

## Unit - 12

### Principles and Processes of Isolation of Elements

Minerals are naturally occurring chemical substances in earth's crust obtainable by mixing Ores of a metal are minerals which are viable to be used as source of that metal profitably.

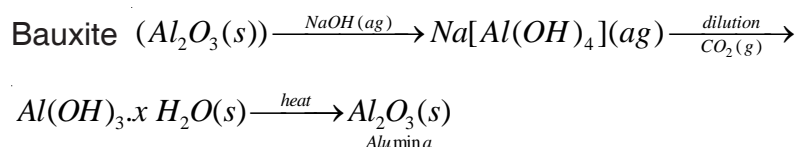
Aluminium is the most abundant metal and the oxygen is most abundant element in the earth's crust. Iron in the second most abundant metal in the earth's crust. Silver, gold, Platinum, sulphur, oxygen and nitrogen are the elements that occur in native of free state.

Many gem-stones are improve form of  $Al_2O_3$ , the impurities range from Cr (in ruby) to Co (in sapphire) [For principal ores of Al, Fe, Cu and Zn, please refer Table 6.1 in the NCERT Text Book, Part I, XII, Page 148] concentration of ores depends upon the difference in physical properties of the compound of metal present and that of the gangue.

Froth floatation process is used for the concentration of sulphide ores. A suspension of powdered ore is made with water. To it collectors (e.g pine oils, fatty acids, xanthates etc.) and froth stabilisers (e.g., cresols, aniline enhance non-wettability of mineral particles stabilise the froths) are added. Sometimes depressants are added to separate the sulphide ores.

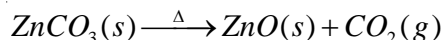
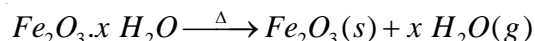
For example NaCN is used as a depressant to selectively prevent Zns from coming to froth but only allows  $P_6S$  to come with froth. NaCN forms a layer of  $Na_2[Zn(CN)_4]$  on the surface of Zns that prevent it from coming to froth.

Leaching, is useful in case the ore is soluble in a suitable solvent.

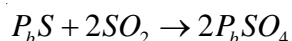
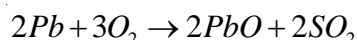
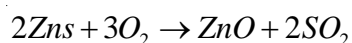


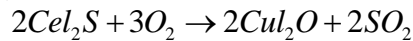
### Conversion of concentrated ore to an oxide

- (a) The hydrated or carbonate ore heated when the volatile matter escapes leaving behind the metal oxide

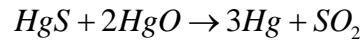
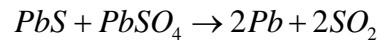
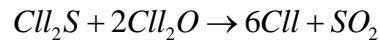


- (b) Roasting : The sulphide ore is heated in a regular supply of air below the melting point of metal to convert the metal into its oxide or sulphite. Sometimes a part of the sulphide may act as reducing agent in the subsequent step.





**Note** :- In auto reduction : For example, the Partially converted  $\text{Cu}_2\text{O}$  reduces  $\text{Cu}_2\text{S}$



**Reduction of oxide to metal** : Reduction means electron gain or electronation. For the reduction of metal oxides heating is required. To understand the variation in temperature requirement for thermal reduction (pyrometallurgy) and to predict which element will suit as reducing agent for a metal oxide ( $\text{M}_x\text{O}_y$ ), Gibbs energy interpretation are made at any specified temperature

$$\Delta G = \Delta H - T\Delta S$$

For any reaction :-

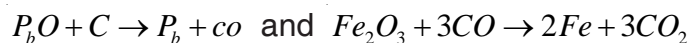
$$\Delta G^\theta = -2.303RT \log k$$

when a reaction proceeds towards products K will be positive which implies that  $\Delta G$  will be negative and vice-versa.

When the value of  $\Delta G$  is negative only then the reaction proceed. If  $\Delta S$  is positive, On increasing the temperature (T), the value of  $T\Delta S$  would increase (i.e.;  $(\Delta H < T\Delta S)$ ) and then, - ve, the overall reaction will occur.

**Ellingham diagram** :- Gibbs energy ( $\Delta G^\theta$ ) for formation of oxides (per mol of  $\text{O}_2$ ) are plotted against temperature T. It is evident that elements, for which Gibbs energy of formation of oxides (per mol of Oxygen) is more negative, can reduce the oxides of elements for which Gibbs energy of formation (per  $\text{mol}^{-1} \text{O}_2$ ) is less negative, that is, the reduction of oxide represented by upper line is feasible by the element represented by lower line.

**Reduction by Carbon** :- (Smelting) : It is the process of extraction of metal from its roasted or calcined ore by heating with powdered coke in presence of a flux. In smelting oxides are reduced to molten metal by carbon or carbonmonoxide.



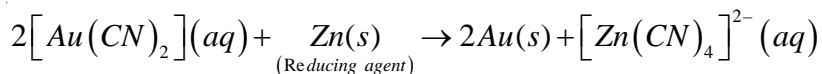
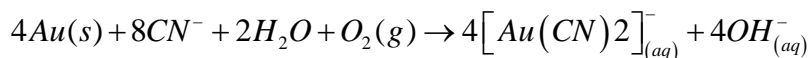
**Electrochemical Principles of metallurgy** : In simple electrolysis molten salt  $\text{M}^{n+}$  are discharged at negative electrodes sometimes a flux is added for making molten mass more conducting as in the electrolysis of molten alumina,  $\text{CaF}_2$  or  $\text{Na}_3[\text{AlF}_6]$  is added

to lower the melting point of mix and bring the conductivity.

Some extractions are based on oxidation for non-metals. For example, extraction of  $Cl_2$  from brine is the oxidation of  $Cl^-$  in aqueous medium



Leaching of Ag of Au with  $CN^-$  involves  $\Delta G^\circ = +422KJ$  the oxidation of  $Ag \rightarrow Ag^+$  or  $Au \rightarrow Au^+$



**Refining** : Distillation : Useful for low boiling metals like Zinc and mercury.

**Liquation** : Useful for low boiling metal like Zinc.

**Electrolytic refining** : Anode : Impure metal.

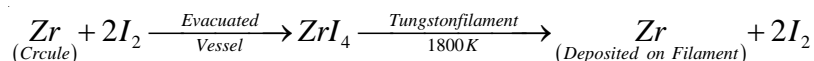
**Cathode** : Strip of pure metal soluble metal salt as an electrolyte.

**Zone refining** is based on the principle that impurities are more soluble in the melt than in the solid state of metal. Pure metals are crystallised out of the melt and impurities move into molten zone. This is used for metals of very high purity, e.g., Ge, Si, B, Ga and In.

**Vapour phase refining** : Impure Metal is converted into volatile compound which is then decomposed to get pure metal.



**Van Arkel method for refining Zr or Ti** : This method is used to remove all oxygen and nitrogen present in the form of impurity in certain metals like Zr or Ti.

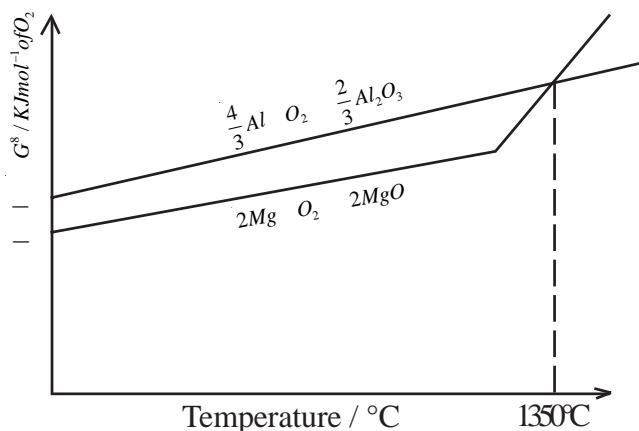


**Chromatographic methods** : This method is based on the principle that different components of a mixture are differently adsorbed on a adsorbent. The adsorbed components are removed (eluted) by using suitable solvent (elutant).

# MOCK TEST

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- (i) How is cast iron different from pig iron?
- (ii) Why is the reduction of metal oxide easier if metal formed is in the liquid state at the temperature of reduction?
- (iii) Does the PH of the solution of brine decrease/increase when the solution is subjected to electrolysis. Explain.
- (iv) In the metallurgy of iron CO acts a reducing agent at lower temperature range but carbon reduces iron oxide at higher temperature range. Explain why?
- (v)



Is it true that under certain conditions, Mg can reduce  $Al_2O_3$  and Al can reduce  $MgO$ ? What are those conditions? [Hint :- (Take the help of Ellingham diagram)]

- (1) Froth floatation process may be used to increase concentration of the mineral in
  - (a) Bauxite
  - (b) Calamine
  - (c) Haemelite
  - (d) Cheiloplasties
- (2) The slag obtained during the extraction of copper from copper pyrites is mainly of :-
  - (a)  $CuSiO_3$
  - (b)  $FeSiO_3$
  - (c)  $Cu_2O$
  - (d)  $Cu_2S$
- (3) Heating the ore with carbon with the simultaneous removal of slag is called :-
  - (a) Roasting
  - (b) Calcination
  - (c) Smelting
  - (d) leaching
- (4) Cryolite is used in electrolysis of alumina :-
  - (a) to increase the conductivity and decrease the melting point of mix.
  - (b) to decrease the conductivity and increase the melting point of mix.

- (c) to increase the conductivity and melting point of mix.  
 (d) to decrease the conductivity and melting point of mix.
- (5) In the extraction of copper from sulphide ore, the metal is formed by reduction of  $Cu_2O$  with :-
- (a)  $FeS$                       (b)  $CO$   
 (c)  $Cu_2S$                       (d)  $SO_2$
- (6) The method of zone refining of metals is based on the principle of :-
- (a) greater mobility of pure metal than that of impurity  
 (b) higher melting point of impurity than that of pure metal  
 (c) higher noble character of solid metal than that of impurity  
 (d) greater solubility of impurity in molten state than in the solid.
- (7) Pyrolusite is an :-
- (a) Sulphide ore    (b) Oxide ore  
 (c) Carbonate ore    (d) Phosphate ore
- (8) Pick out the incorrect statement :-
- (a) Calamine and siderite are carbonates.  
 (b) Argentite and cuprite are oxides.  
 (c) Zinc blende and iron pyrites are sulphides  
 (d) Malachite and azurite are the ores of copper
- (9) 'German silver' does not have :-
- (a)  $Cu$                       (b)  $Zn$   
 (c)  $Ni$                       (d)  $Ag$
- (10) The metal which purified by fractional distillation is :-
- (a)  $Zn$                       (b)  $Cu$   
 (c)  $Al$                       (d)  $Si$
- (11) Identify the reaction that does not take place in Blast furnace :-
- (a)  $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$   
 (b)  $CO_2 + C \rightarrow 2CO$   
 (c)  $CaCO_3 \rightarrow CaO + CO_2$   
 (d)  $FeO + SiO_2 \rightarrow FeSiO_3$

(12) Native silver forms a water soluble complex with dilute solution of NaCN in presence of :-

- (a) nitrogen
- (b) oxygen
- (c) Carbon dioxide
- (d) argon

(13) Extraction of Zinc from zinc blende is achieved by :-

- (a) electrolytic reduction
- (b) roasting followed by reduction with carbon
- (c) roasting followed by reduction with other metal
- (d) roasting followed by self-reduction

(14) Blister copper is :-

- (a) impure copper
- (b) Copper alloy
- (c) pure copper
- (d) copper having  $\sim 1\%$  impurity

(15) Which metal has greater tendency to form oxide

- (a) Al
- (b) Mg
- (c) Cr
- (d) Fe

## Unit - 13

### Hydrogen

Hydrogen (IS') can gain one electron to form  $H^-$  ion like halogens. It can also lose its electron to form  $H^+$  ion like alkali metals.

It also differs from them.  $H^+$  does not exist freely and is always associated with other atoms or molecules. It is unique in behaviour and is, therefore, placed separately in periodic table.

It is the most abundant element in the universal Earth does not possess enough gravitational pull to retain the light  $H_2$  molecules, so it is not found in the atmosphere.

#### Isotopes of Hydrogen :-

- (i) Protium,  ${}^1_1H$
- (ii) Deuterium  ${}^2_1H$  or D
- (iii) Tritium,  ${}^3_1H$  or T

Tritium is radioactive and shows  $\beta^-$ -activity ( $t_{1/2} = 12.33 \text{ years}$ )

Harold C. Urey was awarded Nobel Prize for separating deuterium.

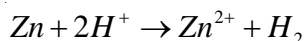
They almost show similar chemical properties but they show different rates of reactions mainly due to their different bond dissociation enthalpies.

$$\left[ D.H_{(D-D)} = 443.35 \text{ and } \Delta H_{(H-H)} = 435.88 \text{ kJ mol}^{-1} \right]$$

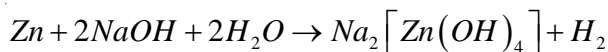
Hydrogen forms more chemical compounds than any other element.

#### Preparation of dehydrogen ( $H_2$ ) :-

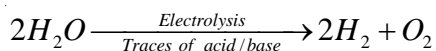
- (i) By the action of dilute acids on Zinc



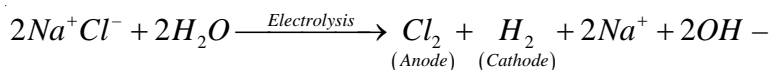
- (ii) By the action of aqueous alkali on Zinc



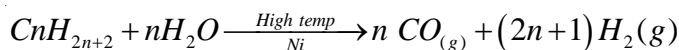
- (iii) By the electrolysis of acidified water

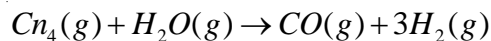


- (iv) By the electrolysis of aq. solution of NaCl

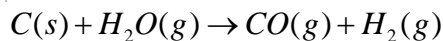


- (v) By the reaction of steam on hydrocarbons or coke

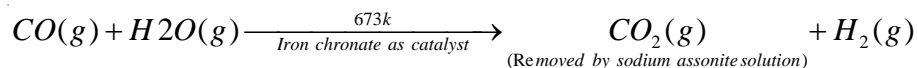




Mixture of CO and  $H_2$  is called water gas or synthesis gas or syngas. The process of producing syngas from coal is called coal gasification.



Water gas – shift reaction is used to increase. The production of dehydrogen by reacting CO of syngas with steam .



Dehydrogen has two nuclear spin isomers called ortho and para-dehydrogen. Their nuclear have parallel and anti parallel nuclear spins respectively.

**Chemical Properties** : It is relatively unreactive at room temperature due to high bond dissociation enthalpy of H–H bond. It shows reactions by (i) loss of electron to form  $H^+$  (ii) the gain an electron to form  $H^-$  ion (iii) sharing of electrons to form single covalent bond.

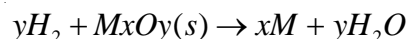
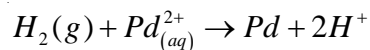
**Reaction with** :  $H_2 + X_2 \rightarrow 2HX$  ( $X = F, Cl, Br, I$ ) reactivity increases in the order  $I_2 < Br_2 < Cl_2 < F_2$ .

