

FOR STUDENTS OF B.Sc AND M.Sc

A TEXT BOOK OF
INORGANIC CO-ORDINATION

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CHAPTER -1 CHEMISTRY OF INDIVIDUAL ELEMENT-BERYLLIUM

INTRODUCTION :- Beryllium is a member of IIA in the periodic table. Its atomic no. is 4. The members of IIA is as Be, Mg, Ca, Sr, Ba and Ra. It is known as alkaline earth metal. These members have almost 2 valence electron.

General properties of Be :-

1) Electronic configuration :- $1s^2 2s^2$

2) Position in the periodic table :-

<u>Element</u>	<u>Outermost conf.</u>	<u>Valence elec.</u>	<u>Gr.</u>	<u>Outer Orbit</u>	<u>Period</u>
Be	$2s^2$	2	II	2	2

Hence alkaline earth metals or Be is in IIA of the periodic table.

3) Atomic radius :- The outer most configuration of Be metal is ns^2 . The value of outer most orbit increases from Be to Cs and hence radius of atom increases from Be to Ba.

Be, Mg, Ca, Sr, Ba
Increases atomic radius.

4) Ionic radius :-

Ionic radius increases from Be^{+2} to Ba^{+2}
 $Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}$
Increases Ionic radius

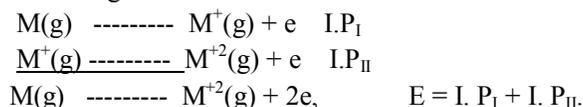
5) Ionization potential :-

As radius increases from Be to Ba I.P. decreases from Be to Ba.

Be, Mg, Ca, Sr, Ba
Decreases

When two electrons are removed from M, M becomes, M^{+2} .

The sum of $I.P_I$ and $I.P_{II}$ is high



6) Effective nuclear charge :-

Effective nuclear charge of Be is lower than that of other members which have equal Z^* .

$$\begin{array}{l} Be^4 - 1s^2 2s^2 \equiv 1s^2 \quad \left| \begin{array}{l} 2s^1 \quad 2s^1 \\ 0.85 \quad 0.30 \quad 0. \end{array} \right. \\ S = 2 \times 0.85 + 0.30 + 0. \\ = 1.70 + 0.30. \\ = 2.0 \\ Z^* = 4 - 2 = 2 \end{array}$$

7) Hydration energy :-

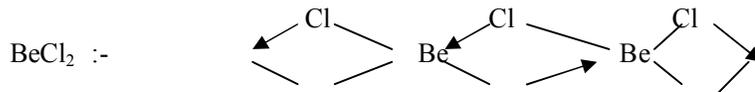
As radius increases from Be^{+2} to Ba^{+2} , hydration energy decreases from Be^{+2} to Ba^{+2} .

8) Oxidation state :-

It has sized +2 oxidation state M^{+2} is formed in solution +2 oxidation state is most stable.

9) Nature of bonds in compounds :-

Compounds of Be have covalent character in anh. Salt $BeCl_2$. But hydrated salts are ionic $BeCl_2 \cdot 4H_2O \equiv [Be(H_2O)_4]^{+2} 2Cl^-$. Anhydrous $BeCl_2$ is purely covalent and has the following structures Polymeric.

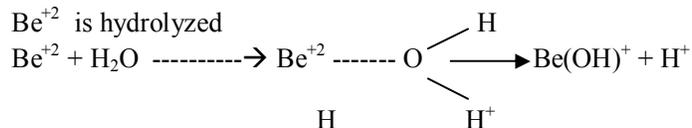


10) Acid base nature of compounds :

All oxides and hydroxides are basic only BeO and Be(OH)₂ are amphoteric.



c) Be^{+2} is hydrolyzed

11) Magnetic property :-

Beryllium and their compounds are diamagnetic.

12) Complex formation :-

Due to small ionic radius of Be^{+2} these form better complex than rest of the members. Be^{+2} acts as Lewis acid.

13) Colour of compound :-

Compounds of Be^{+2} (and all alkaline earth metals) are colourless.

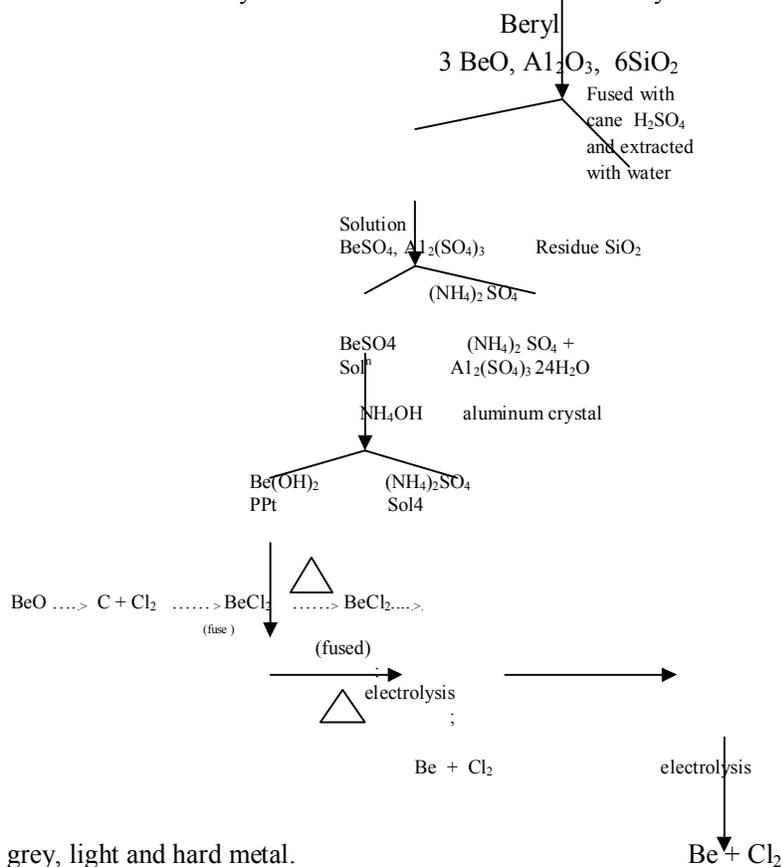
14) Detection of Be metal :-

Be^{+2} is in IIIA group of the analytical table. With NH_4OH , Be^{+2} gives white ppt. in group III A. BeCl_2
 $+ 2\text{NH}_4\text{OH} \rightarrow \text{Be(OH)}_2 \downarrow + 2\text{NH}_4\text{Cl}$

Occurrence :- Beryllium element derived from the mineral beryl (3 BeO, Al₂O₃, 6SiO₂).

It is not found in free state. It occurs mostly in the complex silicate (3 BeO, Al₂O₃, 6SiO₂).

Extraction : This metal is obtained from electrolysis method. Extraction is exhibited by the flow sheet.

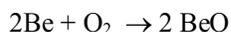
Physical properties :-

1) Beryllium is a steel grey, light and hard metal.

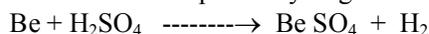
- 2) It has the highest melting and boiling point with respect to all the elements of group IIA.

Chemical properties :-

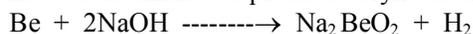
- 1) When beryllium is heated till redness in the presence of oxygen or air, it burns to form beryllium oxide.



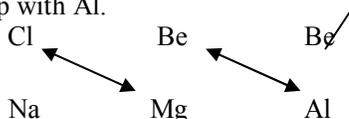
- 2) Beryllium does not react with hydrogen under any known conditions.
 3) Beryllium is treated with halogens (except iodine) to form the halides.
 4) Beryllium dissolve in dilute acid and displaces hydrogen.



