

## (D) Coordination isomerism :

Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are :  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6](\text{Co}(\text{CN})_6)$

## (E) Ligand isomerism :

Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source.

## (F) Polymerisation isomerism :

Considered to be a special case of coordination isomerism, in this the various isomers differ in formula weight from one another, so not true isomers in real sense.

**(2) STEREOISOMERISM :**

The isomers in which atoms are bonded to each other in the same order but that differ in the arrangement of these atoms in the space are called as stereoisomers and the phenomenon as stereoisomerism.

**Geometrical Isomerism**

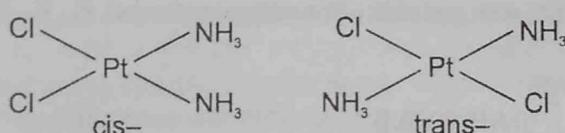
This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

**Coordination Number Four :**

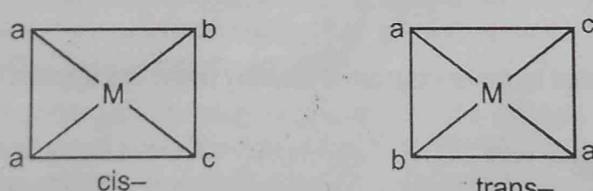
**Tetrahedral Complex :** The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

**Square Planar Complex :**

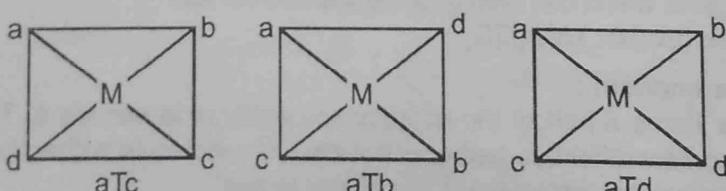
In a square planar complex of formula,  $[\text{Ma}_2\text{b}_2]$  [a and b are unidentates], the two ligands 'a' may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.

**Geometrical isomers (cis and trans) of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ .**

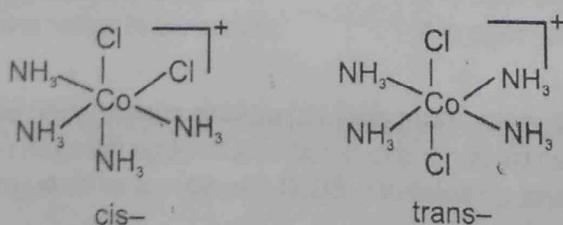
Square planar complex of the type  $\text{Ma}_2\text{bc}$  (where a,b,c are unidentates) shows two geometrical isomers.



Square planar complex of the type  $\text{Mabcd}$  (where a,b,c,d are unidentates) shows three geometrical isomers.

**Coordination Number Six :**

Geometrical isomerism is also possible in octahedral complexes.

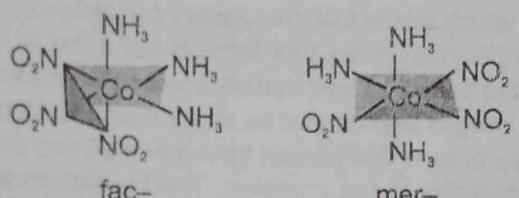
**Geometrical isomers (cis and trans) of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$**

Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(I) Complexes containing only unidentate ligands

(i) $Ma_2b_4$	-	2	;	(ii) $Ma_4bc$	-	2
(iii) $Ma_3b_3$	-	2				

Complexes of the formula  $Ma_3b_3$ , where a and b are monodentate ligands, may show two isomeric forms called fac- and mer-. Facial isomers have three identical ligands on one triangular face whereas meridional isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands.



The facial(fac) and meridional(mer) isomers of  $[Co(NH_3)_3(NO_2)_3]$ .

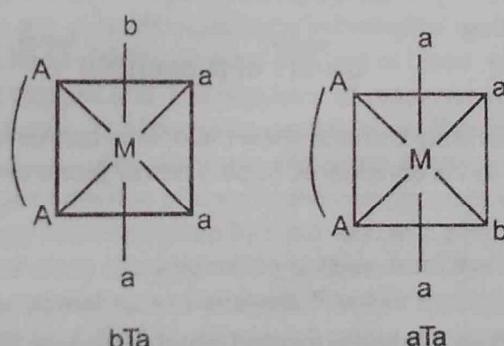
Unsymmetrical bidentate ligands also show fac-mer isomerism.

(iv) $Ma_3b_2c$	-	3	;	(v) $Ma_3bcd$	-	4
(vi) $Ma_2b_2c_2$	-	5	;	(vii) $Ma_2b_2cd$	-	6
(viii) $Ma_2bode$	-	9	;	(ix) Mabcdef, $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$	-	15

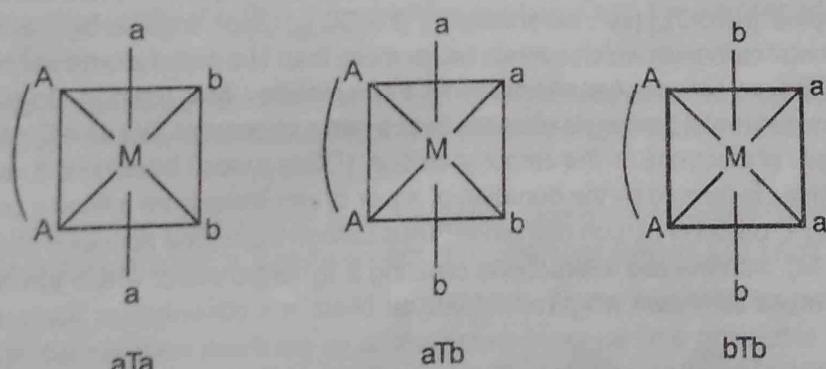
Note:  $Ma_6$  and  $Ma_5b$  have only one form.

(II) Compounds containing bidentate ligand and unidentate ligands.

- (i)  $M(AA)a_3b$  – Two geometrical isomers are possible.

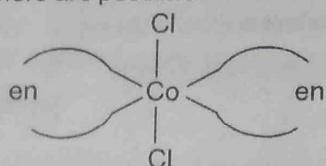
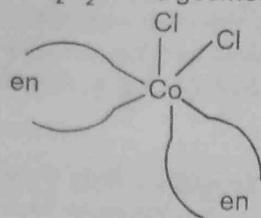


- (ii)  $M(AA)a_2b_2$  – Three geometrical isomers are possible.



Note: With  $[M(AA)b_4]$ , only one form is possible.  $M(AA)abcd$  have six geometrical isomers.

(iii)  $M(AA)_2O_2$  – Two geometrical isomers are possible.



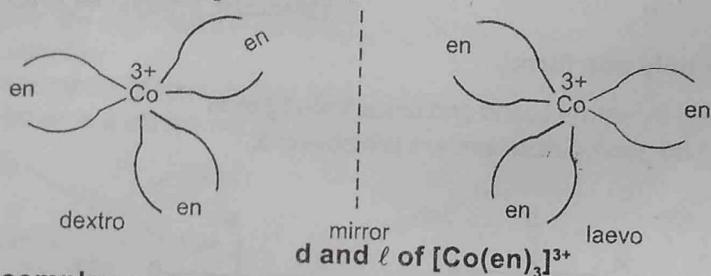
Geometrical isomers (cis and trans) of  $[CoCl_2(en)_2]$

### Optical Isomerism :

A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. This is due to the absence of elements of symmetry in the complex. The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left).

### Octahedral complex :

Optical isomerism is common in octahedral complexes involving didentate ligands. For example,  $[Co(en)_3]^{3+}$  has d and l forms as given below.



### Square planar complex :

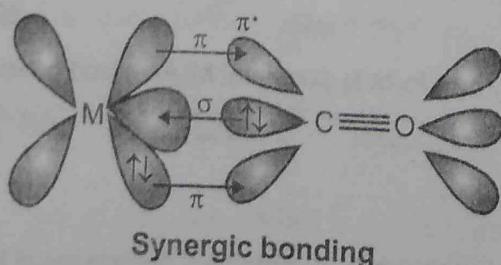
Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality.

## Organometallic compounds

### Metal Carbonyls :

Compounds of metals with CO as a ligand are called metal carbonyls. They are of two types.

- (a) **Monomeric** : Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples :  $[Ni(CO)_4]$  ( $sp^3$ , tetrahedral) ;  $[Fe(CO)_5]$  ( $dsp^3$ , trigonal bipyramidal).
- (b) **Polymeric** : Those metal carbonyls which contain two or more than two metal atoms per molecule and they have metal-metal bonds are called polymeric carbonyl. For example :  $Mn_2(CO)_{10}$ ,  $Co_2(CO)_9$ , etc. The metal–carbon bond in metal carbonyls possess both s and p character. The M—C  $\sigma$  bond is formed by the donation of lone pair of electrons on the carbonyl carbon (CO is a weak base) into a vacant orbital of the metal. The M — C  $\pi$  bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. Thus carbon monoxide acts as  $\sigma$  donor ( $OC \rightarrow M$ ) and  $\pi$  acceptor ( $OC \leftarrow M$ ), with the two interactions creating a synergic effect which strengthens the bond between CO and the metal as shown in figure.



**Sigma ( $\sigma$ ) bonded organometallic compounds :**

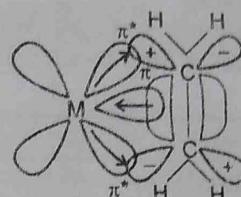
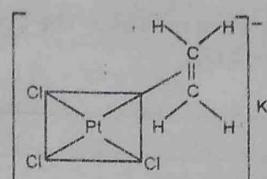
In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond in which ligand contributes one electron and is therefore called one electron donor. For example :

- (a) Grignard's Reagent  $R - Mg - X$  where R is a alkyl or aryl group and X is halogen.
- (b)  $(CH_3)_4 Sn$ ,  $(C_2H_5)_4 Pb$ ,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$  etc.

**Pi ( $\pi$ )-bonded organometallic compounds :**

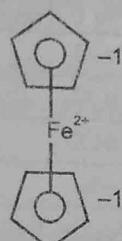
These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

Zeise's salt :  $K [PtCl_3(\eta^2 - C_2H_4)]$

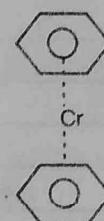


Ferrocene and bis(benzene)chromium :

$Fe(\eta^5 - C_5H_5)_2$



and  $Cr(\eta^6 - C_6H_6)_2$

**Applications of coordination and organometallic compounds :**

- (i) Coordination compounds are of great importance in biological systems. Example being – chlorophyll (the green pigment in plants); haemoglobin (the red pigment of blood, which acts as oxygen carrier) along with myoglobin (which stores oxygen and is a regulator of respiration); Vitamin B<sub>12</sub>, cyanocobalaminne, the anti-pernicious anaemia factor. All of these, respectively, are the coordination compounds of magnesium, iron and cobalt with the macrocyclic porphyrin and corrin ligands.
- (ii) There are many examples of the use of coordination compounds in qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially the chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Familiar examples of such reagents are : ethylenediaminetetraacetic acid (EDTA), dimethylglyoxime, α-nitroso β-naphthol, cupron, etc.
- (iii) Some important extraction processes of metals, like those of extraction of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity  $[Au(CN)_2]^-$  in aqueous solution. Gold can be precipitated from this solution by the addition of Zinc.
- (iv) Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to  $[Ni(CO)_4]$ , which is decomposed to yield pure nickel.
- (v) EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumors. Examples are : cis-platin ( $cis-[Pt(NH_3)_2Cl_2]$ ) and related compounds.
- (vi) Organometallic compounds are used as catalysts. These catalysts are either of the homogeneous type (soluble in the reaction medium) or of the heterogeneous type (insoluble in the reaction medium). The catalysed polymerisation of alkenes at atmospheric pressure and ambient temperature using Ziegler-Natta catalyst (titanium tetrachloride plus triethylaluminium) is one of the important discoveries of organometallic chemistry. The first effective homogeneous catalyst chloridotris(triphenylphosphine) rhodium(I),  $[RhCl(PPh_3)_3]$  for hydrogenation was given by Wilkinson.
- (vii) Tetra ethyl lead (TEL) is used as antiknock compound in gasoline.

## METALLURGY

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue.

- (a) Native ores contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
- (b) Oxidised ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.
- (c) Sulphurised ores consist of sulphides of metals like iron, lead, zinc, mercury etc.
- (d) Halide ores consist of halides of metals.

Metal	Ores	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < X < 1$ ] $\text{Al}_2\text{O}_3$
	Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	Corundam	$\text{Al}_2\text{O}_3$
	Kaolinite (a form of clay)	$[\text{Al}_2(\text{OH})_4 \text{Si}_2\text{O}_5]$
Iron	Haematite	$\text{Fe}_2\text{O}_3$
	Magnetite	$\text{Fe}_3\text{O}_4$
	Siderite	$\text{FeCO}_3$
	Iron pyrite	$\text{FeS}_2$
	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Copper	Copper pyrite	$\text{CuFeS}_2$
	Copper glance	$\text{Cu}_2\text{S}$
	Cuprite	$\text{Cu}_2\text{O}$
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Zinc	Zinc blende or Sphalerite	$\text{ZnS}$
	Calamine	$\text{ZnCO}_3$
	Zincite	$\text{ZnO}$
Lead	Galena	$\text{PbS}$
	Anglesite	$\text{PbSO}_4$
	Cerrusite	$\text{PbCO}_3$
Magnesium	Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ( $\text{K}_2\text{MgCl}_4 \cdot 6\text{H}_2\text{O}$ )
	Magnesite	$\text{MgCO}_3$
	Dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3$
	Epsomsalt (Epsomite)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
	Langbeinite	$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$
Tin	Cassiterite (Tin stone)	$\text{SnO}_2$
Silver	Silver glance (Argentite)	$\text{Ag}_2\text{S}$
	Chlorargyrite (Horn silver)	$\text{AgCl}$

### Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

- (A) **Crushing and Grinding** : The ore is first crushed by jaw crushers and ground to a powder.
- (B) **Concentration** : The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.
- (i) **Hydraulic washing or Gravity separation or Levigation method** : It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.
- (ii) **Electromagnetic separation** : It is based on differences in magnetic properties of the ore components. Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is separated from non-magnetic siliceous impurities and cassiterite ore ( $\text{SnO}_2$ ) is separated from magnetic Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ).
- (iii) **Froth floatation process** : This method is commonly used for the concentration of the low grade sulphide ores like galena,  $\text{PbS}$  (ore of Pb); copper pyrites  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{CuFeS}_2$  (ore of copper); zinc blende,  $\text{ZnS}$  (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.
- (iv) **Leaching** : Leaching is often used if the ore is soluble in some suitable solvent, e.g., acids, bases and suitable chemical reagents.

(C) **Extraction of crude metal from concentrated ore** :

The isolation of metals from concentrated ore involves two major steps as given below.

(i) **Conversion to oxide** :

**Calcination**. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

(a) The carbonate ore gets decomposed to form the oxide of the metal.

(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture.

(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

**Roasting**. It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or  $\text{O}_2$  below its melting point. Roasting is an exothermic process once started it does not require additional heating.

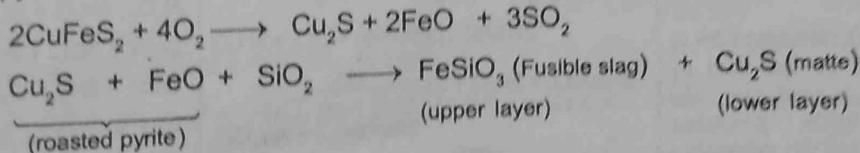
**Smelting** :

**Slag formation** : In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting.

The principle of slag formation is essentially the following :

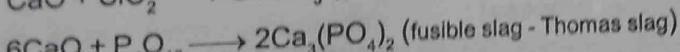
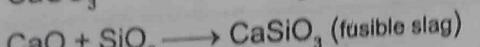
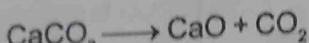
Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide)  $\longrightarrow$  Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example,  $\text{FeO}$  is the impurity in extraction of Cu from copper pyrite.



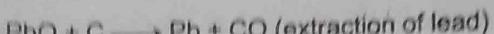
Matte also contains a very small amount of iron(II) sulphide.

To remove unwanted acidic impurities like sand and  $\text{P}_4\text{O}_{10}$ , smelting is done in the presence of limestone.



(ii) **Reduction of a metal oxide** :

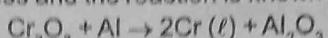
The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

**Chemical reduction method :****Reduction with carbon :**

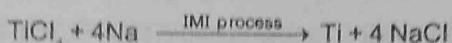
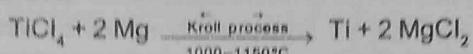
**Reduction with CO :** In some cases CO produced in the furnace itself is used as a reducing agent.