**Rxn. with Oxygen** :  $2H_2 + O_2 \rightarrow 2H_2O$ ;  $\Delta H^\theta < 0$ .

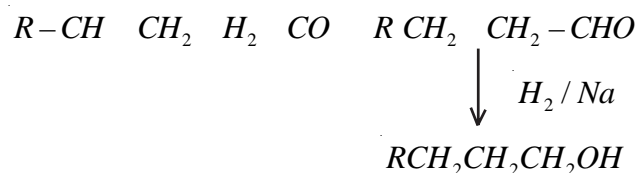
**Rxn. with Metals** :  $H_2 + 2M(g) \rightarrow 2M^+ H^-$

M = an alkali metal

**Rxn. with metal ions and metal oxide** :



**Hydroformylation of alkene** :



**Hydrides** :-

(1) Ionic hydrides are formed with most of S-block elements significant covalent

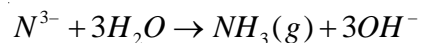
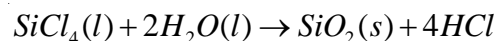
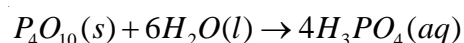
character is found in  $\text{LiH}$ ,  $\text{BeH}_2$  and  $\text{MgH}_2$ . Infact  $\text{BeH}_2$  and  $\text{MgH}_2$  are polymeric in nature.

- (2) Covalent or molecular hydrides are formed with most of p-block elements. They are further classified as :-
- (a) Electron deficient hydrides are formed by group 13 elements e.g.,  $\text{B}_2\text{H}_6$ . They act as Lewis acids.
  - (b) Electron precise hydrides are formed by group 14 elements, e.g.,  $\text{CH}_4$ .
  - (c) Electron rich hydrides have lone pair(s) of electrons on the central atoms of the molecules. Elements of group 15-17 form this type of hydrides. Examples are  $\text{NH}_3$ ,  $\text{HF}$  etc. Presence of lone pair(s) on highly electronegative atoms like N, O and F in hydrides results in intermolecular hydrogen bond formation leading to the association of molecules resulting in exceptionally high m.p and b.p.
- (3) Metalki or non-stoichiometric or interstitial hydrides are formed by d-and t-block elements. For example,  $\text{LaH}_{2.87}$ ,  $\text{TiH}_{1.5-1.8}$ ,  $\text{Zr, H}_{1.3-1.75}$  etc.

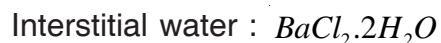
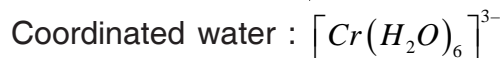
**Water :** Water shows unusual properties in condensed phase due to presence of extensive hydrogen bonding. Polar Covalent compounds are also soluble in water due the formation of hydrogen bonds with water molecules.

**Ice :** Each O-atom is tetrahedrally surrounded by four other oxygen atoms, i.e. a water molecule can form a maximum of four hydrogen bonds with the four other molecules of water.

**Chemical properties of Water :** Water is amphoteric in nature. It has the ability of undergoing oxidation as well as reduction due to high dielectric constant, it has strong hydrating tendency. Covalent and some conic substances are hydrolysed water.



Many salt are crystallised in water as hydrated salt :-



Hydrogen bonded water :  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  : Here fifth water molecule, outside the coordination sphere, is hydrogen bonded to  $\text{SO}_4^{2-}$  ion.

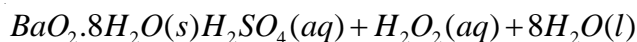
**Hard and Soft Water** : For cause and removal of temporary and permanent hardness please refer the NCERT Text book XI Class Part II pages 283-284.

**Heavy Water** ( $D_2O$ ): It is manufactured by electrolytic enrichment of normal water and used as moderator in nuclear reactors.

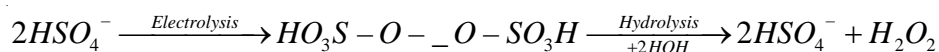
**Hydrogen peroxide ( $H_2O_2$ ) :**

**Preparation :-**

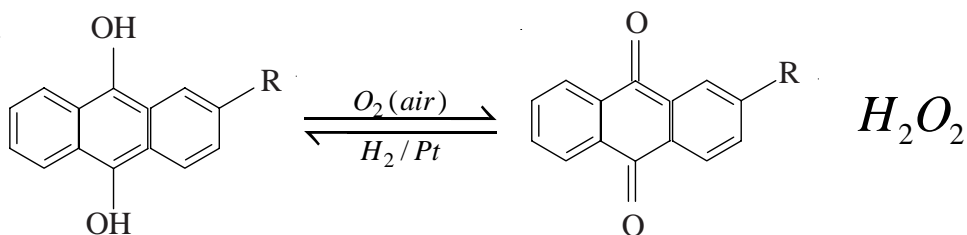
(a) by acidifying the barium peroxide



(b) Peroxodisulphate obtained by the electrolytic oxidation of acidified sulphate solution, on hydrolysis gives  $H_2O_2$

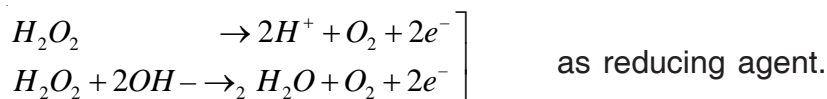
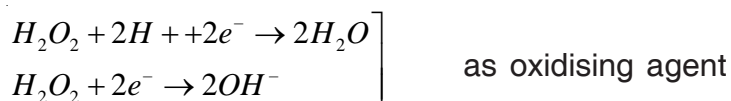


(c) **Industrial preparation :**



$H_2O_2$  is not stored in glass bottles because of traces of alkali present in glass catalyse the decomposition reaction :  $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ . It is also decomposed by exposure of light. Therefore it is stored in wax-lined glass or plastic vessels.

It acts both as oxidising and reducing agent in acidic as well as alkali medium.



It acts as a bleaching agent and its bleaching action is due to the oxidation of colouring matter.

The strength of  $H_2O_2$  solution is expressed as percentage strength or as volume strength as given below :

$$\text{Molarity} \times 11.2 = \text{volume strength}$$

$$\text{Normality} \times 5.6 = \text{volume strength}$$

# MOCK TEST

## UNIT – 13

- (i) Consider the reactions of  $H_2$  with (a) Na and (b)  $Cu_2O$  which species are oxidised/ reduced.
- (ii) Compare the structure of  $H_2O$  and  $H_2O_2$ .
- (iii) How does  $H_2O_2$  act as a bleaching agent?
- (iv) What is the molarity of 30 vol  $H_2O_2$  solution?
- (v) The process  $\frac{1}{2}H_2(g) + e^- \rightarrow H^-(g)$ ,  $\Delta H = +151 \text{ kJ mol}^{-1}$ , yet salt like hydrides are known. How do you account for this formation of salt-like hydrides.
- (1) The oxidation states of most electronegative element is the products of the reaction of  $BaO_2$  with dil  $H_2SO_4$  :-  
(a) 0 and -1            (b) -1 and -2  
(c) -2 and 0            (d) -2 and +1
- (2) The O–O–H bond angle in  $H_2O_2$  is :-  
(a)  $109^\circ.28'$             (b)  $106^\circ.28'$   
(c)  $120^\circ$             (d)  $94.8^\circ$
- (3) The volume strength of 1.5 N.  $H_2O_2$  solution is :-  
(a) 4.8            (b) 5.2  
(c) 8.8            (d) 8.4
- (4) Ortho and para-hydrogen differ in :-  
(a) atomic number    (b) atomic mass  
(c) spins of protons    (d) number of neutrons
- (5) Polyphosphates are used as water softening agents because they :-  
(a) form soluble complexes with anionic species  
(b) precipitate anionic species  
(c) form soluble complexes with cationic species  
(d) precipitates anionic species.

(6) Which of the following pairs of substances on reaction will not evolve  $H_2$  gas?

- (a) Fe and  $H_2SO_4$
- (b) Cu and HCl (aq)
- (c) Sodium and ethanol
- (d) Iron and Steam

(7) Heavy water ( $D_2O$ ) is obtained by :-

- (a) boiling water
- (b) fractional distillation of water
- (c) prolonged electrolysis of water
- (d) heating  $H_2O_2$

(8) The correct order, in which O–O bond length increases in the following, is :-

- (a)  $O_3 < H_2O_2 < O_2$     (b)  $H_2O_2 < O_2 < O_3$
- (c)  $O_2 < H_2O_2 < O_3$     (d)  $O_2 < O_3 < H_2O_2$

**Hint** - Compare the bond order of  $O_2$  and  $O_2^{2-}$ ,  $O_3$  has partial double bond character due to resonance.

$$B.O. \propto \frac{1}{\text{bond length}}$$

(9) 11.2 volume  $H_2O_2$  solution has a molarity of :-

- (a) 1.0                      (b) 0.5
- (c) 11.2                    (d) 1.12

(10) Hydrolysis of one mol of peroxodisulphuric acid produces :-

- (a) two mol of  $H_2SO_4$
- (b) two mol of peroxomonosulphuric acid
- (c) one mol Sulphuric acid and one mol of peroxomonosulphuric acid and one mol of hydrogen peroxide.

# Unit - 14

## S-block Elements

### I. Trends in atomic and physical properties

1. **Electronic configuration.** Alkali metals are s-block elements. These contain only one electron in the s-orbital of the valence shell outside the noble gas core and hence their valence shell electronic configuration is  $ns^1$  or  $(n-1)s^2p^6ns^1$  when  $n = 2$  to  $7$ .
11. **Flame colouration.** All the alkali metals impart characteristic colours to the flame. Due to the low ionization enthalpy, the electrons of alkali metals can be easily excited to the higher energy levels by the small energy provided by the Bunsen flame. When these excited electrons return to the ground state, the absorbed energy is emitted in the visible region of the electromagnetic spectrum and hence the flame appears coloured.
12. **Photoelectric effect.** Due to low ionization enthalpies, alkali metals especially K and Cs show photoelectric effect (i.e. eject electrons when exposed to light) and hence are used in photoelectric cells.
13. **Electrical conductivity.**  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$  as the ionization energy decreases in that order.
14. **Reducing character.** All the alkali metals are good reducing agents due to their low ionization enthalpies. Their reducing character, however, follows the order :

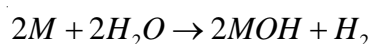


The reducing character of any metal is best measured in terms of its electrode potential which among other things depends upon its (i) heat of vaporization (ii) ionization energy and (iii) heat of hydration. Since  $Li^+$  ion has the smallest size, its heat of hydration has the highest value. Therefore, among the alkali metals Li has the highest negative electrode potential ( $E^\circ = -3.05\text{volts}$ ) and hence is the strongest reducing agents.

15. **Mobility of ions in aqueous solution.** The alkali metal ions exist as hydrated ions  $M^+(H_2O)_x$  in the aqueous solution. The degree of hydration, however, decreases with the ionic size as we move from  $Li^+$  to  $Cs^+$ . In other words,  $Li^+$  ion is most highly hydrated e.g.  $[Li(H_2O)_6]^+$ . Since the mobility of ions is inversely proportional to the size of their hydrated ions, therefore, amongst the alkali metal ions, lithium has the lowest ionic mobility.

### II. Chemical properties

3. **Reaction with water.** All the alkali metals readily react with water evolving hydrogen.



The reactivity, however, increase down the group as the electropositive character

of the metal increases :-



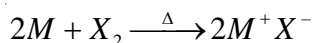
5. **Reaction with oxygen.** All the alkali metals when heated with oxygen form different types of oxides. For example, lithium forms lithium oxide ( $Li_2O$ ), sodium forms sodium peroxide ( $Na_2O_2$ ), while K, Rb and Cs form their respective superoxides ( $MO_2$  where M = K, Rb or Cs). Super oxides are coloured and paramagnetic as these possess three electron bond ( $:O \text{---} \text{---} O:$ )<sup>-</sup> where one unpaired electron is present. Sodium peroxide acquires yellow colour due to the presence of traces of superoxide as an impurity.  $KO_2$  is orange,  $RbO_2$  is brown and  $CsO_2$  is orange in colour. All oxides, peroxides and superoxides are basic in nature. To protect the alkali metals from air and moisture, they are usually kept in hydrocarbon solvents such as hexane, benzene, toluene and kerosene oil.

6. **Reaction with hydrogen.** All the alkali metals when heated with hydrogen form ionic crystalline hydrides of the general formula  $M^+H^-$

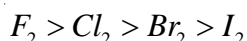


The reactivity of alkali metals towards hydrogen decreases as we move down the group i.e.  $Li > Na > K > Rb > Cs$ . This is mainly due to the reason that the lattice energy of these hydrides decrease progressively as the size of the metal cation increases. Thus, the stability of hydrides decreases from LiH to CsH.

7. **Reaction with halogens.** All the alkali metals react vigorously with halogens to form their respective ionic crystalline halides of the general formula,  $M^+X^-$  where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I.

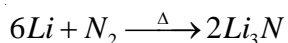


The reactivity of alkali metals towards a particular halogen increases in the order :  $Li < Na < K < Rb < Cs$  while that of halogen towards a particular alkali metal decreases in the order :

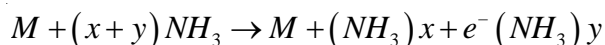


With the exception of LiF, all other lithium halides are covalent. Being covalent, LiCl, LiBr and LiI are insoluble in water but are soluble in organic solvents like pyridine, benzene, alcohols and ethers.

9. **Reaction with nitrogen.** Only lithium reacts with nitrogen to form lithium nitride ( $Li_3N$ ).



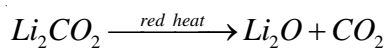
11. **Solubility in liquid ammonia.** All the alkali metals dissolve in liquid ammonia giving deep blue solutions when dilute, due to the presence of ammoniated (solvated) electrons in the solution :



These electrons are excited to higher energy levels and the absorption of photons occurs in the red region of the spectrum. Thus the solution appears blue.

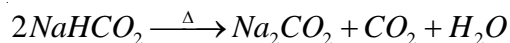
12. **Nature of carbonates and bicarbonates.**  $Li_2CO_3$  is much less stable and

decomposes on heating to red heat to give  $Li_2O$  and  $CO_2$



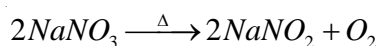
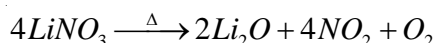
The stability of the other carbonates increases from  $Na_2CO_3$  to  $Cs_2CO_3$  as the basic strength of the corresponding metal hydroxide increases from  $LiOH$  to  $CsOH$ .

Similarly, the bicarbonates of all the alkali metals are known.  $LiHCO_3$  does not exist as a solid but exists in solution while all other bicarbonates exist as solids. All bicarbonates on heating form carbonates with the evolution of  $CO_2$



The solubility of the carbonates and bicarbonates increases as we move down the group probably due to lower lattice energies.

13. **Nature of Nitrates.**  $LiNO_3$  on heating decomposes to give  $v$  and  $O_2$  while the nitrates of the other alkali metals decompose on heating to form nitrites and .



All nitrates are very soluble in water.

### III. Diagonal relationship

Lithium shows diagonal relationship with magnesium since they have almost the same ionic radii.

Lithium resembles magnesium in the following respects :-

(vii) both combine with oxygen to form monoxides, e.g.,  $Li_2O$  and  $MgO$

(viii) both  $LiOH$  and  $Mg(OH)_2$  are weak bases

(ix) both  $LiCl$  and  $MgCl_2$  are predominantly covalent and hence are soluble in organic solvents, such as alcohol and pyridine.

(x) both  $Li$  and  $Mg$  combine with nitrogen to form their respective nitrides,  $Li_3N$  and  $Mg_3N_2$ .