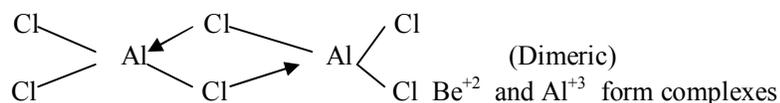
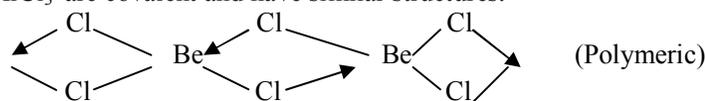
- 5) Beryllium dissolves in hot caustic alkali's to produce beryllates and hydrogen.



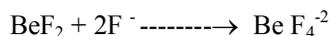
- 6) It shows diagonal relationship with Al.



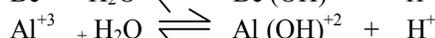
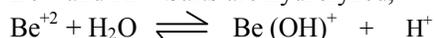
- a) BeCl_2 and AlCl_3 are covalent and have similar structures.



Be^{+2} and Al^{+3} form complexes



- b) Be^{+2} and Al^{+3} Salts are hydrolyzed,



- c) BeCl_2 and AlCl_3 dissolve in organic solvents. USES :-

- 1) In making alloys :

Beryllium alloys are used in industry

- 2) In X-ray tubes :

Beryllium sheets are used for windows of the x-ray tubes.

- 3) In nuclear reactors :

Beryllium salts are used as a source of neutrons, when a beryllium salt is bombarded with α -particles neutrons are formed.



Ques.: How does beryllium differ, from the next of the alkaline earth and why ? Or,

The first member of the group, Be shows properties different from other members.

Ans. : Be has small radius, radius of Be^{+2} is also small, due to small radius of Be^{+2} Potential of Be^{+2} is high and hence its compounds have considerable covalent characters. It is

soluble in organic solvents, salts are hydrolyzed and form hydrates.

The following properties of Be are different from other members :-

- Be compounds such as BeCl_2 are covalent.
- Be compounds such as BeCl_2 are soluble in organic solvents.
- BeCl_2 forms hydrates as $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$
- Maximum covalency of Be is 4, others have 6,
- Be is amphoteric $\text{Be} + 2\text{HCl} \rightarrow \text{BeCl}_2 + \text{H}_2$
 $\text{Be} + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$
- $\text{Be}(\text{OH})_3$, BeO are amphoteric, BeX_2 is lewis acid and forms BeX_4^{2-} . Be^{+2} salts are hydrolyzed $\text{Be}^{+2} + \text{H}_2\text{O} \rightleftharpoons \text{Be}(\text{OH})^+ + \text{H}^+$ Q.-

Qn. Explain why Be shows covalence whereas other members of the family shows electrovalency 2

Ans.- Due to high sublimation energy and high ionization energy of Be in group IIA elements, the energy requires in the formation of Be^{++} ion is not compensated by the lattice energy released. Hence Be shows covalency with various oxides halides etc.

Be (Beryllium)

ELECTRONIC CONFIGURATION :-

Be (4) ----> $1s^2 2s^2$

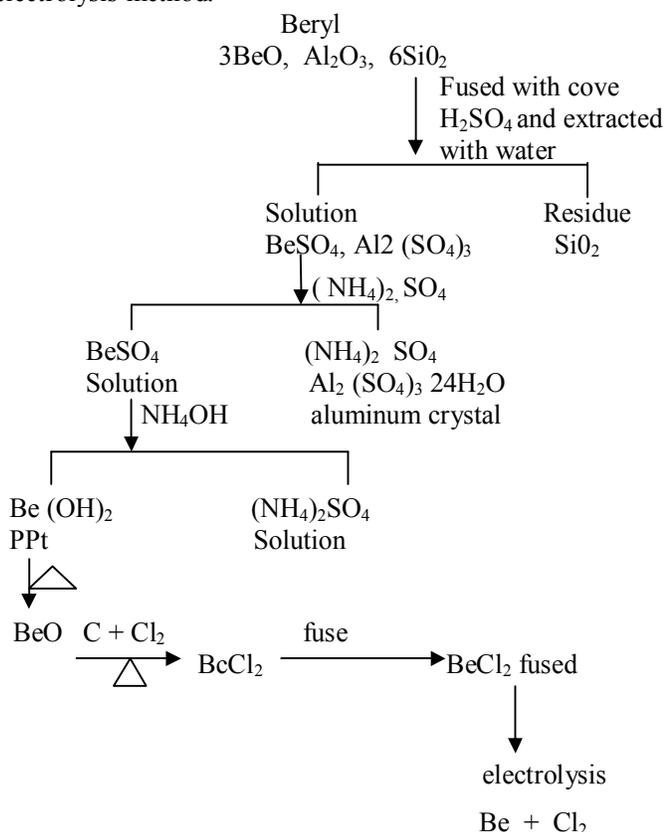
Position in the periodic table :-

Be	-	$2s^2$	2	II	2	2
element	Outer most Conf.	Valence electron	group	outer most orGt	period	

It is alkaline earth metal because it is earth like material and give alkaline Solution with water.

OCCURRENCE :- Beryllium element was derived from the mineral beryl ($3\text{BeO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$). It is not found in free state. It occurs mostly in the complex silicate ($3\text{BeO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$)

EXTRACTION :- This metal is obtained by the electrolysis method.



PHYSICAL PROPERTIES :-

- 1) Beryllium is a steel grey, light and hard metal.
- 2) It has the highest melting and boiling point with respect to all the elements of group II.

CHEMICAL PROPERTY :-

- 1) When beryllium is heated till redness in the presence of oxygen or air, it burns to form beryllium oxide.



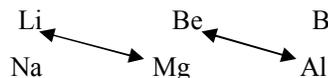
- 2) It does not react with hydrogen under any known conditions.
 3) Beryllium is treated with halogens (except iodine) to form the halides.
 4) Beryllium dissolves in dilute acids and displaces hydrogen :

$$\text{Be} + \text{H}_2\text{SO}_4 \longrightarrow \text{BeSO}_4 + \text{H}_2$$

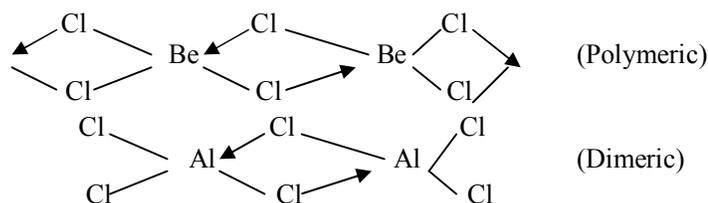
 5) Beryllium dissolves in hot caustic alkalis to produce beryllates and hydrogen:

$$\text{Be} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$$

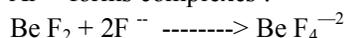
 6) It shows diagonal relationship with Al :



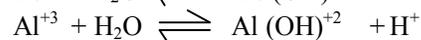
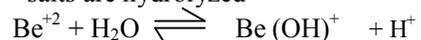
- i) BeCl_2 and AlCl_3 are covalent and have similar structures :



- ii) Be^{+2} and Al^{+3} forms complexes :-



- iii) Be^{+2} and Al^{+3} salts are hydrolyzed



- iv) BeCl_2 and AlCl_3 dissolve in organic solvents.

USES :- 1 In making alloys :-

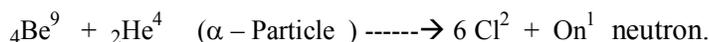
Beryllium alloys are used in industry.

2 In X-ray tubes :-

Beryllium in sheets are used for windows of the α -ray tubes.