**Reduction by other metals :**

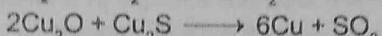
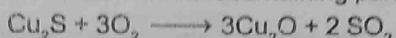
Metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to  $\text{Al}_2\text{O}_3$ . The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.



**Magnesium reduction method :** Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.

**Self-reduction method :**

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and  $\text{SO}_2$ .

**Electrolytic reduction :**

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or aluminum or for production of samples of high purity.

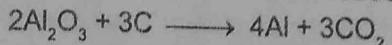
1. **In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
2. **In fused melts :** Aluminum is obtained by electrolysis of a fused mixture of  $\text{Al}_2\text{O}_3$  and cryolite  $\text{Na}_3[\text{AlF}_6]$ .

**Extraction of Aluminium :** It involves the following processes(a) **Purification of bauxite :**

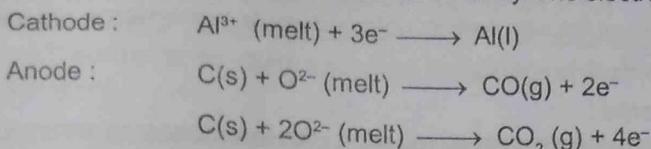
(i) Bayer's Method (used for red bauxite containing $\text{Fe}_2\text{O}_3$ and silicates as impurities)	(II) Hall's Method (used for red bauxite containing $\text{Fe}_2\text{O}_3$ and silicates as impurities)	(III) Serpeck's Method (used for white bauxite containing silica as impurities)
$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \xrightarrow[8\text{ atm}]{190^\circ\text{C}}$ $2\text{NaAlO}_2 \text{ (soluble)} + 3\text{H}_2\text{O}$ <p><math>\text{Fe}_2\text{O}_3</math> (insoluble) separated as red mud by filtration solution is diluted with water and seeded with freshly prepared <math>\text{Al}(\text{OH})_3</math>. It induces the precipitation of <math>\text{Al}(\text{OH})_3</math>. <math>\text{Al}(\text{OH})_3</math> is filtered leaving behind silicates in solution.</p> $\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3 \downarrow$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{Fuse}}$ $2\text{NaAlO}_2 \text{ (soluble)} + \text{CO}_2 + 2\text{H}_2\text{O}$ $2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{60^\circ\text{C}}$ $2\text{Al}(\text{OH})_3 \downarrow + \text{Na}_2\text{CO}_3$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{C} + \text{N}_2 \xrightarrow[1800^\circ\text{C}]{\text{Electro fusion}}$ $2\text{AlN} + 3\text{CO} + 2\text{H}_2\text{O}$ $2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NH}_3$ $\text{SiO}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{Si}$ <p>Silicone volatilises at this temp.</p> $2\text{Al}(\text{OH})_3 \xrightarrow{1473\text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

(b) **Electrolytic reduction (Hall-Heroult process) :**

The purified  $\text{Al}_2\text{O}_3$  is mixed with  $\text{Na}_3\text{AlF}_6$  (cryolite) or  $\text{CaF}_2$  (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as:



The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and  $\text{CO}_2$ . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



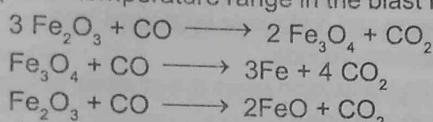
### Metallurgy of some important metals

#### 1. Extraction of iron from ore haematite :

Oxide ores of iron, after concentration through calcination / roasting in reverberatory furnace (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with lime stone and coke and fed into a Blast furnace from its top with the help of a cup and cone arrangement. Here, the oxide is reduced to the metal.

**Reactions involved :** The reactions proceed in several stages at different temperatures. Since the air passes through in a few seconds, the individual reactions does not reach equilibrium.

At 500 – 800 K (lower temperature range in the blast furnace)



At 900 – 1500 K (higher temperature range in the blast furnace):

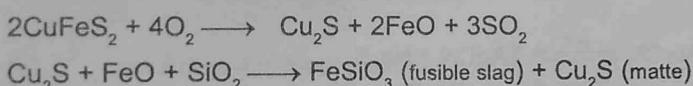


Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

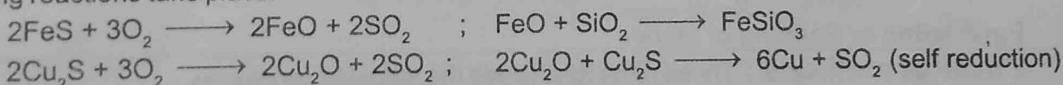


#### 2. Extraction of copper :

**From copper glance / copper pyrite (self reduction) :** In actual process the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte. This contains mostly  $\text{Cu}_2\text{S}$  and some FeS.



Copper matte is then charged into silica lined convertor (Bessemer convertor). Some silica is also added and hot air blast is blown to convert the remaining  $\text{FeS}_2$ , FeO and  $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$  to the metallic copper. Following reactions take place:

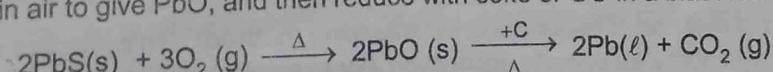


The solidified copper obtained has blistered appearance due to the evolution of  $\text{SO}_2$  and so it is called blister copper.

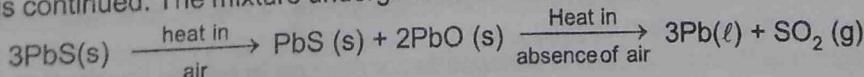
#### 3. Extraction of lead :

There are two methods of extracting the element :

(i) Roast in air to give  $\text{PbO}$ , and then reduce with coke or CO in a blast furnace.

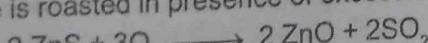


(ii)  $\text{PbS}$  is partially oxidized by heating and blowing air through it. After some time the air is turned off and heating is continued. The mixture undergoes self reduction as given below.

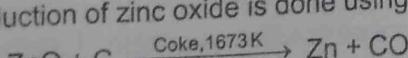


#### 4. Extraction of zinc from zinc blende :

The ore is roasted in presence of excess of air at temperature 1200 K.



The reduction of zinc oxide is done using coke.

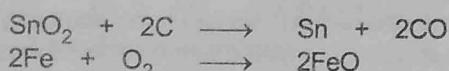


**Note :**  $ZnO$  may be reduced by carbon monoxide at  $1473\text{ K}$  (i.e.  $1200^\circ\text{C}$ ) in smelter. The reaction is reversible, and the high temperature is required to move the equilibrium to the right. At this temperature the  $Zn$  is gaseous. If the gaseous mixture of  $Zn$  and  $CO_2$  was simply removed from the furnace and cooled, then reoxidation of  $Zn$  would occur. Thus the zinc powder obtained would contain large amounts of  $ZnO$ .



#### 5. Extraction of tin from cassiterite :

The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite.  $SnO_2$  is reduced to metal using carbon at  $1200 - 1300^\circ\text{C}$  in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise  $FeO$  which then floats to the surface.

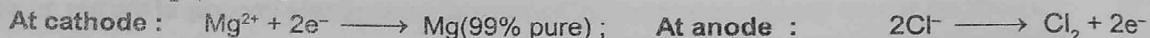
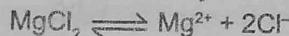


#### 6. Extraction of Magnesium :

##### From Sea water (Dow's process) :

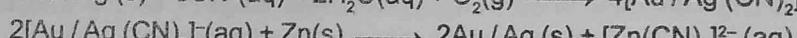
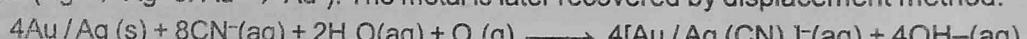
Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

- (a) Precipitation of magnesium as magnesium hydroxide by slaked lime.
- (b) Preparation of hexahydrated magnesium chloride.
- (c) The solution on concentration and crystallisation gives the crystals of  $MgCl_2 \cdot 6H_2O$ .
- (d) Preparation of anhydrous magnesium chloride.
- (e) Electrolysis of fused anhydrous  $MgCl_2$  in presence of  $NaCl$ .

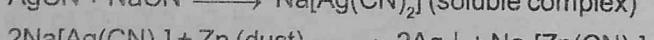
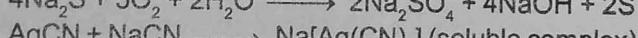
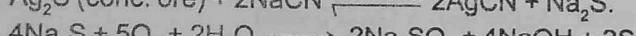
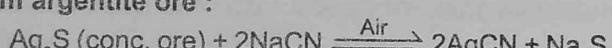


#### 7. Extraction of gold and silver (MacArthur-Forrest cyanide process) :

- (a) **From native ores :** Extraction of gold and silver involves leaching the metal with  $CN^-$ . This is also an oxidation reaction ( $Ag \rightarrow Ag^+$  or  $Au \rightarrow Au^+$ ). The metal is later recovered by displacement method.



- (b) **From argentite ore :**



#### (D) Purification or Refining of metals :

**Physical methods :** These methods include the following processes :

**(I) Liquation process :** This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy.

**(II) Fractional distillation process :** This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

**(III) Zone refining method (Fractional crystallisation method) :** This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

Germanium metal, which is used in semiconductor devices, is refined (purified) by the zone refining method.

**Chemical methods :** These methods include the following methods :

**(I) OXIDATIVE REFINING :**

The method is used when the impurities present in the metal have a greater affinity for oxygen and are more readily oxidized than the metal. Then these oxides may be removed as follows :

(a) These oxide may form a scum on the surface of the metal. This scum can easily be removed by skimming.

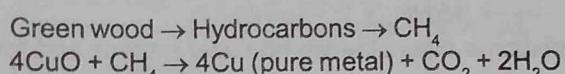
(b) If the oxides are volatile, they escape from the mouth of the furnace.

(c) The oxides may form a slag with the lining on the inside surface of the furnace and may thus be removed. In the formation of the slag, the lining acts as a flux.

This method is usually employed for refining metals like Pb, Ag, Cu, Fe, etc. In this method the molten impure metal is subjected to oxidation by various ways.

**(II) POLING PROCESS :**

This process is used for the purification of copper and tin which contains the impurities of their own oxides. Impure copper is remelted in a reverberatory furnace lined with  $\text{SiO}_2$  and a blast of  $\text{O}_2$  is blown into the furnace. This molten copper is treated with powdered anthracite and then stirred with a pole of green wood.

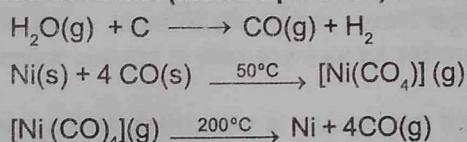


**(III) ELECTROLYTIC REFINING :**

Some metals such as Cu, Ni, and Al are refined electrolytically.

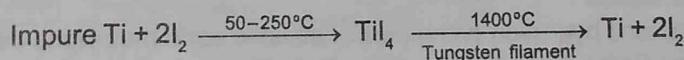
**(IV) VAPOR PHASE REFINING :**

**(i) Extraction of Nickel (Mond's process) :** The sequence of reaction is



**(ii) Van Arkel-De Boer process :**

Small amounts of very pure metals (Ti, Zr, or Bi) can be produced by this method. This process is based on the fact that iodides are the least stable of the halides.



## s-BLOCK ELEMENTS

Group 1 of the periodic table consists of the elements : lithium, sodium, potassium, rubidium, caesium and francium . They are collectively known as the alkali metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature.

The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because their oxide and hydroxide are alkaline in nature and these metal oxides are found in the earth's crust.

### Hydration Enthalpy :

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.  $\text{Li}^+$  has maximum degree of hydration and for this reason lithium salts are mostly hydrated e.g.,  $\text{LiCl} \cdot 2\text{H}_2\text{O}$

### Physical properties :

All the alkali metal have one valence electron,  $n\text{s}^1$  outside the noble gas core. All the alkali metal are silvery white, soft and light metals. Because of the larger size, these element have low density which increases down the group from Li to Cs. The melting and boiling point of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colour to an oxidizing flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet/Lilac	Red violet	Blue

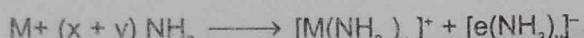
### Chemical Properties:

The alkali metals are highly reactive due to their larger size and low ionization enthalpy. The reactivity of these metals increases down the group.

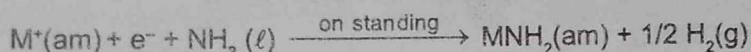
**O Reactivity towards air :** They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxide. The superoxide  $O_2^-$  ion is stable only in the presence of bigger cations such as K, Rb, Cs.

**O Reducing nature:** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful with the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative  $E^\circ$  value and its high reducing power.

**O Solution in liquid ammonia:** The alkali metals dissolve in liquid ammonia giving deep blue solution which are conducting in nature.



The blue colour of the solution is due to the ammoniated electron and the solution is paramagnetic.



In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

### ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/radius ratio). As a result, there is increased covalent character of lithium compound which is responsible for their solubility in organic solvent. Further, lithium shows diagonal relationship to magnesium.

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii :  $Li^+ = 76$  pm,  $Mg^{2+} = 72$  pm.

### GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium.

#### Hydration Enthalpies

Like alkali metal ions hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group ;  $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ . The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g.,  $MgCl_2$  and  $CaCl_2$  exist as  $MgCl_2 \cdot 6H_2O$  and  $CaCl_2 \cdot 6H_2O$  while  $NaCl$  and  $KCl$  do not form such hydrates.

#### Physical Properties

Alkaline earth metals have two electrons in the s-orbital of valence shell. The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. The melting and boiling point of these metals are higher due to smaller sizes. Because of the low ionisation enthalpies they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence these elements do not impart any colour to the flame.

Calcium, strontium and barium impart characteristic colour to the flame.

Metal	Be	Mg	Ca	Sr	Ba
Colour	No colour	No colour	Brick red	Crimson	Apple green

The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence these elements do not impart any colour to the flame.

The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

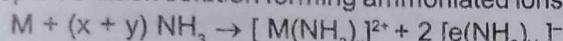
### Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

**O Reactivity towards air and water :** Beryllium and magnesium are inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give  $\text{BeO}$  and  $\text{Be}_3\text{N}_2$ . Magnesium is more electropositive and burns with dazzling brilliance in air to give  $\text{MgO}$  and  $\text{Mg}_3\text{N}_2$ . Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

**O Reducing nature :** Like alkali metals, the alkaline earth metals are strong reducing agent. This is indicated by large negative value of their reduction potentials. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of  $\text{Be}^{2+}$  ion and relatively large value of the atomization enthalpy of the metal.

**O Solution in liquid ammonia:** Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solution forming ammoniated ions.



From these solutions, the ammoniates,  $[\text{M}(\text{NH}_3)_\text{x}]^{2+}$  can be recovered.

### ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium.

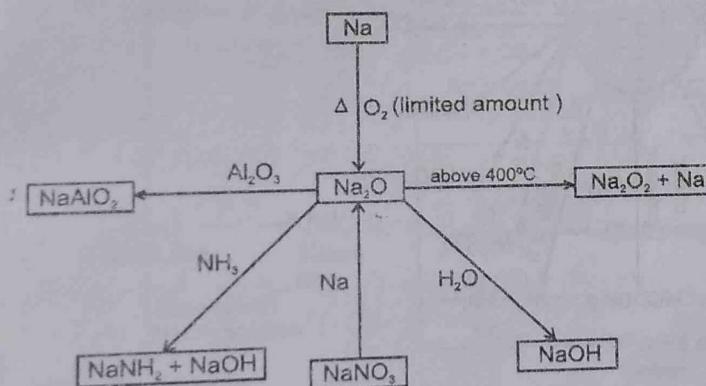
### Diagonal Relationship between Beryllium and Aluminium

The ionic radius of  $\text{Be}^{2+}$  is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the  $\text{Al}^{3+}$  ion. Hence beryllium resembles aluminium in some ways.

### Compounds of s-block elements :

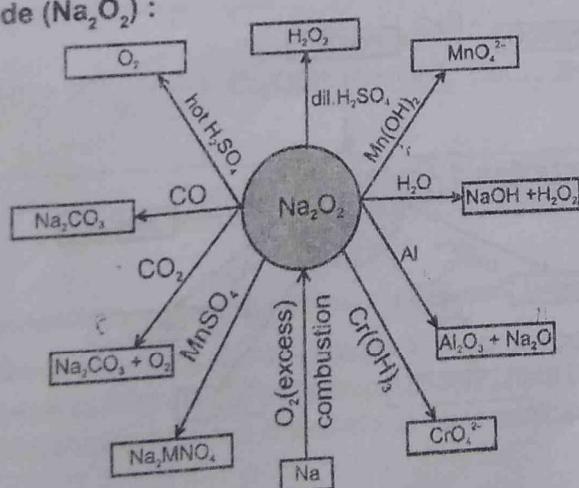
1.