### IV. Anomalous behaviour of lithium.

10. **Flame colouration.** Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration. As we move down the group from  $Ca$  to  $Ba$ , the ionization energy decreases, hence the energy or the frequency of the emitted light increases. Consequently, the colour imparted to the flame shows a gradual shift from red to violet. Thus :

**Ca** : Brick red      **Sr** : Crimson red      **Ba** : Apple green      **Ra** : Crimson

$Be$  and  $Mg$  because of their high ionization energies, however, do not impart any characteristic colour to the Bunsen flame.

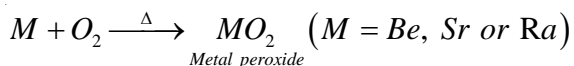
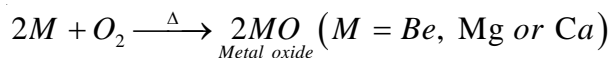
## II. Chemical properties

1. **Reaction with water.** They react with  $H_2O$  evolving  $H_2$  gas.



The chemical reactivity of the metal with  $H_2O$ , however, increases as we move from Mg to Ba. For example, Be does not react even with boiling water, Mg reacts with boiling water while Ca, Sr and Ba react vigorously even with cold water.

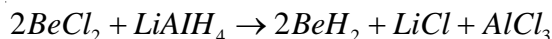
3. **Reaction with oxygen.** The affinity for oxygen increases down the group. Thus, Be, Mg and Ca when heated with oxygen form monoxides while Sr, Ba and Ra form peroxides.



4. **Reaction with hydrogen.** All the alkaline earth metals except Be, combine with  $H_2$  directly on heating to form metal hydrides of the general formula,  $MH_2$ .



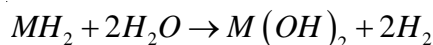
$BeH_2$  can, however, be prepared by reducing  $BeCl_2$  with  $LiAlH_4$ .



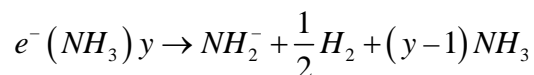
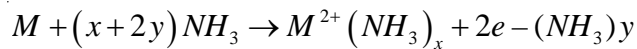
$BeH_2$  is covalent,  $MgH_2$  are polymeric while others are monomeric.

$CaH_2$  is also called hydrolith.

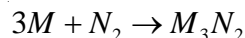
All the hydrides react with water to evolve  $H_2$  and thus behave as strong reducing agents.



5. **Solubility in liquid ammonia.** Like alkali metals, all alkaline earth metals dissolve in liquid ammonia giving bright blue solutions (when dilute) due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters. These solutions decompose very slowly forming amides and evolving  $H_2$ .

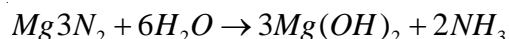


6. **Reaction with nitrogen.** When heated with  $N_2$ , alkaline earth metals form their respective nitrides.



The ease of formation of nitrides increases from Be to Ba.

These nitrides react with water to evolve  $NH_3$ , e.g.,

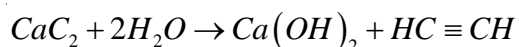


7. **Reaction with carbon.** When heated with carbon, alkaline earth metals form their respective carbides of the general formula  $MC_2$  (except beryllium) and are called acetylides containing the discrete  $C_2^{2-}$  anion.

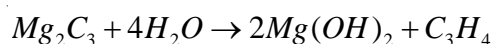


Under the conditions beryllium, however, forms  $Be_2C$  called methanide containing the discrete  $C^{4-}$  anion.

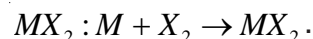
All these carbides are ionic in nature and react with water to form acetylene.  $Be_2C$ , however gives methane.



On heating  $MgC_2$  gives  $Mg_2C_3$  called allylide which contains the discrete  $C_3^{4-}$  anion and gives allylene (methyl acetylene) on hydrolysis.



8. **Reaction with halogens.** When heated with halogens ( $F_2$ ,  $Cl_2$ ,  $Br_2$ , or  $I_2$ ), all the alkaline earth metals form halides of the general formula,

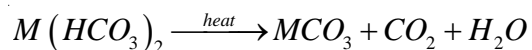


12. **Solubilities of sulphates.** The solubilities of sulphates of alkaline earth metals decrease as we move down the group from Be to Ba. This is mainly due to the reason that as the size of the cation increases, the heat of hydration decreases while the lattice energy remains about the same (because the sulphate anion is so big that increase in size of the cations down the group does not make any difference). Thus, the solubilities decrease in the order :

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ . The negligible solubility of  $BaSO_4$  in water is used in both qualitative and quantitative analysis.

13. **Solubilities of bicarbonates and carbonates.** The bicarbonates of the

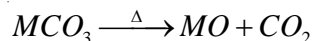
alkaline earth metals do not exist in the solid state but are known only in solution. On heating, these bicarbonates decompose forming carbonates with the evolution of  $CO_2$ .



The solubilities of the carbonates decrease as we move down the group from Be to Ba i.e.,  $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ . This is mainly due to the reason that as the size of the cation increases, the lattice energies of their carbonates remain almost unchanged as in case of sulphates whereas the heats of hydration of the cations decrease.

The extremely low solubility of alkaline earth metal carbonates in water is used in the precipitation of  $Ba^{2+}$ ,  $Sr^{2+}$  and  $Ca^{2+}$  as their carbonates in the V group of qualitative analysis of basic radicals.

14. **Thermal stabilities of carbonates.** The carbonates of alkaline earth metals decompose on heating forming metal oxide and carbon dioxide.



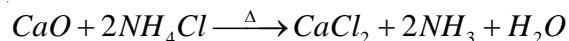
15. **Thermal stabilities of sulphates.** Like carbonates, thermal stabilities of sulphates also increase as the basic character of the metal hydroxide increases. This is shown by the temperature at which decompositions occur:

$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
773 K	1168 K	1422 K	1647 K

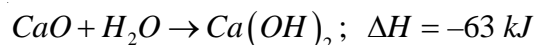
- (i) **Calcium oxide, Quick lime, Burnt lime, lime, CaO.** It is obtained by thermal decomposition of calcium carbonate at 1070 –1270 K.



It is a basic oxide and hence reacts with acids,  $SO_2$  etc. On heating with ammonium salts, it gives ammonia :



- (ii) **Calcium hydroxide, Slaked lime,  $Ca(OH)_2$ .** It is also called lime water and is obtained by dissolving quick lime in water.

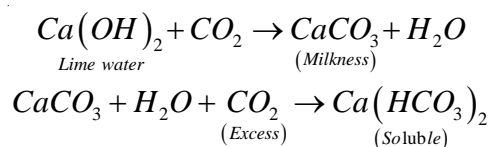


The reaction is highly exothermic and produces a hissing sound. Its suspension in water is called milk of lime.

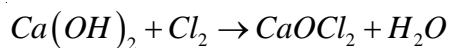
When  $CO_2$  is passed through lime water, it first turns milky due to the

formation of insoluble  $CaCO_3$  but if the passage of  $CO_2$  is continued, the solution becomes clear

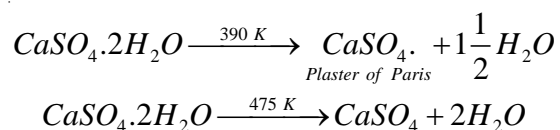
due to the formation of soluble calcium bicarbonate.



It reacts with  $Cl_2$  to give bleaching powder ( $CaOCl_2$ )

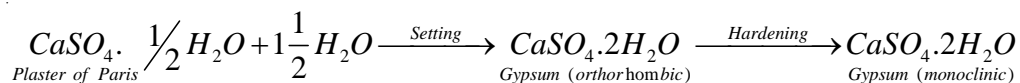


- (iii) **Gypsum, Calcium sulphate dihydrate**,  $CaSO_4 \cdot 2H_2O$ . When heated to 390 K, it gives Plaster of Paris and when heated to 475 K, it loses water of crystallization completely to form anhydrous  $CaSO_4$ . It is also called dead burnt plaster since it has no tendency to set.



Gypsum is added to cement to slow down its rate of setting.

- (iv) **Plaster of Paris, Calcium sulphate hemihydrate**,  $CaSO_4 \cdot \frac{1}{2}H_2O$ . When mixed with water, it forms first a plastic mass which sets into a solid mass (setting of Plaster of Paris) within 5-15 minutes. The setting of Plaster of Paris is believed to be due to rehydration and its reconversion into gypsum.



During setting, it undergoes slight expansion.

- (v) **Calcium chloride**,  $CaCl_2 \cdot 6H_2O$ . It is a deliquescent solid, by product of Solvay's process. In fused state, it is a good desiccant (drying agent). It can not be used to dry alcohol or  $NH_3$  as it forms addition products with them.

# MOCK TEST

## UNIT – 14

- (i) The active constituent of bleaching powder is :-
- (a)  $Ca(OCl)_2$                       (b)  $Ca(OCl)Cl$   
(c)  $Ca(ClO_2)_2$                   (d)  $Ca(ClO_2)Cl$
- (ii) Bleaching powder loses its power on keeping for a long time because :-
- (a) it changes into calcium hypochlorate  
(b) it changes into calcium chloride and calcium hydroxide  
(c) it absorbs moisture  
(d) it changes into calcium chloride and calcium chlorate.
- (iii)  $KO_2$  (potassium superoxide) is used in oxygen cylinders in space and submarines because it :-
- (a) absorbs  $CO_2$  and increase  $O_2$  content  
(b) eliminates moisture  
(c) absorbs  $CO_2$   
(d) produces ozone
- (iv) A metal M readily forms water soluble sulphate  $MSO_4$  . water insoluble hydroxide  $M(OH)_2$  and oxide MO which becomes inert on heating. The hydroxide is soluble in NaOH. The metal M is :-
- (a) Be                                  (b) Mg  
(c) Ca                                  (d) Sr
- (v) The paramagnetic species is :-
- (a)  $KO_2$                               (b)  $SiO_2$   
(c)  $TiO_2$                               (d)  $BaO_2$
- (vi) On dissolving moderate amount of sodium metal in liquid  $NH_3$  at low temperature, which one of the following does not occur?
- (a) Blue coloured solution is obtained  
(b)  $N^{a+}$  ions are formed in the solution  
(c) Liquid ammonia becomes good conductor of electricity  
(d) Liquid ammonia remains diamagnetic.

- (vii) The substance not likely to contain  $CaCO_3$  is
- (a) dolomite                      (b) a marble statue  
(c) calcined gypsum              (d) sea shells
- (viii) Solubilities of carbonates decrease down the magnesium group due to decrease in :-
- (a) entropy of solution formation  
(b) lattice energies of solids  
(c) hydration energy of cations  
(d) inter-ionic attraction
- (ix) In curing cement plasters, water is sprinkled from time to time. This helps in
- (a) converting sand into silicic acid  
(b) keeping it cool  
(c) developing interlocking needle like crystals of hydrated silicates  
(d) hydrating sand and gravel mixed with cement.
- (x) Photoelectric effect is maximum in :-
- (a) Cs                                  (b) Na  
(c) K                                    (d) Li
- (xi) Which of the following metal has most stable carbonate?
- (a) Na                                  (b) Mg  
(c) Al                                    (d) Si
- (xii) A sodium salt of unknown anion when treated with  $MgCl_2$  gives white precipitate only on boiling. The anion is :-
- (a)  $SO_4^{2-}$                               (b)  $HCO_3^-$   
(c)  $CO_3^{2-}$                               (d)  $NO_3^-$
- (xiii) A solid compound 'X' on heating gives  $CO_2$  gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of  $CO_2$  through 'Y' in water, clear solution 'Z' is obtained. On boiling 'Z', compound 'X' is reformed. The compound 'X' is
- (a)  $Ca(HCO_3)_2$                       (b)  $CaCO_3$   
(c)  $Na_2CO_3$                             (d)  $K_2CO_3$

(xiv) One mole of magnesium nitride on reaction with an excess of water gives :-

- (a) one mole of ammonia
- (b) one mole of nitric acid
- (c) two moles of ammonia
- (d) two moles of nitric acid

(xv) The ionic mobility of alkali metal ions in aqueous solution is maximum for :-

- (a)  $K^+$
- (b)  $Rb^+$
- (c)  $Li^+$
- (d)  $Na^+$

(xvi) The correct order of mobility of the alkali metal ions in aqueous solution is:-

- (a)  $Rb^+ > K^+ > Na^+ > Li^+$
- (b)  $Li^+ > Na^+ > K^+ > Rb^+$
- (c)  $Na^+ > K^+ > Rb^+ > Li^+$
- (d)  $K^+ > Rb^+ > Na^+ > Li^+$

(xvii) Pick out the statement(s) which is (are) not true about the diagonal relationship of Li and Mg.

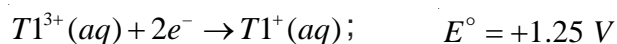
- (A) Polarising powers of  $Li^+$  and  $Mg^{2+}$  are almost same
  - (B) Like Li, Mg decomposes water very fast.
  - (C) Like Li,  $MgCl_2$  are deliquescent.
  - (D) Like Li, Mg readily reacts with liquid bromine at ordinary temperature.
- (a) A and D
  - (b) B and E
  - (c) only B
  - (d) only A
  - (e) B and D

## Unit - 15

### The P-block Elements

#### Group 13 Elements : Boron Family

3. **Inert pair effect.** It is the reluctance of the s-electrons of the valence shell to take part in bonding. It arises due to poor or ineffective shielding of the  $ns^2$  electrons of the valence shell by the intervening d- and f-electrons. Inert pair effect increases down a group and thus the elements present in the lower part of the group show lower oxidation states. In group 13 elements, inert pair effect is more pronounced in Tl.
4. **Oxidation states.** B and Al show an oxidation state of + 3 only while, In and Tl show oxidation states of both + 1 and + 3. Further due to inert pair effect, as we move down the group, the stability of + 3 oxidation state decreases while that of + 1 oxidation state increases. So much so for Tl, it is the + 1 oxidation state which is more stable than + 3 as shown by the redox potential data

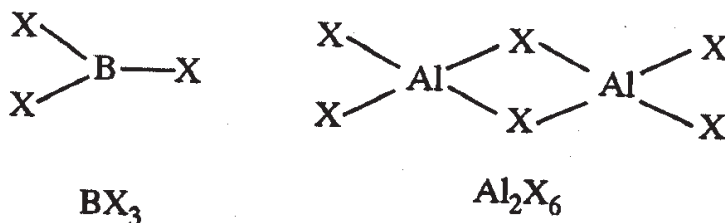


The decrease in stability of + 3 oxidation state with increasing atomic number is due to decrease in bond energy with size from Al to Tl. As a result, the energy required to unpair the  $ns^2$  electrons is not compensated by the energy released in forming two additional bonds.

Stability of +1 oxidation state follows the trend  $Ga < In < Tl$

9. **Halides.** All the elements of group 13 (except thallium which preferably forms thallos monohalides) form trihalides of the general formula  $MX_3$  where X = F, Cl, Br and I.

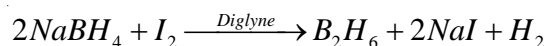
All the boron trihalides, i.e.  $BF_3$ ,  $BCl_3$ ,  $BBr_3$  and  $BI_3$  and aluminium trihalides i.e.  $AlCl_3$ ,  $AlBr_3$  and  $AlI_3$  ( $AlF_3$  being ionic) are covalent compounds. Whereas boron trihalides exist as only monomers, aluminium trihalides exist as dimers.