3 In nuclear reactors :-

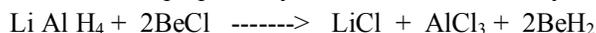
Beryllium salts are used as a source of neutrons when a beryllium salt is bombarded with and α -particles, neutrons are formed.



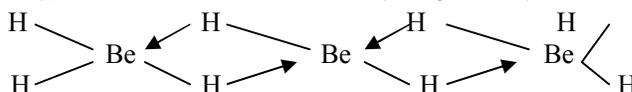
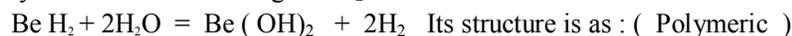
COMPOUNDS OF BERYLLIUM

- (i) BeHO_2 (ii) BeCl_2 (iii) $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$

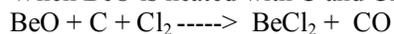
- (i) BeH_2 :- It is prepared by the reaction of Li Al Hy and BeCl_2 in ethereal solution.



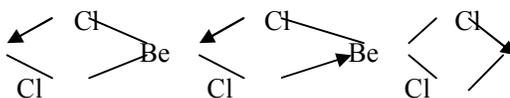
It is polymeric and with water gives H_2



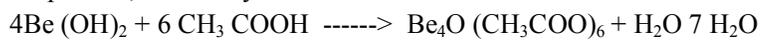
- (ii) BeCl_2 :- When BeO is heated with C and Cl_2 , BeCl_2 is formed.



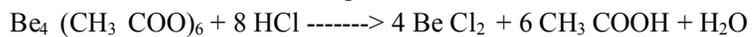
It is covalent forms hydrate $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ with water. It dissolves in organic solvent. Its structure is as -



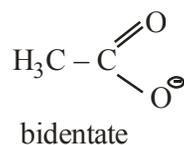
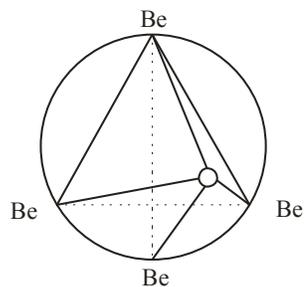
(iii) $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$:- (Basic beryllium acetate) : When $\text{Be}(\text{OH})_2$ is dissolve in glacial acetic acid and evaporated, basic beryllium acetate is formed.



It is covalent and soluble in organic solvents. It reacts with mineral acids as



Its structure content is O which is four co-ordinate, Be atoms are at the corners of tetrahedral,



CHAPTER-02 CHEMISTRY OF INDIVIDUAL ELEMENTS-VANADIUM

INTRODUCTION :- Vanadium is the member of group V. The members of this group is Vanadium (V) , niobium (Nb) and Tantalum (Ta). General formula of this group is $(n-1)d^3ns^2$. Outer electron is d^3ns^2 i.e. group VB. The electron is incompletely filled inner d- orbital in these members, hence it is said to be a transition elements. Atomic no of vanadium is 23.

GENERAL PROPERTIES

1) Electronic configuration :-

The outer most electronic configuration of vanadium (23) is $3d^3 4s^2$. General formula is $(n-1)d^3ns^2$

2) Position in the periodic table :-

<u>A.N.</u>	<u>Element</u>	<u>Symbol</u>	<u>Out. Ele.</u>	<u>V.E.</u>	<u>Outer orbit</u>
23	Vanadium	V	$3d^3 4s^2$	5	4

Hence from the valence electron and outer orbit it is clear that it has the group of VB and period 4.

OXIDATION STATE

+5 Oxidation states becomes more stable from V \rightarrow Nb \rightarrow Ta, because vanadium V compounds are good oxidizing agent while Nb V and Ta V being stable but are not oxidizing agent.

Lower oxidation state becomes too more stable from Ta \rightarrow Nb \rightarrow V. There are following characteristics points are given below :-

i) Vanadium exhibits + 2, +3, +4, +5,

ii) Lower oxidation states are good reducing state.

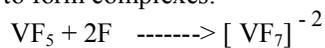
iii) From +5 oxidation state of vanadium step wise reduction occurs by addition of Zinc in it. First forms +4 having blue colour, then +3 having green and finally +2 having violet colours. It is done due to incomplete inner d- orbital. But +5 oxidation state of vanadium is colourless due to completely filled d-orbital i.e. electrons are fully paired.

COLOURS OF COMPOUNDS

The compounds with lower oxidation states have incomplete d-electron and are therefore coloured while these with higher oxidation states which have completely filled –d-electrons shells are colourless. V_2O_5 has orange red colour.

COMPLEX FORMATION

It has tendency to form complexes:



ACID BASE CHARACTERS

Vanadium is unreacted at ordinary temperature. It dissolves in nitric acid, concentrated H_2SO_4 and aquaregia, when it is fused with alkali, it gives the corresponding van date evolving hydrogen.

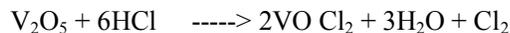
OXIDES OF VANADIUM

Vanadium V oxides, V_2O_5 :-



It is amphoteric in character,

It dissolves in acid solutions to give salts such as $VOCl_2$ (vanadyl chloride) or VCl_5 (Vanadium penta chloride),



Vanadium IV oxide, VO_2 :-

It is formed by the reduction of V_2O_5 . It is blue amphoteric solid with rutile structure. It reacts with non oxidizing acids to form vanadyl and vanadium salts.



Vanadyl Chloride



It reacts with alkalis to form vanadites.



Vanadium III Oxide, V_2O_3 :-

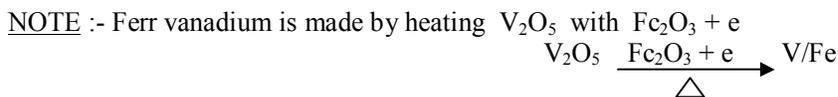
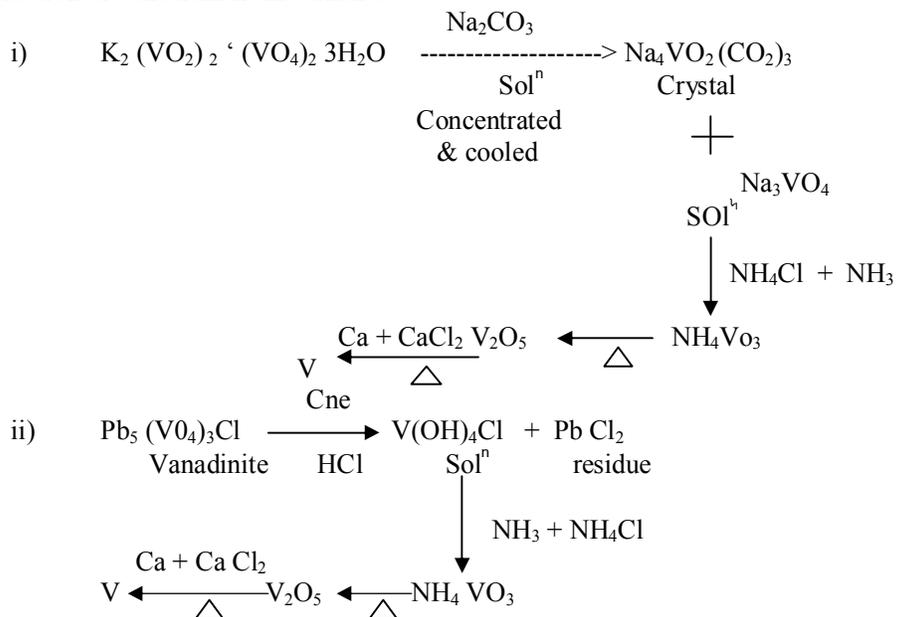
It is obtained by the reduction of V_2O_5 with C or H at high temperature.