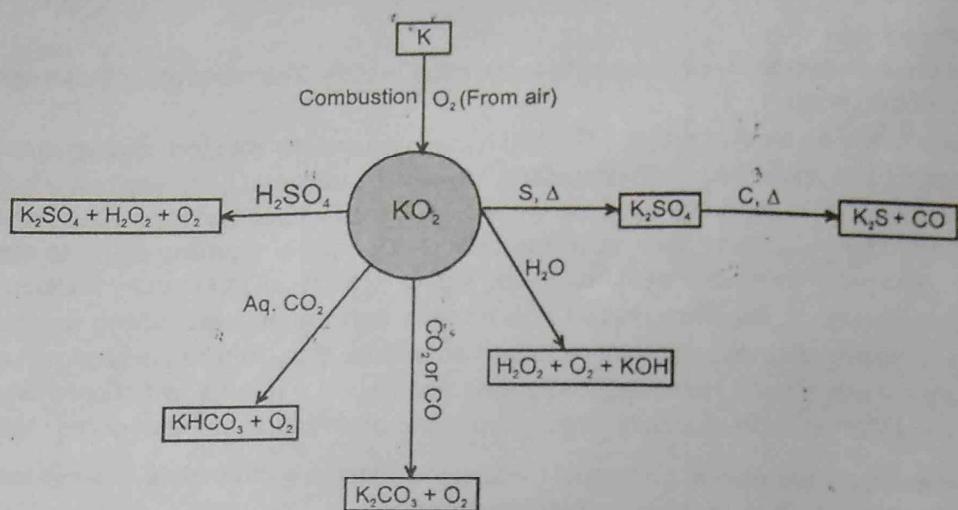
#### Sodium Oxide ( $\text{Na}_2\text{O}$ ) :



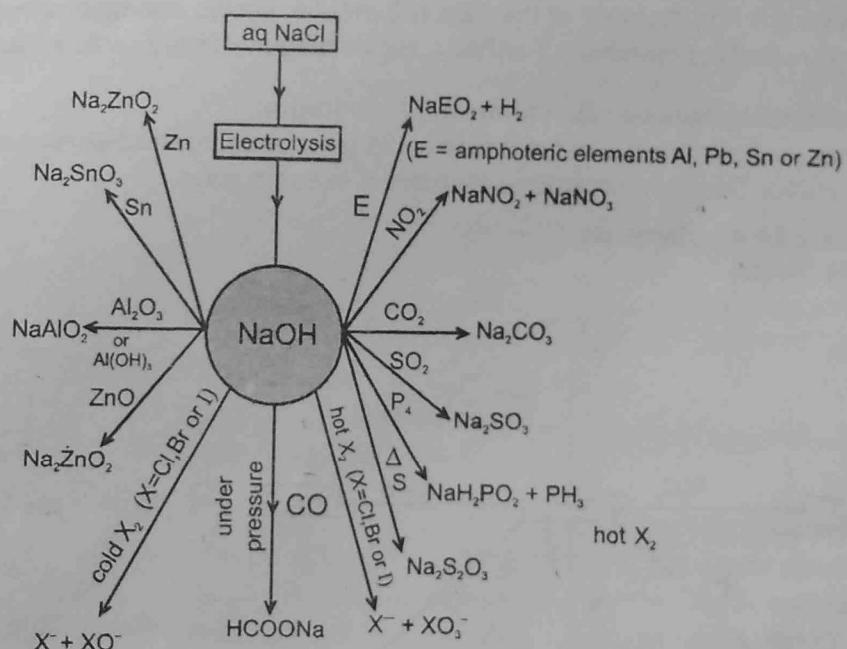
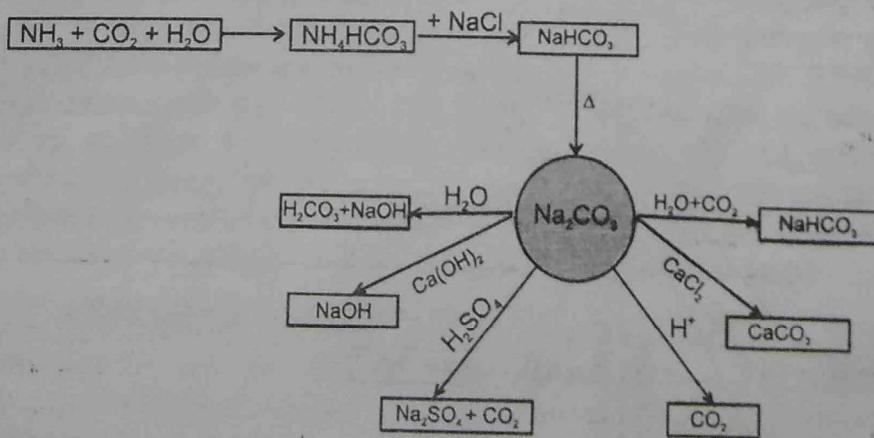
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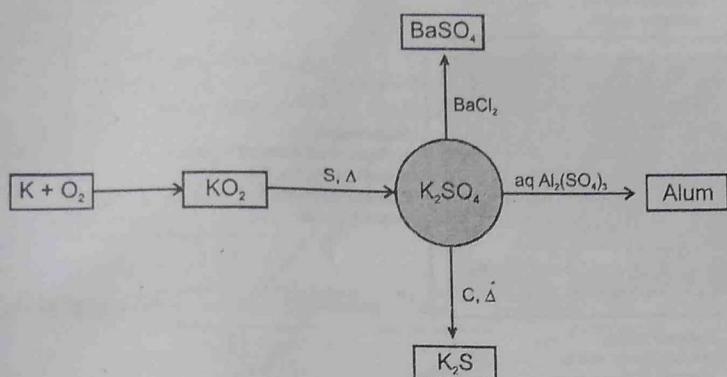
#### Sodium peroxide ( $\text{Na}_2\text{O}_2$ ) :



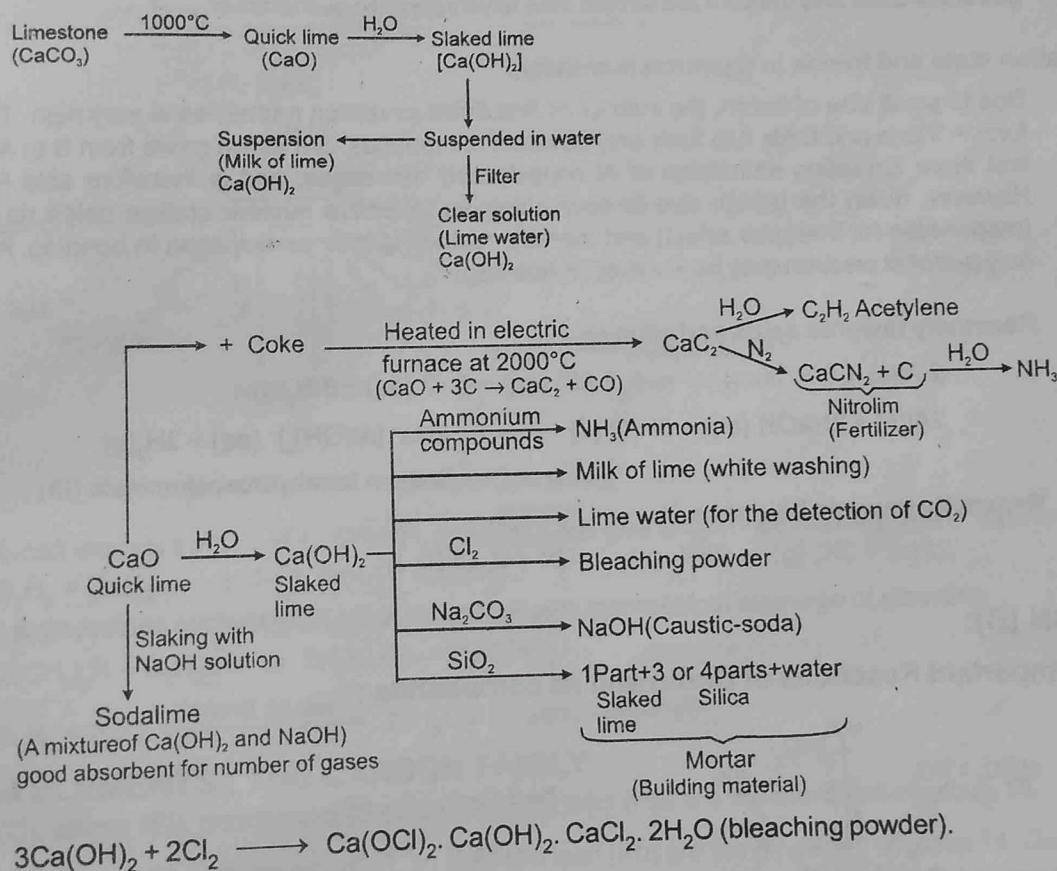
3. Potassium Super oxide ( $KO_2$ ) :

## 4. Sodium Hydroxide (NaOH) :

5. Sodium Carbonate ( $Na_2CO_3$ ) :

6. Potassium sulphate ( $K_2SO_4$ ):

## 7. Quick Lime, Slaked Lime and Lime Water :



## p-BLOCK ELEMENTS

## Introduction :

The p-block elements have general valence shell electronic configuration  $ns^2 np^{1-6}$ .

The highest oxidation of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding).

## TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.

Electronegativity, ionization enthalpy, oxidizing power.						
B	C	N	O	F	Ne	
Al	Si	P	S	Cl	Ar	
Ga	Ge	As	Se	Br	Kr	
In	Sn	Sb	Te	I	Xe	
Tl	Pb	Bi	Po	At	Rn	

Covalent radius,  
van der Waals' radius,  
metallic character

Covalent radius,  
van der Waals' radius,  
enthalpy of atomization  
(upto group 14),  
metallic character

Electronegativity,  
enthalpy of atomization  
(except for N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>),  
ionization enthalpy,  
oxidizing power.

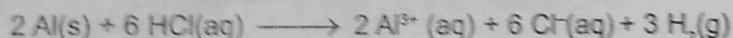
## (A) GROUP 13 ELEMENTS : THE BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron , and gallium, indium and thallium are almost exclusively metallic in character.

## Oxidation state and trends in chemical reactivity :

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form + 3 ions and force it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al<sup>3+</sup> ions. However, down the group, due to poor shielding, effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding.

## Reactivity towards acids and alkalies

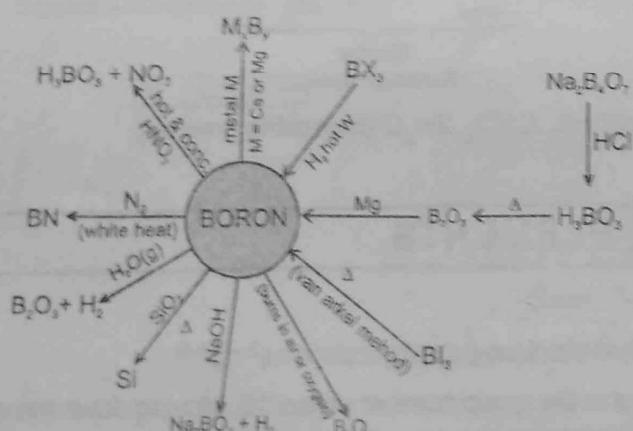


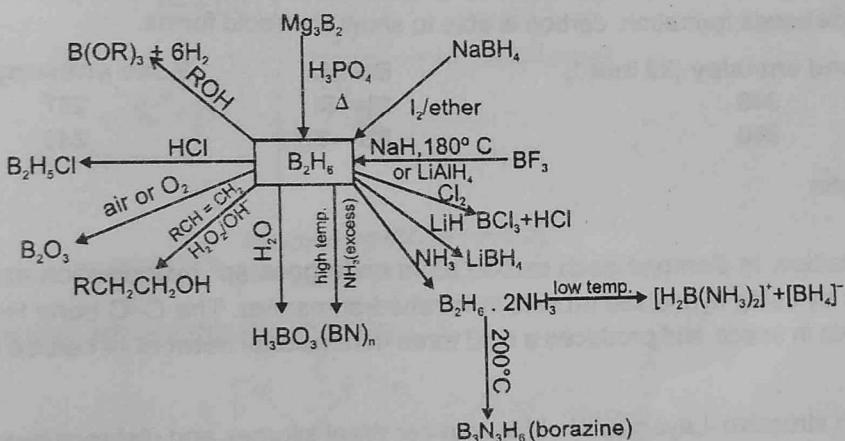
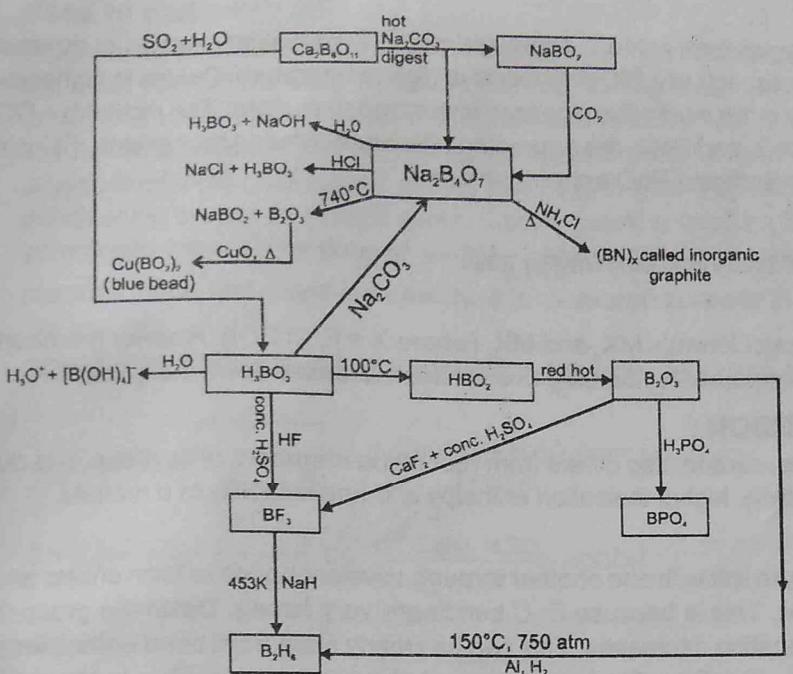
## Reactivity towards halogens



## BORON (B):

## Some Important Reactions of Boron and its compounds :





- Small amines such as  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$  give unsymmetrical cleavage of diborane.  

$$\text{B}_2\text{H}_6 + 2\text{NH}_3 \longrightarrow [\text{H}_2\text{B}(\text{NH}_3)_2]^+ + [\text{BH}_4]^-$$
- Large amines such as  $(\text{CH}_3)_3\text{N}$  and pyridine give symmetrical cleavage of diborane.  

$$2(\text{CH}_3)_3\text{N} + \text{B}_2\text{H}_6 \longrightarrow 2\text{H}_3\text{B} \leftarrow \text{N}(\text{CH}_3)_3$$
- $\text{B}_2\text{H}_6 + 2\text{CO} \xrightarrow{200^\circ\text{C}, 20 \text{ atm}} 2\text{BH}_3\text{CO}$  (borane carbonyl)

## (B) GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Germanium exists only in traces. Tin occurs mainly as cassiterite,  $\text{SnO}_2$  and lead as galena,  $\text{PbS}$ . Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

### Electronic Configuration

The valence shell electronic configuration of these elements is  $\text{ns}^2 \text{np}^2$ .

### Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of  $\text{ns}^2$  electrons of valence shell to participate in bonding (inert pair effect). The relative stabilities of these two oxidation states vary down the group.

**(i) Reactivity towards oxygen :**

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula  $MO$  and  $MO_2$ , respectively.  $SiO$  only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation state. The dioxides –  $CO_2$ ,  $SiO_2$  and  $GeO_2$  are acidic, whereas  $SnO_2$  and  $PbO_2$  are amphoteric in nature. Among monoxides,  $CO$  is neutral,  $GeO$  is distinctly acidic whereas  $SnO$  and  $PbO$  are amphoteric.

**(ii) Reactivity towards water :**

Tin decomposes steam to form dioxide and dihydrogen gas.

**(iii) Reactivity towards halogen :**

These elements can form halides of formula  $MX_2$  and  $MX_4$  (where  $X = F, Cl, Br, I$ ). Heavier members  $Ge$  to  $Pb$  are able to make halides of formula  $MX_2$ . Stability of dihalides increases down the group.

**ANOMALOUS BEHAVIOUR OF CARBON :**

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals.

**Catenation :**

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C–C bonds are very strong. Down the group the size increases tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is  $C > > Si > Ge \approx Sn$ . Lead does not show catenation. Due to the property of catenation and  $p\pi-p\pi$  bonds formation, carbon is able to show allotropic forms.

Bond	Bond enthalpy ( $\text{kJ mol}^{-1}$ )	Bond	Bond enthalpy ( $\text{kJ mol}^{-1}$ )
C—C	348	Si—Si	297
Ge—Ge	260	Sn—Sn	240

**Allotropes of Carbon****Diamond :**

It has a crystalline lattice. In diamond each carbon atom undergoes  $sp^3$  hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral manner. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms.