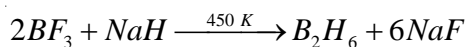
**Nature of Trihalides.** The trihalides of group 13 elements have only six electrons in the valence shell and hence have a strong tendency to accept a pair of electrons to acquire the nearest inert gas configuration. Consequently trihalides of group 13 elements behave as Lewis acids.

(ii) Diborane is prepared in the laboratory by the oxidation of sodium

borohydride ( $\text{NaBH}_4$ ) with iodine in diglyme ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_3$ ) as solvent

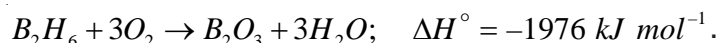


(iii) On the industrial scale, diborane is prepared by the reduction of  $\text{BF}_3$  with sodium hydride.

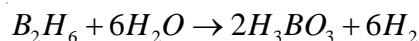


### Properties.

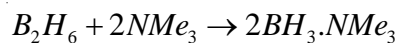
(i) Diborane is a colourless highly toxic gas which burns in oxygen evolving enormous amount of heat



(ii) It is readily hydrolysed by water to form boric acid.

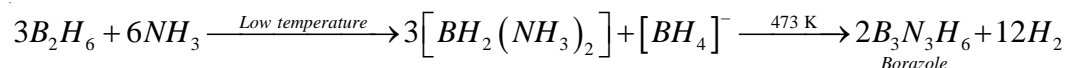


(iii) With Lewis bases, diborane first undergoes cleavage to form borane ( $\text{BH}_3$ ) which then reacts to form adducts.

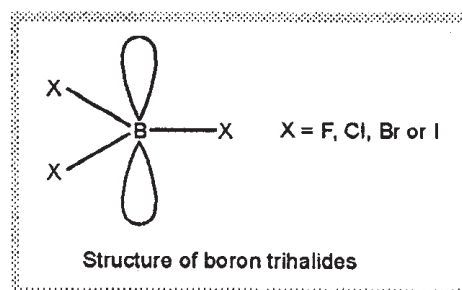


(iv) With ammonia an addition product  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$  formulated as

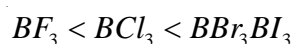
$[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$  is formed which then decomposes on heating at 473 K to give a volatile compound called borazole.



**Structure.** Trihalides of boron ( $\text{BX}_3$ ) are planar molecules in which B atom is  $sp^2$ -hybridized and contains one unhybridized empty p-orbital perpendicular to the plane of three of  $\sigma\text{B}-\text{X}$  bonds. As B atom has only six electrons in its valence shell, all  $\text{BX}_3$  molecules are electron deficient and behave as Lewis acids.

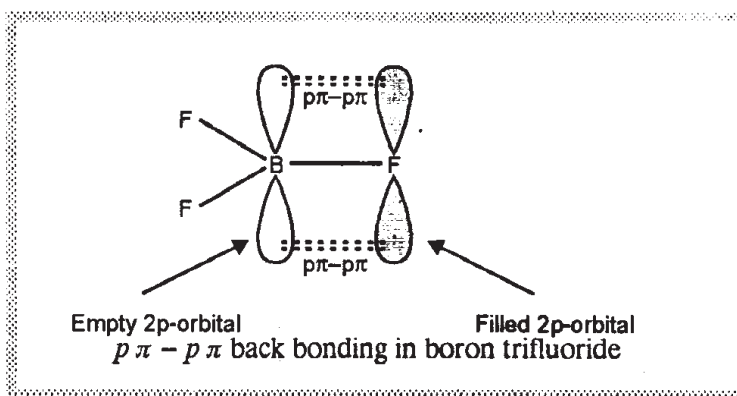


Relative acid strength of  $\text{BX}_3$ . It increases in the order :



This order can be explained on the basis of the tendency of halogen atom to back donate its lone pair of electrons to the empty p-orbital of B atom through  $p\pi - p\pi$  bonding. As this tendency is higher in case of F (due to identical size of 2 p-orbitals of

B and F), the electron deficiency of B decreases and thus  $BF_3$  behaves as the weakest Lewis acid. As the size of halogen atom increases from Cl to I, the tendency for back donation decreases and consequently the electron deficiency of B increases and the Lewis acid character increases accordingly from  $BF_3$  to  $BI_3$ .



Due to back donation by three F atoms,  $BF_3$  can be represented as a resonance hybrid of the following three structures :

The relative strength of Lewis acids of boron trihalides increases in the order  $BF_3 < BCl_3 < BBr_3 < BI_3$ . This order can be explained on the basis of the tendency of the halogen atom to back donate its electrons to the boron atom and makes it less electron deficient. Amongst the trihalides of group 13,  $BF_3$  and  $AlCl_3$  are widely used as Lewis acid catalysts.  $BF_3$  is used as a catalyst in Friedel-Crafts reactions, in esterification and in polymerization of olefines. Similarly, anhydrous  $AlCl_3$  is used as a catalyst in Friedel Crafts reactions.

Halides of other elements of group 13 also behave as Lewis acids. The Lewis acidity decreases as  $BX_3 > AlX_3 > GaX_3 > InX_3$  (where X = Cl, Br or I )

5. **Oxidation states.** All the elements show an oxidation state of + 4. However, as we move down the group from C to Pb, the stability of + 4 oxidation state decrease while that of + 2 oxidation state increases due to inert pair effect. Thus + 4 oxidation state is important for C and Si while + 2 state becomes increasingly important for Ge, Sn and Pb. The stability of the divalent state increases in the sequence  $Ge < Sn < Pb$ .

7. **Catenation.** The property of self-linking of atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called **catenation**. The tendency of an element to form chains depends upon the strength of the element-element bond. Amongst the group 14 elements, C – C bond strength ( $355 \text{ kJ mol}^{-1}$ ) is maximum, therefore, carbon shows maximum tendency for catenation. As we move down the group, the element-element bond strength decreases very rapidly, i.e.,

Element-element	C – C	Si – Si	Ge – Ge	Sn – Sn
Bond strength ( $\text{kJ mol}^{-1}$ )	355	215	165	152

Therefore, the tendency for catenation decreases in the order : C > > > Si > Ge ≈ Sn > > Pb

Tin and lead, however, do not show any tendency for catenation.

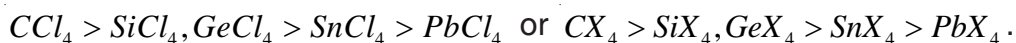
10.  **$p\pi - p\pi$  and  $P\pi - d\pi$  multiple bonding.** Amongst group 14 elements, carbon shows a pronounced ability to form  $p\pi - p\pi$  multiple bonds with itself (e.g., in graphite) and with other non-metals especially nitrogen and oxygen. Silicon and other heavier elements of this group show negligible tendency of this type. This is the reason that silicon exists only in the diamond structure.

$p\pi - d\pi$  multiple bonding has been observed particularly in case of silicon linked to oxygen and nitrogen. Thus trimethylamine,  $N(CH_3)_3$  is pyramidal (N is  $sp^3$ -hybridized) and is more basic whereas similar silicon compound trisilylamine,  $N(SiH_3)_3$  is planar (N is  $sp^2$ -hybridized) and is less basic. In this case, the lone pair on nitrogen atom is transferred to the empty d-orbital of silicon ( $p\pi - d\pi$  overlapping) leading to the planar structure.

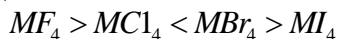
## II. Chemical properties

1. **Nature of bonding.** The compounds of group 14 elements which show an oxidation state of + 4 are covalent while those which show an oxidation of + 2 are ionic in nature. Further, as we move down the group, the tendency of the elements to form covalent compounds decreases but the tendency to form ionic compounds increases.

4. Formation of halides (i) Tetrahalides. All the elements of group 14 form tetrahalides of the general formula,  $MX_4$  where X = F, Cl, Br or I. All these tetrahalides are covalent compounds and have tetrahedral structures. The stability of these tetrahalides decreases as we move from C to Pb i.e.,



On the other hand, the thermal stability and volatility of tetrahalides with a common central atom fall with increase in molecular weight of the tetrahalide i.e.,



In fact  $PbBr_4$  and  $PbI_4$  do not exist because  $Pb^{4+}$  (being a strong oxidant) does not survive in presence of strong reductants  $Br^-$  and  $I^-$  and is immediately reduced to  $Pb^{2+}$ .

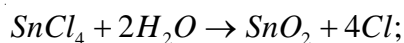
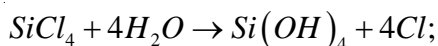
Tetrahalides of Ge, Sn and Pb behave as oxidizing agents and the oxidizing character of  $M^{4+}$  species increases in the order e.g.,



The tetrahalides of carbon; for example, carbon tetrachloride ( $CCl_4$ ) cannot be hydrolysed by water since it cannot expand its coordination number beyond 4 due to the absence of d-orbitals. The tetrachlorides of other elements, i.e.,

$SiCl_4, GeCl_4, SnCl_4$  and  $SiCl_4, GeCl_4, SnCl_4$  are easily hydrolysed and the ease of

hydrolysis follows the sequence  $SiCl_4 < GeCl_4 < SnCl_4 < PbCl_4$ .



Further, the tetrahalides of all the elements except carbon form complexes (due to the presence of vacant d-orbitals in them) when dissolved in halogen acids and thus act as Lewis acids :

- (ii) **Dihalides.** All the elements of group 14 form dihalides of the formula,  $MX_2$  where  $X = F, Cl, Br$  or  $I$ . The stability of these dihalides increases as we move down the group from  $C$  to  $Pb$ . Thus, the dihalides of tin and  $Pb$ , i.e.,  $SnCl_2$  and  $PbCl_2$  are quite stable. Dihalides are generally ionic in nature and behave as reducing agents, the reducing character (of  $M^{2+}$  species) decreases in the order e.g.,  $GeCl_2 > SnCl_2 > PbCl_2$

5. **Formation of oxides :** All the elements of this group form two types of oxides : (i) monoxides and (ii) dioxide

(i) **Monoxides.** All the elements of group 14 form monoxides of the general formula  $MO$ , i.e.,  $CO, SiO, GeO, SnO$  and  $PbO$ . These oxides except  $SiO$  and  $GeO$  are quite stable.  $CO$  is neutral while  $SnO$  and  $GeO$  are amphoteric. Red form of  $PbO$  is called litharge and yellow form is called massicot.

(ii) **Dioxides.** All these elements form dioxides of the general formula,  $MO_2$  i.e.,  $CO_2, SiO_2, GeO_2, SnO_2$  and  $PbO_2$ . All these dioxides can be prepared by heating the elements in oxygen except lead which forms lead monoxide.

$CO_2$  is a monomeric, linear molecule and hence exists as a gas while the dioxides of all other elements are crystalline solids with high melting points.

7. **Silicones.** Silicones are synthetic organosilicon compounds containing repeated  $R_2SiO$  units held by  $Si-O-Si$  linkages. Since the empirical formula  $R_2SiO$  (where  $R = CH_3$  or  $C_6H_5$  group) is similar to that of a ketone ( $R_2CO$ ), the name silicones have been given to these materials.

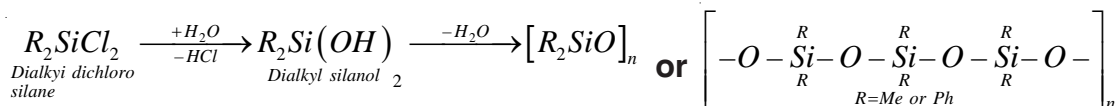
Short chains silicones are oily liquids, medium chains silicones behave as viscous oils, jellies and greases and those with very long chains behave as rubbery elastomers and resins.

Silicones are water repellent, heat resistant, chemically inert, resistant to oxidation and attack by organic acids and good electrical insulators.

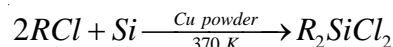
Silicones are used for making water proof papers, wool, textiles, wood, etc., as lubricants at high and low temperatures, as antifoaming agents, as sealants, as surgical and cosmetic implants.

**Preparation.** Silicons are prepared by the hydrolysis of dialkyl or diaryl dichlorosilanes ( $R_2SiCl_2$ ) followed by dehydration of the resultant dialkyl or diaryl

silanol  $[R_2Si(OH)_2]$  compounds where condensation-polymerization occurs on heating. e.g.,



The starting monomers  $R_2SiCl_2$  are industrially manufactured by the direct reaction of RCl with Si at 370 K in the presence of metallic copper as a catalyst.



6. **Oxidation states.** (i) Negative oxidation states. The elements of group 15 contain five electrons ( $ns^2 - np^3$ ) in their valence shell and hence can acquire the nearest gas configuration by gaining three more electrons from more metallic elements to form triply charged negative ions such as nitrides,  $N^{3-}$  and phosphides,  $P^{3-}$  ions. Therefore, the elements of this group show an oxidation state of  $-3$ . However, the tendency of these elements to show  $-3$  oxidation states decreases as we move down the group from N to Bi due to a gradual decrease in the electronegativity and ionization enthalpy.

(ii) Positive oxidation states. The elements of this group also show positive oxidation states such as  $+3$  and  $+5$ . The stability of  $+3$  oxidation state increases while that of  $+5$  decreases as we go down the group. This is due to inert pair effect. The  $+5$  oxidation state in Bi is less stable than in Sb. The only well characterized Bi (V) compound is  $BiF_5$ .

Nitrogen shows  $-1, -2, -3, +1, +2, +3, +4$  and  $+5$  oxidation states in  $NH_2OH$ ,  $N_2H_4$ ,  $NH_3$ ,  $N_2$ ,  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $N_2O_4$  and  $N_2O_5$  respectively.

9. **Catenation**, the property of self linkage which is characteristic of carbon, is also shown by these elements though to a lesser extent. Since the bond energy of P-P bond is very large ( $201 \text{ kJ mol}^{-1}$ ), phosphorus has a distinct tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorus atoms. Nitrogen has little tendency for catenation since  $N-N$  single bond is weak ( $167 \text{ kJ mol}^{-1}$ ) due to repulsion between non bonded electron pairs in a smaller nitrogen atom. As we move down the group, the element-element bond energies decrease rapidly viz. P-P ( $201 \text{ kJ mol}^{-1}$ ), N-N ( $167 \text{ kJ mol}^{-1}$ ), As-As ( $146 \text{ kJ mol}^{-1}$ ) and Sb-Sb ( $121 \text{ kJ mol}^{-1}$ ) and therefore, tendency for catenation decreases in the order  $P > N > As > Sb > Bi$ .

10. **Elemental state.** Because of small size and high electronegativity, nitrogen has a strong tendency to form multiple ( $p\pi - p\pi$ ) bonds but other elements do not form multiple bonds. Thus, nitrogen exists as a diatomic gas in which two nitrogen

atoms are linked by a triple bond (one  $\sigma$  and two  $\pi$ -bonds),  $:N \equiv N:$ . Because of short bond length ( $1.09 \text{ \AA}$ ) and high bond strength ( $946 \text{ kJ mol}^{-1}$ ) nitrogen is inert at ordinary temperature. Other elements of this group do not exist as diatomic molecules due to their reluctance to form multiple bonds. Phosphorus, arsenic and antimony exist as discrete tetraatomic tetrahedral molecules, i.e.,  $P_4$ ,  $As_4$  and  $Sb_4$  in which the four atoms lie at the corners of a regular tetrahedron. Each atom is linked to three other atoms by covalent bonds and the angle between any two adjacent bonds is  $60^\circ$ . There are total six single bonds and four lone pairs of electrons in a  $P_4$  molecule. Theoretically required bond angle is  $90^\circ$  molecule. Theoretically required bond angle is  $90^\circ$  if pure 3 p orbitals are involved. This suggests that the structure is under strain and unstable. The high chemical reactivity of white P is due to this strained nature of  $P_4$  molecule. Bismuth, however, has metallic bonding.