It acts as strong reducing agent, V_2O_3 is basic in nature and dissolve in acids to give solutions of the V III hexaquo i.e $[V(H_2O)_6]^{+3}$.

Extraction of Vanadium :-

Extraction of vanadium from carnalite :-

Chemical Properties :-

- i) Treating with alkali to give vanadate.

$$2V + 6NaOH + 2H_2O \xrightarrow{\Delta} 2Na_3VO_4 + 5H_2$$

Sodium
Vanadate
- ii) Treating with oxygen : to give vanadium penta oxide

$$4V + 5O_2 \xrightarrow{\Delta} 2V_2O_5$$
- iii) Treating with Cl_2 .

$$V + 2Cl_2 \xrightarrow{\Delta} VCl_4$$

Uses :-

- i) It is used in steel industry as a ferro vanadium alloy for making special steels.
 - ii) It acts as a scavenger and makes the steel stronger, tougher and resistant to shock.
 - iii) It makes the steel more ductile.
 - iv) More tensile strength steel containing chromium and vanadium is used in making parts of the motor vehicle.
 - v) Treating with alkali to give sodium vanadate.

$$(1) 2V + 6NaOH + 2H_2O \xrightarrow{\Delta} 2Na_3VO_4 + 5H_2$$

Sodium vanadate
 - Treating with oxygen to give vanadium pentaoxide

$$(2) 4V + 5O_2 \xrightarrow{\Delta} 2V_2O_5$$
 - Treating with Cl_2

$$V + 2Cl_2 \xrightarrow{\Delta} VCl_4$$

(Vanadium Chloride)
-

CHAPTER-03 CHEMISTRY OF NON-TRANSITION ELEMENTS

Trimethyl amine and trisilyl amine differ in structure, donor property and basic property. I – Trisilyl Amine, nitrogen forms dative π – bonds to the silicon atoms. In the planar state of $N(SiH_3)_3$, the nonbonding electrons of nitrogen would occupy the $2p_x$ orbital, if we assume that the N-Si bonds are formed using sp^3 py trigonal, hybrid orbitals of nitrogen. Silicon has empty $3d$ orbitals which are of low enough energy to be able to interact appreciably with the nitrogen $2p_z$ orbital. Thus the N – Si π bonding is due to the kind of overlap indicated in the figure.

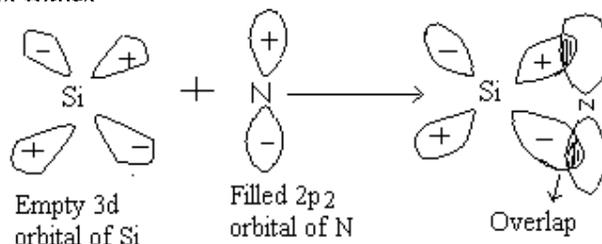


Fig. – Formation of $d\pi - p\pi$ bond between Si and N in tri silylamine. It is the additional bond strength to be gain by this $p\pi - d\pi$ bonding which causes the $N Si_3$ skeleton to take up a planar configuration whereas with $N(CH_3)_3$ where the carbon has no low energy d – orbitals the $6 -$ bonding alone determines the configuration, which is pyramidal as expected $N(SiH_3)_3$ is weaker base than $N(CH_3)_3$ due to its less ability to form donor – acceptor complexes.

Ionic mobility of Li^+ is lowest among alkali metal cations.

Li^+ ion has the highest hydration energy among the alkali metal ions and the most tensively hydrated. Due to excessive hydration, the effective size of Li^+ ion in aqueous solution is larger even than that of Cs^+ ion. The highly hydrated Li^+ ion moves slowly. That is why the ionic mobility of Li^+ is lowest among alkali metal cations. The order of ionic mobility of alkali metal ions is –

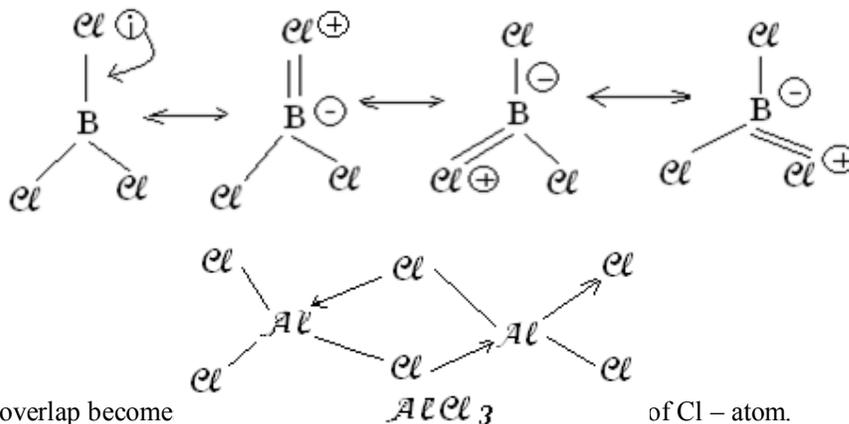
$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ is aqueous solutions.

INORGANIC

Q. N. -8

BCl_3 does not dime rise but $AlCl_3$ dime rises.

BCl_3 are stabilized by resonance and exist as monomers where as $AlCl_3$ is stabilized by dime rization in which Cl atom forms co-ordinate bond.

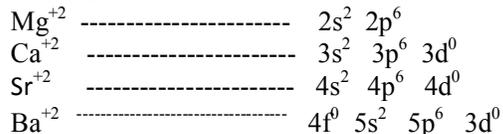


Further $p\pi - p\pi$ overlap become

$AlCl_3$

of Cl – atom.

In solid state alkaline earth metals exist as M^{+2} , $2e$ in lattice. Radius of M^{+2} decreases from Be^{+2} to Ba^{+2} and hence electro-static attraction decreases from Be to Ba. On this basis it is expected that m.p. should have the order $Be > Mg > Ca > Sr > Ba$. However, the order is $Be > Mg < Ca > Sr < Ba$.



It is reported that due to participate on of d-orbital in Ca and f – orbital in Ba, bond strength increases in M^{+2} , $2e$ due to d – d – and f – f overlap and in p of Ca and Ba show deviation. Due to greater extension of 4d in Sr relative to 3d, d – d overlap is not so effective.

Stability of N – 2 oxidation state for p block metals.

P block metals show variable oxidation states of +1 and +3. For lighter elements +3 state is more stable than +1 state but for the heavier element +1 state is more stable than +3 state.

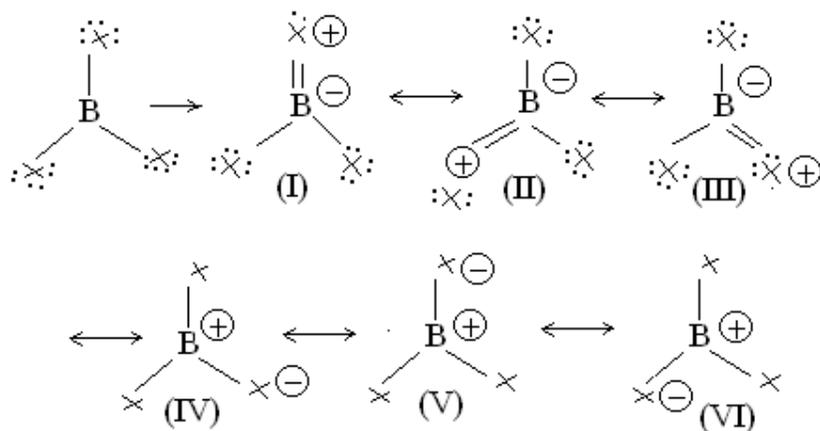
+3 state arises due to involvement of all the electrons in $ns^2 np^1$ and is termed as N – state. +1 state arises due to involvement of only np^1 and non participation of ns^2 electron and is termed N-2 states. The N-2 state thus arises due to inert pair effect.