**Graphite :**

Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C–C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes  $sp^2$  hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a  $\pi$  bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

**Fullerenes :**

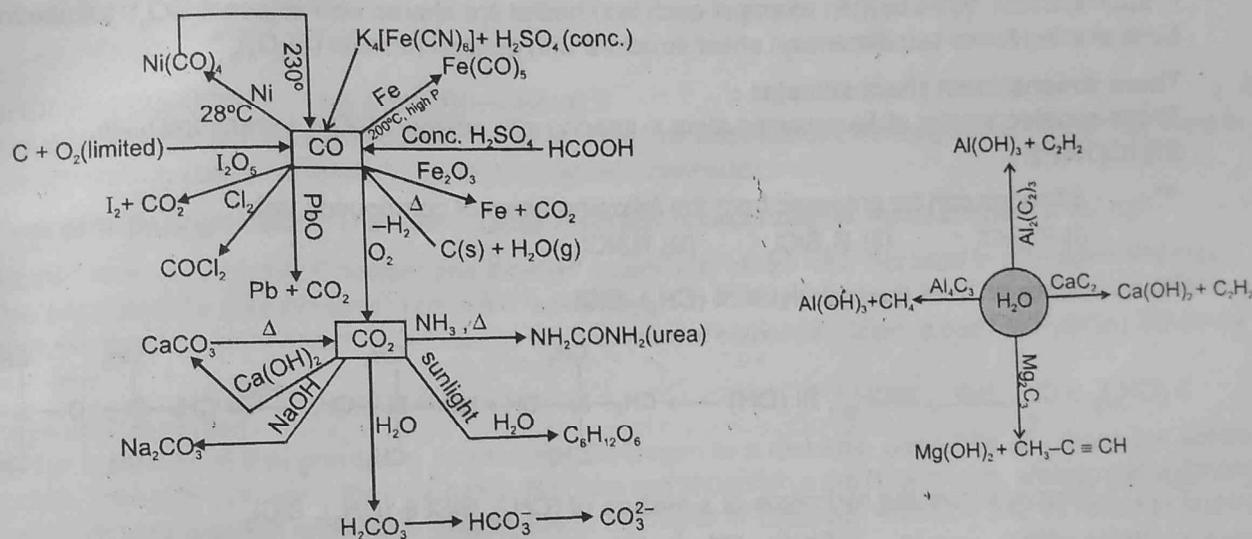
Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerene are cage like molecules.  $C_{60}$  molecule has a shape like soccer ball and called **Buckminster fullerene**.

It contains twenty six -membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are called bucky balls in short. Carbon black is obtained by burning hydrocarbons in a limited supply of air.

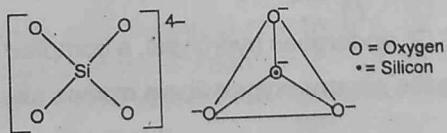
**Uses of carbon**

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircraft and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous and having enormous surface area activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg.).

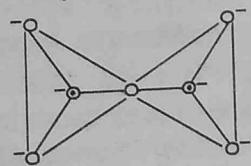
CO and CO<sub>2</sub>

**SOME IMPORTANT REACTIONS OF CO, CO<sub>2</sub> AND METAL CARBIDES :****CLASSIFICATION OF SILICATES :**

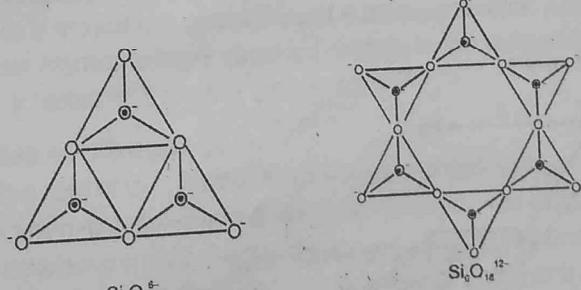
## (A) Orthosilicates :



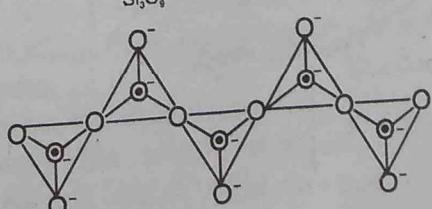
## (B) Pyrosilicate :

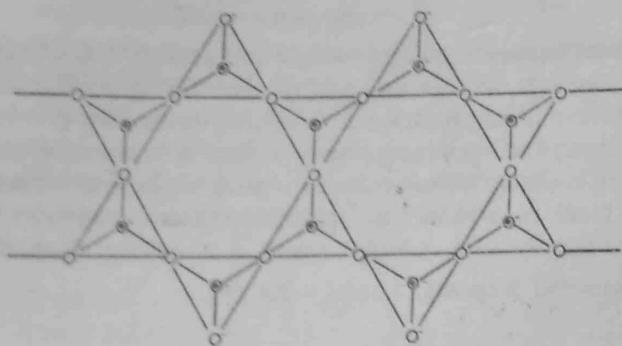


## (C) Cyclic silicates :



## (D) Chain silicates :





## (E) Two dimensional sheet silicates :

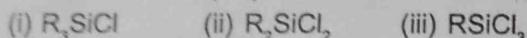
In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent  $\text{SiO}_4^{4-}$  tetrahedrals. Such sharing forms two dimension sheet structure with general formula  $(\text{Si}_2\text{O}_5)_n^{2n-}$

## (F) Three dimensional sheet silicates :

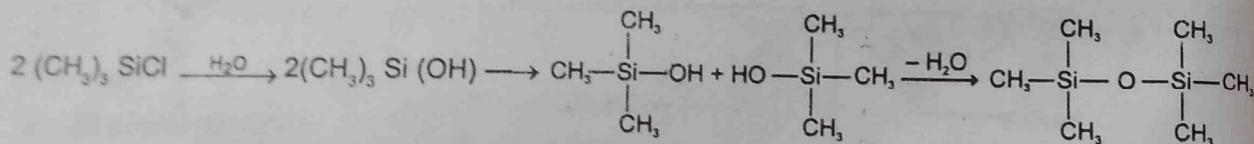
These silicates involve all four oxygen atom in sharing with adjacent  $\text{SiO}_4^{4-}$  tetrahedral units.

## ● SILICONES :

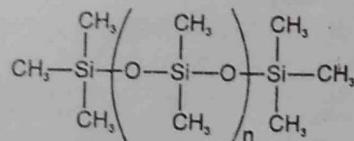
☞ Silicones can be prepared from the following types of compounds only.



☞ Silicones from the hydrolysis of  $(\text{CH}_3)_3\text{SiCl}$



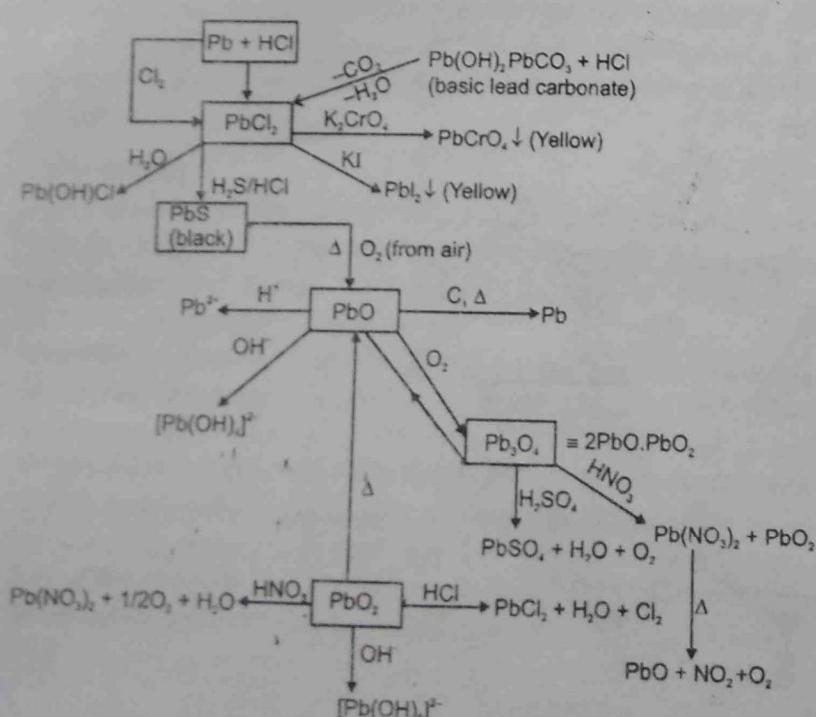
☞ Silicones from the hydrolysis of a mixture of  $(\text{CH}_3)_3\text{SiCl}$  &  $(\text{CH}_3)_2\text{SiCl}_2$



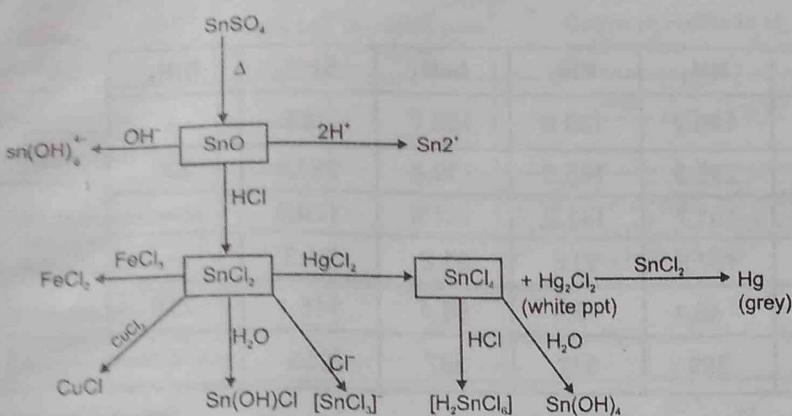
☞ When a compound like  $\text{CH}_3\text{SiCl}_3$  undergoes hydrolysis, a complex cross-linked polymer is obtained.

☞ The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

## COMPOUNDS OF LEAD :



## COMPOUNDS OF TIN :



## (C) GROUP 15 ELEMENTS : THE NITROGEN FAMILY

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloid character.

**Electronic Configuration :** The valence shell electronic configuration of these elements is  $ns^2 np^3$ .

**Atomic and Ionic Radii :** Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.

**Physical Properties:**

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

**Chemical Properties :****Oxidation States and trends in a chemical reactivity :**

The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group ;  $Bi^{3+} > Sb^{3+} > As^{3+}$ ;  $Bi^{5+} < Sb^{5+} < As^{5+}$

Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

For example,  $3 HNO_2 \longrightarrow HNO_3 + H_2O + 2 NO$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding. The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in  $PF_6^-$ .

**Anomalous properties of nitrogen :**

Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, high ionisation enthalpy and non-availability of d orbitals. Nitrogen has unique ability to form  $p\pi-p\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form  $p\pi-p\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms.

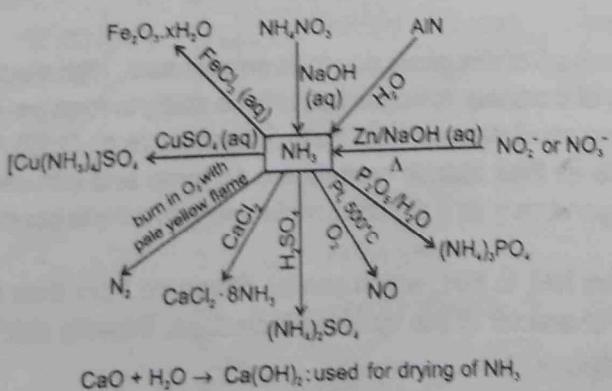
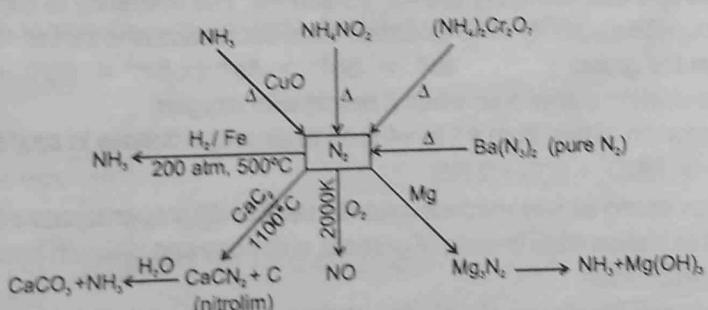
The stability of hydrides decreases from  $NH_3$  to  $BiH_3$  which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Basicity also decreases in the order  $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$ .

## PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS

Property	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	BiH <sub>3</sub>
Melting point / K	195.2	139.5	156.7	185	—
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	—
HEH angle (°)	107.8	93.6	91.8	91.3	—
$\Delta_{\text{diss}}^{\text{H}^-}$ / kJ mol <sup>-1</sup>	-46.1	13.4	66.4	145.1	278
$\Delta_{\text{diss}}^{\text{H}^-}(\text{E} - \text{H})$ / kJ mol <sup>-1</sup>	389	322	297	255	—

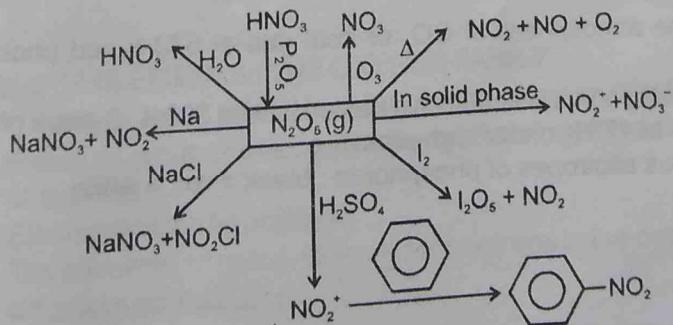
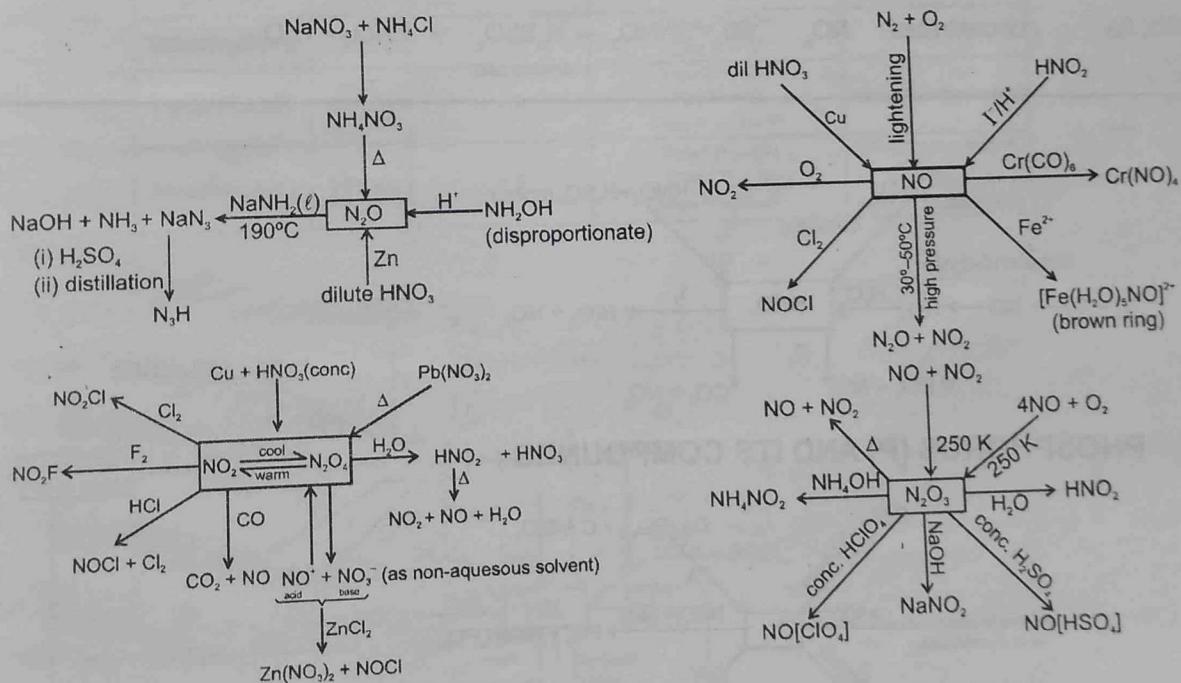
- (ii) The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E<sub>2</sub>O<sub>3</sub> of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.
- (iii) Nitrogen does not form pentahalide due to non-availability of the d-orbitals in its valence shell. Pentahalides are more covalent than trihalides. Halides are hydrolysed in water forming oxyacids or oxychlorides;
- $$\text{PCl}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + \text{HCl};$$
- $$\text{SbCl}_3 + \text{H}_2\text{O} \rightarrow \text{SbOCl} \downarrow (\text{orange}) + 2\text{HCl};$$
- $$\text{BiCl}_3 + \text{H}_2\text{O} \rightarrow \text{BiOCl} \downarrow (\text{white}) + 2\text{HCl}$$
- (iv) These elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca<sub>3</sub>N<sub>2</sub> (calcium nitride) Ca<sub>3</sub>P<sub>2</sub> (calcium phosphide) and Na<sub>3</sub>As<sub>2</sub> (sodium arsenide).

