. The impurities like Fe, Zn, Ni, Co etc., dissolve in the solution as sulphates and others like Au and Ag settle down below the anode as anode mud. The process gives copper of about 99.99 percent purity.

## Properties of Copper.

- (i) It has reddish brown colour.
- (ii) It is highly malleable and ductile.
- (iii) It has high electrical conductivity and high thermal conductivity.
- (iv) In presence of CO<sub>2</sub> and moisture Cu is covered with a green layer of CuCO<sub>3</sub>. Cu(OH)<sub>2</sub>.  
$$2\text{Cu} + \text{H}_2\text{O} + \text{CO}_2 + \text{O}_2 \rightarrow \text{CuCO}_3 \cdot \text{Cu(OH)}_2$$
- (v) It undergoes displacement reactions with lesser reactive metals e.g., with Ag. It can displace Ag from AgNO<sub>3</sub>. The family divided Ag so obtained is black in colour.

## Compounds of Copper.

1. **Cuprous oxide, Cu<sub>2</sub>O:** It is a reddish brown powder insoluble in water but soluble in ammonia solution, where it forms diammine copper (I) ion.



It is used to impart red colour to glass in glass industry.

2. **Cupric oxide, CuO:** It is dark black, hygroscopic powder which is reduced to Cu by hydrogen, CO etc. It is used to impart light blue colour to glass. It is prepared by heating copper nitrate



3. **Copper sulphate: CuSO<sub>4</sub>·5H<sub>2</sub>O (Blue vitriol).** It is prepared by action of dil H<sub>2</sub>SO<sub>4</sub> on copper scrap in presence of air.



- (i) On heating this blue salt becomes white due to loss of water of crystallization.



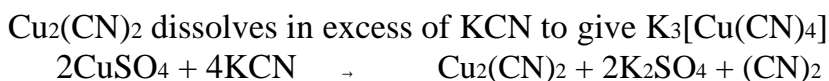
At about 1000 K, CuSO<sub>4</sub> decomposes to give CuO and SO<sub>3</sub>.



- (ii) It gives a deep blue solution of tetrammine copper (II) sulphate with NH<sub>4</sub>OH.

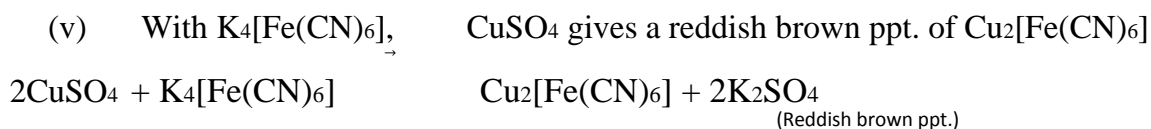


- (iii) With KCN it first gives yellow precipitate of CuCN which decomposes to give Cu<sub>2</sub>(CN)<sub>2</sub>.



- (iv) With KI it gives white ppt. of Cu<sub>2</sub>I<sub>2</sub>





### Uses:

- (i) For electroplating and electrorefining of copper.
- (ii) As a mordant in dyeing.
- (iii) For making Bordeaux mixture (ii parts lime as milk of lime + 16 parts copper sulphate in 1,000 parts of water). It is an excellent fungicide.
- (iv) For making green pigments containing copper carbonate and other compounds of copper.
- (v) As a fungicide in starch paste for book binding work.

4. **Cupric sulphide,  $CuS$** : It is prepared as follows:



5. **Cupric chloride,  $CuCl_2$** : It is a dark brown solid soluble in water and its aqueous solution first changes to green and then to blue on dilution.

6. **Cuprous chloride,  $Cu_2Cl_2$** : It is a white solid insoluble in water and dissolves in conc. HCl due to formation of  $H[CuCl_2]$  complex.



## SILVER :

Silver is found in the free (native) as well as combined state. Native silver usually occurs associated with copper and gold.

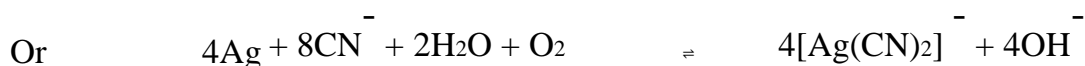
Important ores are;

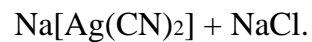
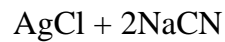
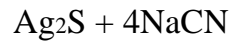
- (i) Argentite (silver glance) :  $Ag_2S$
- (ii) Horn silver :  $AgCl$
- (iii) Ruby silver (pyrargyrite) :  $3Ag_2S.Sb_2S_3$

Lead and copper ores are generally contaminated with silver. Argentiferous galena (lead sulphide containing argentite as impurity) contains 0.01 to 0.1% silver.

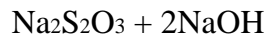
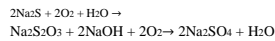
### Extraction of silver by cyanide process or Mac Arthus-Forrest cyanide process.

This method depends on the fact that silver, its sulphide or chloride, forms soluble complex with alkali cyanides in the silver. This implies that silver compound will dissolve in solution of alkali cyanides in the presence of blast of air.

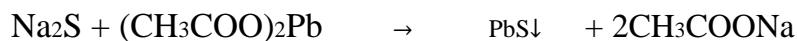




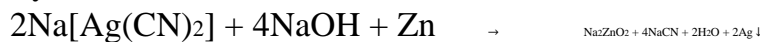
The reaction with the sulphide is reversible and accumulation of  $\text{Na}_2\text{S}$  must be prevented. A free excess of air is continuously passed through the solution which oxidizes  $\text{Na}_2\text{S}$  into sulphate and thiosulphate.



The equilibrium can also be shifted in the forward direction by adding some litharge or lead acetate which precipitates excess sulphide as  $\text{PbS}$  and helps in the dissolution process.



Silver is recovered from solution by precipitation with zinc or aluminium. During precipitation the solution should be strongly alkaline and sometimes caustic soda is added if necessary.



## Refining:

Silver is refined by electrolysis of silver nitrate solution containing 1% nitric acid using pure thin plate of silver as cathode and impure silver slab as anode. On passing electric current, silver is deposited at the cathode and silver from the anode dissolves. Copper, if present as impurity dissolve in the electrolyte solution and gold, if present, is deposited as a anode mud.

## Compound of silver:

$\text{AgNO}_3$ ,  $\text{Ag}_2\text{S}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$  and  $\text{AgO}$  are some of the important compounds of silver.

## GOLD:

Some important **ores**.

(i) Bismuthaurite :  $\text{BiAu}_2$  (ii) Syvanite :  $\text{AgAuTe}_2$  (iii) Calverite :  $\text{AuTe}_2$

## Extraction:

- (i) Extraction of gold by cyanide or Mac Arther Forest cyanide process. This is a very good method for the extraction of gold, even from quartz containing very small amount of gold. The gold bearing quartz is mined by blasting. The rock is crushed to very fine powder in stamp mills and a pulp of powdered ore and water is made alkaline with slaked lime. The slurry is treated with a dilute solution of sodium

cyanide (0.03 to 0.08 per cent) and the solution is agitated by passing air through it. Gold dissolves in sodium cyanide solution forming sodium aurocyanide.



The gold recovered from the solution by precipitation with zinc dust in deaerated cyanide solution.

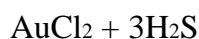
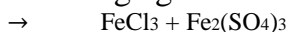


The excess of zinc is removed by dilute acid, when the gold is left as a slime which is collected into a compact mass by fusion. Gold obtained in this way contains some silver and other impurities.

### Refining:

The crude gold is made the anode and the cathode is pure gold. The electrolytic bath contains a solution of gold chloride in hydrochloric acid. On electrolysis, gold is deposited on the cathode.

- (ii) **Plattner chlorine extraction process:** The roasted ore of auriferous pyrite ore is moistened with water and treated with chlorine. Gold chloride is leached with water and the solution is treated with reducing agent like  $\text{H}_2\text{S}$ .



### Quartations process:

Refining of gold is carried by this process. It involves the separation of gold and silver by sulphuric acid.

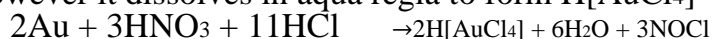
Gold is soft and hence for making ornaments it is generally hardened by adding Ag or Cu. The weight of gold is expressed in terms of Carats. Pure gold is taken as 24 carats.

20 carats means, it contains 20 parts by wt. of gold in 24 parts by wt. of given alloy.

$$\text{Percentage of gold in 20 carat gold sample} = \frac{20}{24} \times 100 = \frac{250}{3} = 83.33\%$$

### Properties of Gold:

- (i) Gold is not affected by conc.  $\text{H}_2\text{SO}_4$ , conc.  $\text{HNO}_3$ , or by strong alkalis.  
 (ii) However it dissolves in aqua regia to form  $\text{H}[\text{AuCl}_4]$



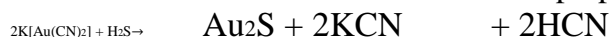
### Compounds of Gold:



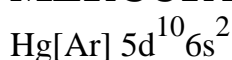
1. **AuCl<sub>3</sub>**: It is a reddish solid soluble in water. It reacts with HCl to give H[Au(Cl)<sub>4</sub>] which is used in toning process in photography.



2. **Au<sub>2</sub>S**: It is a dark brown solid insoluble in water prepared as follows.



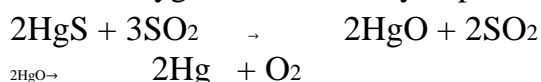
## MERCURY :



**Important ore:** Cinnabar :Hgs

### Extraction of mercury from cinnabar:

- (i) **Concentration:** The powdered ore is concentrated by froth floatation process.
- (ii) **Roasting :** The concentrated ore is roasted in the presence of excess of air at 770 to 780 K to form HgO. At this temperature, mercury oxide formed decomposes into mercury vapours and oxygen. The mercury vapours are then condensed.



- (iii) **Refining:** It is refined by filtering impure mercury through thick canvass or chamois leather. It is then dropped into 5% nitric acid when metallic impurities like Fe, Cu, Zn etc., get converted to their respective nitrates and go into solution and mercury free from impurities is received in the receiver. It is further refined by distillation under reduced pressure. More volatile mercury is distilled first.

### Compounds of Mercury:

1. **Mercuric chloride, HgCl<sub>2</sub>** (Corrosive sublimate).

(i) It is a colourless solid, sparingly soluble in water.

(ii) It forms red ppt. of HgI<sub>2</sub> with KI:



(iii). With NH<sub>4</sub>OH it gives white ppt. of Hg(NH<sub>2</sub>)Cl.

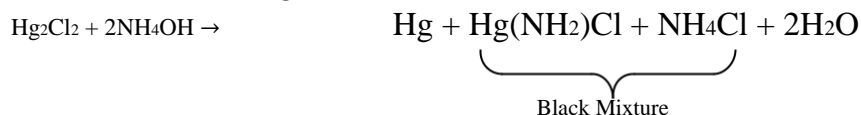


White ppt.

2. **Mercurous chloride, Hg<sub>2</sub>Cl<sub>2</sub>** (Calomel).

(i) It is a white solid insoluble in water.

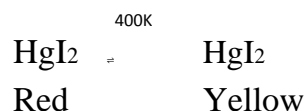
(ii) With  $\text{NH}_4\text{OH}$  it forms a black mixture composed of black metallic mercury and white mercuric aminochloride,  $\text{Hg}(\text{NH}_2)\text{Cl}$ .



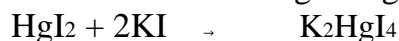
(iii) It is used as purgative in medicine and it sublimes on heating.

### 3. Mercuric iodide, $\text{HgI}_2$ :

(i) It is a yellow solid below 400 K but changes to red solid above 400 K

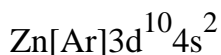


(ii) It dissolves in excess of KI forming  $\text{K}_2\text{HgI}_4$ .



Alkaline solution of  $\text{K}_2\text{HgI}_4$  is called Nessler's reagent.

## ZINC :



### Important ores.

- (i) Znincite (red zinc ore):  $\text{ZnO}$
- (ii) Franklinite :  $\text{ZnOFe}_2\text{O}_3$
- (iii) Zinc blende :  $\text{ZnS}$
- (iv) Calamine (zinc spar) :  $\text{ZnCO}_3$

### Extraction of zinc from zinc blende:

- (i) **Concentration:** The powdered ore is concentrated by froth floatation process.
- (ii) **Roasting:** The concentrated ore is roasted at 1200 K in excess of air.



Some  $\text{ZnSO}_4$  is also formed but at high temperature the sulphate decomposes to give  $\text{ZnO}$ .