The stability of +3 state is because ΔH_s for $M(s) \rightarrow M(r)$ is very high and this is not compensated by the energy released in the formation of three bonds which are predominantly covalent.

Order of acidic strength of BX_3 (X = F, Cl, Br, I)

All boron halides are typical electron deficient compounds as they have only octate of electrons round B-atom in stead of octate of electron. Hence they are bonafide lewis acids. Since the lone pair of electrons of halogen is engaged in $p\pi - p\pi$ overlap therefore, B – atom acquires negative charge. But with the increase in size the strength of IT bonding decreases and thus amount of negative charge on B – atom decreases. Due to which electron accepting power increases and hence the acid strength increases.

$BI_3 > BBr_3 > BCl_3 > BF_3$



Order of acidic strength of oxy acids of Cl

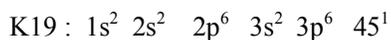
Chloride forms four oxy acids :-

HCl^{+1}O	-----	Hypochlorous acid
$\text{HCl}^{+3}\text{O}_2$	-----	Chlorous acid
$\text{HCl}^{+5}\text{O}_3$	-----	Chloric acid
$\text{HCl}^{+7}\text{O}_4$	-----	Perchloric acid

With the increase in the value of oxidation number of the central halogen atom i. e. Cl, in oxy acids of chlorine, the acid strength increases because more and more electrons are going to be accepted by the central atom of the acid. Therefore, the relative strength of oxy acids of chlorine following the trend.

Effective nuclear charge for K(19) and Cu (29)

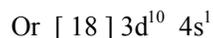
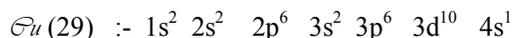
Potassium :



$$\begin{aligned} \therefore \text{Screening constant, } S &= 10 + 8 \times 0.85 + 0 \\ &= 10 + 6.80 \\ &= 16.80 \end{aligned}$$

$$\begin{aligned} \therefore \text{Effective nuclear charge } Z^* &= Z - S \\ Z^*_{\text{K}} &= 19 - 16.80 \\ &= 2.20 \text{ Units} \end{aligned}$$

Copper :

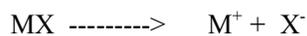


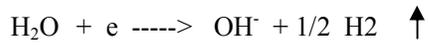
$$\begin{aligned} \therefore \text{Screening constant } S &= 18 + 10 \times 0.85 + 0 \\ &= 18 + 8.5 \\ &= 26.5 \end{aligned}$$

$$\begin{aligned} \therefore \text{Effective nuclear charge } (Z^*) \\ Z^*_{\text{Cu}} &= Z - S \\ &= 29 - 26.5 \\ &= 2.5 \text{ Units} \end{aligned}$$

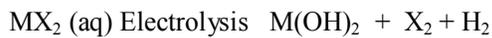
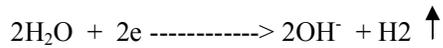
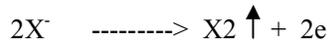
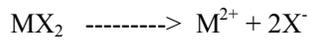
Alkali and alkaline earth metals are not isolated by the electrolysis of aqueous salt solution.

The aqueous solutions of alkali and alkaline earths upon electrolysis give metal hydroxides M(OH) or M(OH)_2 instead of pure metal, M. Hence alkali or alkaline earth metals are not obtained by the electrolysis of their aqueous solutions. :





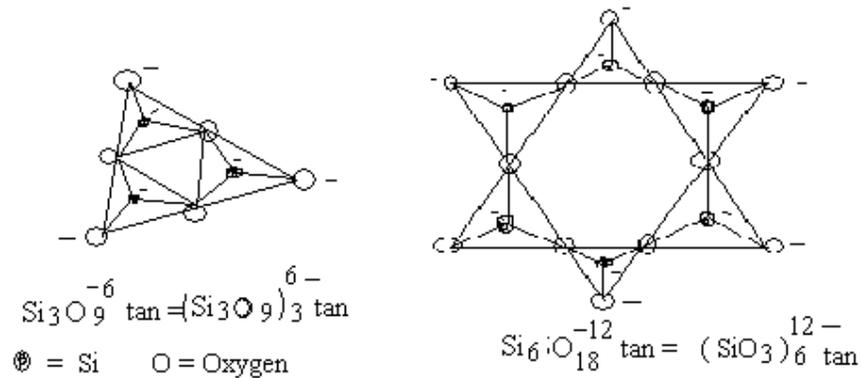
And,



Silicate form chain and ring structures.

Simple silicates has SiO_4^{-2} tetrahedral Si - O bond energy is high (106 K cal), Si has the property of forming complex silicates like chain and ring structures by forming - Si - O - Si - O - linkage. The complex silicates are formed by sharing of O of SiO_4^{-2} - tetrahedral.

When two oxygen atoms of SiO_4 tetrahedral is shared (i) cycle or ring silicates and (ii) chain silicates are obtained.

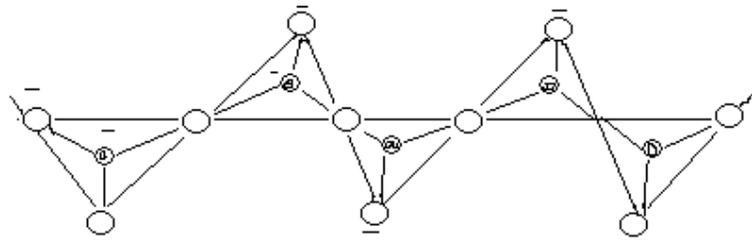


(Cycle silicates)

Examples (i) $Ca_3 (Si_3O_9)$ [Wollastonite]

(ii) $Be_2Al (Si_6O_{18})$ [Beryl]

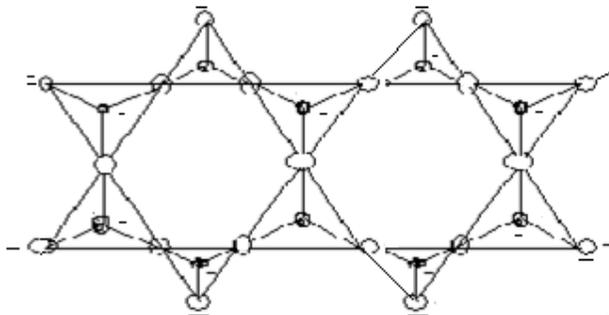
Chain Silicates :



(SiO_3)₂ 2n⁻ Chain

Example :- $Li Al (SiO_3)_2$ [Spodumenu]

Double chains are formed when two SiO_3 units are joined together the formula forms out to be $(\text{Si}_4\text{O}_n)^{-6n}$



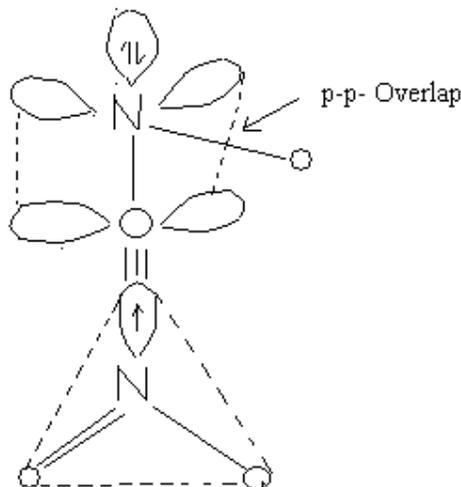
In this chain some tetrahedral share two O and some share three O- atoms –

Example :- $\text{Ca}_2\text{Mg}_5\text{Si}_4\text{O}_{22}(\text{OH})_2$ [Tremolite or Amphibole]

N_2O , No , No_2 exist but the corresponding p – compounds do not exist.