## NITROGEN (N) AND ITS COMPOUNDS :



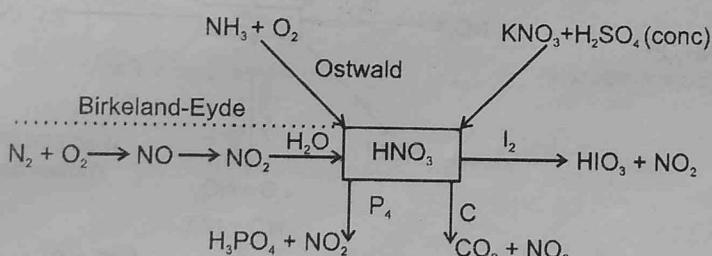
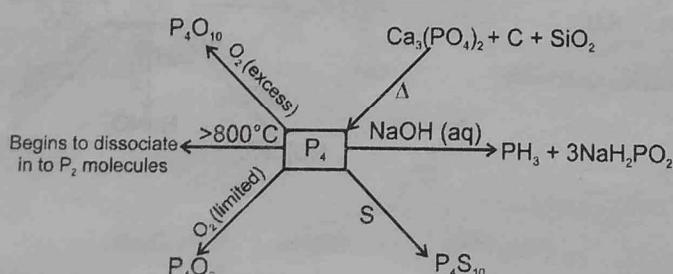
## Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N <sub>2</sub> O	+ 1	NH <sub>4</sub> NO <sub>3</sub> $\xrightarrow{\text{Heat}}$ N <sub>2</sub> O + 2 H <sub>2</sub> O	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide] (Nitric acid)	NO	+ 2	2 NaNO <sub>2</sub> + 2 FeSO <sub>4</sub> + 3 H <sub>2</sub> SO <sub>4</sub> $\longrightarrow$ Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2 NaHSO <sub>4</sub> + 2 H <sub>2</sub> O + 2 NO	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide] (Nitrogen sesquioxide)	N <sub>2</sub> O <sub>3</sub>	+ 3	2 NO + N <sub>2</sub> O <sub>4</sub> $\xrightarrow{250\text{ K}}$ 2 N <sub>2</sub> O <sub>3</sub>	blue solid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO <sub>2</sub>	+ 4	2 Pb(NO <sub>3</sub> ) <sub>2</sub> $\xrightarrow{673\text{ K}}$ 4NO <sub>2</sub> + 2PbO + O <sub>2</sub>	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>4</sub>	+ 4	2 NO <sub>2</sub> $\xrightleftharpoons[\text{Heat}]{\text{cool}}$ N <sub>2</sub> O <sub>4</sub>	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>5</sub>	+ 5	4 HNO <sub>3</sub> + P <sub>4</sub> O <sub>10</sub> $\longrightarrow$ 4 HPO <sub>3</sub> + 2 N <sub>2</sub> O <sub>5</sub>	colourless solid, acidic



Reactions of Elements (Metals/Metalloids) with  $\text{HNO}_3$ 

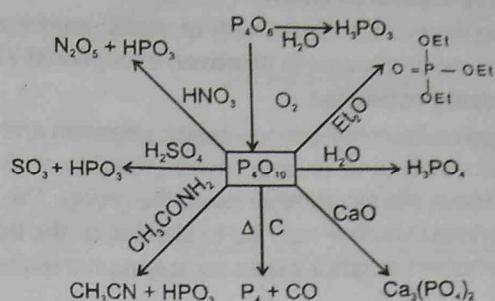
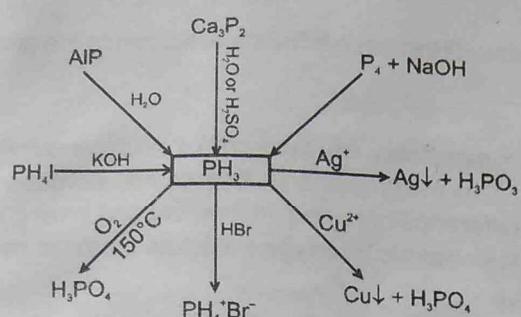
Element	Nature of $\text{HNO}_3$	Changes to	Reactions
<b>(A) Metals placed above H in electrochemical series (ECS)</b>			
1. Mg, Mn	cold and dilute	$\text{M}(\text{NO}_3)_2$	$\text{M} + 2\text{HNO}_3 \rightarrow \text{M}(\text{NO}_3)_2 + \text{H}_2$
2. Zn, Fe	(a) very dilute	$\text{NH}_4\text{NO}_3$	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) dilute	$\text{N}_2\text{O}$	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
	(c) concentrated	$\text{NO}_2$	$\text{Zn} + 4\text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
			Fe becomes passive with 80% $\text{HNO}_3$
3. Sn	(a) dilute	$\text{NH}_4\text{NO}_3$	$4\text{Sn} + 10\text{HNO}_3 \rightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) concentrated	$\text{NO}_2$	$\text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$ meta stannic acid
4. Pb	(a) dilute	NO	$3\text{Pb} + 8\text{HNO}_3 \rightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
	(b) concentrated	$\text{NO}_2$	$\text{Pb} + 4\text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
<b>(B) Metals below H in ECS</b>			
5. Cu, Ag	(a) dilute	NO	$3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
Hg	Hg forms $\text{Hg}_2(\text{NO}_3)_2$		
	(b) concentrated	$\text{NO}_2$	$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
<b>(C) Metalloids</b>			
Sb, As	concentrated	$\text{NO}_2$	$\text{Sb} + 5\text{HNO}_3 \rightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$ antimonic acid

**PHOSPHORUS (P) AND ITS COMPOUNDS :**

When white phosphorus is heated in the atmosphere of  $\text{CO}_2$  or coal gas at 573 K red phosphorus is produced.

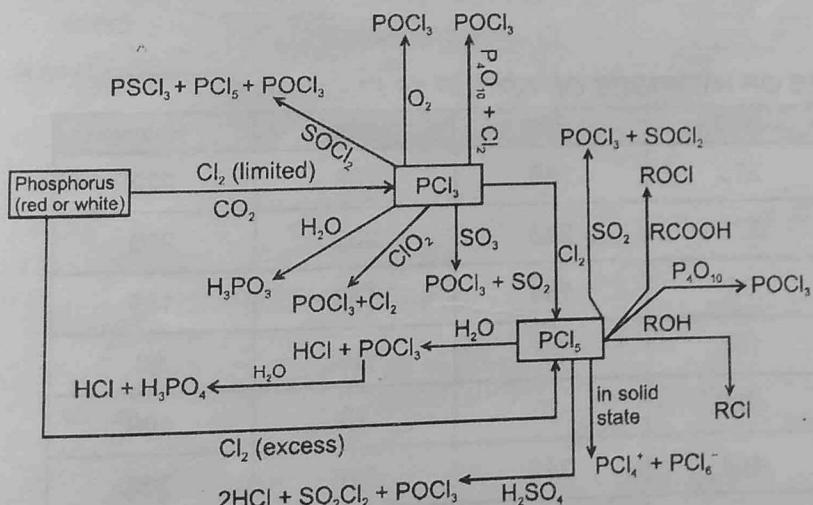
$\alpha$ -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.  $\beta$ -black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

Order of thermodynamic stability of various allotropes of phosphorus : black > red > white



### Oxoacids of Phosphorus

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous	$\text{H}_3\text{PO}_2$	+ 1	One $\text{P} - \text{OH}$ Two $\text{P} - \text{H}$ One $\text{P} = \text{O}$	white $\text{P}_4$ + alkali
Orthophosphorous	$\text{H}_3\text{PO}_3$	+ 3	Two $\text{P} - \text{OH}$ One $\text{P} - \text{H}$ One $\text{P} = \text{O}$	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+ 3	Two $\text{P} - \text{OH}$ Two $\text{P} - \text{H}$ Two $\text{P} = \text{O}$	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+ 4	Four $\text{P} - \text{OH}$ Two $\text{P} = \text{O}$ One $\text{P} - \text{P}$	red $\text{P}_4$ + alkali
Orthophosphoric	$\text{H}_3\text{PO}_4$	+ 5	Three $\text{P} - \text{OH}$ One $\text{P} = \text{O}$	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+ 5	Four $\text{P} - \text{OH}$ Two $\text{P} = \text{O}$ One $\text{P} - \text{O} - \text{P}$	heat phosphoric acid
Metaphosphoric	$(\text{HPO}_3)_3$	+ 5	Three $\text{P} - \text{OH}$ Three $\text{P} = \text{O}$ Three $\text{P} - \text{O} - \text{P}$	phosphorus acid + $\text{Br}_2$ , heat in sealed tube



### (D) GROUP 16 ELEMENTS : THE OXYGEN FAMILY

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens the ore forming elements because a large number of metals ores are oxides or sulphides.

#### Electronic Configuration :

The elements of group 16 have six electrons in the outermost shell and have  $ns^2 np^4$  general valence shell electronic configuration.

**Atomic and Ionic Radii :**

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

**Physical Properties :**

Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecules ( $O_2$ ) whereas sulphur exists as polyatomic molecule ( $S_8$ ).

**Catenation :**

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur ( $S_8$ ). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

**Chemical Properties****Oxidation states and trends in chemical reactivity :**

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states. Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of  $OF_2$  where its oxidation state is +2. Other elements of the group exhibit +2, +4, +6 oxidation states but +4 and +6 are more common. The stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases (inert pair effect).

**Anomalous behaviour of oxygen :**

The anomalous behaviour of oxygen is due to its small size and high electronegativity. The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely increases beyond two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

- (i) Their acidic character increases from  $H_2O$  to  $H_2Te$ . The increase in acidic character can be understood in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group, the thermal stability of hydrides also decreases from  $H_2O$  to  $H_2Po$ . All the hydrides except water possess reducing property and this property increases from  $H_2S$  to  $H_2Te$ .

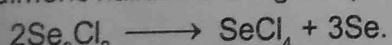
**PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS**

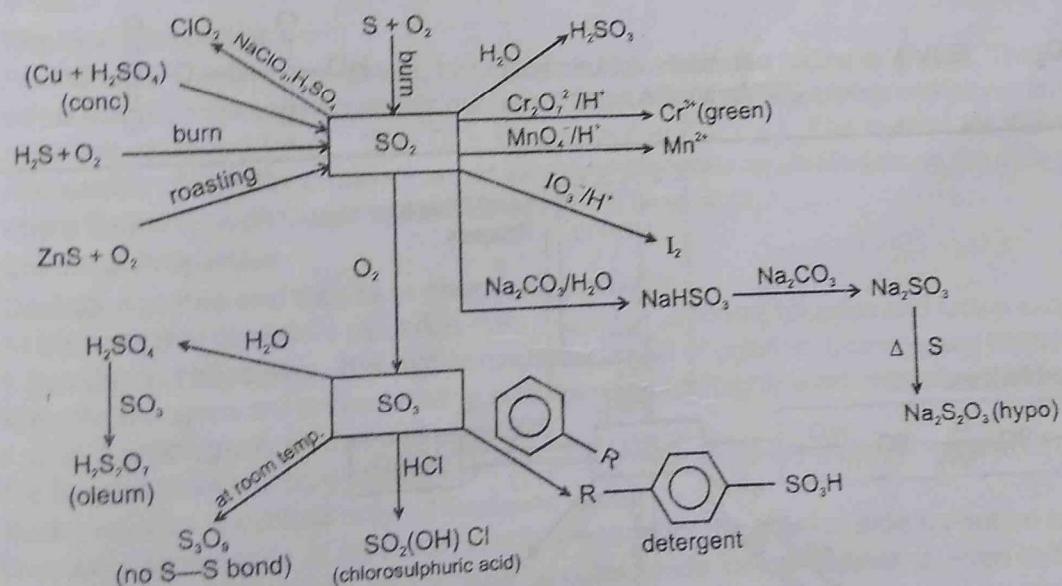
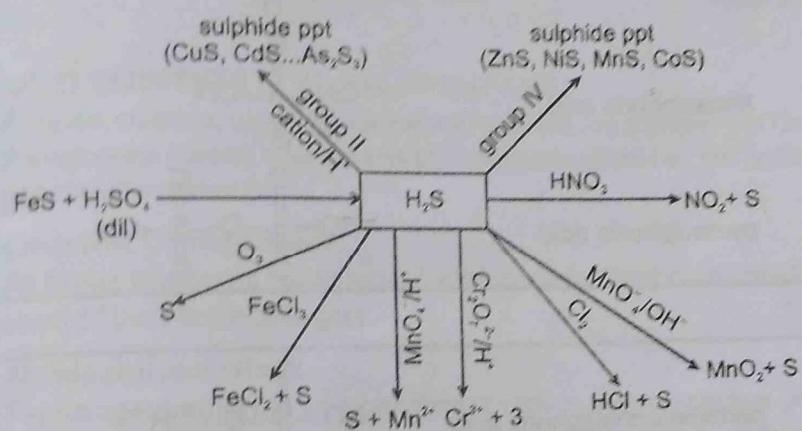
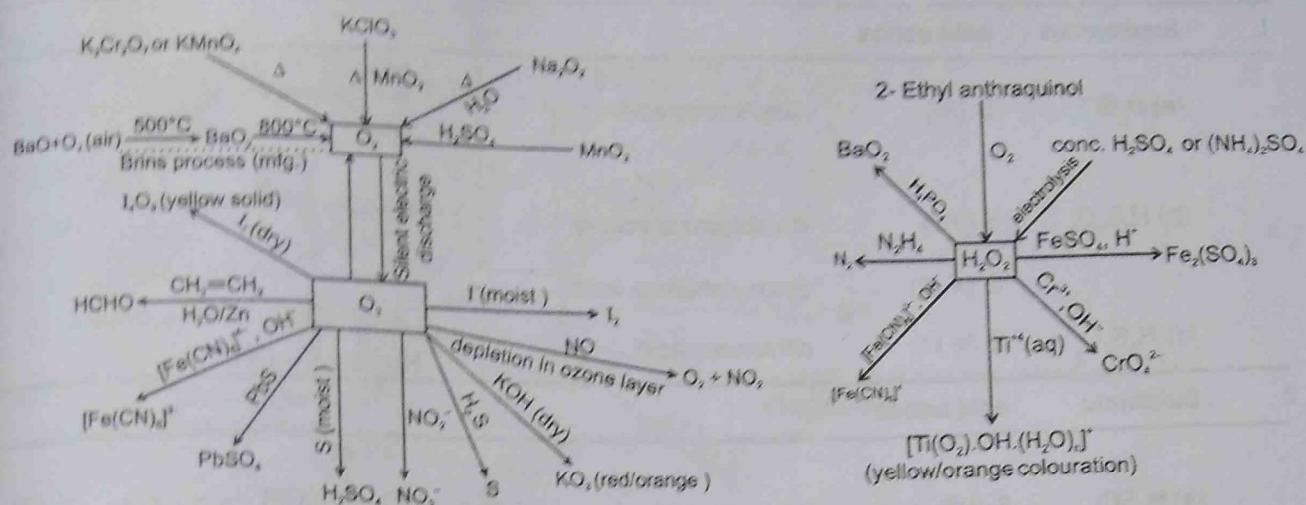
Property	$H_2O$	$H_2S$	$H_2Se$	$H_2Te$
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H/kJ\ mol^{-1}$	-286	-20	73	100
$\Delta_{diss} H\ (H-E)/kJ\ mol^{-1}$	463	347	276	238
Dissociation constant <sup>a</sup>	$1.8 \times 10^{-16}$	$1.3 \times 10^{-7}$	$1.3 \times 10^{-4}$	$2.3 \times 10^{-3}$

- (ii) Reducing property of dioxide decreases from  $SO_2$  to  $TeO_2$ ;  $SO_2$  is reducing while  $TeO_2$  is an oxidising agent. Oxides are generally acidic in nature.

- (iii) The stabilities of the halides decrease in the order  $F > Cl > Br > I$ . Sulphur hexafluoride  $SF_6$  is exceptionally stable for steric reasons.