- (iii) **Reduction of  $\text{ZnO}$ :** The oxide ore is mixed with crushed coke and heated to about 1670 K in fire clay retorts (Belgian process) zinc being volatile distils over and is received in an earthen ware pot where it condenses. The crude metal obtained is called zinc spelter.

- (iv) **Refining:** It is refined by distillation and by electrolytic method. The electrolytic used is acidified zinc sulphate. The anode is made of spelter and cathode of pure zinc wire.

## Compounds of Zinc:

### 1. Zinc oxide, ZnO:

- (i) Zincite (ZnO) is also called Philosopher's wool.
- (ii) ZnO is white powder, become yellow on heating and again white on cooling.
- (iii) ZnO is amphoteric in nature.
- (iv) ZnO is used as a white pigment under the name Zinc white or Chinese white.

### 2. Zinc Sulphate (White vitriol), ZnSO<sub>4</sub>.7H<sub>2</sub>O:

- (i) It is a colourless transparent crystal highly soluble in water.
- (ii) On heating it loses its molecules of water as:

ZnSO<sub>4</sub>.7H<sub>2</sub>O →

375°K ZnSO<sub>4</sub>.H<sub>2</sub>O → 725°K ZnSO<sub>4</sub> → Δ



- (iii) It is used as an eye-lotion and for preparing double salts.

## PREPARATION, PROPERTIES AND USES OF KMnO<sub>4</sub> AND K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:

### Potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:

**Preparation:** It is prepared from chromite ore or ferro chromes (FeCr<sub>2</sub>O<sub>4</sub> or FeOCr<sub>2</sub>O<sub>3</sub>) by following steps.

- (a) Fusion of the ore with molten alkali in presence of air

4FeCr<sub>2</sub>O<sub>4</sub> + 16 NaOH + 7O<sub>2</sub> →



The fused mass is extracted with water and filtered.

- (b) Conversion of sodium chromate into sodium dichromate by treating the filtrate with dil H<sub>2</sub>SO<sub>4</sub>

2Na<sub>2</sub>CrO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> →



Na<sub>2</sub>SO<sub>4</sub> being less soluble is separated as Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O by fractional crystallization.

- (c) Conversion of sodium dichromate into potassium dichromate by heating with KCl.

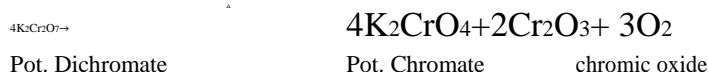
Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2KCl → K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2NaCl

Potassium dichromate being less soluble is obtained by fractional crystallization.

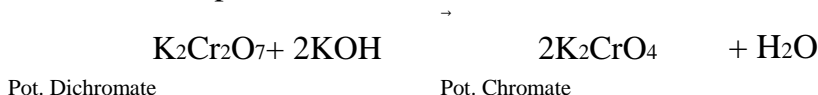
### Properties:

- (i) **Physical state :** Potassium dichromate forms orange red crystals which melts at 669 K. It is moderately soluble in cold water but freely soluble in hot water.

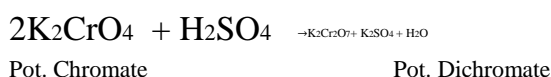
- (ii) **Action of heat** : When heated strongly to white heat, it decomposes with the evolution of oxygen.



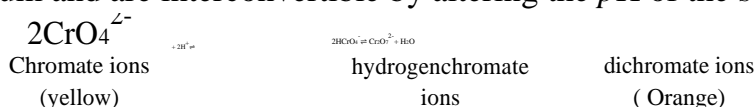
- (iii) **Action of alkalis**: When an alkali is added to an orange red solution containing dichromate ions, a yellow solution is obtained due to the formation of chromate ions. For example,



On acidifying the above yellow solution containing chromate ions, it again change to orange red due to the formation of dichromate ions.



In fact, in any given solution, dichromate ions and chromate ions exist in equilibrium and are interconvertible by altering the pH of the solution.



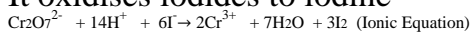
- (iv) **Action of concentrated sulphuric acid** : In cold, red crystals of chromic anhydride ( $\text{CrO}_3$ ) are formed



- (v) **Oxidising properties** : Potassium dichromate is a powerful oxidizing agent. In acidic solution, its oxidizing action can be represented as follows.

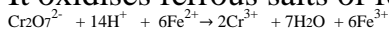


- (a) It oxidises iodides to iodine



This reaction is used in the estimation of iodide ions in the volumetric analysis.

- (b) It oxidises ferrous salts to ferric salts:

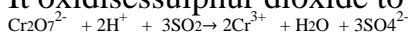


This reaction is used in the estimation of ferrous ions in the volumetric analysis.

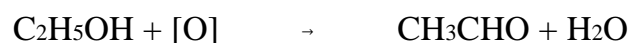
- (c) It oxidises  $\text{H}_2\text{S}$  to S :



- (d) It oxidises sulphur dioxide to sulphuric acid :



(e) It oxidises ethyl alcohol to acetaldehyde and acetic acid :



(vi) **With hydrogen peroxide** : Acidified potassium dichromate forms a deep blue colour with hydrogen peroxide due to the formation of  $\text{CrO}_5$ .



The blue colour fades away gradually due to decomposition of  $\text{CrO}_5$  into  $\text{Cr}^{3+}$  ions and oxygen.

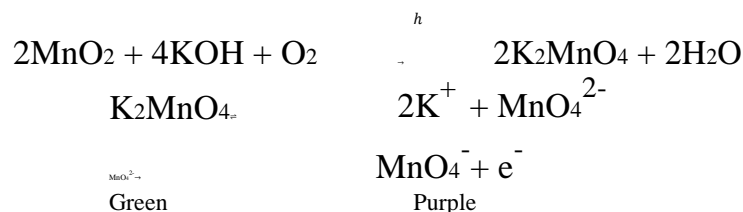
### Uses.

- (i) In volumetric estimation of reducing agents e.g., ferrous salts, iodides and sulphites. This is due to the fact that  $\text{K}_2\text{Cr}_2\text{O}_7$  is obtained in a much higher degree of purity than  $\text{Na}_2\text{Cr}_2\text{O}_7$
- (ii) In the preparation of chromium compounds e.g., chrome alum.
- (iii) In photography for hardening of gelatin.
- (iv) In dyeing for producing  $\text{Cr}(\text{OH})_3$  as mordant.
- (v) Chromic acid mixture ( $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4$ ) is used for cleaning glasswares in the laboratory.
- (vi) As an oxidizing agent.

### Potassium permanganate, $\text{KMnO}_4$ :

It is prepared by fusing pyrolusite ore ( $\text{MnO}_2$ ) with  $\text{KOH}$  in the presence of atmospheric oxygen or an oxidizing agent like  $\text{KNO}_3$  or  $\text{KClO}_3$  to get potassium manganate,  $\text{K}_2\text{MnO}_4$  (green mass). The green mass is extracted with water and is oxidized to potassium

permanganate, either electrolytically or by passing chlorine or ozone into the solution. The purple solution is concentrated by evaporation which on cooling deposits crystals of  $\text{KMnO}_4$ .

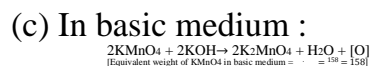


### Properties:

- (i) Potassium permanganate exists as dark purple black prismatic crystals having a greenish metallic lustre. It melts at 523 K. It is moderately soluble in water at room temperature giving a purple solution. However, its solubility in water increases with temperature.



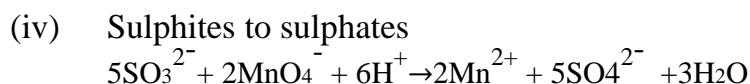
(iii) **Oxidising properties.**



In basic medium,  $\text{MnO}_4^-$  (manganate ions) is further reduced to  $\text{MnO}_2$  in the presence of reducing agent. As such equivalent weight of  $\text{KMnO}_4$  in basic medium is same as in neutral medium.

In acidic medium potassium permanganate oxidises.

- (i) Ferrous to ferric salt  
 $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$
- (ii) Oxalates to carbon dioxide  
 $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$
- (iii) Iodides to iodine  
 $10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$



### In alkaline solution

- (i) Iodides to iodates



### Uses.

- (i) As oxidizing agent in laboratory and industry.
- (ii) In volumetric estimation of ferrous salts, oxalates and other reducing agents in redox titration.
- (iii) As disinfectant in water.
- (iv) For qualitative detection of halides, oxalates, tartarates.

### Use of $\text{KMnO}_4$ in redox – titrations:

Potassium permanganate is a powerful and versatile oxidizing agent and is widely used for titration against reducing agents like oxalic acid and Mohr's salt. During the titration, the reduction of potassium permanganate by a reducing agent e.g., oxalic acid or Mohr's salt, produces manganous ions which are nearly colourless.



As the titration proceeds and when the whole of the reducing agent is consumed up, then the addition of an excess drop of potassium permanganate solution gives its own colour (pink) to the solution. Therefore, at the end point the colour changes from colourless to pink. Thus, potassium permanganate acts as a self indicator.

## SOME OTHER COMPOUNDS OF TRANSITION METALS :

### Halides of transition metals:

- (i) Halides of transition metals in higher oxidation states exhibit a greater tendency to hydrolysis  
e.g.  $\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}$
- (ii) Bonding in fluorides is essentially ionic. In the chlorides, bromides and iodides, the ionic character decreases with increase in atomic mass of the halogens. For example  $\text{CuF}_2$  is ionic while  $\text{CuCl}_2$  and  $\text{CuBr}_2$  are covalent compounds consisting of infinite chains. The structure of copper (II) chloride is given below.

### Sulphides of transition metals.

- (i) Sulphides of transition metals can be obtained direct union of sulphur with the transition metals



- (ii) In sulphides, the oxidation state of the metal is generally low because sulphur is a weak oxidizing agent.
- (iii) The sulphides of transition metals are usually coloured or black. For example CuS, NiS, CoS are black, MnS is light pink, CdS is yellow etc. They are insoluble in water.

### Silver Nitrate or Lunar Caustic, AgNO<sub>3</sub>:

Silver nitrate can be prepared by heating silver with dilute nitric acid.



### Properties:

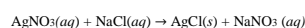
- (i) It is a colourless, crystalline compound, soluble in water and alcohol. It melts at 484 K.
- (ii) In contact with organic substances (skin, clothes, paper etc.) it blackens due to decomposition into metallic silver and thus leaves black stains when comes in contact with skin and clothes.
- (iii) It decomposes on exposure to light and hence is stored in brown coloured bottles. On heating strongly, at red hot it decomposes to metallic silver.



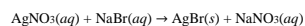


- (iv) With potassium chromate it gives a red ppt. of silver chromate.  
 (v) Aqueous solutions of halides, phosphates, sulphides, chromates, thiocyanates, give a precipitate of the corresponding silver salt with silver nitrate solution

e.g.,



(white)



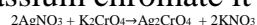
(pale Yellow)

- (vi) It forms precipitate of silver oxide with  $\text{NaOH}(aq)$ . Originally, the ppt., has a brown colour but turns black when dried.



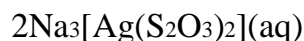
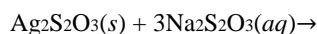
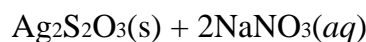
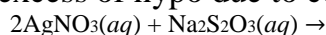
- (vii) Solid  $\text{AgNO}_3$  absorbs ammonia gas with the formation of an addition compound,  $\text{AgNO}_3 \cdot 2\text{NH}_3$ .

- (viii) With potassium chromate it gives a red ppt. of silver chromate.



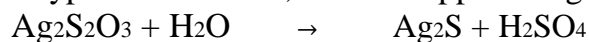
Red PPT

- (ix) It gives white precipitate with hypo (sodium thiosulphate) which however dissolves in excess of hypo due to complex formation.



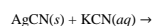
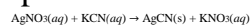
Sodium argentothiosulphate

However if hypo is not excess, the white ppt. changes to black  $\text{Ag}_2\text{S}$ , slowly.

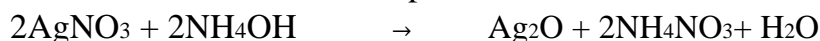


Black ppt.

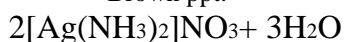
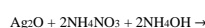
- (x) It gives white precipitate of  $\text{AgCN}$  with  $\text{KCN}$  which dissolves in excess of  $\text{KCN}$  due to complex formation.



- (xi) **Tollen's reagent:** It gives brown precipitate with  $\text{NH}_4\text{OH}$  which however dissolves in excess of  $\text{NH}_4\text{OH}$  due to complex formation.