Size of N is small relative to size of P. Hence due to small size and lack of d – orbital in its outer most configuration N shows properties different from P.

Due to small size N, p- p overlap in N_2O , NO & NO_2 is possible and these compounds exist. But in case of ρ , due to its large size $\rho - \rho$ overlap is not effective. Hence the corresponding compounds of ρ do not exist.

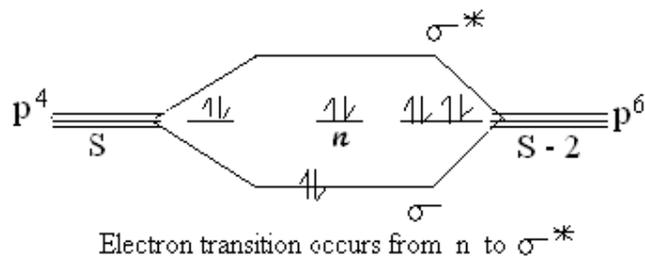


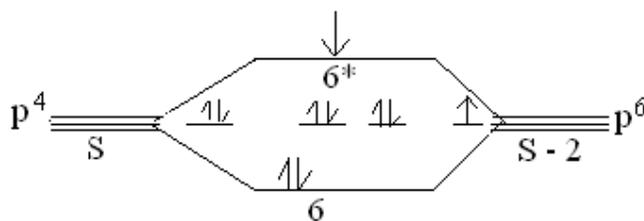
Oxy acid of S in +6 oxidation state is H_2SO_4 but of Te is H_6TeO_6 .

The maximum covalence of S is 6 and of Te is 8. Due to maximum covalence 8 for Te, the oxyacid of Te in +6 state is H_6TcO_6 .

$(\text{NH}_4)_2\text{S}_2$ is Yellow:

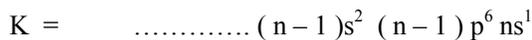
$(\text{NH}_4)_2\text{S}_2$ is yellow due to charge transfer from $\text{S}^{-2} - \text{S}$ in S_2^{2-} . Charge transfer occurs from non-bonding (n) to σ^* (anti bonding) orbital.



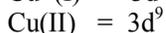
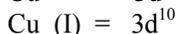
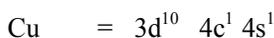


Fixed oxidation state of K is variable oxidation states for Cu.

In case of K fixed oxidation state of +1 is found, the +1 oxidation state is formed by electron loss as I. P₁ is low.

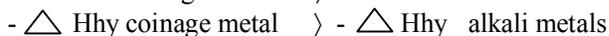
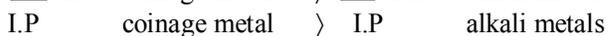
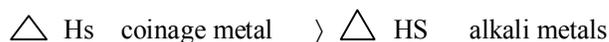
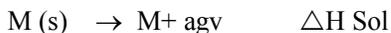


Due to stable $(n-1)s^2 (n-1)p^6$, I. P II is very high and so +2 oxidation state is not possible. In case of Cu, due to participation of $(n-1)d^{10}$ electron, it has variable oxidation states i.e.



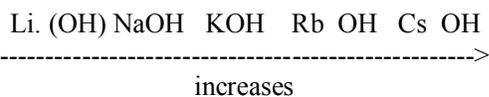
K is a base metal but Ag is noble metal.

Oxidation potential of coinage metal is less positive than alkali metals. The less positive oxidation potential is due to high sublimation energy and high I.P. of the coinage metals. Thus coinage metals are poor reducing agent relative to alkali metals.



Alkali metals for example K, due to low I. P. and low ΔH sublimation have high value of E° and easily react with H_2O to form HOH base i. e. KOH base one recalled base metals. Coinage metals for example due to high I. P. and high ΔH sublimation and are E° and does not react with water to form base. Hence Ag is noble metal.

Order of basic strength for MoH (M = alkali metals)- The metallic character increases from Li to Cs and so basic character of Metal hydroxides increases from Li to Cs. In MOH, radius of M^+ increases from Li^+ to Cs^+ and hence attraction between M^+ and OH^- decreases from Li^+ to Cs^+ consequently dissociation of MOH to $M^+ + OH^-$ increases and basic strength increases. Hence Basic character :



As a matter of fact MOH are strong bases and are 100% ionized.



CHAPTER-4 CHEMISTRY OF LANTHANIDES

The fourteen elements after Lanthanum from cerium (Z-58) to lutetium (Z-71) are called lanthanides. The properties of La itself resembles very much with these elements, therefore, lanthanum (Z-57) is also considered in lanthanides.

In the periodic table all these elements are placed in IIIrd and VIth period. They are inner transition elements.

ELECTRONIC CONFIGURATION :-

Their electronic configuration are not contain completely because the electronic spectra of these atoms and ions are very close and their analysis is different.

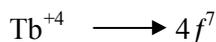
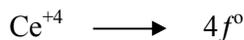
However, it may be considered that La has electronic configuration $5d^1 6s^2$. From Ce, filling of electron in $4f$ orbitals start which finishes at **Lu**. The general electronic configuration can be given as $(n-2) f^{1-14} ns^2$. The individual electronic configuration of all these elements are as follows :-

Atomic no.	Name of element	Symbol	Ele. Conf.
57	Lanthanum	La	$[\text{Xe}]5d^1 6s^2$
58	Cerium	Ce	$[\text{Xe}]4f^2 6s^2$
59	Praseodymium	Pr	$[\text{Xe}]4f^3 6s^2$
60	Neodymium	Nd	$[\text{Xe}]4f^4 6s^2$
61	Promethium	Pm	$[\text{Xe}]4f^5 6s^2$
62	Samarium	Sm	$[\text{Xe}]4f^6 6s^2$
63	Europium	Eu	$[\text{Xe}]4f^7 6s^2$
64	Gadolinium	Gd	$[\text{Xe}]4f^7 5d^1$
65	Terbium	Tb	$[\text{Xe}]4f^9 6s^2$
.....	Dysprosium	Dy	$[\text{Xe}]4f^{10} 6s^2$
69	Thulium	Tm	$[\text{Xe}]4f^{13} 6s^2$
70	Ytterbium	Yb	$[\text{Xe}]4f^{14} 6s^2$
71	Lutetium	Lu	$[\text{Xe}]4f^{14} 5d^1 6s^2$

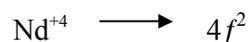
OXIDATION STATE

Here f orbitals are well shielded from outer sphere, therefore, f orbitals do not take part in bonding. Due to the stability of +3 oxidation states and non availability of f orbitals all these lanthanides are very similar to each other and also similar to Y and La.

Some of the lanthanides also turn M^{+2} and M^{+4} ions. The stability of these oxidation states may be partially correlated with the empty half filled and fully filled f orbital configuration i. e. f^0 , f^7 and f^{14} configuration –



These are known as stable ions. In addition to the above ions, so we M^{+2} and M^{+4} ions are also known. Their stability may be due to other thermodynamic and kinetic factors.



Of lanthanides between Lu and Hf a decrease in size, nearly 0.01 Å results in almost identical radii of Zr^{+4} (0.79 Å) and Hf^{+4} (0.78 Å). Further all the elements in II and III transition series also have identical radii due to this lanthanide contraction effect.