The well known monohalides are dimeric in nature, Examples are  $S_2F_2$ ,  $S_2Cl_2$ ,  $S_2Br_2$ ,  $Se_2Cl_2$  and  $Se_2Br_2$ . These dimeric halides undergo disproportionation as given below :



OXYGEN ( $O_2$ ) AND ITS COMPOUNDS :

## Oxo-acids of Sulphur

## 1. Sulphurous acid series

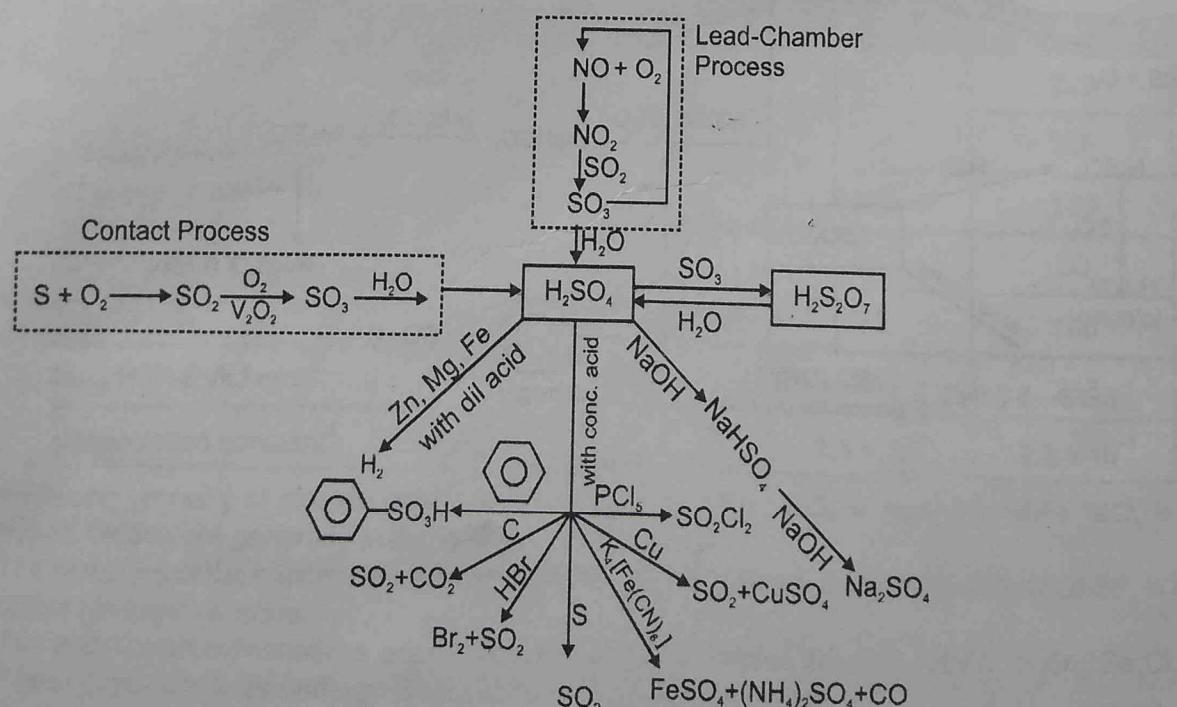
(a) $\text{H}_2\text{SO}_3$	S (IV)	sulphurous acid	$\begin{array}{c} \text{HO} \\   \\ \text{S}=\text{O} \\   \\ \text{HO} \end{array}$
(b) $\text{H}_2\text{S}_2\text{O}_5$	S (+V)	disulphurous acid or	$\begin{array}{c} \text{H}-\text{O} \\    \\ \text{S}=\text{O} \\    \\ \text{S}-\text{OH} \end{array}$
	S (+ III)	pyrosulphurous acid	$\begin{array}{c} \text{H} \\   \\ \text{S}=\text{O} \\   \\ \text{S}-\text{OH} \end{array}$
(c) $\text{H}_2\text{S}_2\text{O}_4$	S (+ III)	dithionous acid	

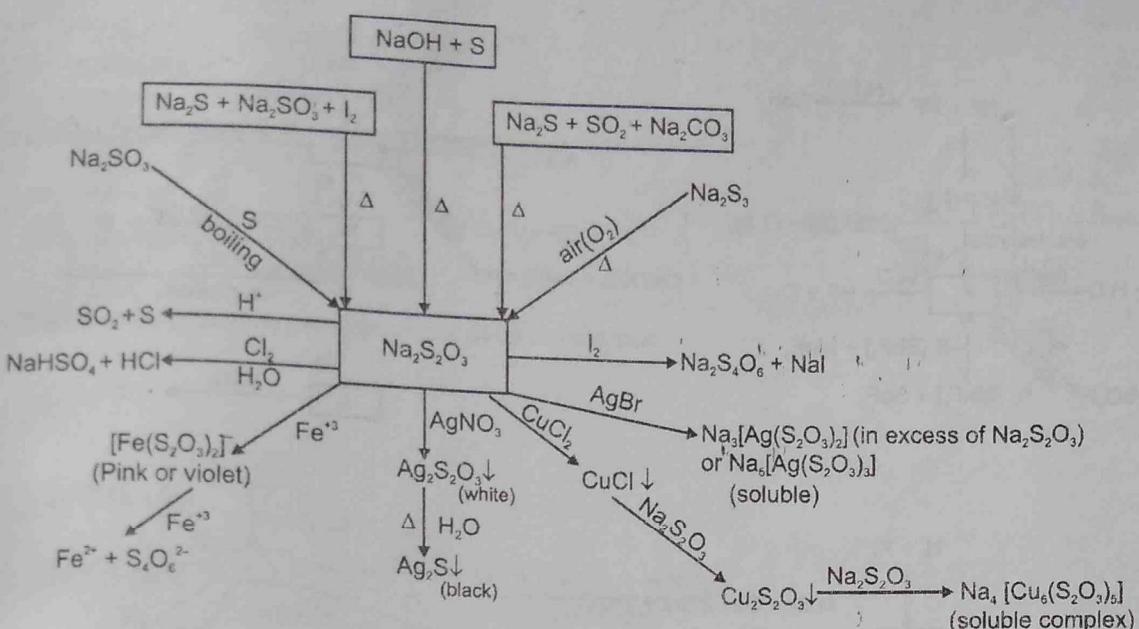
## 2. Sulphuric acid series

(a) $\text{H}_2\text{SO}_4$	S (VI)	sulphuric acid	$\begin{array}{c} \text{HO} \\    \\ \text{S}=\text{O} \\    \\ \text{OH} \end{array}$
(b) $\text{H}_2\text{S}_2\text{O}_3$	S (IV)	thiosulphuric acid	$\begin{array}{c} \text{OH} \\   \\ \text{S}-\text{OH} \\   \\ \text{S} \end{array}$
(c) $\text{H}_2\text{S}_2\text{O}_7$	S (IV)	pyrosulphuric acid	$\begin{array}{c} \text{HO} \\    \\ \text{S}=\text{O} \\    \\ \text{O}-\text{S}-\text{OH} \\    \\ \text{O} \end{array}$

## 3. Peroxo acid series

(a) $\text{H}_2\text{SO}_5$	S (VI)	peroxomonosulphuric acid	$\begin{array}{c} \text{HO} \\    \\ \text{S}=\text{O} \\    \\ \text{O}-\text{O}-\text{OH} \end{array}$
(b) $\text{H}_2\text{S}_2\text{O}_8$	S (VI)	peroxodisulphuric acid (Marshall's acid)	$\begin{array}{c} \text{HO} \\    \\ \text{S}=\text{O} \\    \\ \text{O}-\text{O}-\text{O}-\text{S}=\text{O} \\    \\ \text{O} \end{array}$





### (E) GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the halogens (Greek halo means salt and genes born i.e., salt producers). The halogens are highly reactive non-metallic elements.

#### Electronic Configuration

All these elements have seven electrons in their outermost shell ( $ns^2 np^5$ ) which is one electron short of the next noble gas.

#### Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

#### Physical Properties

Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid. Their melting and boiling points steadily increase with atomic number. The X-X bond dissociation enthalpies from chlorine onwards show the expected trend :  $\text{Cl} - \text{Cl} > \text{Br} - \text{Br} > \text{F} - \text{F} > \text{I} - \text{I}$ . The reason for the smaller enthalpy of dissociation of  $\text{F}_2$  is the relatively larger electrons-electrons repulsion among the lone pairs in  $\text{F}_2$  molecule where they are much closer to each other than in case of  $\text{Cl}_2$ .

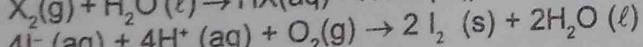
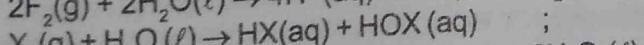
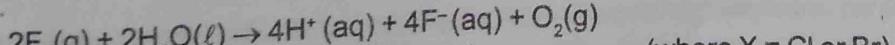
#### Chemical Properties

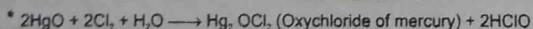
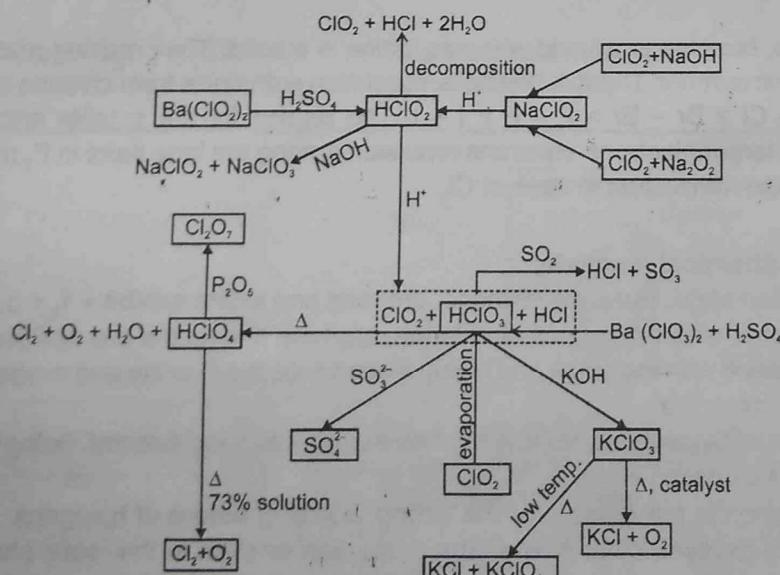
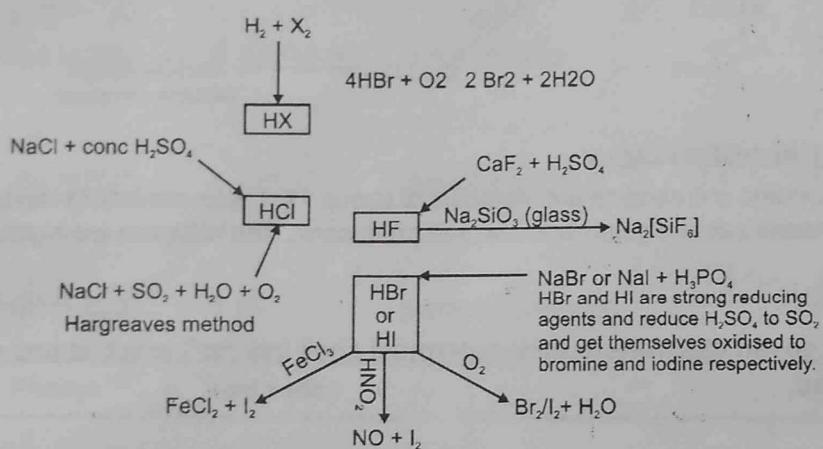
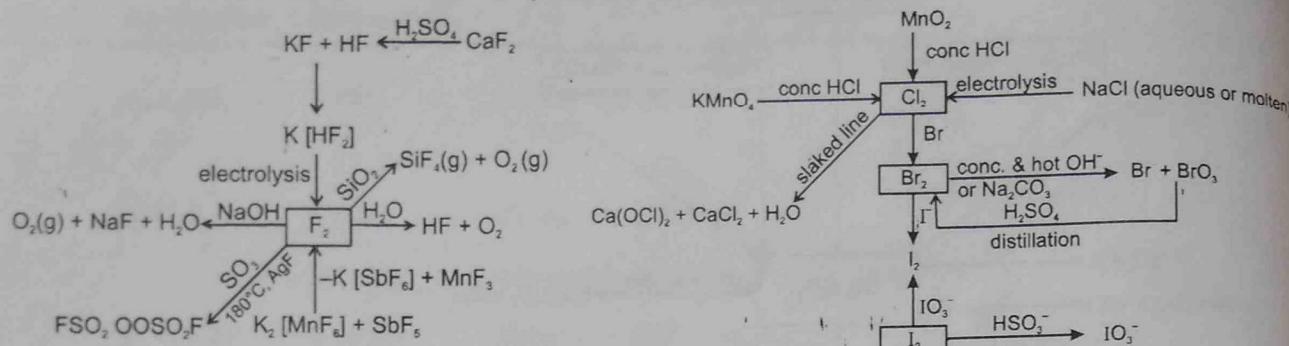
##### Oxidation states and trends in chemical reactivity

All the halogens exhibit  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.

The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only  $-1$  oxidation state.

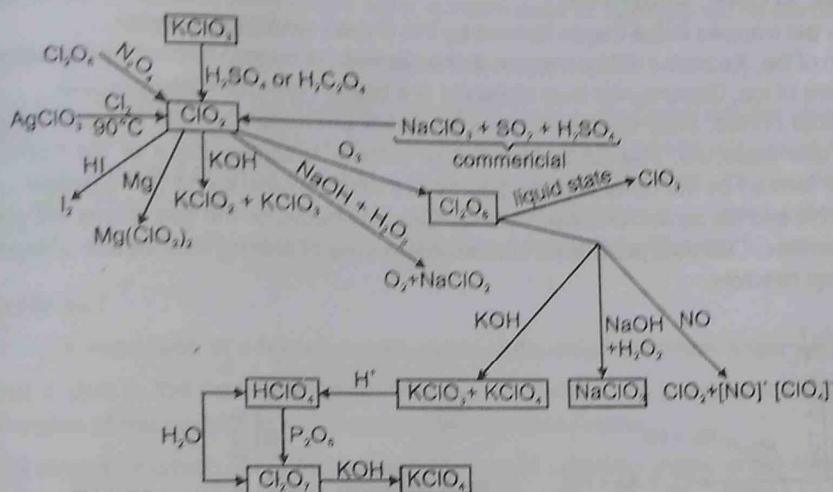
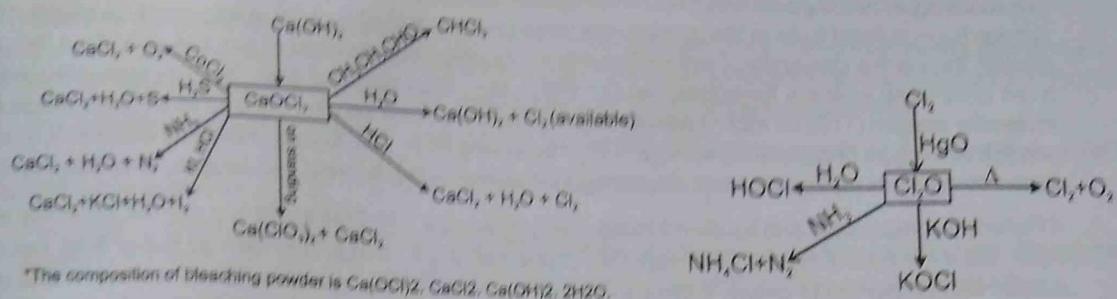
The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.  $\text{F}_2$  is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reactions of iodine with water is non-spontaneous.  $\text{I}^-$  can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.





(F) GROUP

(i)  
(ii)



## (F) GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

Group 18 consists of six elements: helium, neon, argon, krypton , xenon and radon . All these are gases and chemically unreactive. They form very few compounds . Because of this they are termed noble gases.

- Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

### Electronic Configuration

All noble gases have general electronic configuration  $ns^2 np^6$  except helium which has  $1s^2$  . Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

### Atomic Radii

Atomic radii increase down the group with increase in atomic number.