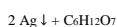
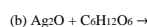
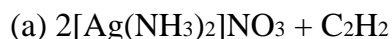


Brown ppt.



## Diamminesilver(I)nitrate

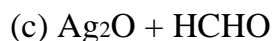
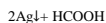
The ammonical solution of  $\text{AgNO}_3$  is known as Tollens reagent and gives following reactions.  
 $\rightarrow \text{Ag}_2\text{C}_2\text{O}_4 + 2\text{NH}_4\text{NO}_3 + 2\text{H}_2\text{O}$



Silver Acetylide

Silver mirror

$\rightarrow$



Silver mirror

### Uses.

- (i) It is used as a laboratory reagent for the identification of various acidic radicals especially for halides. Tollen's reagent is used in organic chemistry for testing aldehydes, reducing sugars, etc.
- (ii) It is used for making silver halides which are used in photography.
- (iii) It is used in the preparation of inks and hair dyes.
- (iv) A very dilute solution of silver nitrate is used in cauterisation of eyes and as dental antiseptic.
- (v) **Silvering of mirror** or for the preparation of silvered mirrors.
- (vi)  $\text{AgNO}_3$  is popularly used both the quantitative and qualitative analysis. Presence of chloride ( $\text{Cl}^-$ ) bromide ( $\text{Br}^-$ ) and iodide ( $\text{I}^-$ ) ions can be detected with the help of silver nitrate. However, Fluoride ion ( $\text{F}^-$ ) cannot be detected by this method as silver fluoride so formed on treatment with  $\text{AgNO}_3$  solution is soluble in water.

## INNER TRANSITION ELEMENTS :

The elements which in their atomic or ionic form, in addition to their incomplete  $d$ -subshell of the penultimate shell have partly filled  $f$ -subshell of the ante-penultimate (inner to the penultimate shell i.e.  $n-2$ ) shell are called as  $f$ -block elements. They are also known as inner transition elements. These are so called because these form a series within the transition series. The general electronic configuration of the  $f$ -block elements is  $(n-2)f^{1-14} (n-1)s^2 (n-1)p^6 (n-1)d^{10} ns^2$ .

### Classification of $f$ -block elements:

The  $f$ -block elements can be subdivided into two series depending upon the nature of the  $f$ -orbital of the antepenultimate shell ( $4f$  or  $5f$ ) in which the differentiating electron enters.

- (i)  $4f$ -series (First inner transition series). In these the differentiating electron goes to  $4f$  orbitals. This series consists of lanthanum ( $Z = 57$ ) and the next 14 elements ( $Z = 58$  to  $71$ ). These are known as Lanthanides.
- (ii)  $5f$ -series (Second inner transition series). In these elements differentiating electron goes to  $5f$ -orbitals. This series includes fifteen elements from actinium ( $Z=89$ ) to Lawrencium ( $Z = 103$ ). These are known as actinides. Inner transition elements are

placed outside the body of the periodic table. The reason for this is the remarkable similarities among the chemical properties of lanthanides and also among the various members of the actinides. The similarities in properties, in turn is due to the similar electronic configuration of the outermost shell. These elements differ only in the number of f electrons which do not take part in chemical bonding (difference from d-block elements in which the differentiating d-electrons are involved in chemical interaction).

## LANTHANIDES OR LANTHANONS :

In these elements differentiating electron goes to  $4f$ -subshell. This series consists of 14 elements which follow lanthanum ( $Z = 57$ ). It should be noted that fifteen elements starting from  $La_{57}$  to  $Lu_{71}$  are generally considered as lanthanides because they resemble one another closely. The name lanthanide has been derived from lanthanum which is the prototype of lanthanides. However, lanthanum is not an element of  $f$ -block of the periodic table.

Originally these elements were called rare earths because for many years pure compounds of these elements were difficult to obtain. Now a days the term rare earth is avoided because many of these elements are far from rare

Lanthanides				Actinides			
Name	Symbol	At. No.	Configuration	Name	Symbol	At.No.	Configuration
Cerium	Ce	58	$[Xe]4f^2 5d^0 6s^2$	Thorium	Th	90	$[Rn]5f^0 6d^2 7s^2$
Praseodymium	Pr	59	$[Xe]4f^3 5d^0 6s^2$	Protactinium	Pa	91	$[Rn]5f^2 6d^1 7s^2$
Neodymium	Nd	60	$[Xe]4f^4 5d^0 6s^2$	Uranium	U	92	$[Rn]5f^3 6d^1 7s^2$
Promethium	Pm	61	$[Xe]4f^5 5d^0 6s^2$	Neptunium	Np	93	$[Rn]5f^4 6d^1 7s^2$
Samarium	Sm	62	$[Xe]4f^6 5d^0 6s^2$	Plutonium	Pu	94	$[Rn]5f^6 6d^0 7s^2$
Europium	Eu	63	$[Xe]4f^7 5d^0 6s^2$	Americium	Am	95	$[Rn]5f^7 6d^0 7s^2$
Gadolinium	Gd	64	$[Xe]4f^7 5d^1 6s^2$	Curium	Cm	96	$[Rn]5f^7 6d^1 7s^2$
Terbium	Tb	65	$[Xe]4f^9 5d^0 6s^2$	Berkelium	Bk	97	$[Rn]5f^8 6d^1 7s^2$
Dysprosium	Dy	66	$[Xe]4f^{10} 5d^0 6s^2$	Californium	Cf	98	$[Rn]5f^{10} 6d^0 7s^2$
Holmium	Ho	67	$[Xe]4f^{11} 5d^0 6s^2$	Einsteinium	Es	99	$[Rn]5f^{11} 6d^0 7s^2$
Erbium	Er	68	$[Xe]4f^{12} 5d^0 6s^2$	Fermium	Fm	100	$[Rn]5f^{12} 6d^0 7s^2$
Thulium	Tm	69	$[Xe]4f^{13} 5d^0 6s^2$	Mendelevium	Md	101	$[Rn]5f^{13} 6d^0 7s^2$
Ytterbium	Yb	70	$[Xe]4f^{14} 5d^0 6s^2$	Nobelium	No	102	$[Rn]5f^{14} 6d^0 7s^2$
Lutetium	Lu	71	$[Xe]4f^{14} 5d^1 6s^2$	Lawrencium	Lr	103	$[Rn]5f^{14} 6d^1 7s^2$

## GENERAL CHARACTERISTICS OF LANTHANIDES:

1. There are hard metals with high melting points.
2. **Oxidation state.** The lanthanides too display variable oxidation states. The characteristic and the most stable oxidation state of lanthanides is + 3 ( $\text{Ln}^{3+}$ ). This oxidation state is obtained by the loss of one  $5d$ -electron and two  $6s$ -electrons. Along with + 3 oxidation state, certain metals show + 2 and + 4 oxidation states so as to attain  $f^0$ ,  $f^7$  and  $f^{14}$  configurations.
3. **Ionic radii-Lanthanide contraction.** There is a regular decrease in the size of atoms/ions with increase in atomic number as we move across from La to Lu. Thus among lanthanides, lanthanum has the largest and lutetium has the smallest radii. This slow decrease in size is known as lanthanide contraction.

### Cause of lanthanide contraction:

The configurations of lanthanides show that the additional electron enters the  $4f$ -subshell. The shielding of one  $4f$ -electron by another is very little (imperfect), being even smaller than that encountered in case of  $d$ -electrons ( $d$ -transition series). The imperfect shielding of  $f$ -electrons is due to the shape of  $f$ -orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity of each step, while no comparable increase in the mutual shielding effect of  $4f$ -electrons occurs. This causes a contraction in the size of the  $4f$ -subshell. Consequently the atomic and ionic size goes on decreasing systematically from *La* to *Lu*.

It must be noted that the decrease in atomic radii, although continuous, is not regular. The decrease is much more in the case of first six elements than in the subsequent elements. Hence the properties of lanthanide compounds show some divergence from regularity. However, decrease in ionic radii is more regular.

### Consequences of Lanthanide Contraction:

- (i) **Separation of Lanthanides:** Separation of lanthanides is possible only due to lanthanide contraction. All the lanthanides have quite similar properties and due to this reason they are difficult to separate. However, because of lanthanide contraction their properties (such as ability to form complexes) vary slightly. This slight variation in properties is utilized in the separation of lanthanides by ion exchange methods.
- (ii) **Variation in basic strength of hydroxides:** The basic strength of oxides and hydroxides decreases from  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ . Due to lanthanide contraction size of  $\text{M}^{3+}$  ions decreases and there is increase in the covalent character in  $\text{M}-\text{OH}$  bond.
- (iii) **Similarity of second and third transition series:** The atomic radii of second row of transition elements are almost similar to those of the third row of transition elements. For example, among the elements of group 3, there is normal increase in size from Sc to Y to La. But after lanthanide the atomic radii from second to third transition series do not increase for group 4 and group 5.

i.e., for Zr – Hf and Nb – Ta pairs which have element same atomic radii. After group 5 the effect of lanthanide contraction is not so predominant.

4. **Colour:** The lanthanide metals are silvery white but the trivalent lanthanide ions are coloured both in the solid state and in the aqueous solutions.
5. **Magnetic properties:**  $\text{La}^{3+} (4f^0)$  and  $\text{Lu}^{3+} (4f^{14})$  having no unpaired electron do not show paramagnetism while all other tripositive ions of lanthanides are paramagnetic.
6. They have low ionization energy and are highly electropositive. Their ionization values are quite comparable with those of alkaline earth metals particularly calcium.
7. These metals do not have much tendency to form complexes.
8. The lanthanides are highly reactive. This is in agreement with the low value of their ionization energies.
9. The solubility of compounds of lanthanides follow the same order as group 2 elements. Their fluorides, oxides, hydroxides carbonates are insoluble in water. However halides (except fluorides), nitrates, acetates are soluble in water.

## GENERAL CHARACTERISTICS OF ACTINIDES :

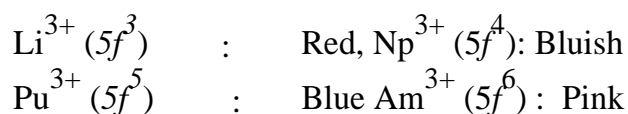
### Actinides:

The elements with atomic numbers 90 to 103 i.e. thorium to lutetium (which come immediately after actinium,  $Z = 89$ ) are called actinides or actinones. These elements involve the filling of  $5f$  orbitals. Their general electronic configuration is  $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$ .

They include three naturally occurring elements thorium, protoactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or man made. All actinides are radioactive.

### Physico-chemical characteristics of Actinides:

- (i) **Oxidation states:** These elements usually exhibit oxidation state of +2. However, they also show oxidation states of +4, +5 and +6.
- (ii) **Physical state:** These are silvery white metals and get tarnished with alkalis.
- (iii) **Density:** All the actinides except thorium and americium have high densities.
- (iv) **Colour:** The actinide ions, in general are coloured. The colour depends upon the number of  $5f$  electrons. The ions of  $5f^0$  and  $5f^7$  configurations are colourless while ions with  $5f^3$  to  $5f^6$  configurations are coloured.



- (v) **Ionisation energies:** These elements have low values of ionization energies.
- (vi) **Electropositive character:** All the actinides are highly electropositive and as such are strong reducing agents.
- (vii) **Complex formation:** Actinides have a strong tendency towards complex formation and form cations like  $\text{UO}^{2+}$ ,  $\text{PuO}_2^{2+}$ ,  $\text{UO}^+$  etc.

- (viii) **Actinide contraction:** Actinides show actinide contraction. The size of atom/cation decreases regularly along the actinide series. The steady decrease in ionic radii with increase in atomic number is referred to as a actinide contraction. This is due to poor shielding of  $5f$  electrons.

### **Uses of Actinides:**

- (i) Polonium as fuel for atomic reactors and in atomic bombs.
- (ii) Uranium as nuclear fuel, its salts in glass industry (to impart colour), textile industry and in medicines.
- (iii) Thorium in atomic reactors as fuel rods, in treatment of cancer, in gas mantles (as a mixture of thorium and cerium nitrate 99:1)

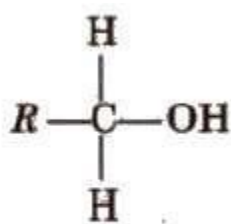
# Alcohols, Phenols and Ethers

## Alcohols and Phenols

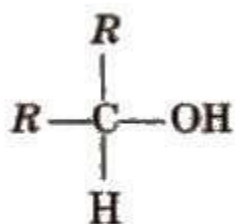
Alcohols and phenols are formed when a hydrogen atom in hydrocarbon, aliphatic and aromatic respectively, is replaced by hydroxyl group (-OR group).