1. **Formation of hydrides.** All the elements of group 15 form volatile hydrides of the type  $MH_3$  i.e., ammonia ( $NH_3$ ), phosphine ( $PH_3$ ), arsine ( $AsH_3$ ), stibine ( $SbH_3$ ), and bismuthine ( $BiH_3$ ). They have a pyramidal structure.

- (i) **Thermal stability** of these hydrides decreases gradually from  $NH_3$  to  $BiH_3$ , i.e.,

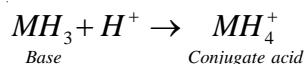


The reason being that as we move down the group, the strength of the M-H bond decreases due to an increase in the atomic size of the element.

- (ii) **Reducing character.** Because of decrease in thermal stability, the tendency of these hydrides to give hydrogen and thus act as reducing agents gradually increases in the order :



- (iii) **Basic character.** The presence of a lone pair of electrons on the central atom M in  $MH_3$  makes these hydrides as Lewis bases.



As the size of the central atom increases, the stability of the conjugate acid decreases and hence the basic character decreases in the order :

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ . Thus  $NH_3$  is distinctly basic.  $PH_3$  is a much weaker base than  $NH_3$  but  $AsH_3$ ,  $SbH_3$  and  $BiH_3$  are not at all basic.

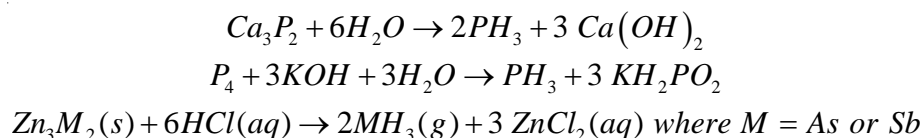
- (iv) **Hydrogen bonding.** Due to small size and high electronegativity of nitrogen,  $NH_3$  forms H-bonds but the other hydrides of this group do not exhibit H-bonding, resulting in high m.P & b.p.

- (v) **Melting points and boiling points.** Due to H-bonding, the m.p. of  $NH_3$  is the

highest amongst the hydrides of group 15 elements and b.p. is higher than  $PH_3$ . As we move from  $NH_3$  to  $PH_3$ , there is a sharp decrease in the m.p. and b.p. of  $PH_3$  as compared to  $NH_3$  due to absence of H-bonding. However, the m.p. and b.p. of the hydrides of rest of the elements increase gradually as we move down the group from  $PH_3$  to  $BiH_3$ . This is due to increase in molecular size resulting in increased van der Waals forces of attraction holding the molecules together. Thus  $PH_3$  has the lowest and  $NH_3$  and  $SbH_3$  has the highest m.p. and b.p. respectively.

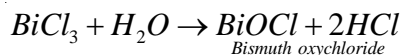
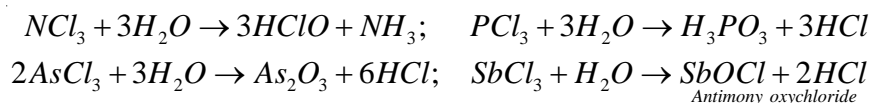
- (vi) Bond angles. The hydrides of group 15 have pyramidal shapes, i.e., the central atom undergoes  $sp^3$ -hybridization. The HNH bond angle in  $NH_3$  is  $107^\circ$ . However, as we move down the group the bond angles gradually decrease due to decrease in bond pair-bond pair repulsion.  $NH_3$  ( $107.8^\circ$ ),  $PH_3$  ( $93.5^\circ$ ),  $AsH_3$  ( $91.8^\circ$ ),  $SbH_3$  ( $91.3^\circ$ ) and  $BiH_3$  ( $90^\circ$ ). Thus, the bond angles show the following trend :  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ .

The hydrides can be prepared by the following reactions :



- (2) **Formation of halides, (a) Trihalides.** All the elements of this group form trihalides of the type  $MX_3$ . All the trihalides of these elements except  $NBr_3$  and  $NI_3$  are stable. The instability of  $NBr_3$  and  $NI_3$  is due to the weakness of N – Br and N – I bonds because of the large size difference between N and the halogens. The stability decreases in the order  $NF_3 > NCl_3 > NBr_3$ . These halides are predominantly covalent in nature and have pyramidal structures (the central atom is  $sp^3$ -hybridized) with a lone pair of electrons in the fourth orbital.  $BiF_3$  and to some extent  $SbF_3$  are ionic. Except  $NF_3$  and  $PF_3$ , the trihalides of these elements are readily hydrolysed by water.

$NF_3$  is not hydrolysed due to lack of vacant d-orbitals in N and F.  $PF_3$  is not hydrolysed due to stronger P – F bond as compared to P – O bond.

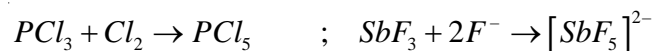


The ease of hydrolysis decreases on moving down the group i.e.,  $NCl_3$  is easily hydrolysed but  $SbCl_3$  and  $BiCl_3$  are partly hydrolysed. Thus ease of

hydrolysis decreases in the order

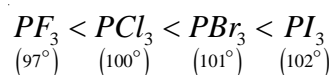


Basic nature. Due to the presence of lone pair of electrons, the trihalides act as Lewis-bases. However,  $NF_3$  has a little tendency to donate a pair of electrons because of the high electronegativity of F. Increasing order of Lewis base strength of trihalides is  $NF_3 < NCl_3 < NBr_3 < NI_3$ . The trihalides of P, As and Sb also behave as Lewis acids by accommodating the additional pair of electrons in the vacant d-orbitals. The Lewis acid strength decreases down the group and increases with the increase in E.N. of the halogen (X).



Thus  $PCl_3 > AsCl_3 > SbCl_3$  and  $PF_3 > PCl_3 > PBr_3 > PI_3$  in Lewis acidic strength.

The bond angle decreases as the E.N. of X in  $PX_3$  increases i.e.



- (b) **Pentahalides.** P, As and Sb also form pentachlorides. Nitrogen, however, does not form pentahalides due to the absence of d-orbitals in its valence shell.

Phosphorus pentaiodide,  $PI_5$ , does not exist probably due to steric factors. Bismuth forms only pentafluoride. The non-existence of pentachloride, bromide and iodide of Bi is probably due to the strongly oxidizing properties of  $Bi^{5+}$  due to inert pair effect.

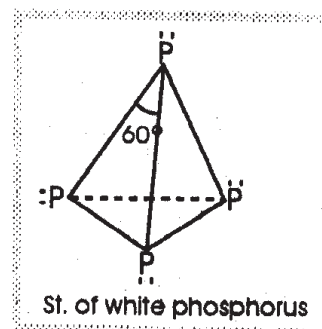
These pentahalides have trigonal bipyramid shapes in the vapour phase involving  $sp^3d$ -hybridization.  $PF_5$  is not hydrolysed because the P–F bond is stronger than P–O covalent bond.  $PCl_5$  is not very stable due to its unsymmetrical (trigonal bipyramidal) shape where some bond angles are of  $90^\circ$  and the others are of  $120^\circ$ . It decomposes to give  $PCl_5 \rightarrow PCl_3 + Cl_2$ . It is due to this reason that  $PCl_5$  behaves as a good chlorinating agent. Solid  $PCl_5$  is an ionic compound consisting of  $[PCl_4]^+$  and  $[PCl_6]^-$  ions. Solid  $PbBr_5$  exists as  $[PbBr_4]^{+Br^-}$ .

3. **Oxides.** All the elements of this group form two types of oxides, i.e.,  $M_2O_3$  and  $M_2O_5$  and are called trioxides and pentoxides.

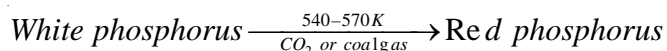
The trioxides of N, P and As are acidic. Their acidic strength decreases in the order  $N_2O_3 > P_2O_3 > As_2O_3$ .

- (c) **Allotropic forms of phosphorus.** Phosphorus exists in three allotropic forms. (i) White (or yellow) phosphorus (ii) Red (or violet) phosphorus and (iii) Black phosphorus.

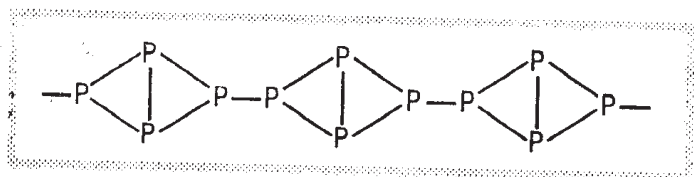
(i) **White or yellow phosphorus.** It is obtained from phosphate rock or phosphorite as explained above. It exists as  $P_4$  units where four P atoms lie at the corners of a regular tetrahedron with  $\angle PPP = 60^\circ$ . Each P atom is linked to three other P atoms by covalent bonds. There are total six bonds and four lone pairs of electrons present in a  $\angle PPP = 60^\circ$  molecule of white phosphorus.



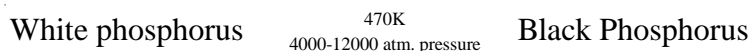
(ii) **Red phosphorus.** It is obtained by heating white phosphorus at 540–570 K out of contact with air in an inert atmosphere ( $CO_2$  or coal gas) for several hours.



Red phosphorus exists as chains of  $P_4$  tetrahedra linked together through covalent bonds to give a polymeric amorphous structure as shown :



(iii) **Black phosphorus.** It is obtained by heating white phosphorus at 470 K under high pressure (4000–12000 atm.) in an inert atmosphere.



It has a double layered structure in which each P is bound to three neighbours by single bonds. Each layer is made up of zig zag chains with P – P – P bond angle of  $99^\circ$ . Since it is highly polymeric, it has high density. It is the most stable (inactive) form of phosphorus and has a black metallic luster. It is a good conductor of heat and electricity.

5. **Electron gain enthalpies.** The elements of group 16 have relatively high electron gain enthalpy values which decrease down the group from S to Po. Oxygen has low electron gain enthalpy. This is due to its small size which makes electron density high and repels the incoming electrons.

Element	O	S	Se	Po
Electron gain enthalpy	-140.9	-200.7	-195.1	-180.0

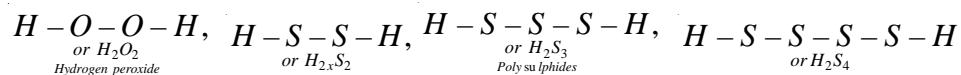
(kJ mol<sup>-1</sup>)

6. **Oxidation states.** Since elements of group 16 have  $n_s^2 n_p^4$  configuration in their valence shell, they can attain noble gas configuration viz.,  $n_s^2 n_p^6$  either by gaining or by sharing electrons. These elements, therefore, show two types of oxidation states.

(i) Negative oxidation states. Oxygen because of its high electronegativity and ionization enthalpy shows an oxidation state of  $-2$  in most of its compounds preferably by gaining electrons in order to complete its octet. Because of this, almost all metal oxides are ionic and contain  $O^{2-}$  ions. However in  $OF_2$ , it shows an oxidation state of  $+2$  and in peroxides ( $H_2O_2$ ,  $Na_2O_2$ ) an oxidation state of  $-1$ . The other elements of this group have less tendency to show  $-2$  oxidation state due to low electronegativity and low ionization enthalpy. The last element, i.e., Po does not show  $-2$  oxidation state at all. Thus, the tendency to show  $-2$  oxidation state (i.e., to form chalcogenide dianions) decreases on moving down the group from S to Po.

(ii) Positive oxidation state. These elements show positive oxidation states of  $+2$ ,  $+4$  and  $+6$ . Oxygen shows only  $+2$  oxidation state (in  $OF_2$ ) but does not show  $+4$  and  $+6$  oxidation states due to absence of d-orbitals in its valence shell. Therefore, oxygen behaves as a divalent element only. Other elements besides  $+2$ , also show oxidation states of  $+4$  and  $+6$  (in their compounds with oxygen and fluorine) due to the presence of vacant d-orbitals in the valence shell. However, as we move down the group, the stability of  $+4$  oxidation state increases while that of  $+6$  oxidation state decreases due to **inert pair effect**. Thus, in Po,  $+4$  oxidation state is more important than  $+6$  oxidation state. Thus S, Se and Te are tetravalent in their typical compounds with oxygen and hexavalent in their compounds with fluorine.

10. **Catenation.** Oxygen has some but sulphur has greater tendency for catenation. Oxygen chains are limited to two atoms as in peroxides but sulphur chains contain upto four atoms as in polysulphides.



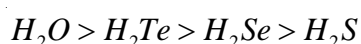
Sulphur possesses the maximum tendency of catenation due to the highest bond strength of S-S bond (O-O = 142, S-S = 226, Se-Se = 172 and Te-Te = 126  $\text{kJ mol}^{-1}$ ). The tendency for catenation decreases markedly as we go down the group from S to Te. Oxygen possesses this property to less extent. The decreasing order of catenation amongst group 16 elements is



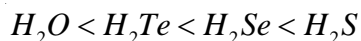
## II. Chemical properties

1. **Formation of hydrides.** All these elements form volatile, stable, bivalent hydrides of the formula  $H_2M$  i.e.,  $H_2O$ ,  $H_2S$ ,  $H_2Se$ ,  $H_2Te$  and  $H_2Po$ . The central atom (M) in these hydrides is  $sp^3$  hybridized. Due to the presence of two lone pairs on the central atom, these have bent (V) shapes.

(i) **Melting points and boiling points.**  $H_2O$  has the highest and  $H_2S$  has the lowest values of melting and boiling points. Their decreasing order is



(ii) **Volatility.** As  $H_2O$  has the highest and  $H_2S$  has the lowest boiling point, the volatility increases abruptly from  $H_2O$  to  $H_2S$  and then decreases from  $H_2S$  to  $H_2Te$ . Thus,  $H_2O$  is least volatile and  $H_2S$  is most volatile hydrides of group 16 elements. Therefore, volatility increases in the order



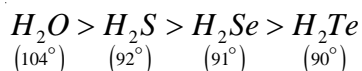
(iii) **Thermal stability** of the hydrides decreases from  $H_2O$  to  $H_2Te$  i.e.

$H_2O > H_2S > H_2Se > H_2Te$ . This is due to the reason that as the size of the central atom in  $H_2M$  increases, the H–M bond becomes weaker and breaks easily on heating.

(iv) **Reducing character.** Hydrides of all these elements except that of oxygen, i.e.  $H_2O$  behave as reducing agents. The reducing character of these hydrides increases as the thermal stability decreases from  $H_2S$  to  $H_2Te$  i.e.