### Physical properties

All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,. Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

### Chemical Properties :

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

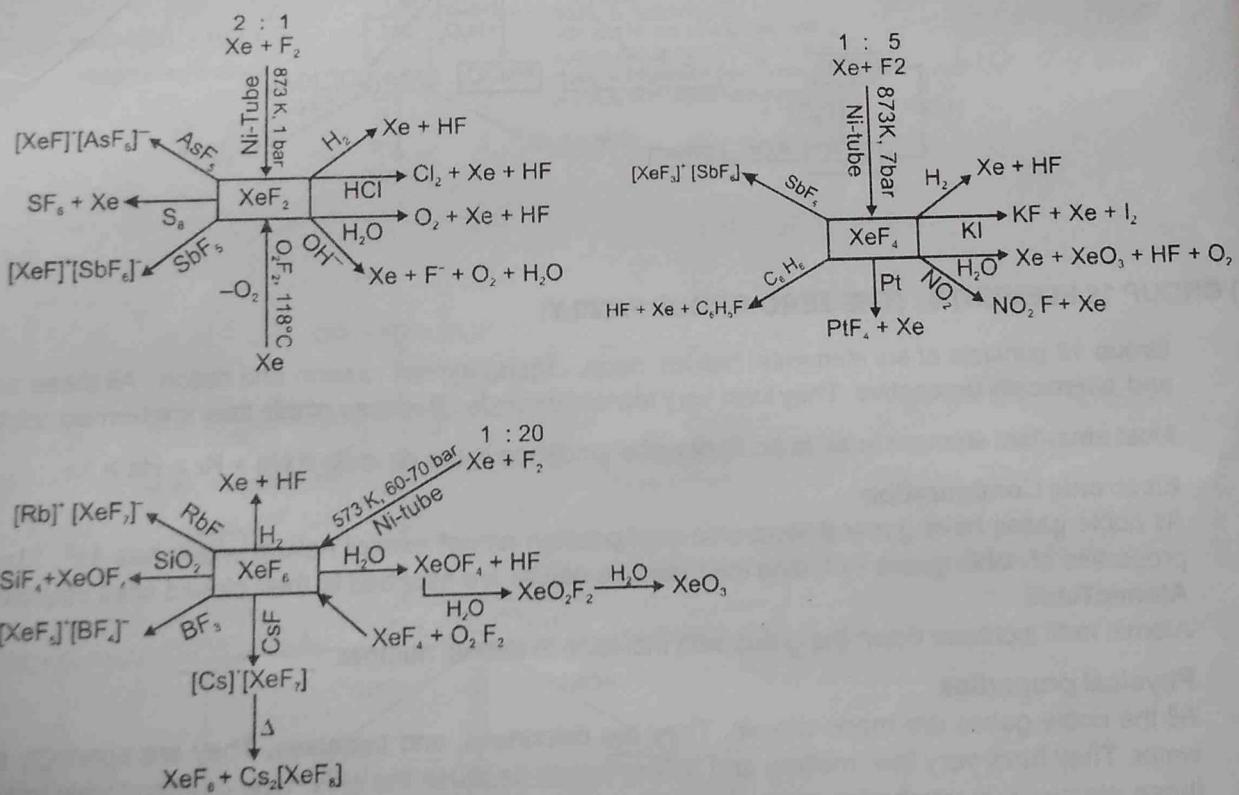
- The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2 np^6$  electronic configuration in their valence shell.
- They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempts to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+ PtF_6^-$ . He then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with  $Xe^+ PtF_6^-$  by mixing  $PtF_6^-$  and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

If Helium is compressed and liquified it forms  $He(I)$  liquid at  $4.2 \text{ K}$ . This liquid is a normal liquid like any other liquid. But if it is further cooled then  $He(II)$  is obtained at  $2.2 \text{ K}$ , which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

### CLATHRATE COMPOUNDS :

Inert gas molecules get trapped in the cages formed by the crystal structure of water. During the formation of ice, Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clathrate compounds. There are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules : 1 inert gas molecule. The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol). The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.



### d-BLOCK ELEMENTS

Four series of elements are formed by filling the 3d, 4d, 5d and 6d shells of electrons. Together these comprise the d-block elements. A transition element may be defined as the element whose atom in ground state or ion in one of common oxidation states, has partly filled d-sub shell i.e. having electrons between 1 to 9.

The general electronic configuration of d-block elements is  $(n-1)d^{1-10} ns^{0-2}$ , where n is the outer most shell.

General trends in the chemistry of transition elements.

**Metallic character :**

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

The transition elements (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.

**Melting and boiling points :**

The melting and boiling points of the transition series elements are generally very high. Strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points.

★ The dip in melting points of Mn, Tc & Re can be attributed to their exactly half filled d-orbital. Due to this stable electronic configuration the electrons are held tightly by the nucleus and hence the delocalisation of electrons is less and the metallic bond is much weaker than preceding elements.

**Density :**

The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high. The densities of the second row are high and third row values are even higher. Elements with the highest densities are osmium  $22.57 \text{ g cm}^{-3}$  and iridium  $22.61 \text{ g cm}^{-3}$ .

**Oxidation states :**

With the exception of a few elements, most of transition elements show variable oxidation states.

This is due to the participation of inner  $(n - 1)$  d-electrons in addition to outer ns-electrons because, the energies of the ns and  $(n - 1)$  d-subshells are nearly same.

The elements which show the greater number of oxidation states occur in or near the middle of the series. Unlike p-block elements where the lower oxidation states are favoured by heavier members (due to inert pair effect), the higher oxidation states are more stable in heavier transition elements.

**Different oxidation states of first transition series.**

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+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

## Characteristics of Oxides and Some Ions of V and Cr

O.S.	Oxide/ Hydroxide	Behaviour	Ion	Name of Ion	Colour of ion
+2	VO	basic	$V^{2+}$	vanadium (II) (vanadous)	violet
+3	$V_2O_5$	basic	$V^{3+}$	vanadium (III) (vanadic)	green
+4	$VO_2$	amphoteric	$VO^{2+}$	oxovanadium (IV) (vanadyl)	blue
+5	$V_2O_5$	amphoteric	$V_2O_9^{2-}$ $VO_2^+$ $VO_4^{3-}$	hypovanadate (vanadite)	brown
+2	$CrO$ $Cr(OH)_2$	basic	$Cr^{2+}$	dioxovanadium (V) orthovanadate	yellow colourless
+2	$CrO$ $Cr(OH)_2$	basic	$Cr^{2+}$	chromium (II) (chromous)	light blue
+3	$Cr_2O_3$ $Cr(OH)_3$	amphoteric	$Cr^{3+}$ $Cr(OH)^-$	chromium (III) chromic chromite	violet
+5	$CrO_3$ $CrO_2(OH)_2$ $H_2Cr_2O_7$	acidic	$CrO_4^{2-}$ $Cr_2O_7^{2-}$	chromate dichromate	green yellow orange

**Standard electrode potentials :**

The value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is the compound.

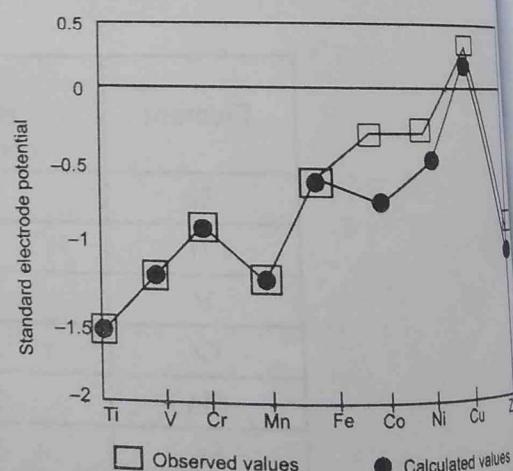
**Electrode potentials :**

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution.

The overall energy change is

$$\Delta H = \Delta_{\text{sub}} H^\circ + IE + \Delta_{\text{hyd}} H$$

The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitatively, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode potential data. The lower the electrode potential i.e., more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

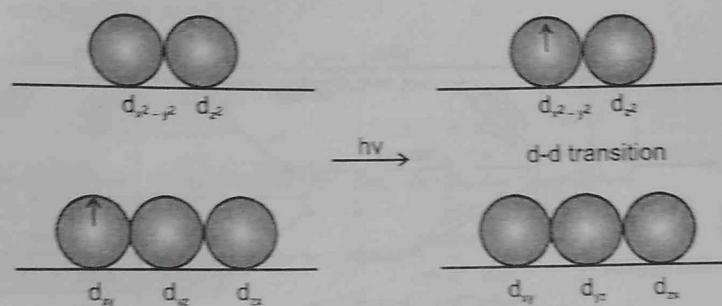


Thermochemical data ( $\text{kJ mol}^{-1}$ ) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of  $M^{\text{II}}$  to  $M$

Element (M)	$\Delta_f H^{\circ} (\text{M})$	$\Delta_f H_1^{\circ}$	$\Delta_f H_2^{\circ}$	$\Delta_{\text{red}} H^{\circ} (\text{M}^{2+})$	$E^{\circ} / \text{V}$
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

### Formation of Coloured Ions :

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete ( $n - 1$ ) d-subshell.



The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance.

### Magnetic Properties :

- (i) **Paramagnetic substances :** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.
- (ii) **Diamagnetic substances :** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals.
- The 'spin only' magnetic moment can be calculated from the relation :

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

where  $n$  is the number of unpaired electrons and  $\mu$  is magnetic moment in Bohr magneton (BM) units. The paramagnetism first increases in any transition series and then decreases. The maximum paramagnetism is observed around the middle of the series (as contains maximum number of unpaired electrons).

### Formation of Interstitial Compounds :

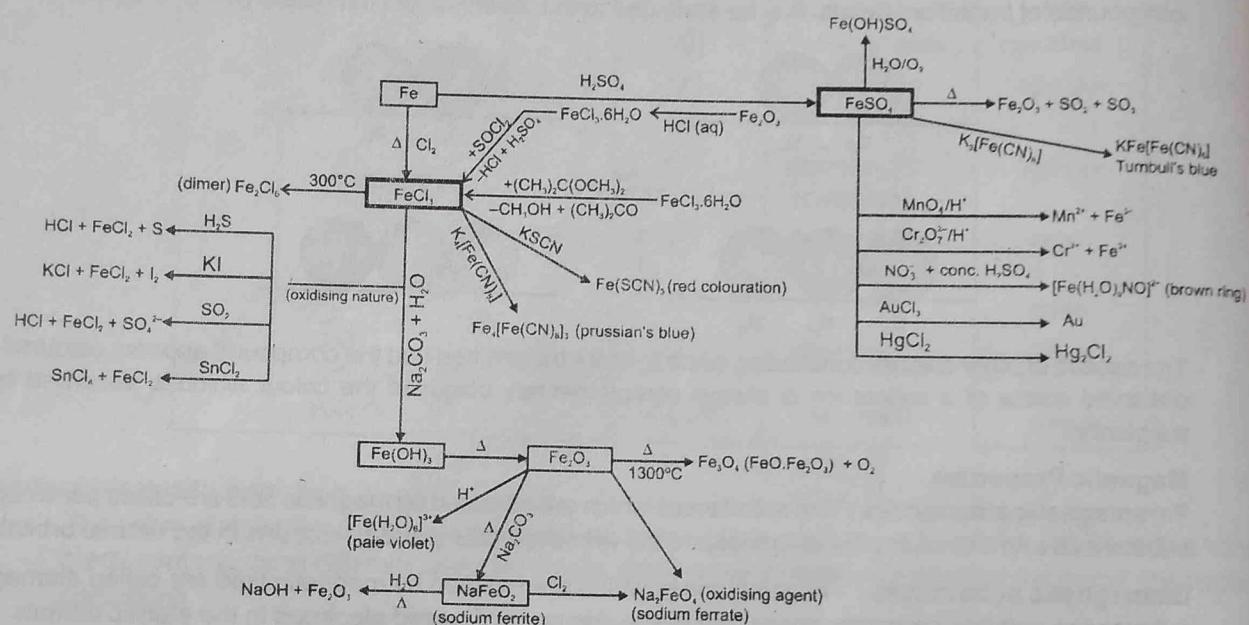
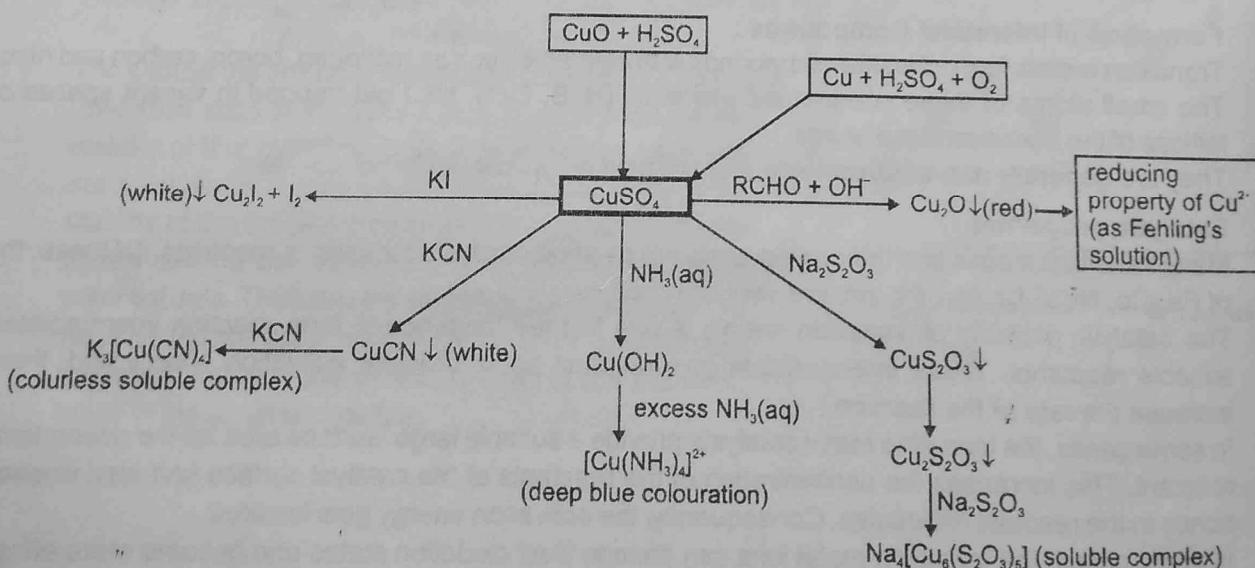
Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms. They are generally non-stoichiometric and are neither typically ionic nor covalent.

### Catalytic properties :

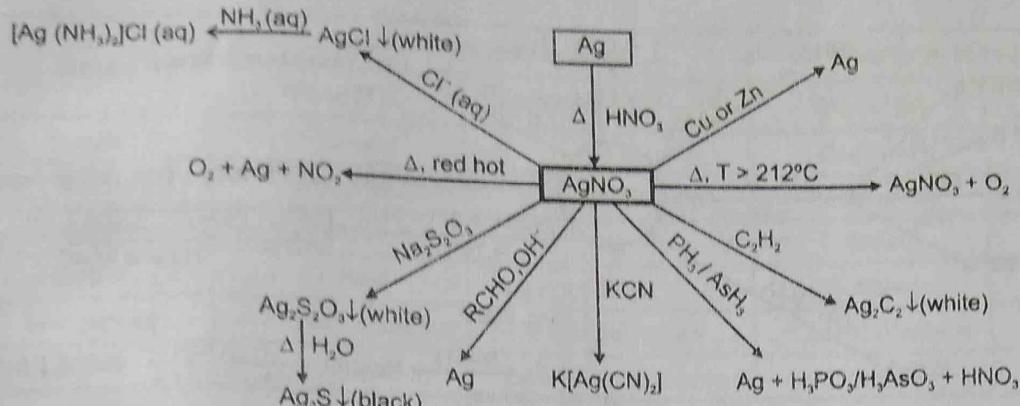
- Many transition metals and their compounds act as good catalysts for various reactions. Of these, the use of Fe, Co, Ni, V, Cr, Mn, Pt, etc. are very common.
- (i) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.
- (ii) In some cases, the transition metal catalysts provide a suitable large surface area for the adsorption of the reactant. This increases the concentration of the reactants at the catalyst surface and also weakens the bonds in the reactant molecules. Consequently, the activation energy gets lowered.
- (iii) In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts.