## Classification of Alcohols and Phenols

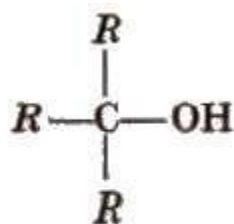
In alcohols, -OR group is attached to  $sp^3$  hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



primary ( $1^\circ$ )



secondary ( $2^\circ$ )



tertiary ( $3^\circ$ )

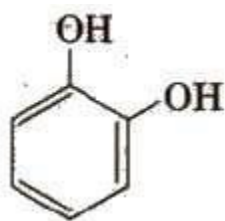
Alcohols may be

- v) monohydric-containing one -OR group,
- vi) dihydric-containing two -OR groups and
- vii) polyhydric-containing three or more -OR groups.

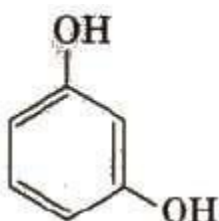
In phenols, -OR group is attached to  $sp^2$  hybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further may be ortho, meta or para derivative.



phenol



catechol



resorcinol



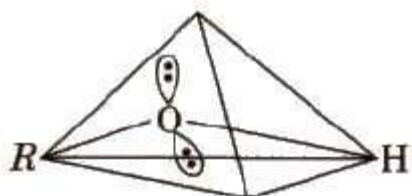
quinol or hydroquinone

In allylic alcohols, -OH group is attached to  $sp^3$  hybridised carbon but next to  $C=C$  bond.

e.g.,  $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$ , Benzylic alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ )

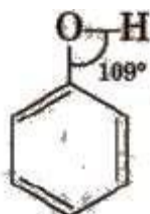
## Structure of Alcohols and Phenols

The oxygen atom of alcohols is  $\text{Sp}^3$  hybridised and they have tetrahedral position of hybrid atomic orbitals .



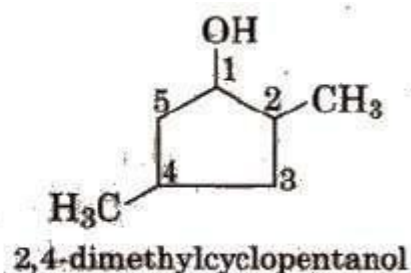
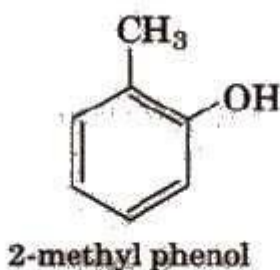
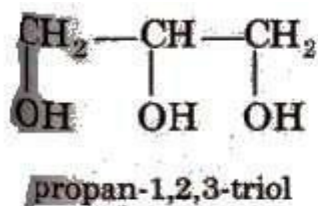
The value of  $\angle\text{ROH}$  bond angle depends upon the R group. For methyl alcohol, it is ( $\angle\text{C} - \text{O} - \text{H}$ )  $108.9^\circ$  due to repulsion of lone pairs.

In phenols, the  $-\text{OH}$  group is attached to  $\text{Sp}^2$  hybridised carbon and thus, the  $\text{C} - \text{O}$  bond acquires a partial double bond character.



## Nomenclature of Alcohols and Phenol

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,

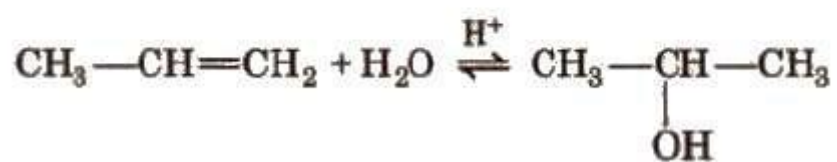
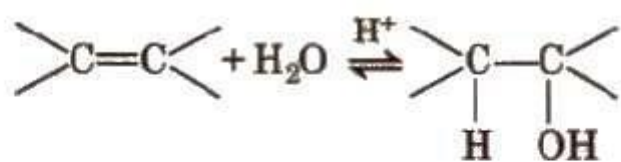


## Preparation of Alcohols

### 2. From alkenes

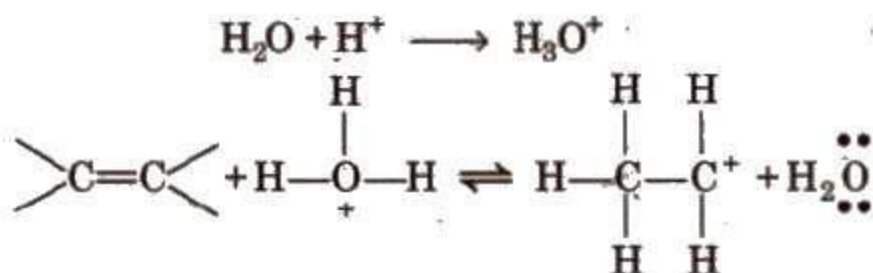
(a) By acid catalysed hydration in accordance with Markownikoff's rule.



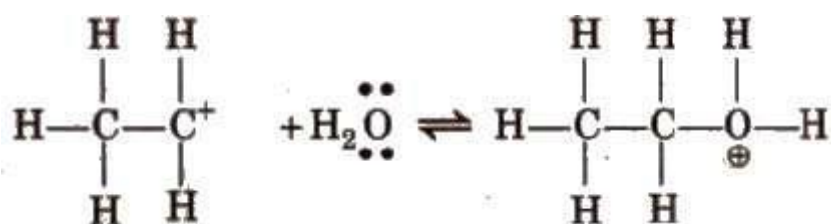


## Mechanism

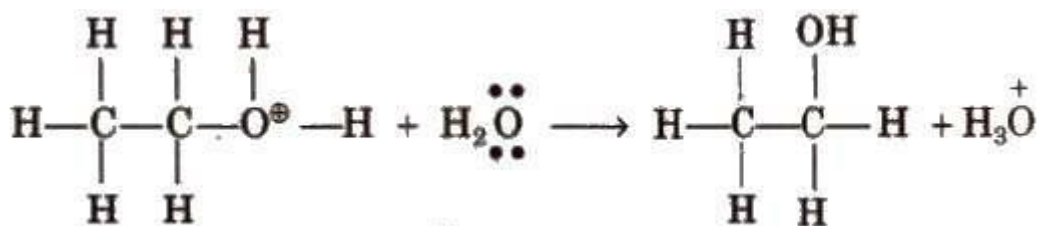
**Step I** Protonation of alkene by attack of  $\text{H}_3\text{O}^+$



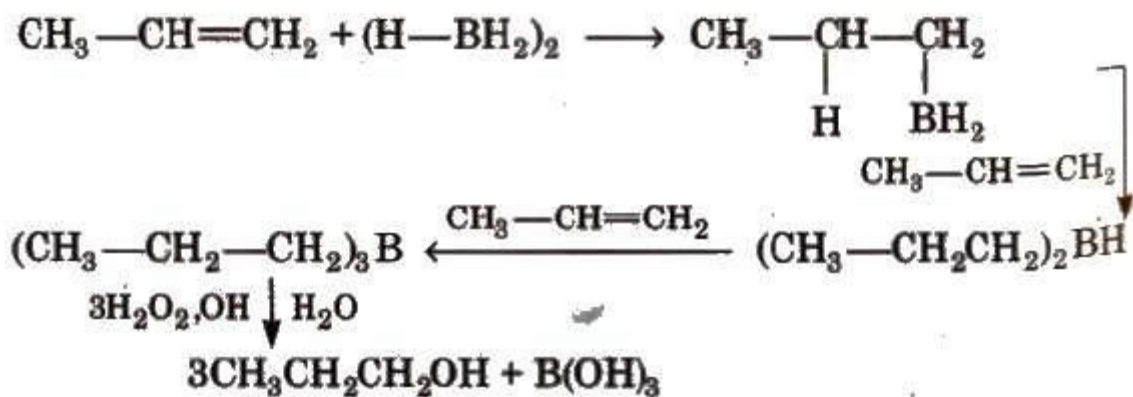
**Step II** Nucleophilic attack



**Step III** Deprotonation to form an alcohol

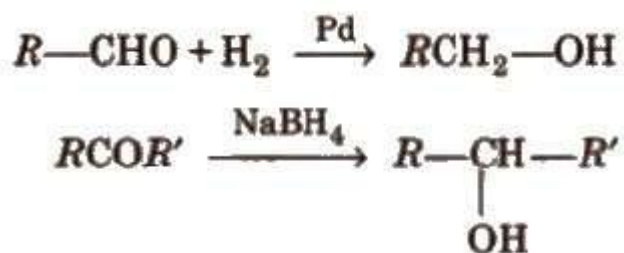


4. By hydroboration-oxidation



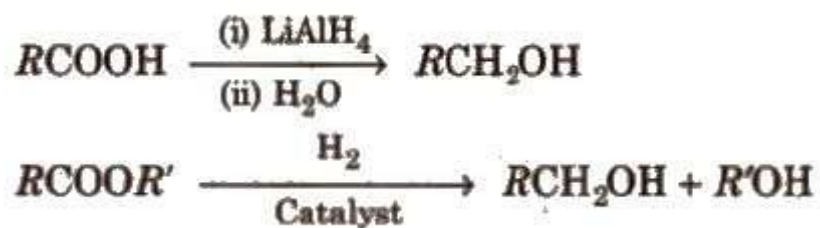
## From carbonyl compounds

(a) By reduction of aldehydes and ketones

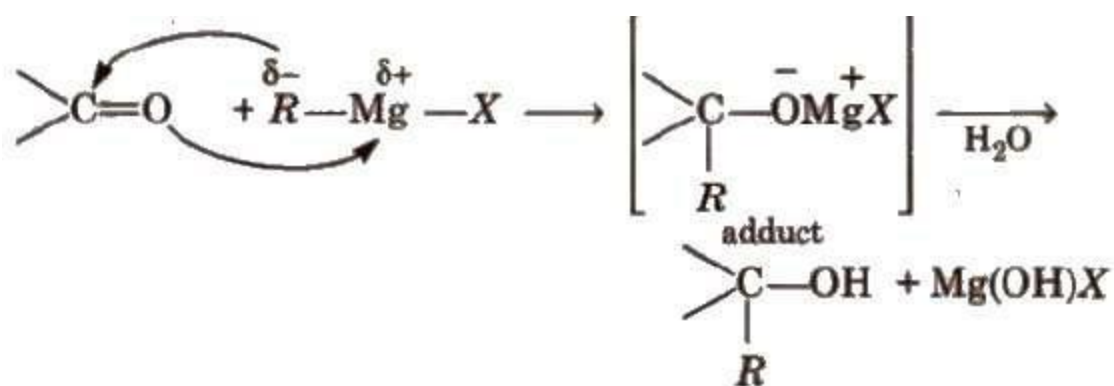


Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction.

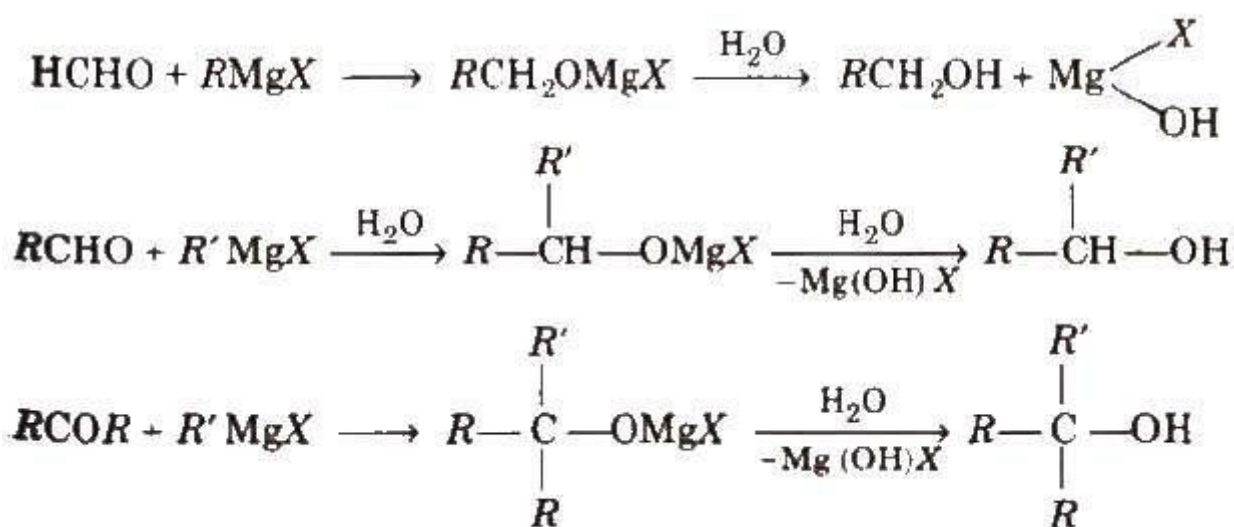
(b) By reduction of carboxylic acids and ester



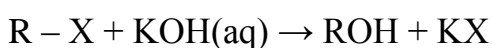
Reduction of aldehyde, ketones and esters with No Alcohol is called Bouveault-blanc reduction.