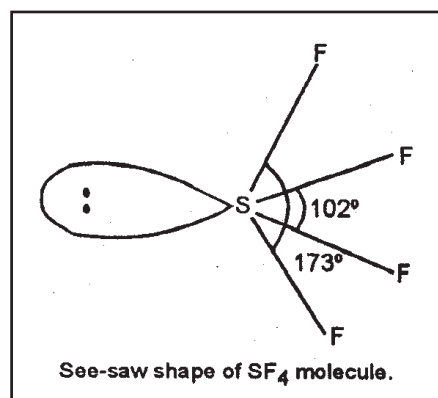


(vii) **Bond angles.** The hydrides of group 16 are V-shaped in which the bond angles decrease on moving down the group as the electronegativity of the central atom decreases from O to TE. Consequently, the bond pairs of electrons move away from the central atom and the bond pair-bond pair repulsion decreases. The bond angles, therefore, decrease in the order



(i) **Hexahalides.** All the elements except oxygen form hexafluorides, i.e.  $SF_6$ ,  $SeF_6$  and  $TeF_6$ . No other halogen forms hexahalides. The hexafluorides have octahedral ( $sp^3d^2$ ) shapes. The stability of these hexafluorides decreases from  $SF_6$  to  $TeF_6$ , i.e.,  $SF_6$  is practically inert,  $SeF_6$  is slightly more reactive while  $TeF_6$  is hydrolysed by water. This is due to the reason that as the size of the atom increases, the polarity of the M – X bond increases and hence the hexafluoride molecule becomes more susceptible to nucleophilic attack by water. Thus, the ease of hydrolysis varies as  $SF_6 < SeF_6 < TeF_6$

(ii) **Tetrahalides.** All the elements except oxygen form tetrafluorides ( $SF_4$ ,  $SeF_4$ , and  $TeF_4$ ) and tetrachlorides ( $SCL_4$ ,  $SeCl_4$ ,  $TeCl_4$ ). These have trigonal bipyramid ( $sp^3d$ ) geometry. As one equatorial position is occupied by a lone pair of electrons which repels the axial bond pairs thereby decreasing the angle from  $180^\circ$  to  $180^\circ$  to  $173^\circ$ , these halides have see-saw shape.



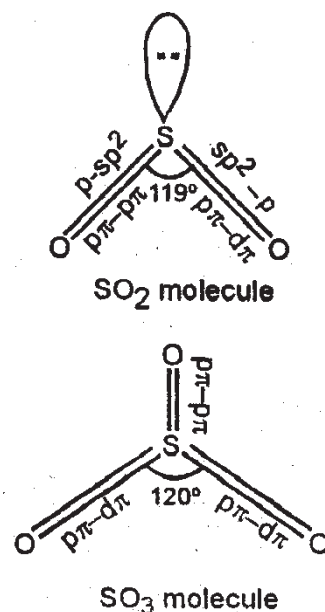
3. **Formation of oxides.** These elements form a variety of oxides in different oxidation states from + 2 to + 6. Some of their important features are listed below :
- (i) The acidic character of oxides of these elements (in the same oxidation state) decreases as we move down the group. Thus  $SO_2$  and  $SeO_2$  are acidic while  $TeO_2$  and  $ToO_2$  are amphoteric. The order varies as  $SO_2 > SeO_2 > TeO_2 > PoO_2$  and  $SO_3 > SeO_3 > TeO_3$

**(a) Sulphur dioxide,  $SO_2$**  is a gas and forms discrete molecules even in the solid state. It is acidic in nature and is also called anhydride of sulphurous acid ( $H_2SO_3$ ). It can act as a reducing agent and also as an oxidising agent. It can also act as a bleaching agent in the presence of a moisture. It bleaches due to reduction and the bleaching action is temporary ( $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$ ). The colour is, however, restored when the bleached article is exposed to air since the oxygen of the air oxidises the colourless compound back to the original coloured substance.  $SO_2$  acts as a Lewis base due to the presence of a lone pair of electrons on S atom. It also acts as a ligand and forms numerous coordination compounds.

$SO_2$  molecule has a bent structure with a O–S–O bond angle of  $119^\circ$ . The  $\sigma$ -bonds between S and O are formed by  $sp^2 - p$  overlap while one of the

$\pi$ -bonds arises from  $p\pi - p\pi$  overlap and the other from  $p\pi - d\pi$  overlap but even then both of the S – O bonds are identical (143 pm) due to resonance.

**(b) Sulphur trioxide,  $SO_3$ .** It is an acidic oxide and is regarded as an anhydride of  $H_2SO_4$ . It acts as an oxidising agent. In the gas phase it exists as planar triangular molecular species involving  $sp^2$ -hybridization of the sulphur atom. It has three S – O  $\sigma$ -bonds formed by  $sp^2 - p$  overlap and three S – O  $\pi$ -bonds, one formed by  $p\pi - p\pi$  overlap and two formed by  $p\pi - d\pi$  overlap. The O–S–O bond angle is of  $120^\circ$  and all S – O bonds are equivalent (142 pm).



## Group - 17 – Elements

4. **Electronegativity.** Fluorine is the most electronegative element in the periodic table. With increase in atomic number down the group, the electronegativity decrease.

Element	F	Cl	Br	I	At
Electronegativity	4.0	3.2	3.0	2.7	2.2

The decreasing order of electronegativity is  $F > Cl > Br > I$

5. Electron gain enthalpy. Electron gain enthalpies of chlorine, bromine and iodine become less negative as the size of the atom increases. The electron gain enthalpy of fluorine is, however, less negative than that of Cl because of its small size as a result of which inter - electronic repulsions present in its 2p-subshell are comparatively large. Thus, chlorine has the highest negative electron gain enthalpy.

Element	F	Cl	Br	I	
Electron gain enthalpy (kJ $mol^{-1}$ )		-333	-349	-325	-296

The decreasing order of negative electron gain enthalpy is  $Cl > F > Br > I$

6. Oxidation states. All the halogens show an oxidation state of -1. Fluorine being the most electronegative element always shows an oxidation state of -1 while other halogens also show positive oxidation states up to a maximum of +7 (i.e. -1, +3, +5, and +7) due to the availability of vacant d-orbitals in the valence shell of these atoms. Some halogens also show +4 and +6 oxidation states in oxides and oxo acids.

10. **Colour.** All the halogens have characteristic colours.  $F_2$  is light yellow,  $Cl_2$  is greenish yellow,  $Br_2$  is reddish brown and  $I_2$  is deep violet. The colour of halogens is due to the reason that their molecules absorb light in the visible region as a result of which electrons are excited to higher energy levels. The amount of energy needed for excitation decreases progressively from  $F_2$  to  $I_2$ . Since, fluorine atom requires large amount of energy for excitation of electrons and therefore absorbs violet light and appears yellow. On the other hand, iodine requires low energy for excitation of electrons (absorbs yellow light) and appears deep violet.

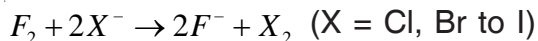
11. **Bond dissociation energy or enthalpy of dissociation.** Bond dissociation energies of chlorine, bromine and iodine decrease down the group as the size of the atom increases. The bond dissociation energy of fluorine, is however, lower than those of chlorine and bromine because of inter electronic repulsions present in the small atom of fluorine

$X_2$	$F_2$	$Cl_2$	$Br_2$	$I_2$
Bond dissociation energy (kJ $mol^{-1}$ )	158.8	242.6	192.8	151.1

Hence bond energy decreases in the order  $Cl_2 > Br_2 > F_2 > I_2$

15. Oxidising power. All the halogens act as strong oxidising agents since they have a strong tendency to attract electrons and have positive values of electrode potential ( $E^\circ$ ). The oxidising power, however, decreases as we move down the group from F to I. i.e.  $F_2 > Cl_2 > Br_2 > I_2$ .

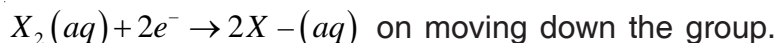
Since  $F_2$  is the strongest oxidising agent, it will oxidise all other halide ions to halogens in solution or even in the solid phase.



Similarly,  $Cl_2$  will displace  $Br^-$  and  $I^-$  ions from their solutions while  $Br_2$  will displace  $I^-$  ions only.



Hence  $F_2$  is the strongest and  $I_2$  is the weakest oxidising agent. This is also indicated by the decrease in the electrode potential ( $E^\circ$ ) for the reaction



2. **Formation of halides.** Halogens combine with all the elements except He, Ne and Ar forming a large number of binary halides.

(a) **Halides of metals.** (i) There is a regular gradation from ionic to covalent bonding as the atomic number of the halogen increases for the same metal atom (M).

The ionic character of M–X bond and m.p. and b.p. of halides decrease in the order  $M - F > M - Cl > M - Br > M - I$ .

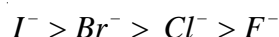
(ii) Metals of low ionization enthalpies such as alkali metals form ionic halides whereas metals with high ionization enthalpies such as transition metals form covalent halides. Molecular halides show decrease in m.p. and b.p. as  $MI > MBr > MCl > MF$ .

(iii) Halides of metals in their higher oxidation states are more covalent than those formed in lower oxidation states. For example,  $SnCl_4$  is more covalent than  $SnCl_2$ ;  $PbCl_4$ ,  $SbCl_5$  are more covalent than  $PbCl_2$  and  $SbCl_3$  respectively. Less ionic halides such as AgX show the solubility trends as  $AgI < AgBr < AgCl < AgF$  in water.

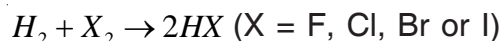
(b) **Halides of non-metals.** (i) Halides of non-metals are generally covalent in nature.

(ii) The strength of M–X bond for a particular non metal (M) decreases in the order  $M - F > M - Cl > M - Br > M - I$ . Thus for hydrogen halides HX, the bond strength of H–X bond decreases from HF to HI as the atomic size of the halogen increases from F to I i.e.  $H - F > H - Cl > H - Br > H - I$ .

(c) **Reducing character of halides.** The halide ions ( $X^-$ ) behave as reducing agents and their reducing power decreases in the order.



3. **Hydrogen halides.** All the halogens combine directly with hydrogen to form covalent molecular but their reactivity progressively decreases from fluorine to iodine.



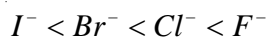
Aqueous solutions of hydrogen halides are known as hydrohalic acids.

(ii) **Thermal stability** of the hydrogen halides decrease from HF to HI i.e.,

HF > HCl > HBr > HI. This is due to the reason that as the size of the halogen increases from F to I, the bond dissociation energy decreases.

HX	HF	HCl	HBr	HI
$\Delta_{diss}H(kJ mol^{-1})$	574	432	363	295

(iii) **Acidic strength.** The acidic strength of hydrogen halides from HI to HF i.e., HI > HBr > HCl > HF. This is due to the reason that as the size of halogen increases, H–X bond becomes weaker and hence breaks easily to spilt off a proton. The conjugate base strength of these acids increases in the order

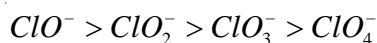


as the charge density on the anion increases : The  $pK_a$  values of HX are

HX	HF	HCl	HBr	HI
$pK_a$	3.2	-7.0	-9.5	-10.0

5. **Oxoacids of halogens.** Fluorine forms only one oxoacid HOF since it is the strongest oxidising agent Chlorine, bromine and iodine mainly form four series of oxoacids – namely **halic (I) acid** or hypohalous acid (HOX), **halic (III) acid** or halous acid (HOXO), **halic (V) acid** or halic acid ( $HOXO_2$ ) and perhalic acid ( $HOXO_3$ ).

(ii) **Acidic character.** All these acids are monoprotic containing an – OH group. The acidic character of the oxoacids increases with increase in oxidation number of the halogen, i.e.,  $HClO < HClO_2 < HClO_3 < HClO_4$



Oxoacids	$HOCl$	$HOClO$	$HOClO_2$	$HOClO_3$
$pK_a$	7.5	2.0	-1.2	-10

(iii) **Oxidising power and thermal stability.** The oxidising power of these acids decreases as the oxidation number of the halogen increases, i.e.,

$HClO > HClO_2 > HClO_3 > HClO_4$ . This is due to the reason that as the oxidation number increases, the halogen-oxygen bond becomes more covalent. As a result, the thermal stability increases. Thus, hypohalites are stronger oxidising agents than perhalates.

7. **Interhalogen compounds.** The compounds of one halogen with the other are called interhalogens or interhalogen compounds. The main reason for their formation is the large electronegativity and the size differences between the different halogens. Taking A as the less electronegative and B as the more electronegative halogen, they are divided into the following four types the less electronegative halogen (A) is always written first.

# MOCK TEST

## UNIT – 15

31. Borax is used as a cleansing agent because on dissolving in water, it gives :-  
(a) alkaline solution      (b) acidic solution  
(c) bleaching solution      (d) amphoteric solution
32. A metal, M forms chlorides in +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?  
(a)  $MCl_2$  is more volatile than  $MCl_4$ .  
(b)  $MCl_2$  is more soluble in anhydrous ethanol than  $MCl_4$ .  
(c)  $MCl_2$  is more ionic than  $MCl_4$ .  
(d)  $MCl_2$  is more easily hydrolysed than  $MCl_4$ .
35.  $Al_2O_3$  can be converted to anhydrous  $AlCl_3$  by heating :-  
(a)  $Al_2O_3$  with  $Cl_2$  gas  
(b)  $Al_2O_3$  with HCl gas  
(c)  $Al_2O_3$  with NaCl in solid state  
(d) a mixture of  $Al_2O_3$  and carbon in dry  $Cl_2$  gas.
38. Which of the following statements about diborane is not true?  
(a) the B atoms in it are  $sp^3$ -hybridized  
(b) it contains two 3-centre-2-electron bonds  
(c) All B–H bond lengths are equal due to resonance  
(d) the molecule is non-planar  
(e) the molecule contains 12 valence electrons
39. Which is strongest Lewis acid?  
(a)  $BF_3$                       (b)  $BCl_3$   
(c)  $BBr_3$                       (d)  $BI_3$
42. Which of the following is not true?  
(a) Among halide ions, iodide ion is the most powerful reducing agent  
(b) Fluorine is the only halogen which does not show a variable oxidation state  
(c) HOCl is a stronger acid than HOBr

- (d) HF is a stronger acid than HCl.
45. Which of the following are isoelectronic and isostructural?  $NO_3^-$ ,  $CO_3^{2-}$ ,  $ClO_3^-$ ,  $SO_3$
- (a)  $NO_3^-$ ,  $CO_3^{2-}$       (b)  $SO_3$ ,  $NO_3^-$   
 (c)  $ClO_3^-$ ,  $CO_3^{2-}$       (d)  $CO_3^{2-}$ ,  $SO_3$
50. Total number of lone pair of electrons in  $XeOF_4$  is
- (a) 0                              (b) 1  
 (c) 2                              (d) 3
51. The acid having O–O bond is
- (a)  $H_2S_2O_3$                       (b)  $H_2S_2O_6$   
 (c)  $H_2S_2O_8$                       (d)  $H_2S_4O_6$
54. The shape of  $O_2F_2$  is similar to that of
- (a)  $O_2F_2$                               (b)  $H_2O_2$   
 (c)  $H_2F_2$                               (d)  $C_2H_2$
56. Among the following, the pair in which the two species are not isostructural is
- (a)  $SiF_4$  and  $SF_4$       (b)  $IO_3^-$  and  $XeO_3$   
 (c)  $BH_4^-$  and  $NH_4^+$       (d)  $PF_6^-$  and  $SF_6$
58. The ONO angle is maximum in
- (a)  $NO_3^-$                               (b)  $NO_2^-$   
 (c)  $NO_2$                               (d)  $NO_2^+$
60. The correct order of bond angles (smallest first) in  $H_2S$ ,  $NH_3$ ,  $BF_3$  and  $SiH_4$  is
- (a)  $H_2S < SiH_4 < NH_3 < BF_3$   
 (b)  $NH_3 < H_2S < SiH_4 < BF_3$   
 (c)  $H_2S < NH_3 < SiH_4 < BF_3$   
 (d)  $H_2S < NH_3 < BF_3 < SiH_4$

64. Among  $Al_2O_3$ ,  $SiO_2$ ,  $P_2O_3$  and  $SO_2$ , the correct order of acid strength is
- (a)  $SO_2 < P_2O_3 < SiO_2 < As_2O_3$
  - (b)  $SiO_2 < SO_2 < As_2O_3 < P_2O_3$
  - (c)  $As_2O_3 < SiO_2 < SO_2 < P_2O_3$
  - (d)  $As_2O_3 < SiO_2 < P_2O_3 < SO_2$
68. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?
- (a)  $F < Cl < O < S$
  - (b)  $S < O < Cl < F$
  - (c)  $O < S < F < Cl$
  - (d)  $Cl < F < S < O$

## Unit - 16

### The d - and f - block Elements

3. **Melting and boiling points.** These metals have very high melting and boiling points due to stronger metallic bonding. The melting points of the transition elements first rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points.