**Alloy Formation :**

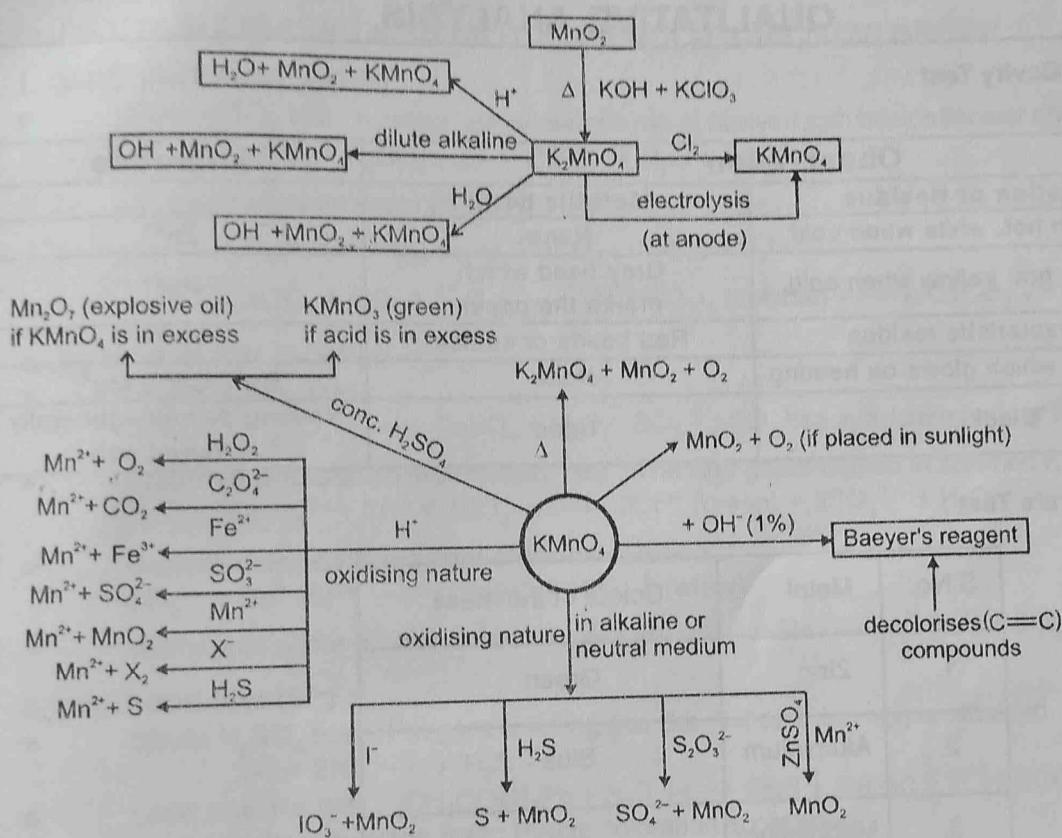
Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in their crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed. Such alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

**d-BLOCK METAL COMPOUNDS :****1. Hydrated Ferrous Sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), Ferric chloride ( $\text{FeCl}_3$ ) and iron (III) oxide ( $\text{Fe}_2\text{O}_3$ )****2. Hydrated copper sulphur ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) :**

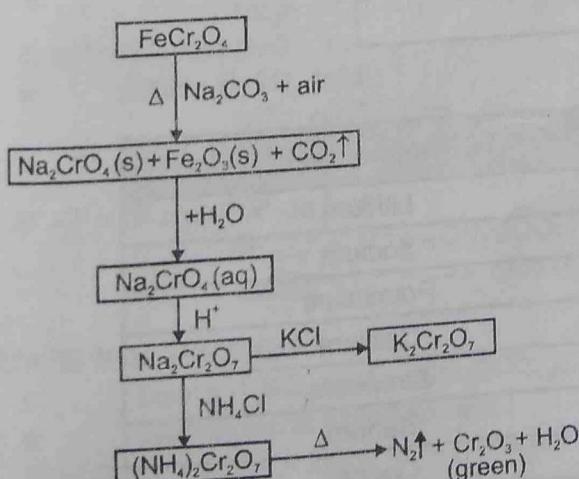
3.

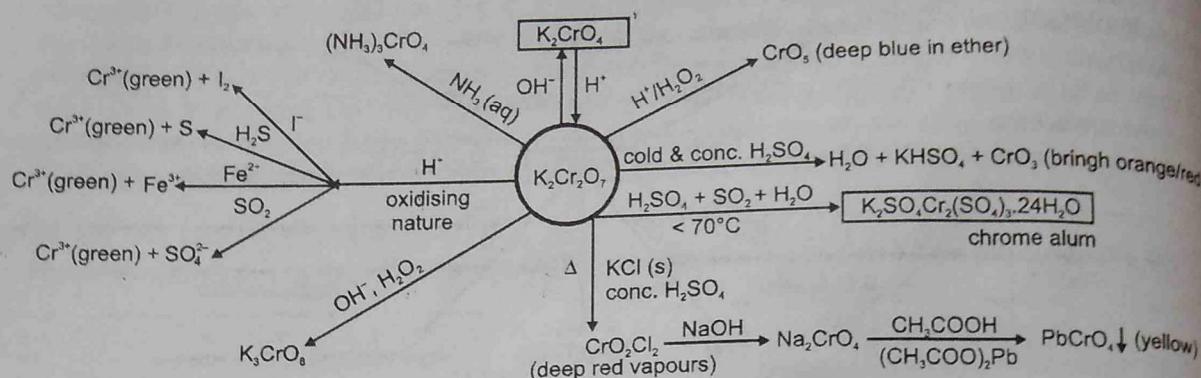
Silver nitrate ( $\text{AgNO}_3$ ) :

4.

Potassium permanganate ( $\text{KMnO}_4$ ) :

5.

Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) :



## QUALITATIVE ANALYSIS

### Charcoal Cavity Test :

Observation		Inference
Incrustation or Residue	Metallic bead	
Yellow when hot, white when cold	None	Zn <sup>2+</sup>
Brown when hot, yellow when cold	Grey bead which marks the paper	Pb <sup>2+</sup>
No characteristic residue	Red beads or scales	Cu <sup>2+</sup>
White residue which glows on heating	None	Ba <sup>2+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>
Black	None	Nothing definite—generally coloured salt

### Cobalt Nitrate Test :

S.No.	Metal	Colour of the mass
1.	Zinc	Green
2.	Aluminium	Blue
3.	Magnesium	Pink
4.	Tin	Bluish - green

### Flame test :

Colour of Flame	Inference
Crimson Red / Carmine Red	Lithium
Golden yellow	Sodium
Violet/Lilac	Potassium
Brick red	Calcium
Crimson	Strontium
Apple Green/Yellowish Green	Barium
Green with a Blue centre/Greenish Blue	Copper

Borax Bead test :

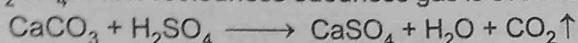
Metal	Colour in oxidising flame		Colour in reducing flame	
	When Hot	When Cold	When Hot	When Cold
Copper	Green	Blue	Colourless	Brown red
Iron	Brown yellow	Pale yellow/Yellow	Bottle green	Bottle green
Chromium	Yellow	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet/Amethyst	Red/Amethyst	Grey/Colourless	Grey/Colourless
Nickel	Violet	Brown/Reddish brown	Grey	Grey

## Analysis of ANIONS (Acidic Radicals) :

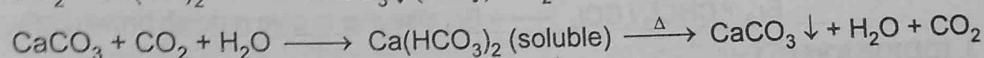
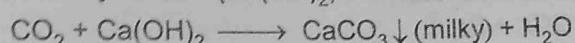
## (a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP :

1. CARBONATE ION ( $\text{CO}_3^{2-}$ ) :

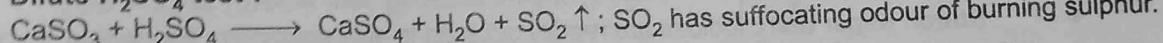
- Dilute  $\text{H}_2\text{SO}_4$  test : A colourless odourless gas is evolved with brisk effervescence.



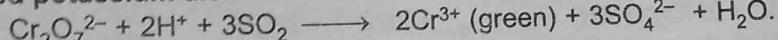
- Lime water/Baryta water ( $\text{Ba}(\text{OH})_2$ ) test :

2. SULPHITE ION ( $\text{SO}_3^{2-}$ ) :

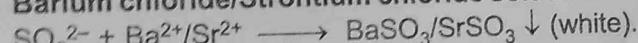
- Dilute  $\text{H}_2\text{SO}_4$  test :



- Acidified potassium dichromate test : The filter paper dipped in acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green.



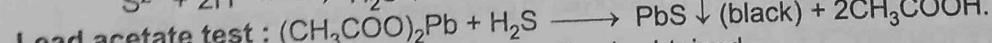
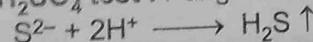
## 3. Barium chloride/Strontium chloride solution :



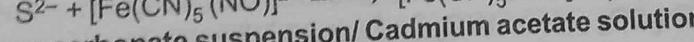
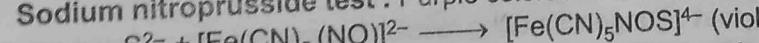
- White precipitate dissolves in dilute HCl.  $\text{BaSO}_3 \downarrow + 2\text{H}^+ \longrightarrow \text{Ba}^{2+} + \text{SO}_2 \uparrow + \text{H}_2\text{O}.$

3. SULPHIDE ION ( $\text{S}^{2-}$ ) :

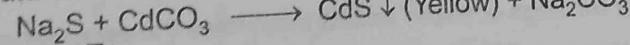
- Dilute  $\text{H}_2\text{SO}_4$  test : Pungent smelling gas like that of rotten egg is obtained.



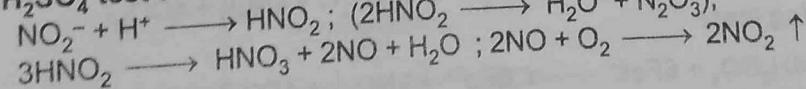
- Lead acetate test :  $(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \longrightarrow \text{PbS} \downarrow \text{(black)} + 2\text{CH}_3\text{COOH}.$



## 4. CADMIUM CARBONATE SUSPENSION/ CADMIUM ACETATE SOLUTION :

4. NITRITE ION ( $\text{NO}_2^-$ ) :

- Dilute  $\text{H}_2\text{SO}_4$  test :

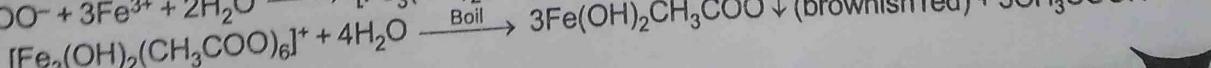
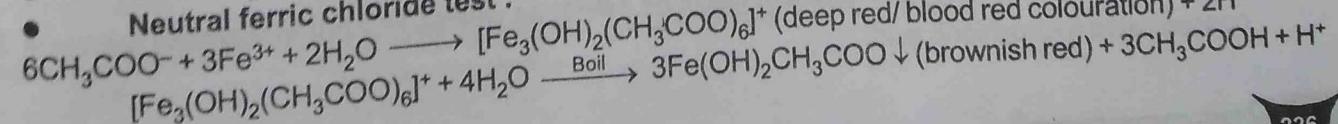


## 5. STARCH IODIDE TEST :

5. ACETATE ION ( $\text{CH}_3\text{COO}^-$ )

- Dilute  $\text{H}_2\text{SO}_4$  test :  $(\text{CH}_3\text{COO})_2\text{Ca} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{CH}_3\text{COOH} \text{ (vinegar like smell)} + \text{CaSO}_4$

## 6. NEUTRAL FERRIC CHLORIDE TEST :



(b) CONC.  $\text{H}_2\text{SO}_4$  GROUP :1. CHLORIDE ION ( $\text{Cl}^-$ ) :

- Concentrated  $\text{H}_2\text{SO}_4$  test :  $\text{Cl}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{HCl}$  (colourless pungent smelling gas) +  $\text{HSO}_4^-$
- $\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} \uparrow$  (white fumes) +  $\text{H}_2\text{O}$ .
- Silver nitrate test :  $\text{Cl}^- + \text{Ag}^+ \longrightarrow \text{AgCl} \downarrow$  (white)  
White precipitate is soluble in aqueous ammonia and precipitate reappears with  $\text{HNO}_3$ .  
 $\text{AgCl} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$  (Soluble) +  $2\text{H}_2\text{O}$ ;  $[\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}^+ \longrightarrow \text{AgCl} \downarrow + 2\text{NH}_4^+$
- Chromyl chloride test :  
 $4\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} + 6\text{H}^+$  (conc.)  $\longrightarrow 2\text{CrO}_2\text{Cl}_2$  (deep red vapours) +  $3\text{H}_2\text{O}$   
 $\text{CrO}_2\text{Cl}_2 + 4\text{OH}^- \longrightarrow \text{CrO}_4^{2-} + 2\text{Cl}^- + 2\text{H}_2\text{O}$ ;  $\text{CrO}_4^{2-} + \text{Pb}^{2+} \longrightarrow \text{PbCrO}_4 \downarrow$  (yellow)

2. BROMIDE ION ( $\text{Br}^-$ ) :

- Concentrated  $\text{H}_2\text{SO}_4$  test :  
 $2\text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HBr}$ ;  $2\text{HBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Br}_2 \uparrow$  (reddish-brown) +  $2\text{H}_2\text{O} + \text{SO}_2$
- Silver nitrate test :  $\text{NaBr} + \text{AgNO}_3 \longrightarrow \text{AgBr} \downarrow$  (pale yellow) +  $\text{NaNO}_3$   
Yellow precipitate is partially soluble in dilute aqueous ammonia but readily dissolves in concentrated ammonia solution.  $\text{AgBr} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Br} + \text{H}_2\text{O}$
- Chlorine water test (organic layer test) :  
 $2\text{Br}^- + \text{Cl}_2 \longrightarrow 2\text{Cl}^- + \text{Br}_2 \uparrow$ .  
 $\text{Br}_2 + \text{CHCl}_3 / \text{CCl}_4 \longrightarrow \text{Br}_2$  dissolve to give reddish brown colour in organic layer.

3. IODIDE ION ( $\text{I}^-$ ) :

- Concentrated  $\text{H}_2\text{SO}_4$  test :  $2\text{NaI} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HI}$   
 $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 \uparrow$  (pungent smelling dark violet) +  $2\text{H}_2\text{O} + \text{SO}_2$
- Starch paper test : Iodides are readily oxidised in acid solution to free iodine; the free iodine may then be identified by deep blue colouration produced with starch solution.  
 $3\text{I}^- + 2\text{NO}_2^- + 4\text{H}^+ \longrightarrow \text{I}_3^- + 2\text{NO} \uparrow + 2\text{H}_2\text{O}$ .
- Silver nitrate test : Bright yellow precipitate is formed.  
 $\text{I}^- + \text{Ag}^+ \longrightarrow \text{AgI} \downarrow$   
Bright yellow precipitate is insoluble in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.
- Chlorine water test (organic layer test) :  
 $2\text{NaI} + \text{Cl}_2 \longrightarrow 2\text{NaCl} + \text{I}_2$   
 $\text{I}_2 + \text{CHCl}_3 \longrightarrow \text{I}_2$  dissolves to give violet colour in organic layer.

4. NITRATE ION ( $\text{NO}_3^-$ ) :

- Concentrated  $\text{H}_2\text{SO}_4$  test : Pungent smelling reddish brown vapours are evolved.  
 $4\text{NO}_3^- + 2\text{H}_2\text{SO}_4 \longrightarrow 4\text{NO}_2 \uparrow + \text{O}_2 + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O}$   
Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.  
 $2\text{NO}_3^- + 4\text{H}_2\text{SO}_4 + 3\text{Cu} \longrightarrow 3\text{Cu}^{2+} + 2\text{NO} \uparrow + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}$ ;  $2\text{NO} \uparrow + \text{O}_2 \longrightarrow 2\text{NO}_2 \uparrow$   
 $4\text{C}$  (paper pellet) +  $4\text{HNO}_3 \longrightarrow 2\text{H}_2\text{O} + 4\text{NO}_2 + 4\text{CO}_2$ .
- Brown ring test :  
 $2\text{NO}_3^- + 4\text{H}_2\text{SO}_4 + 6\text{Fe}^{2+} \longrightarrow 6\text{Fe}^{3+} + 2\text{NO} \downarrow + 4\text{SO}_4^{2-} + 4\text{H}_2\text{O}$ .  
 $\text{Fe}^{2+} + \text{NO} \uparrow + 5\text{H}_2\text{O} \longrightarrow [\text{Fe}^{\text{l}}(\text{H}_2\text{O})_5\text{NO}^+]^{2+}$  (brown ring).

## Miscellaneous Group :

1. SULPHATE ION ( $\text{SO}_4^{2-}$ ) :

- Barium chloride test :  $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow \text{BaSO}_4 \downarrow$  (white) +  $2\text{NaCl}$ .  
White precipitate is insoluble in warm dil.  $\text{HNO}_3$  as well as  $\text{HCl}$  but moderately soluble in boiling concentrated hydrochloric acid.

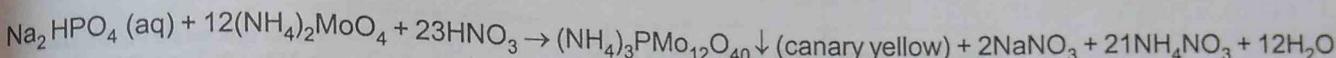
Precip  
(Hg(N)  
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- Lead acetate test :**  $\text{Na}_2\text{SO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbSO}_4 \downarrow (\text{White}) + 2\text{CH}_3\text{COONa}$   
White precipitate soluble in excess of hot ammonium acetate.  

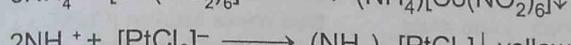
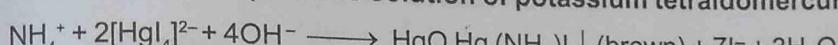
$$\text{PbSO}_4 + 2\text{CH}_3\text{COONH}_4 \longrightarrow (\text{CH}_3\text{COO})_2\text{Pb} \text{ (soluble)} + (\text{NH}_4)_2\text{SO}_4$$

**2. PHOSPHATE ION ( $\text{PO}_4^{3-}$ ) :**

- Ammonium molybdate test :**

**ANALYSIS OF CATIONS****1. AMMONIUM ION ( $\text{NH}_4^+$ ) :**

**Nessler's reagent (Alkaline solution of potassium tetraiodomercurate(II)) :**

**I<sup>st</sup> GROUP ( $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ) :**