The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones



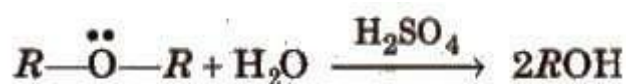
## 8. Hydrolysis of alkyl halides



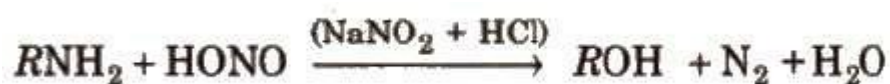
To avoid dehydrohalogenation of RX, mild alkalies like moist

Ease of hydrolysis of alkyl halides  $\text{RI} > \text{R}-\text{Br} > \text{RCI} > \text{and } \text{t} > \text{s} > \text{p}$  alkyl halides.

## 9. Hydrolysis of ethers

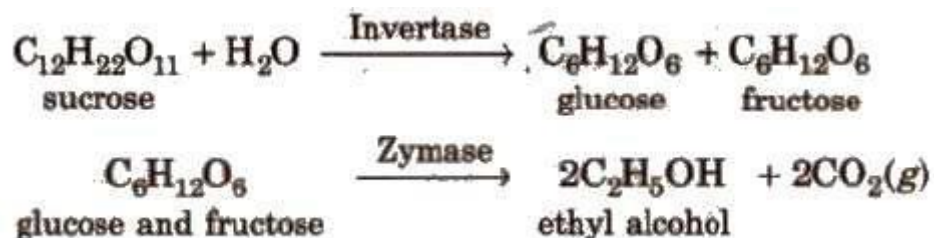


10. From primary amines By treatment with nitrous acid.



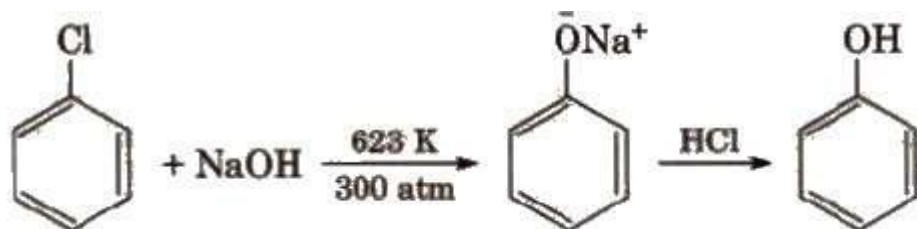
Methylamine does not give methyl alcohol when treated with  $\text{HNO}_2$ . It gives  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{ONO}$ .

### 10. By alcoholic fermentation

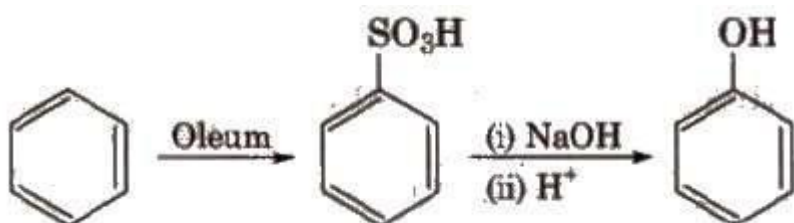


### Preparation of Phenols

#### 13. From haloarenes



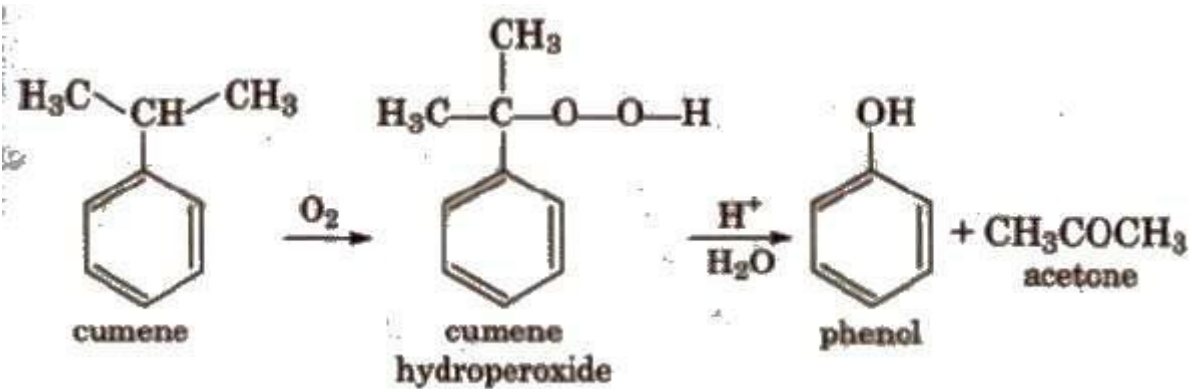
#### 14. From benzene sulphonic acid



#### 15. From diazonium salts

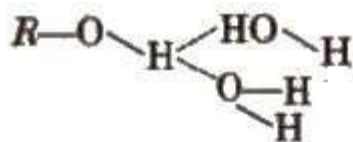


#### N From cumene



## Physical Properties of Alcohols

- iv) Lower alcohols are colourless liquids, members from C<sub>5</sub> – C<sub>11</sub> are oily liquids and higher members are waxy solids.
- v) The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.



- vi) Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.

[The boiling point decreases in the order 1° > 2° > 3° as the van der Waals' forces of attraction decreases]

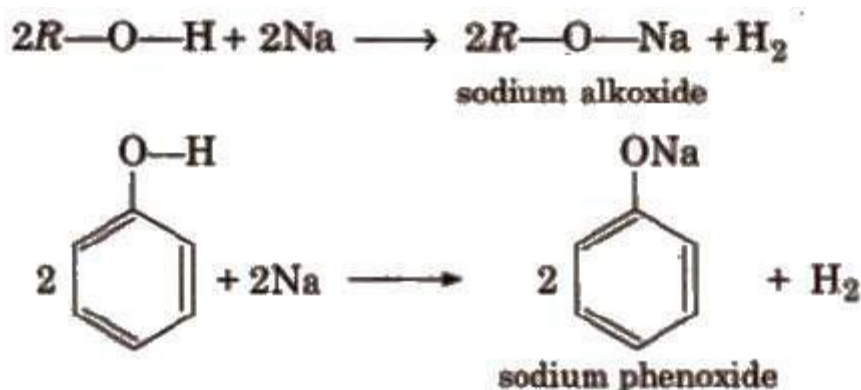
## Physical Properties of Phenols

2. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
3. Phenol is also called carbolic acid.
4. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

## Chemical Reactions of Alcohols and Phenols

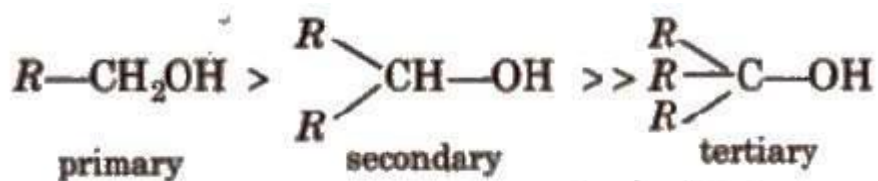
### 3. Reactions involving cleavage of O – H Bond

- (a) Acidity of alcohols and phenols



Alcohols are weaker acids than water due to +I group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols



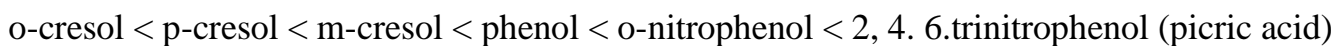
Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond.

Order of acidity is



Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising phenoxide ion.

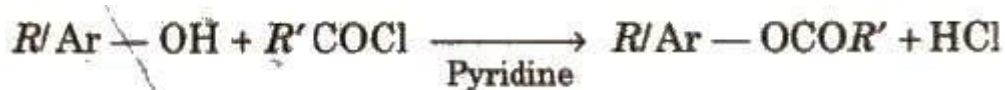
Thus, increasing acidic strength is



Higher  $K_a$  and lower  $pK_a$  value corresponds to the stronger acid.

## 2 Esterification



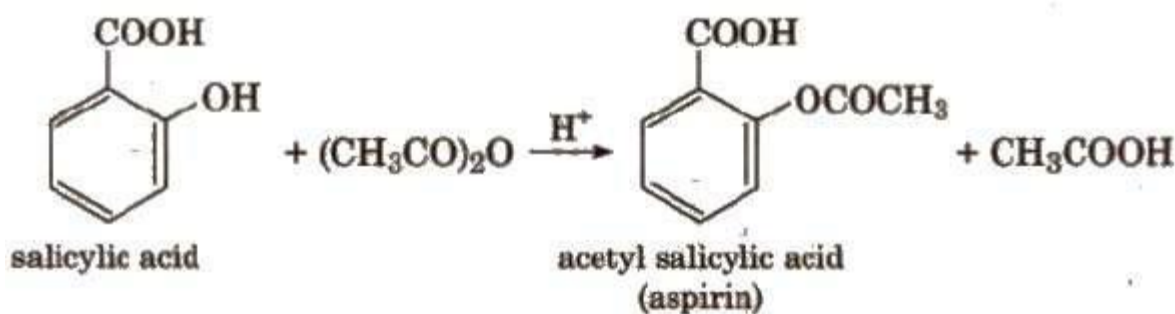


The reaction with R'COOH and (R'CO)<sub>2</sub>O is reversible, so conc. H<sub>2</sub>SO<sub>4</sub> is used to remove water.

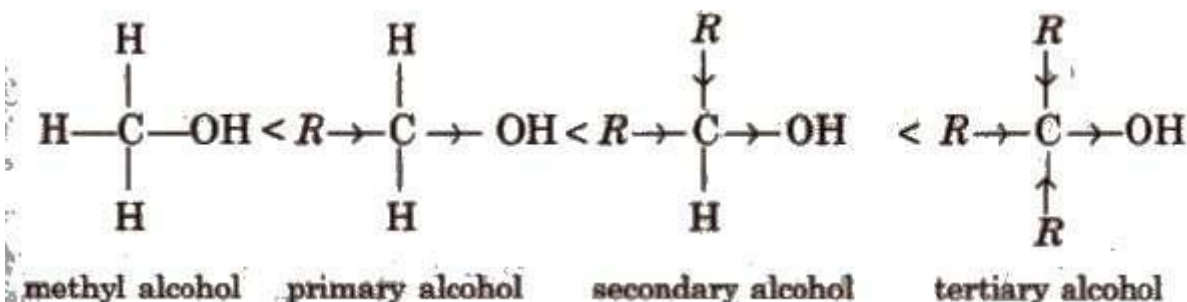
The reaction with R'COCl is carried out in the presence of pyridine so as to neutralise HCl which is formed during the reaction.

The introduction of acetyl (CH<sub>3</sub>CO-) group in phenols is known as acetylation.

Acetylation of salicylic acid produces aspirin.



4. **Reaction involving cleavage of C-O bond in alcohols** In these reactions, the reactivity order of different alcohols :



Alkyl group due to +I effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.



**Reaction with halogen acids** Alcohols can be converted into haloalkanes by the action of halogen acids.



For a given alcohol order of reactivity of HX is



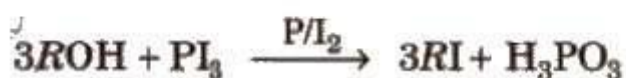
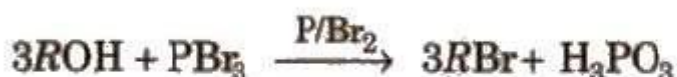
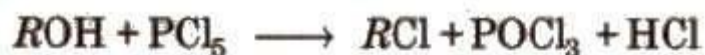
For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

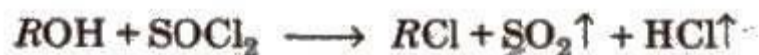
### Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols
$RCH_2OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_2CH-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_3C-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$
No reaction and hence, no white cloudiness or turbidity at room temperature.	$R_2CHCl$ White cloudiness or turbidity appears with in about 5 minutes.	$R_3CCl$ White cloudiness or turbidity appears immediately.