In a particular series, the metallic bond strength increases upto the middle with increasing number of unpaired electrons. Thus Cr, Mo and W have maximum number of unpaired d-electrons and have highest melting points in their respective series. Tungsten has the highest melting point (3683 K) among the d-block elements.

As there are no unpaired electrons in Zn, Cd and Hg, they have low melting points. Hg is liquid at ordinary temperature with lowest melting point (234 K) among the transition metals.

5. **Ionization enthalpies.** The first ionization enthalpies of d-block elements are higher than those of s-block elements and are lesser than those of p-block elements. The ionization enthalpies of 3 d and 4 d-series are irregular but increase across the series while those of 5 d-series are much higher than 3 d and 4 d-elements. This is because of the weak shielding of nucleus by 4 f electrons in 5 d-transition series which results in greater effective nuclear charge acting on the outer valence electrons.

7. **Electrode potentials and reducing character.** Quantitatively the stability of transition metal ions in different oxidation states in solution 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 more stable is the oxidation state of the transition metal ion in aqueous solution. Electrode potential values depend upon energy of sublimation of the metal, the ionization enthalpy and the hydration enthalpy.

8. **Oxidation states.** All transition elements except the first and the last member in each series show variable oxidation states. This is because difference of energy in the (n-1) d and ns orbitals is very little. Hence electrons from both the energy levels can be used for bond formation.

(i) **The highest oxidation states** of transition metals are found in fluorides and oxides since fluorine and oxygen are the most electronegative elements. The highest oxidation state shown by any transition elements is + 8. Both Os and Ru show + 8 oxidation states but the most stable oxidation state is of Os in  $OsO_4$ . Manganese shows + 7 highest oxidation state in  $MnO_4^-$ .

(iv) Higher oxidation states are stabilized by atoms of high electronegativity like O or F whereas lower oxidation states (zero or + 1) are stabilized by ligands which can accept electrons from the metal through  $\pi$ -bonding (such as CO).

(v) In going down a group, the stability of higher oxidation states increases while

that of lower oxidation states decreases.

(vii) The relative stability of different oxidation states of transition metal atoms with respect to oxidation can be determined with the help of standard electrode potential data. For example,  $E^\circ$  values for the couples  $Cr^{3+}/Cr^{2+} = -0.41$  volt and  $Cr^{3+}/Cr^{2+} = -0.41$  volts suggest that  $Cr^{2+}$  is unstable and is oxidised to  $Cr^{3+}$  (which is more stable) and acts as a reducing agent whereas  $Mn^{3+}$  is unstable and is reduced to  $Mn^{2+}$  (which is more stable) and acts as an oxidising agent. It may be noted that both  $Cr^{2+}$  and  $Mn^{3+}$  are  $d^4$  species.

9. **Catalytic properties.** Many transition metals (like Co, Ni, Pt, Fe, Mo etc) and their compounds are used as catalysts because of the following reasons :

(i) Because of variable oxidation states, they easily absorb and re-emit wide range of energies to provide the necessary activation energy.

(ii) Because of variable oxidation states, they easily combine with one of the reactants to form an intermediate which reacts with the second reactant to form the final products.

10. **Coloured ions.** Most of the transition metal compounds are coloured both in the solid state and in aqueous solution. This is because of the presence of incompletely filled d-orbitals. When a transition metal compound is formed the degenerate d-orbitals of the metal split into two sets, one (having three orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  called  $t_{2g}$  orbitals) with slightly higher energy in an octahedral field. This is called crystal field splitting.

When white light falls on these compounds, some wavelength is absorbed for promotion of electrons from one set of lower energy orbitals to another set of slightly higher energy within the same d-subshell. This is called d-d transition. The remainder light is reflected which has a particular colour.

Colours of  $Cr_2O_7^{2-}$ ,  $CrO_4^{2-}$ ,  $MnO_4^-$ ,  $MnO_4^{2-}$ ,  $Cu_2O$  are due to charge transfer transitions.

Compounds of s and p-block elements are generally white as high energy is required for promotion of s and p-electrons of incomplete subshells.

11. **Magnetic properties.** Due to the presence of unpaired electrons in the  $(n-1)$  d-orbitals, the most of the transition metal ions and their compounds are paramagnetic i.e., they are attracted by the magnetic field. As the number of unpaired electrons increases from 1 to 5, the magnetic moment and hence paramagnetic character also increases. Those transition elements which have paired electrons are diamagnetic i.e., they are repelled by the magnetic field. Metals like Fe, Co and Ni possess very high (special type) of paramagnetism where they obtain permanent magnetic moment and are referred to as ferromagnetic Alnico which is an alloy of Al, 12%, Ni, 20%, Co, 50% and rest Fe is used to make permanent magnets.

The magnetic moment is expressed in Bohr magnetons (B.M.)

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

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

The magnetic moment of any species depends upon the sum of orbital and spin contributions for each unpaired electron present. In transition metal ions, the orbital magnetic moment is largely suppressed or quenched by the electrostatic field of other atoms, ions or molecules surrounding the metal ion. Thus the effective magnetic moment arises mainly from the spin of electrons.

A paramagnetic substance is characterised by its effective magnetic moment ( $\mu_{eff}$ ) which is given by the expression  $\mu_{eff} = \sqrt{n(n+2)} B.M.$

where  $n$  is the number of unpaired electrons and B.M. stands for Bohr magneton.

12. **Complex formation.** Transition metal ions form a large number of complexes in which the central metal ion is linked to a number of ligands. This is because of the following characteristic properties of transition metals :

(i) They have high nuclear charge and small size i.e. charge/size ratio (charge density) is large.

(ii) They have empty d-orbitals to accept the lone pairs of electrons donated by the ligands.

Thus in complexes metal ions behave as Lewis acids and ligands behave as Lewis bases.

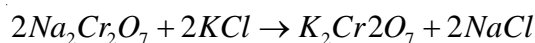
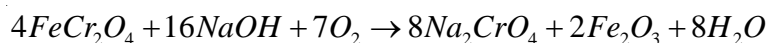
13. **Interstitial compounds.** Transition metals form a number of interstitial compounds in which small non-metal atoms such as H, C, B, N and He occupy the empty spaces (interstitial sites) in their lattices and also form bonds with them.

14. **Alloy formation.** Due to similarity in atomic sizes, atoms of one transition metal can easily take up positions in the crystal lattice of the other in the molten state and are miscible with each other forming solid solutions and smooth alloys on cooling. Alloys are generally harder, have higher melting points and more resistant to corrosion than the individual metals.

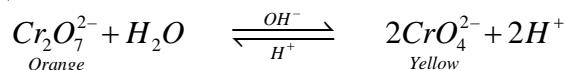
11. **Some more compounds of transition elements**

**(1) Potassium dichromate ( $K_2Cr_2O_7$ )**

**Preparation.** It is prepared from chromite ore ( $FeCr_2O_4$  or  $FeO.Cr_2O_3$ ) through the following reactions :

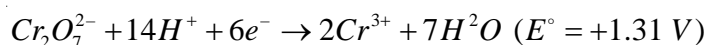


(ii) In the solution, dichromate ions ( $Cr_2O_7^{2-}$ ) exist in equilibrium with chromate ions ( $CrO_4^{2-}$ ) as follows :



In alkaline solution, equilibrium shifts in the forward direction and the solution is yellow. In the acidic medium, equilibrium shifts in the backward direction and the solution is orange. This conversion takes place with change in  $pH$  of the solution.

In other words  $Cr_2O_7^{2-}$  ion takes up electrons and hence acts as an oxidising agent

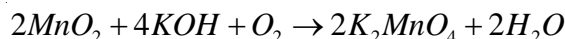


In this reaction Cr (+6) is reduced to Cr (+3)

Therefore, equivalent weight of  $K_2Cr_2O_7$  is one sixth the molecular mass of  $K_2Cr_2O_7$  i.e.,  $294/6 = 49$ .

## (2) Potassium permanganate ( $KMnO_4$ )

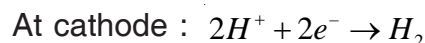
**Preparation.** It is prepared from pyrolusite ore ( $MnO_2$ ) through the following reactions :



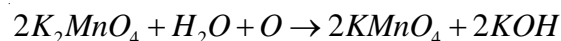
$K_2MnO_4$  undergoes disproportionation in a neutral or acid medium to give  $KMnO_4$ .



(b) Electrolytic oxidation. This is the most preferred method. The manganate solution is electrolysed between iron electrodes separated by diaphragm. The electrode reactions are as follows :



The oxygen evolved at the anode converts manganate to permanganate



The solution is filtered and evaporated to get deep purple black crystals of  $KMnO_4$ .

**Note :-** Refer to NCERT Test Book XII class, Part I page No. for oxidising action of  $K_2Cr_2O_7$  and  $KMnO_4$ .

## 12. Lanthanoids and Actinoids

(a) **Lanthanoids.** The elements with atomic numbers 58 to 71 i.e. cerium to

lutetium (which come immediately after lanthanum  $Z = 57$ ) are called **lanthanoids** or **lanthanides** or **lanthanones** or **rare earths**. These elements involve the filling of 4f-orbitals. Their general electronic configuration is  $[Xe]4f^{1-14}5d^{0-1}6s^2$

Promethium (Pm), At. No. 61 is the only synthetic (man made) radioactive lanthanide.

Because La closely resembles the lanthanoids, it is also included among the lanthanoids for which the general symbol Ln is often used.

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

# MOCK TEST

## UNIT – 16

105.  $MnO_4^{2-}$  (1 mole) in neutral aqueous medium dis-proportionates to
- (a)  $2/3$  mole of  $MnO_4^-$  and  $1/3$  mole of  $MnO_2$
  - (b)  $1/3$  mole of  $MnO_4^-$  and  $2/3$  mole of  $MnO_2$
  - (c)  $1/3$  mole of  $Mn_2O_7$  and  $1/3$  mole of  $MnO_2$
  - (d)  $2/3$  mole of  $Mn_2O_7$  and  $1/3$  mole of  $MnO_2$
109. Lanthanide contraction is due to increase in
- (a) Shielding by 4 f electrons
  - (b) Atomic number
  - (c) Effective nuclear charge
  - (d) Size of 4 f-orbital
112. The basic character of the transition metal monoxide follows the order
- (a)  $VO > CrO > TiO > FeO$
  - (b)  $CrO > VO > FeO > TiO$
  - (c)  $TiO > FeO > VO > CrO$
  - (d)  $TiO > VO > CrO > FeO$
114. When  $MnO_2$  is fused with KOH, a coloured compound is formed. The product and its colour is
- (a)  $K_2MnO_4$ , purple green
  - (b)  $KMnO_4$ , purple
  - (c)  $K_2MnO_4$  brown
  - (d)  $Mn_2O_4$ , black
115. Lanthanoids are
- (a) 14 elements in the sixth period (atomic number 90 to 103) that are filling 4f sub level.
  - (b) 14 elements in the seventh period (atomic number 90 to 103) that are filling 5f subshell.
  - (c) 14 elements in the sixth period (atomic number 58 to 71) that are filling the 4f subshell.
  - (d) 14 elements in the seventh period (atomic number 58 to 71) that are filling the 4f subshell.

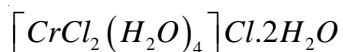
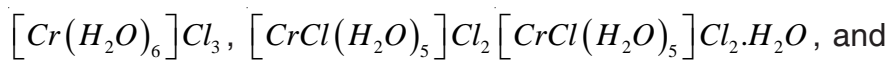
116. The product of oxidation of  $I^-$  with  $MnO_4^-$  in alkaline medium is  
 (a)  $IO_3^-$       (b)  $I_2$       (c)  $IO^-$       (d)  $IO_4^-$
117. Cerium ( $Z = 58$ ) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?  
 (a) The common oxidation states of cerium are + 3 and + 4.  
 (b) The + 3 oxidation state of cerium is more stable than + 4 oxidation state.  
 (c) The + 4 oxidation state of cerium is not known in solutions.  
 (d) Cerium (IV) acts as an oxidizing agent.
118. Lanthanides and actinides resemble in  
 (a) electronic configuration      (b) oxidation state  
 (c) ionization energy      (d) formation of complexes
122. For decolorization of 1 mole of  $KMnO_4$ , the moles of  $H_2O_2$  required is  
 (a) 1/2      (b) 3/2      (c) 5/2      (d) 7/2
124. The value of 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is  
 (a)  $d^4$  (in strong ligand field)  
 (b)  $d^4$  (in weak ligand field)  
 (c)  $d^3$  (in weak as well as strong fields)  
 (d)  $d^5$  (in strong ligand field)
125. Which of the following factor may be regarded as the main cause of lanthanide contraction?  
 (a) Poor shielding of one of the 4 f-electrons by another in the subshell.  
 (b) Effective shielding of one of the 4 f-electrons by another in the subshell.  
 (c) Poorer shielding of 5 d electrons by 4 f-electrons by another in the subshell.  
 (d) Greater shielding of 5 d electrons by 4 f-electrons.
126. The aqueous solution containing which one of the following ions will be colourless?  
 (a)  $Fe^{2+}$       (b)  $Mn^{2+}$       (c)  $Ti^{3+}$       (d)  $Sc^{3+}$
127. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionization enthalpy?  
 (a) Vanadium ( $Z = 23$ )      (b) Manganese ( $Z = 25$ )

## Unit - 17

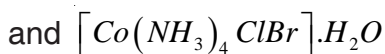
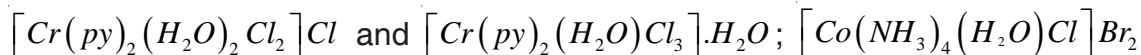
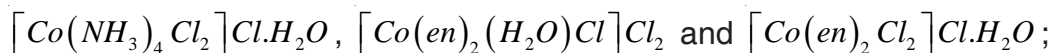
### Coordination Compounds

(i) **Ionization isomerism.** This isomerism results when compounds with same molecular formula give different ions in the solution e.g.  $[CoBr(NH_3)_5]^{2+} SO_4^{2-}$  and  $[CoSO_4(NH_3)_5]^{+Br^-}$ . Here counter ion itself is a potential ligand.