MAGNETIC PROPERTY

The magnetic property of lanthanides are due to unpaired f electrons present in it. The 5s and 5p orbitals remain in between 4f orbitals and opposite external ions or ligands. Therefore, these 4f orbitals are well shielded from such external species. Therefore there is a small variation in magnetic properties among the lanthanides complex and salts. It generally depends upon the nature of metal ions. It is further observed that spin orbit interaction is larger in these cases. The different states arising from a particular term are far apart in energy i.e. the ground state is well isolated and well populated. So J values are significant in determining magnetic properties and magnetic moment may be given by

$$G \sqrt{J(J+1)} \text{ BM.}$$

Where g = gyro magnetic

The various ground state and expected magnetic properties are as follows :-

Ion	Ground state	$G \sqrt{J(J+1)}$ BM.
La ⁺³	Iso	0.00
Co ⁺³	2F 8/2	2.54
Pr ⁺³	3H4	3.58
Nd ⁺³	4I 9/4	3.62
Pm ⁺³	5I4	2.70
Sm ⁺³	6H 3/2	0.84
Eu ⁺³	IFo	0.00
Gd ⁺³	85 7/2	7.94
Lu ⁺³	ISo	0.00
Yb ⁺³	2F 7/2	7.94
Tm ⁺³	3 H6	7.60
Pr ⁺³	4 I 5/2	9.60
Ho ⁺³	5 I 8	10.60
Dy ⁺³	6 H 5/2	10.60
Tb ⁺³	7 F ¹ 6	9.70

SPECIAL PROPERTIES :-

Since f orbitals are well shielded from external field. The splitting in various I states are small. The $f-f$ transition which is also laporte forbidden occurs in these cases but since the energy states are well defined, the absorption are very sharp i.e. line like nature.

However f^4 & f^{14-r} rare identical ground form splitting and identical absorption spectra. Therefore colours are also identical in such cases –

<u>Ion</u>	<u>Gr. State</u>	<u>Colour</u>	<u>Ion.</u>	<u>Gr. State</u>
La ⁺³	Iso	Colour less	I4 ⁺³	Iso
Ce ⁺³	2F 8/2	„ „	Yb ⁺³
Pr ⁺³	3H4	Green		
Sm ⁺³	6H 5/2	Yellow	Dy ⁺³	6HI 8/2
Eu ⁺³	7Fo	Pink	Tb ⁺³	7F 6

Gd ⁺³	85 5/2	Colour less	Gd ⁺³	85 7/2
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It may be observed that f_0 , f_7 , f_{14} ions i.e. Gd⁺³, La⁺³ and Lu⁺³ are colour less. In some cases laporte allowed transition are also absorbed. These transitions are from $4f$ to $5f$. They may give deep pink colour to some lanthanides ions.

COMPLEX FORMATION

The ability to form complexes are lesser in lanthanides as compared to transition elements. It is for two reasons-

- (i) f orbitals are not available for hybridizations and covalent bonding in these elements.
- (ii) The ionic radius of lanthanides are larger than those of metals of 1st transition series, which results the decrease in ionization potential i.e. lower the electrostatic force of attraction.

The bonding complexes are also rare in these cases due to residual tripositive (highly +ve ions). Chelates are oxidation salts of ions formed and one stable e. g. Acetyl acetone dibenzoyl methane etc. forms complex of the composition ML_2 , hydroxyl acids and amino acids like tartaric acid, citric acid etc. also. In some cases complexes of co-ordination no. 8, 9, 10 are also formed cyclopentadienyl form free complexes as $(C_5H_5)_3M$, $C_5H_5MCl_3$, 3THF (Tetra hydrofolran). They are thermally stable air sensitive compounds.

COMPARISON OF d. block AND Lanthanides:

- 1) Lanthanides are more reactive than d-block elements. The reactivity of lanthanides resemble with that of alkaline earth metals.
- 2) The lanthanides are soluble in NH_3 giving deep blue colour while transition metals rarely dissolve in it.
- 3) The lanthanides show nearly oxidation state (+3) with a very few exceptions of +2 and +4 0.5 while d-block elements are famous for their variable valences. In some cases d-varies from +2 to +7.
- 4) The magnetic property depends upon the ground term only in d-block elements while in lanthanides it is very much susceptibility to ground state i.e. $M J$ -value in d-block elements than lanthanides.
- 5) Due to non-participation of f electrons, lanthanides form a fewer complexes while in transition metals d-electrons participate in bonding and forms a large no. of complexes.
- 6) The d-d transitions give rise to broad bands in transition elements O while in lanthanides.
- 7) Due to lanthanides construction the property of lanthanides are very similar and their separation is very much different but d-block elements can be separated without any notable difficulty.

8) Due to larger size co-ordination no. of lanthanides can be intended to 8, 9, 10. It is a rare phenomenon in d-block elements.

SEPARATION

The most important ores of lanthanides are –

- i) Monazite Sand :- Moisture of ortho phosphates of lanthanides.
- ii) Cerite :- Hydrated, Silicated costs of Lanthanides.
- iii) Gadolinite :- Fe or Be Silicate costs of lanthanides.

EXTRACTION OF LANTHANIDES FROM MONAZITE SAND

- a) Concentration of ores :- Since there are heavy, they are concentrated by gravity separation method and by magnetic separation method.
- b) Cracking :- The one is digested with Conc. H_2SO_4 at $210^{\circ}C$ for 4 Hrs and the digested mass is heated with water. The unreacted insoluble part containing SiO_2 , TiO_2 and $ZrSiO_4$. The acid solution containing sulphate.
- c) Lanthanides are treated with sodium pyro phosphate ($Na_2P_2O_7$). Thulium is precipitated as thulium pyro phosphate. The filtrate obtained is treated with oxalic acid ($H_2C_2O_4$) The ppt mixture so obtained is boiled with $(NH_4)_2C_2O_4$. Traces of the $(C_2O_4)_2$ and $(2NO)(C_2O_4)_2$ remains in Soln and $Ln_2(C_2O_4)_3$ are left behind as residue. The residue is converted into sulphate by igniting carefully with Conc. H_2SO_4 Na_2SO_4 is added to the clear Solⁿ of sulphate of La^{+3} . In this way, light lanthanides [La – Ce] as double sulphates while heavy lanthanides [Gd – Lu] remains on the Solⁿ as simple sulphate.

From the ppt of light lanthanides, Ce can be removed as –

- i) Converting them into nitrates (CeO_2 separates out).
- ii) Selective crystallization of double ammonium nitrate.
- iii) Selective elution
- iv) Selective hydrolysis
- v) Selective extraction

Amongst the soluble sulphates of heavy lanthanides, Th can be separated as –

- i) Elective pptⁿ method by H_2F_2 or by $NaOH$. Th mainly

The other lanthanides are separated by following physical methods –

Separation of individual rare earths.

- i) Fractional crystallization methods -

Rare earth salts differ from each other in their solubility in water. The diff. is utilized in this method. The saturated Solⁿ is evaporated to crystallization point. The crystal thus obtained are concentrated least soluble salt. The mother liquor is re crystallized to get the salt of higher solubility.

The process is repeated so many times when pure lanthanides separates out.