### (iii) Reaction with phosphorus halides



### (iv) Reaction with thionyl chloride

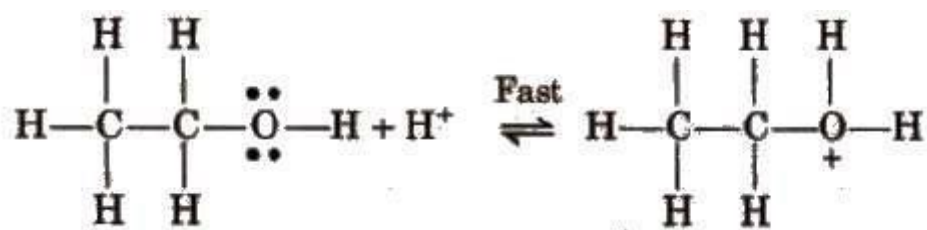


(v) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

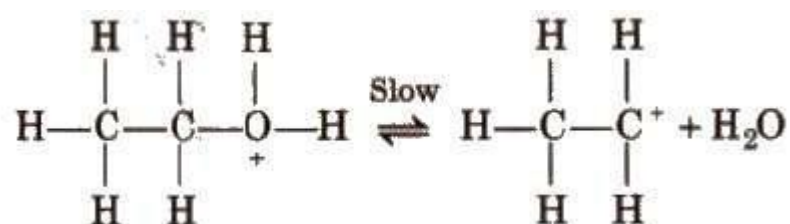
Since, the rate determining step is the formation of carbocation, the ease of dehydration is

## Mechanism

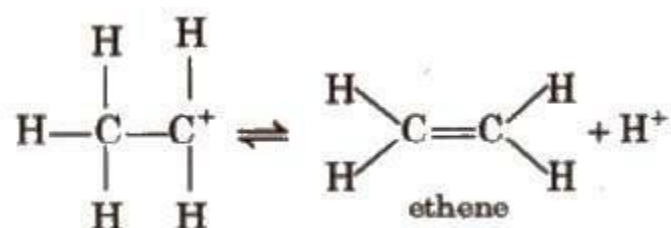
### Step I Formation of protonated alcohol



### Step II Formation of carbocation



### Step III Formation of ethene by elimination of a proton

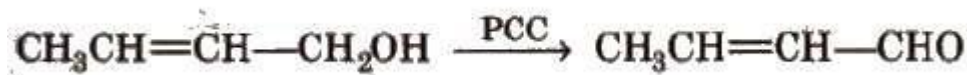


In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

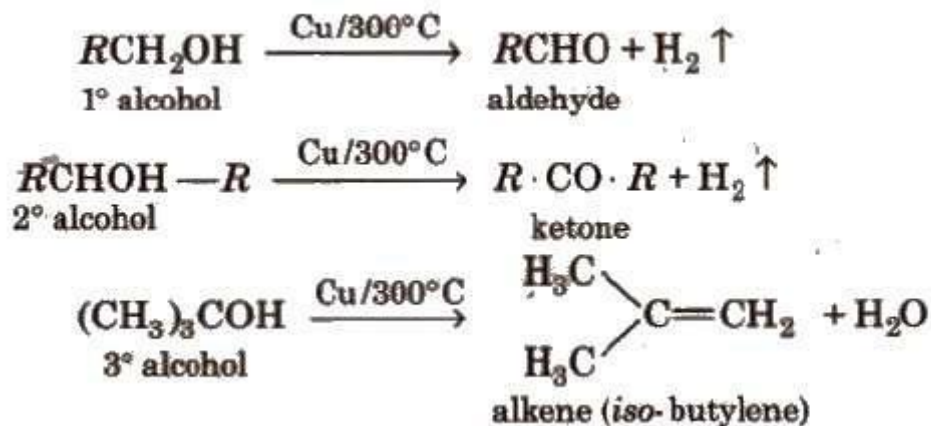
(vi) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline  $\text{KMnO}_4$  and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Primary alcohols	Secondary alcohols	Tertiary alcohols
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHOH}-\text{CH}_3$	$(\text{CH}_3)_3\text{C}-\text{OH}$
↓[O]	↓[O]	↓[O]
$\text{CH}_3\text{CHO}$	$\text{CH}_3\text{COCH}_3$	$\text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$
↓[O]	↓[O]	↓[O]
$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$

A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).



(vii) **Dehydrogenation**

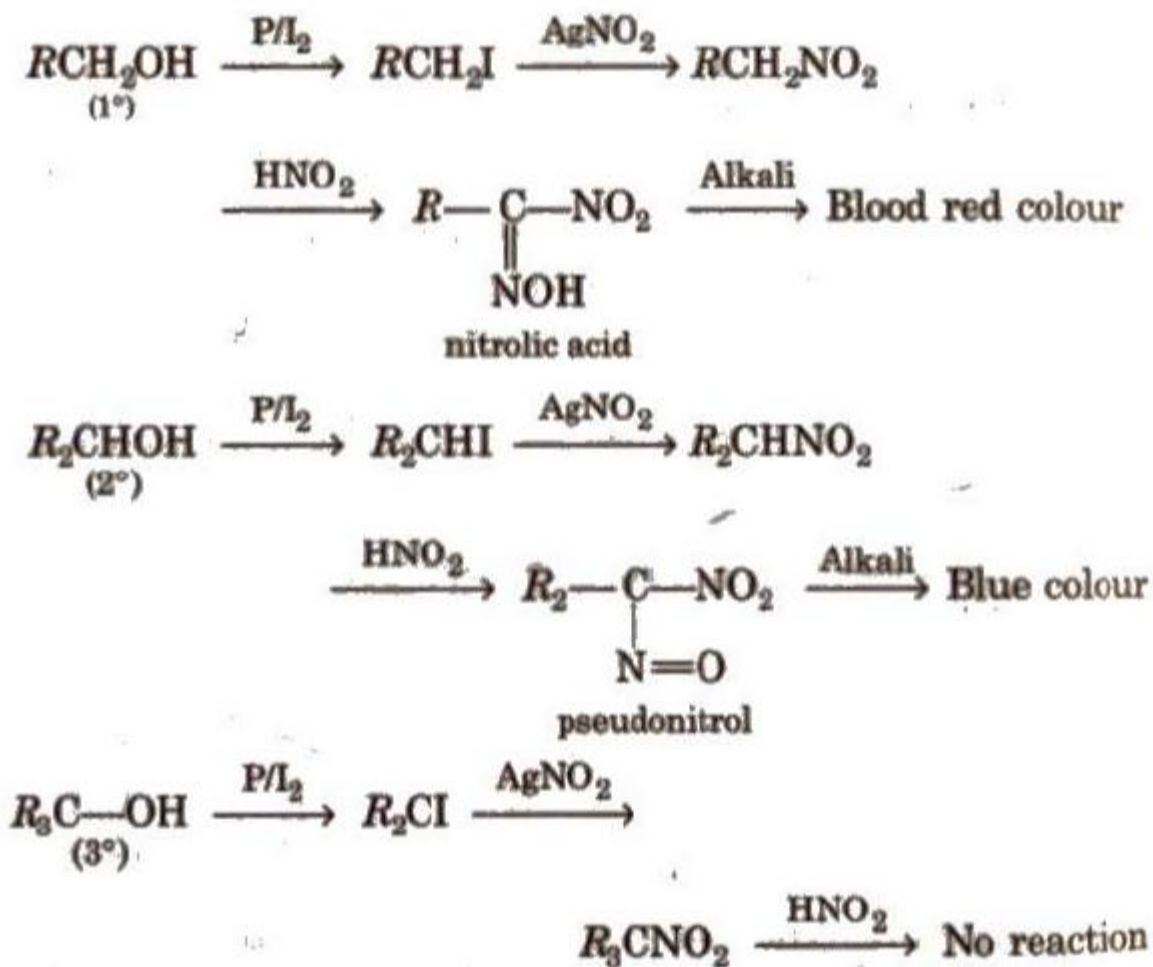


**Distinction among 1°, 2° and 3° Alcohols**

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

**Victor Meyer's test** is also used to distinguish them.

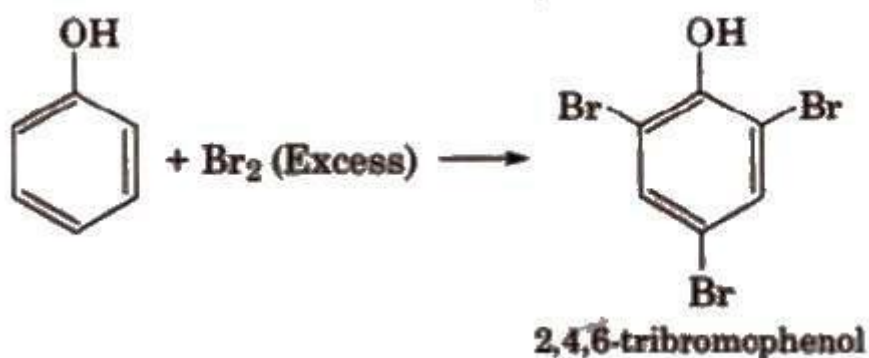
In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.



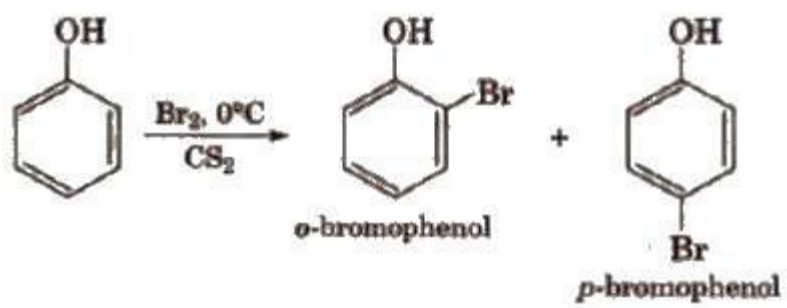
## Reactions of Phenols

4. **Electrophilic substitution reactions** The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions .

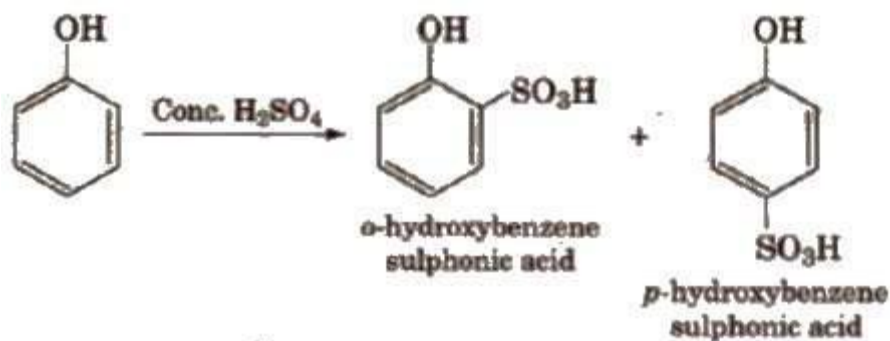
### (vi) Halogenation



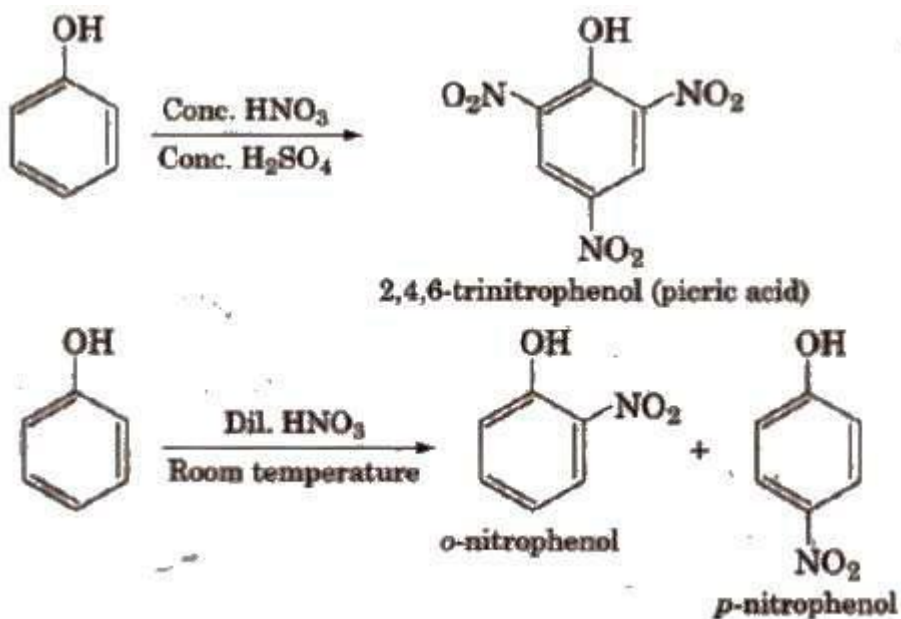
With calculated amount of Br<sub>2</sub> in CS<sub>2</sub> or CHCl<sub>3</sub> it gives ortho and para product.