(ii) **Hydrate isomerism.** It arises when some ligand  $H_2O$  molecules become water of hydration outside the coordination sphere. i.e., here water forms a part of the coordination entity or is outside it. For example, there is three hydrate isomers of the formula  $CrCl_3.6H_2O$  as shown below :

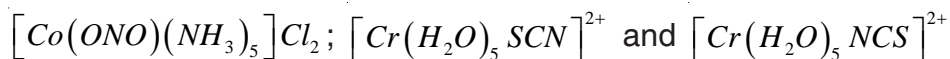


Other examples of hydrate isomerism are :  $[Co(NH_3)_4 H_2O Cl]Cl_2$  and

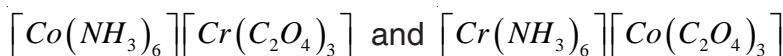


(iii) **Linkage isomerism.** This isomerism results when a monodentate ligand has two possible atoms and attaches in two ways to the central metal atoms i.e., a ligand can ligate. Some common examples of such ligands are : nitro ( $-NO_2^-$ ) and nitrito ( $-ONO^-$ ), cyano ( $-CN^-$ ) and isocyano ( $-NC^-$ ), thiocyanato ( $-SCN^-$ ) and isothiocyanato ( $-NCS^-$ ), cyanato ( $-OCN^-$ ) and isocyanato ( $-NCO^-$ ).

Some examples of linkage isomers are :  $[Co(NO_2)(NH_3)_5]Cl_2$  and



(iv) **Coordination isomerism.** This type of isomerism is shown by compounds in which both cation as well as anion are complexes (coordination entities) and ligands may interchange their positions between the two complex ions. For example.



(i) **Geometrical isomerism.**

(a) **Isomerism in complexes with coordination number 4.** Tetrahedral complexes do not show geometrical isomerism because the relative position of the atoms with respect to each other will be the same. The square planar complexes on the other hand, show this kind of isomerism as discussed below : Square planar complexes of the type  $MA_2X_2$ ,  $MA_2XY$ ,  $MA_2BX_2$  and  $MABXY$  (where A).

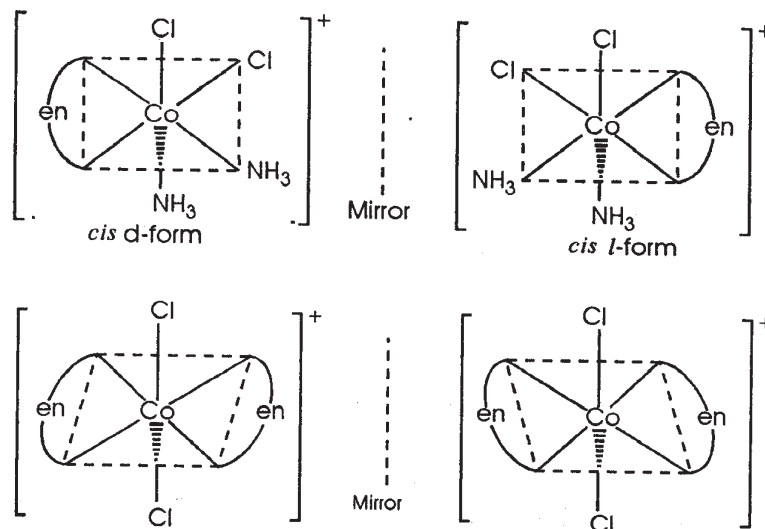
(b) **Isomerism in complexes with coordination number 6.** Octahedral complexes of the type  $MA_4X_2$ ,  $MA_3X_3$ ,  $MA_4XY$  exist as cis and trans isomers. Common examples are :  $[Co(NH_3)_4Cl_2]$ ,  $[Co(NH_3)_4Cl(NO_2)]$

Complexes of the type  $M(AA)_2X_2$  and  $M(AA)_2XY$  can also show cis-trans isomerism (Here (AA) refers to symmetrical bidentate ligands and X and Y refer to anionic ligands. Common examples are :  $Co en_2Cl_2$ ,  $Ni ox_2Cl_2$  etc.

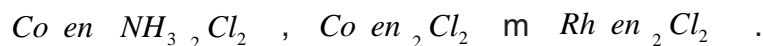
(ii) **Optical isomerism.** Chiral molecules i.e. molecules which do not have plane of symmetry exhibit optical isomerism. The optically active isomers called enantiomers or enantiomorphs are non super imposable mirror images of each other and rotate the plane of polarised light equally but in opposite directions i.e. left called laevorotatory (*l*) or (–) and right called dextrorotatory (*d*) or (+). Complexes with coordination number 6 having chelating ligands show this kind of isomerism. A 1:1 equilibrium mixture of *d* and *l* isomers gives a **racemic mixture** with a net zero rotation.

The optical isomers of a compound have **identical** physical and chemical properties.

(b) **Isomerism in complexes with coordination number 6.** Octahedral complexes of the type  $M(AA)X_2Y_2$ ,  $M(AA)_2X_2$  and  $M(AA)_2XY$  where (AA) is symmetrical bidentate ligand and X and Y are monodentate ligands can be resolved into a pair of enantiomers. As seen earlier, the complexes of these types show geometrical isomerism i.e. exist as cis and trans isomers. The trans isomer does not show optical isomerism since it is symmetrical while only cis isomer shown optical activity as it is unsymmetrical. Thus total three isomers may be possible in such cases.



Some common examples of the above type of complexes are :



- (ii) **Valence bond theory (VBT).** This theory, put forward by Linus Pauling (1931), is used to explain the shapes of complexes and relation between the observed magnetic behaviour and the bond type. It involves the hybridization of empty non equivalent orbitals of the metal atom/ion, each of which then can accept a lone pair of electrons donated by the ligands. The shape is octahedral, tetrahedral, square, planar, trigonal bipyramidal (or square pyramidal) or linear when hybridization is  $d^2sp^3$ ,  $sp^3$ ,  $dsp^2$ ,  $dsp^3$  or  $sp$  respectively.

**Complexes of some transition metal ions/atoms on the basis of V.B. Theory.**

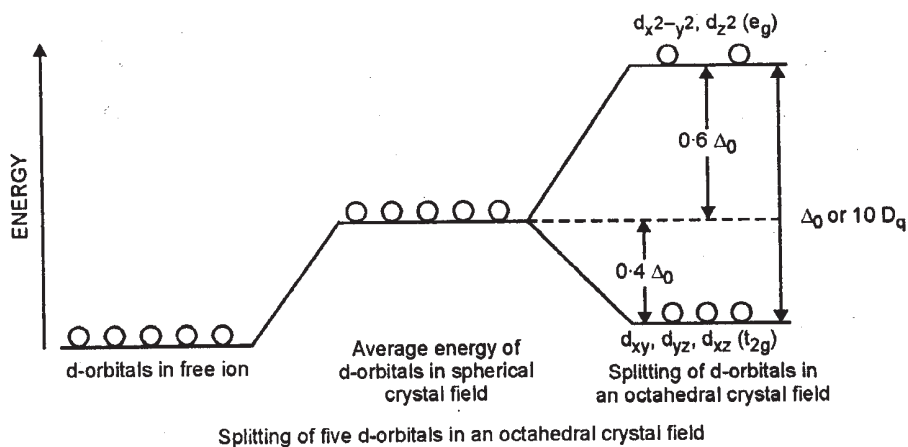
Complex	Metal ion atom	Electron distribution						Type of Hybridisation	No. of unpaired
		3s	3p	3d	4s	4p	4d		
$V(H_2O)_6^{3+}$	$V^{3+}$	2	6	2				$d^2sp^3$	2
$Cr(NH_3)_6^{3+}$	$Cr^{3+}$	2	6	3				$d^2sp^3$	3
$Mn(CN)_6^{3-}$	$Mn^{3+}$	2	6	4 (1e <sup>-</sup> pairs up)				$d^2sp^3$	2
$Fe(CN)_6^{3-}$	$Fe^{3+}$	2	6	5 (2e <sup>-</sup> pair up)				$d^2sp^3$	1
$Fe(CN)_6^{4-}$	$Fe^{2+}$	2	6	6 (2e <sup>-</sup> pair up)				$d^2sp^3$	0
$FeF_6^{3-}$	$Fe^{3+}$	2	6	5				$sp^3d^2$	5
$Co(NH_3)_6^{3+}$	$Co^{3+}$	2	6	6 (2e <sup>-</sup> pair up)				$d^2sp^3$	0
$CoF_6^{3-}$	$Co^{3+}$	2	6	6				$sp^3d^2$	4
$Ni(CN)_4^{2-}$	$Ni^{2+}$	2	6	8 (1e <sup>-</sup> pairs up)				$dsp^2$	0
$Ni(CO)_4$	Ni	2	6	8	2 (jump to 3d)			$sp^3$	0
$Cu(NH_3)_2^+$	$Cu^+$	2	6	10				$sp$	0
$Cu(NH_3)_4^{2+}$	$Cu^{2+}$	2	6	8	0	1	0	$dsp^2$	1
								(1e <sup>-</sup> promoted to 4p)	
$Cu(CN)_4^{3-}$	$Cu^+$	2	6	10				$sp^3$	0
$Zn(NH_3)_4^{2+}$	$Zn^{2+}$	2	6	10				$sp^3$	0
$Cr(CN)_6^{3-}$	$Cr^{3+}$	2	6	3				$d^2sp^3$	3

Cr H <sub>2</sub> O <sub>6</sub> <sup>3+</sup>	Cr <sup>3+</sup>	2	6	3		d <sup>2</sup> sp <sup>3</sup>	3
Co CN <sub>6</sub> <sup>3-</sup>	Co <sup>3+</sup>	2	6	6 (2e <sup>-</sup> pair up)		d <sup>2</sup> sp <sup>3</sup>	0
Co NO <sub>2</sub> <sub>6</sub> <sup>3-</sup>	Co <sup>3+</sup>	2	6	6 (2e <sup>-</sup> pair up)		d <sup>2</sup> sp <sup>3</sup>	0
Co NH <sub>3</sub> <sub>6</sub> <sup>2+</sup>	Co <sup>2+</sup>	2	6	6	0 0 0	d <sup>2</sup> sp <sup>3</sup>	1
(2e <sup>-</sup> pair up, 1e <sup>-</sup> promoted to 4d)							
Ni NH <sub>3</sub> <sub>6</sub> <sup>2+</sup>	Ni <sup>2+</sup>	2	6	8		sp <sup>3</sup> d <sup>2</sup>	2
Fe H <sub>2</sub> O <sub>6</sub> <sup>2+</sup>	Fe <sup>2+</sup>	2	6	6		sp <sup>3</sup> d <sup>2</sup>	4
Fe NH <sub>3</sub> <sub>6</sub> <sup>2+</sup>	Fe <sup>2+</sup>	2	6	6		sp <sup>3</sup> d <sup>2</sup>	4
Cu NH <sub>3</sub> <sub>6</sub> <sup>2+</sup>	Cu <sup>2+</sup>	2	6	9		sp <sup>3</sup> d <sup>2</sup>	1
MnF <sub>6</sub> <sup>3-</sup>	Mn <sup>3+</sup>	2	6	4		sp <sup>3</sup> d <sup>2</sup>	4
Ni H <sub>2</sub> O <sub>6</sub> <sup>2+</sup>	Ni <sup>2+</sup>	2	6	8		sp <sup>3</sup> d <sup>2</sup>	2
NiCl <sub>4</sub> <sup>2-</sup>	Ni <sup>2+</sup>	2	6	8		sp <sup>3</sup>	2
Ni NH <sub>3</sub> <sub>4</sub> <sup>2+</sup>	Ni <sup>2+</sup>	2	6	8		sp <sup>3</sup>	2
FeCl <sub>4</sub> <sup>-</sup>	Fe <sup>3+</sup>	2	6	5		sp <sup>3</sup>	5
MnCl <sub>4</sub> <sup>2-</sup>	Mn <sup>2+</sup>	2	6	5		sp <sup>3</sup>	5
Pt NH <sub>3</sub> <sub>2</sub> Cl <sub>2</sub>	Pt <sup>2+</sup>	5s <sup>2</sup>	5p <sup>6</sup>	5d <sup>8</sup> (1 e <sup>-</sup> pairs up)		dsp <sup>2</sup>	0
CuCl <sub>4</sub> <sup>2-</sup>	Cu <sup>2+</sup>	2	6	9		sp <sup>3</sup>	1

(iii) **Crystal Field Theory (CFT).** Crystal field theory is based on the assumption that the metal ion and the ligands act as point charges and the interaction between them is purely electrostatic, i.e., metal-ligand bonds are 100% ionic. The five d-orbitals in an isolated gaseous metal atom/ion are degenerate. This degeneracy is maintained in a spherically symmetrical field of negative charges.

However, when this negative field is due to real ligands in a complex, the degeneracy of the d-orbitals is lifted due to asymmetrical field. This results in splitting of the d-orbital energies. The pattern of splitting depends upon (a) nature of the crystal field such as octahedral, tetrahedral or square planar and (b) basic strength of ligands.

1. **Crystal field effects in octahedral coordination entities.** In an octahedral complex, the six ligands approach the central metal atom lying at the origin symmetrically **along** the cartesian axes. Initially, there is an increase in the energy of d-orbitals relative to that of the free ion (just like that in a spherical field). Next, the orbitals lying along the axes ( $d_{xy}$  and  $d_{xz}$ ) which are lowered in energy relative to the average energy in the spherical crystal field as shown below :



This splitting of five degenerate d-orbitals of the metal ion into two sets of d-orbitals with different energies is called crystal field splitting. The two sets of d-orbitals, i.e.,  $d_{x^2-y^2}$  and  $d_{z^2}$  and  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  are commonly called  $e_g$  and  $t_{2g}$  orbitals respectively. The crystal field splitting is the energy difference between  $t_{2g}$  and  $e_g$  orbitals and is frequently measured in terms of a parameter  $\Delta_0$  where the subscript (0) stands for octahedral. (This is also measured in terms of another parameter called  $D_q$ . The magnitude of splitting is arbitrarily fixed at  $10 D_q$  so that  $\Delta_0 = 10D_q$ ). The above energy level diagram shows that an electron will prefer to go into more stable  $t_{2g}$  orbital is stabilized by  $-0.4 \Delta_0 = -4D_q$  energy while each electron occupying the  $e_g$  orbital shall be destabilized by an amount  $0.6 \Delta_0 = 6D_q$  energy. This gain in energy achieved by preferential filling of stable  $t_{2g}$  orbitals over the energy of a randomly filled d-orbital is called the crystal field stabilization energy (CFSE). The net CFSE is equal to  $(6x-4y) D_q$  where x and y are the number of electrons in  $e_g$  and  $t_{2g}$  orbitals respectively. The actual configuration adopted is decided by the relative value of  $\Delta_0$  and P (where P is the pairing energy). The energy required to cause pairing of electrons in the same orbital is called pairing energy. If  $\Delta_0 > P$ , we have a weak field and high spin or spin free complex and the fourth electron will enter one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . If now a fifth electron is added to a weak field coordination entity, the configuration becomes  $t_{2g}^3 e_g^2$ . The pairing of electrons will take place only if the gain in stability in terms of  $\Delta_0$  is large enough to overcome the loss in

stability due to electron pairing. When  $\Delta_0 > P$ , we have a strong field and low spin or spin paired complex and pairing will occur in the  $t_{2g}$  level with  $e_g$  level remaining unoccupied in  $d^1$  to  $d^6$  systems. By calculating CFSE values, it can be shown that coordination entities having  $d^4$  to  $d^7$  configurations are more stable for strong field as compared to weak field complexes.