### (v) Sulphonation

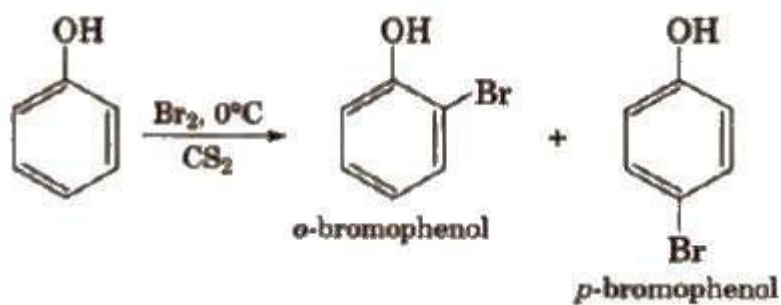


### 2. Nitration

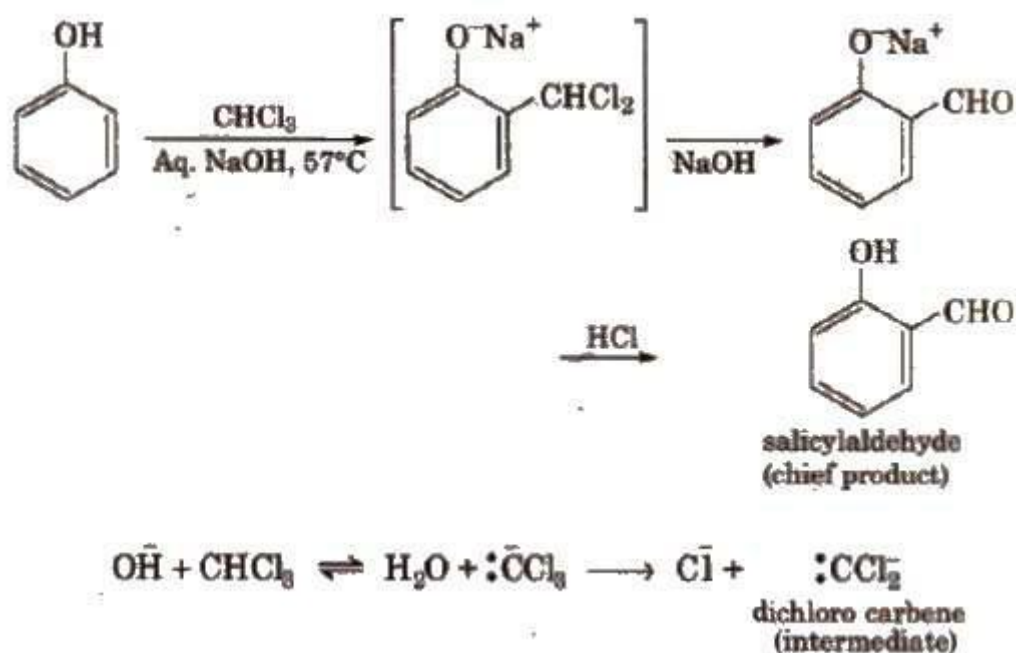


The ortho and para isomers can be separated by steam distillation. This is because *o*-nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



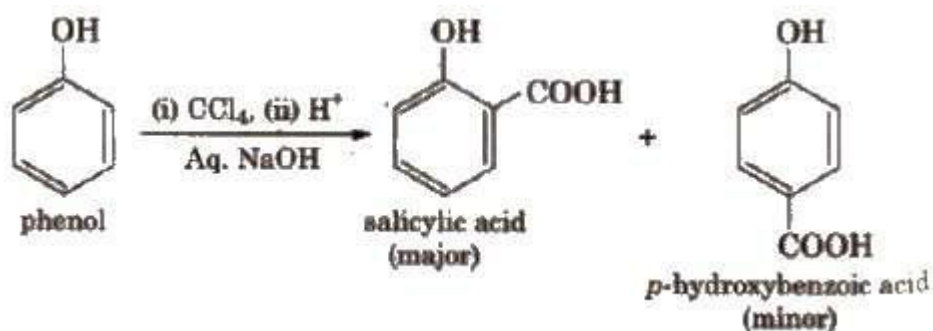


(ii) Reimer-Tiemann reaction

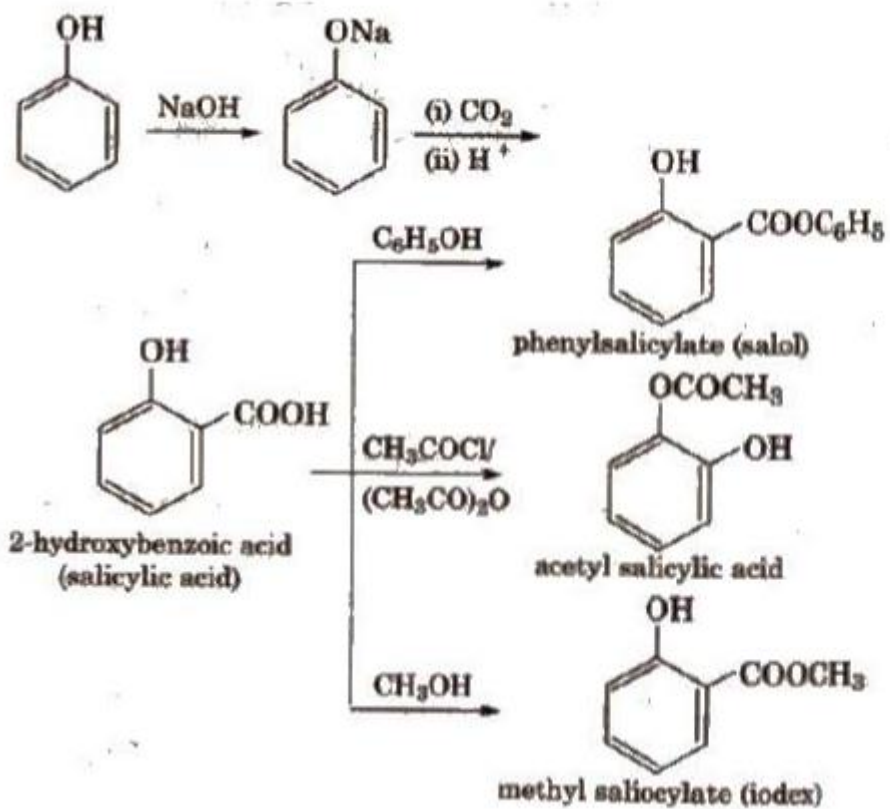


This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene.

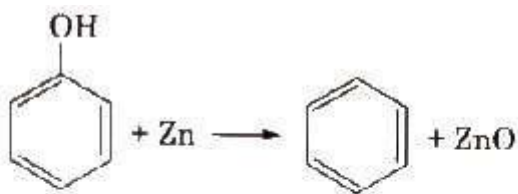
Similarly with carbon tetrachloride and alkali, *c*- and *p*-hydroxybenzoic acid are obtained



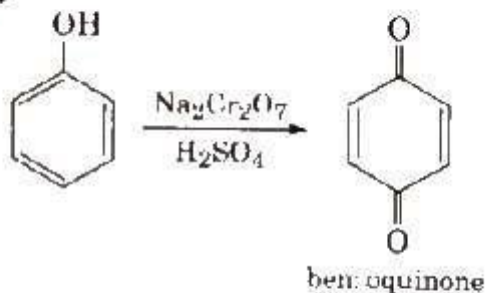
(iii) Kolbe's reaction



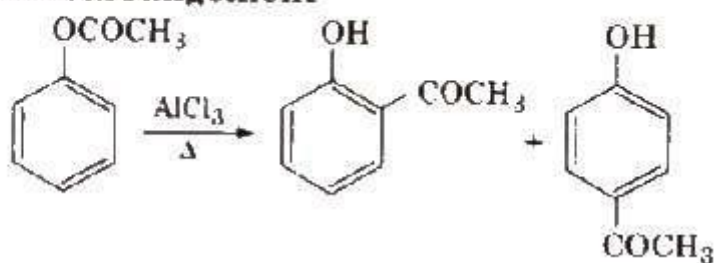
(iv) **Reaction with zinc dust**



(iv) **Oxidation**



(v) **Fries rearrangement**



## Terms Related to Alcohols

3. **Rectified spirit** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74°.

4. **Absolute alcohol** Alcohol containing no water, i.e; 100% C<sub>2</sub>H<sub>5</sub>OH is known as absolute alcohol. It is prepared as follows.

4. Quick lime process

5. Azeotropic method

(iii) **Methylated spirit** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.

(iv) **Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.

(v) **Wood spirit** Methyl alcohol (CH<sub>3</sub>OH) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation

of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.

(vi) **Grain alcohol** Ethyl alcohol  $C_2H_5OH$  is also called grain alcohol. It is used in the preparation of various beverages containing different percentages.

### Dihydric Alcohols

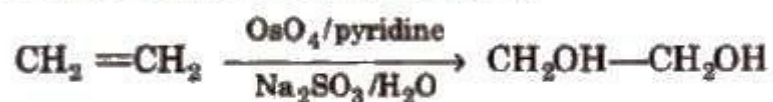
These are generally called glycols because of their sweet taste. Ethylene glycol ( $CH_2OH - CH_2OH$ ) is the first and most important member of dihydric alcohol series.

### Methods of Preparation

#### (i) From ethylene



(1% alkaline  $KMnO_4$  is called Baeyer's reagent)



#### (ii) By reduction of glyoxal



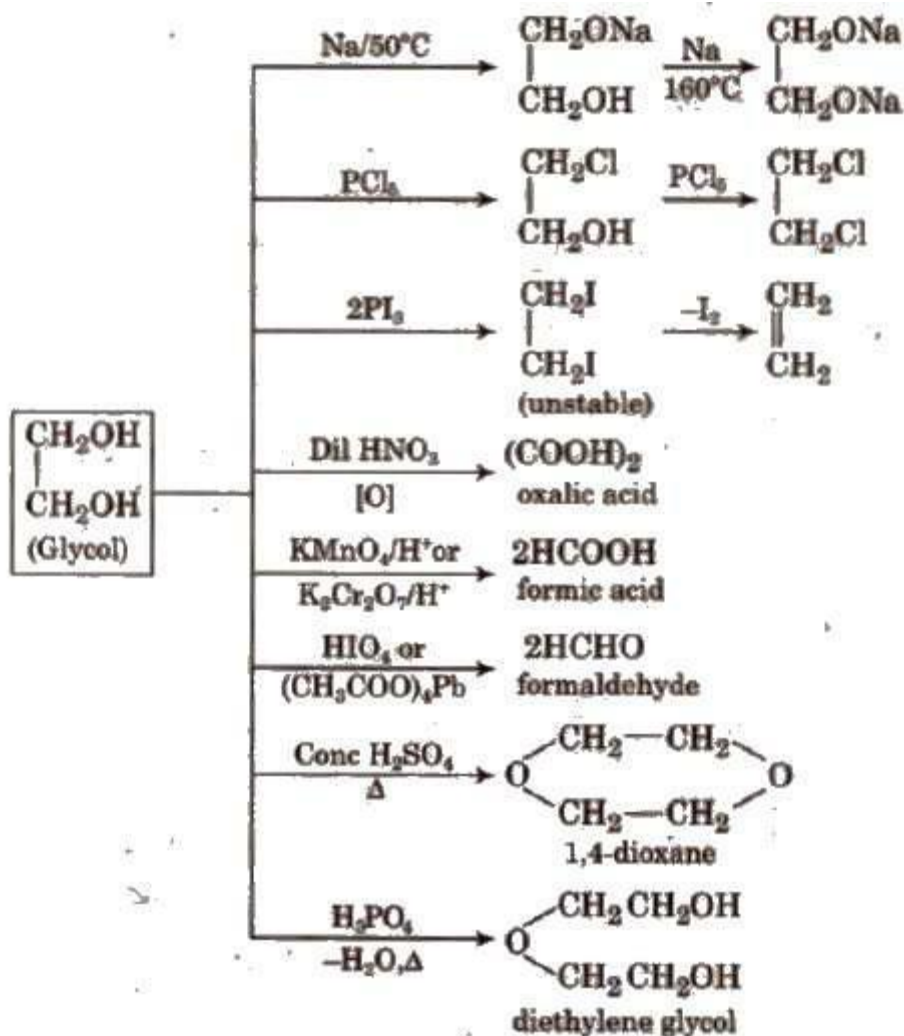


## Physical Properties

- (iv) It is a colourless, syrupy liquid with sweet taste.  
(v) Because of its tendency of formation of H-bonds, it is miscible with H<sub>2</sub>O and ethanol but not with ether.

## Chemical Properties

It gives all the general reactions of -OH group.



The per-iodic acid cleavage of 1,2-glycols is sometimes called Malaprade reaction.

## Trihydric Alcohols

Glycerol or glycerine, CH<sub>2</sub>OH – CH(OH)– CH<sub>2</sub>OH is the first member of this group. Its IUPAC name is propane-1,2,3-triol.

## Method of Preparation

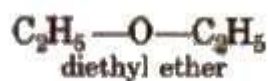
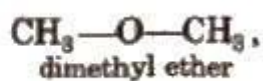
Cone  $\text{HNO}_3$  gives II; dil  $\text{HNO}_3$  gives II and III;  $\text{Bi}(\text{NO}_3)_3$  or  $\text{NaNO}_3$  gives VI; Fenton's reagent or  $\text{NaOBr}$  or  $\text{Br}_2$  water in  $\text{Na}_2\text{CO}_3$  gives a mixture of I and IV.

Solid  $\text{KMnO}_4$  oxidises glycerol to VII and  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

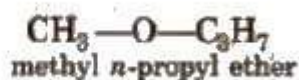
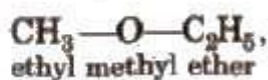
With  $\text{HIO}_4$  (periodic acid), glycerol gives  $\text{HCOOH}$  and  $\text{HCHO}$ .

## Ethers

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen, known as ethereal oxygen. These are represented by the general formula  $\text{R}-\text{O}-\text{R}'$  where R may be alkyl or aryl groups. e.g.,



### Mixed ethers



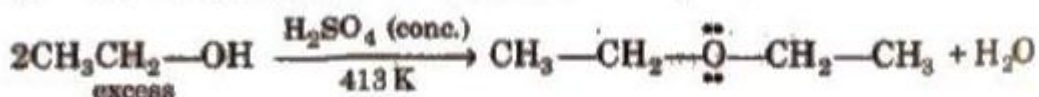
These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

## Nomenclature of Ethers

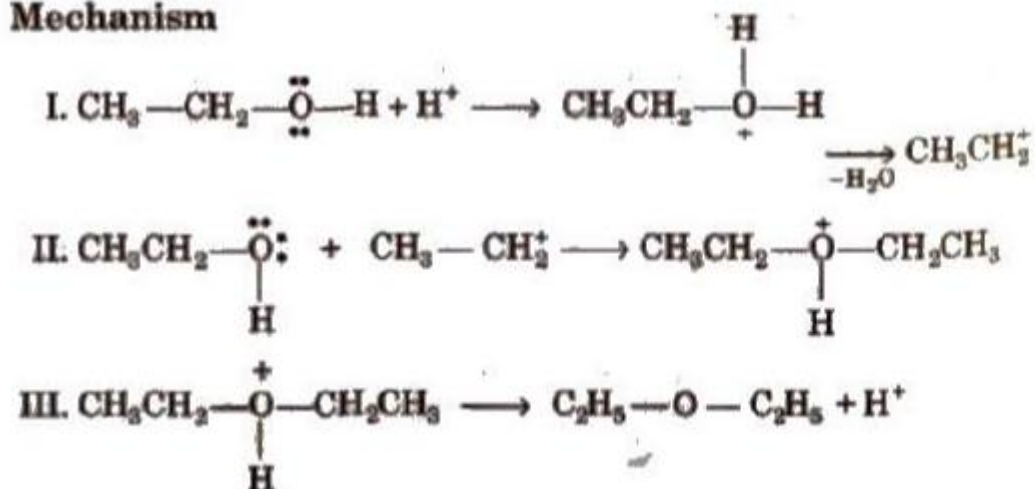
In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

## Preparation of Ethers

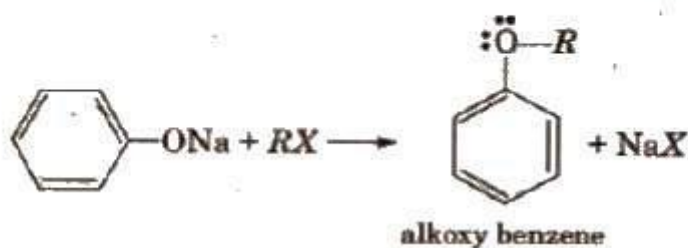
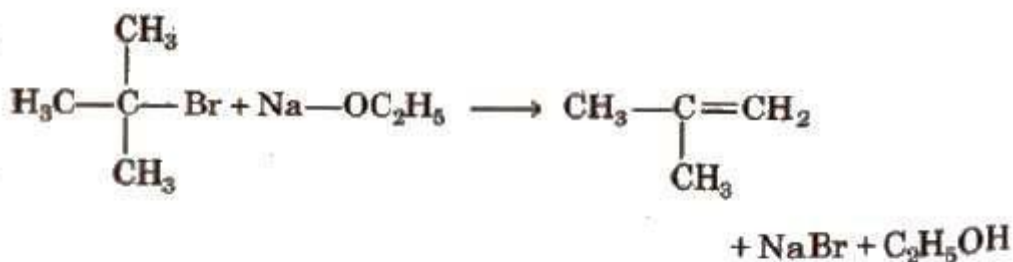
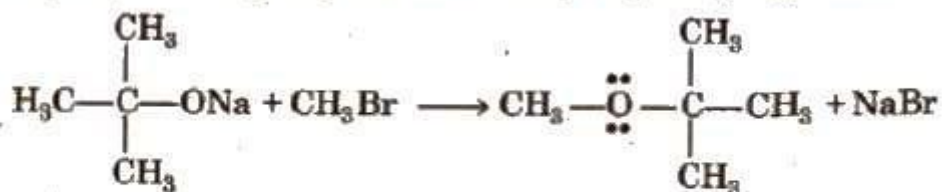
(i) **By dehydration of alcohols**



**Mechanism**



5. **Williamson's synthesis** Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.



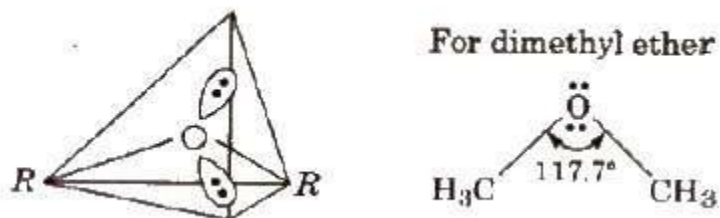
**Physical Properties of Ethers**

Ethers are polar but insoluble in  $\text{H}_2\text{O}$  and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.



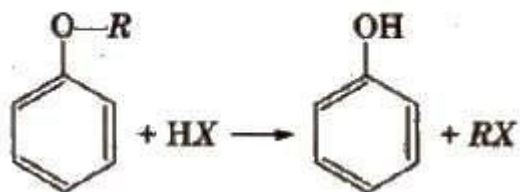
## Structure of Ether

The hybridisation of O atom in ethers is  $sp^3$  (tetrahedral) and its shape is V-shape.

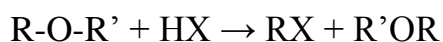


## Chemical Reactions of Ether

### (ii) Reaction with HX



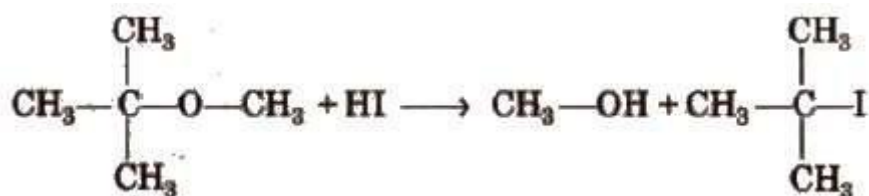
Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by  $S_N^2$  mechanism.



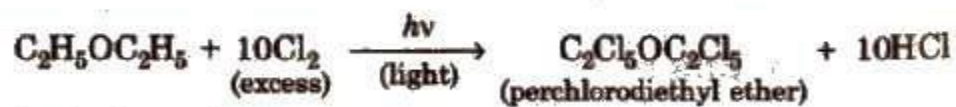
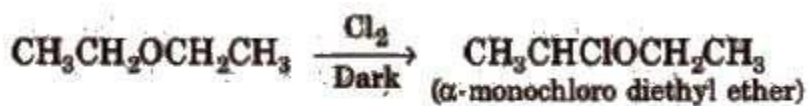
The order of reactivity of hydrogen halides is as follows



In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by  $S_N^1$  mechanism.



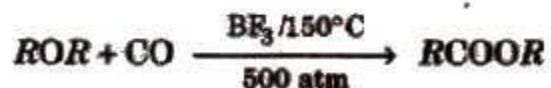
### (iii) Halogenation



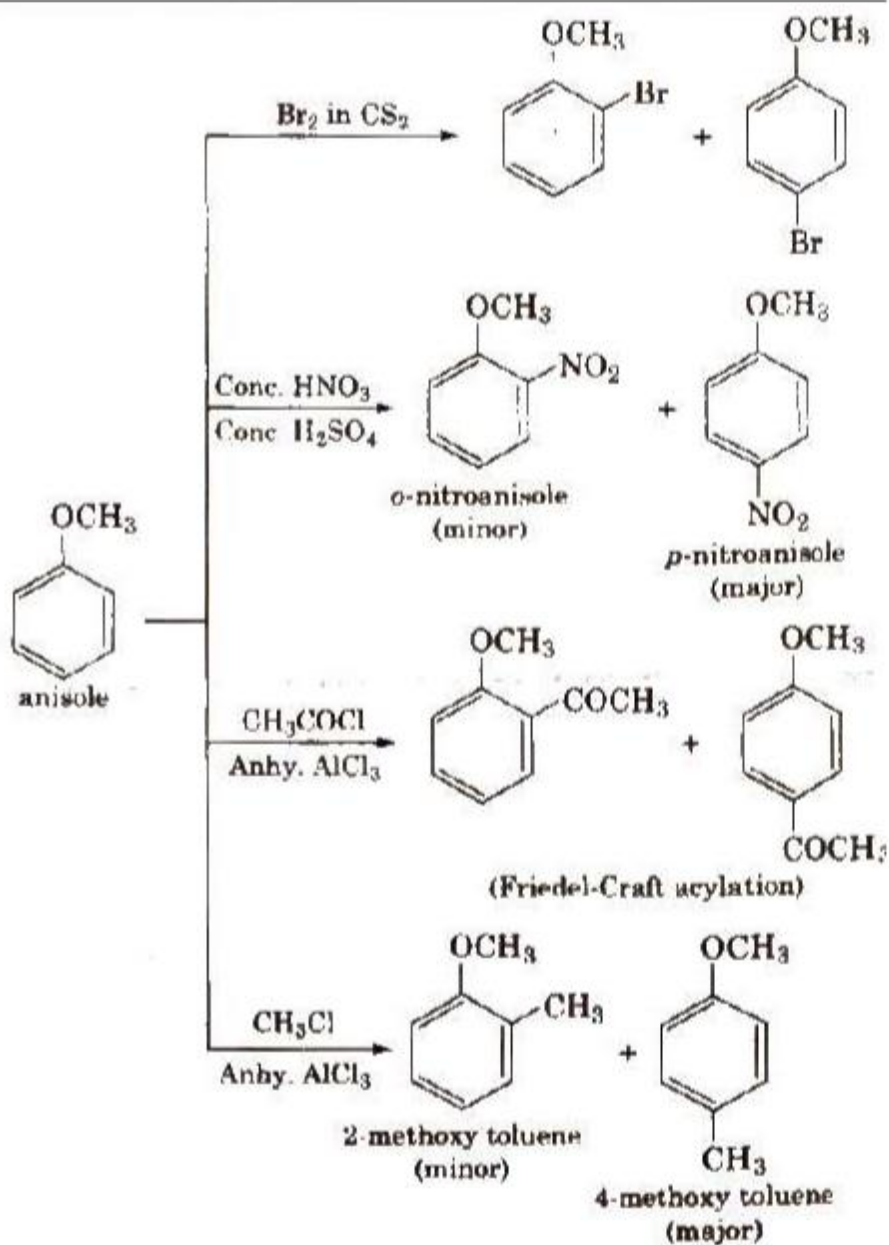
(iii) Reaction with  $\text{PCl}_5$



(iv) Reaction with CO



v) Electrophilic substitution reactions In ethers, -OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction



Ethyl phenyl ester  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$  is also, known as phenetole.

### Uses of Ethers

- (v) Dimethyl ether is used as refrigerant and as a solvent at low temperature.
- (vi) Diethyl Ether is used as an anaesthesia in surgery .