- ii) Fractional precipitation :-

The hydroxides due to diff. basic nature, precipitate preferentially at diff. PH e.g. –
When PH is raised by adding NH_3 in the mixture of lanthanides cerium, Pr etc being less basic ppt out – first at low PH. The more basic lanthanides are ppted at higher PH. This difference can be used to separate the mixture.

iii)position of any salt :-
The separation is based upon the fact that Cr, Pr etc nitrates sulphates decomposed more readily by heating. The heavier lanthanides salt. Thus difference can also be employed for their separation.

iv) By change of oxidation number :-
We know that few lanthanides exist also in +2 or +4 oxidation states in addition to +3 oxidation states. The physical properties like basicity, solubility of elements in these oxidation states are two different than that of +3 +ve ion. So if a particular ion is selectively reduced then its separation becomes easier for e.g. Ce^{+3} can be first converted into Ce^{+4} and precipitates out as $\text{Ce}(\text{OH})_4$ being less basic than the mixture of +3 lanthanide ion.
All the above methods are not sufficient for complete separation. Since difference in the properties is very small now a days moderns techniques like –

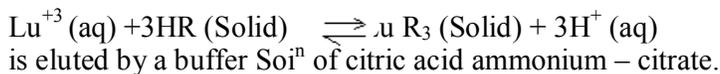
(1) Ion – Exchange Method :-

Lanthanides have different size and therefore they have different behavior towards absorption of cation exchange resin simultaneously, their elution tendency will also be

Ion being lightly absorbed comes at first and vice versa. In lanthanides the size decreases from La to Lu i. e. the hydrated ions increases from La to Lu. The last number being larger is less tightly bonded with resin and come first during elution. In contrast the first member being more tightly bonded comes at last thus the order of elution as Lu, Ph, Tm, Er, Ho, Tb etc.

The separation can be made more effective by choosing a complexing agent at a suitable PH. In actual practice ammonium citrate – citric acid buffer solution is used and PH is maintained between 2 – 8 and 3, 4.

Lanthanides are introduced in the column as chloride, absorption takes place according to the following equilibria. –



In this way diff volume collected will contain concentrated individual lanthanide series.

2) Paper chromatography :-

It has been observed that a gradual increase in RF values takes place with decreasing atomic of lanthanides. If the paper is treated with diethyl – hexyl or the phosphoric acid, the difference in RF values can be caused.

3) Solvent extraction Method :-The extracting solvent is tri-n-butyl phosphate in medium like kerosene or xylene. The lanthanides are dissolved in HNO_3 and can be extracted in organic layer

by complex formation with tri-n-butyl phosphate. The difference in the solubility of complexes formed in water and organic layer is used as the basis of separation.

4) Gas chromatography :-

The lanthanides are converted into stable volatile and monomeric complexes. These complexes can be separated due to their different retention times.

5) Complex formation :-

In this method, lanthanides are dissolved in presence of EDTA where lanthanides EDTA complexes are formed. The solubility of these complexes will be when dilute acid and oxalate Sol^{H} is added in these complexes the least stable EDTA complexes decomposes first and oxalate as pated.

More stable complexes needed more and for decomposition. In this way all oxalates complex can be separated out successively.

Lanthanide

The fourteen elements after lanthanum i. e. from cerium (58) to lutetium (71) are called lanthanide. It is f block elements which is incompletely filled. It is in IIIB and VI per..... thus it is called inner transition element lanthanum resembles very much with these elements so, lanthanum (57) is also considered in lanthanide.

Write out lanthanide electronic configuration.

Lanthanide electronic configurations are not truly complete because the electronic spectra of these atoms and ions are very close and their analysis is difficult. However the general electronic configuration can be given as $(n-2)f^x 5d^1 ns^2$.

<u>Atomic no.</u>	<u>Name of element</u>	<u>Symbol</u>	<u>Electronic Conf.</u>
57	Lanthanum	La	[Xe] $4f^0 5d^1 6s^2$
58	Cerium	Ce	„ $4f^1 5d^1 6s^2$
59	Praseodymium	Pr	„ $4f^2 5d^1 6s^2$
60	Neodymium	Nd	„ $4f^3 5d^1 6s^2$
61	Promethium	pm	„ $4f^4 5d^1 6s^2$
62	Samarium	Sm	„ $4f^5 5d^1 6s^2$
63	Europium	Eu	„ $4f^6 5d^1 6s^2$
64	Gadolinium	Gd	„ $4f^7 5d^1 6s^2$
65	Terbium	Tb	„ $4f^8 5d^1 6s^2$
66	Dysprosium	Dy	„ $4f^9 5d^1 6s^2$
67	Holmium	HO	„ $4f^{10} 5d^1 6s^2$

68	Erbium	Er	„	$4f^{11} 5d^1 6S^2$
69	Thulium	Tm	„	$4f^{12} 5d^1 6S^2$
70	Ytterbium	Yb	„	$4f^{13} 5d^1 6S^2$
71	Lutetium	Lu	„	$4f^{14} 5d^1 6S^2$

OXIDATION STATE

1) f orbitals of lanthanide are well shielded from outer sphere. Therefore f orbitals do not take part in bonding.

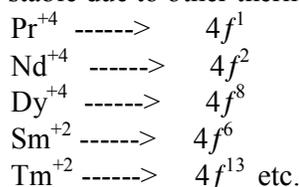
2) Mostly oxidation state of lanthanides are +3. They are all similar to each other. Y and La is also identical.

3) Some of the lanthanide also show M^{+2} and M^{+4} ions.



Obvious oxidation state are stable because f - orbital has empty, half filled and full filled electronic configuration.

4) Some M^{+2} and M^{+4} ions are also stable due to other thermodynamic and kinetic factors.



5) Since after all this, vent other elements have +3.....

LANTHANIDE CONTRACTION

The continuous decrease in the size of the lanthanide ions from La^{+3} to Lu^{+3} is known as lanthanide contraction.

$$\text{Ionic radii of } \text{La}^{+3} = 1.061 \text{ \AA}$$

$$\text{Ionic radii of } \text{Lu}^{+3} = 0.848 \text{ \AA}$$

$$\text{Thus the Contraction} = 0.213 \text{ \AA}$$

It is firstly decreases slowly and the rapidly with increasing atomic number.

<u>Symbol</u>	<u>Radii of M^{+3} (\AA)</u>
La -----	1.061
Ce -----	1.034
Pr -----	1.013
Nd -----	0.995

Pm	-----	0. 976
Sm	-----	0. 964
Eu	-----	0. 950
Gd	-----	0. 938
Tb	-----	0. 923
Dy	-----	0. 908
Ho	-----	0. 884
Er	-----	0. 881
Tm	-----	0. 867
Yb	-----	0. 859
Lu	-----	0. 848

Reason :- In this series nuclear charge is increasing from 5 to 71.

Thus the increasing nuclear charge is shielded by the f - electrons. We know that the shielding of $4f$ electron is very poor. The effective nuclear charge experienced.

EFFECT OF LANTHANIDE CONTRACTION

The continuous variation in the physical and chemical properties of lanthanide are due to lanthanide contraction. The elements are very similar to each other.

1) The radius of lanthanum La^{+3} ion is 1.061 \AA^0 and it decreases to Lu^{+3} ion 0.848 \AA^0 . The size of Y^{+3} is 0.88 \AA^0 so Y can lie in between La^{+3} and Lu^{+3} because its properties are very near to lanthanide. Therefore Y is always found above of the lanthanide which is very difficult to separate from lanthanide. Its ions Y^{+3} resemble very much with Dy^{+3} and Hf^{+3} .

2) In IIIB group of periodic table lanthanum is larger than Y , the IVB group Zr is smaller than Y . With respect to Zr , Hf should be larger than Zr . But due to the inclusion of lanthanide La and Hf a decrease in size nearly 0.21 \AA^0 which shows almost identical radii of Zr^{+4} (0.79 \AA^0) and Hf^{+4} (0.78 \AA^0). Further all the elements in II and III transition series also have identical radii due to this lanthanide contraction effect.

Effect of lanthanide contraction :-

a) Radii of La^{+3} to Lu^{+3} is similar due to lanthanide contraction and their is similar. The basic character of metals show slight increase with increasing atomic number.

b) Due to lanthanide contraction radii of second and third transition series elements are similar and consequently chemistry is similar.

- c) Due to lanthanide contraction, Y^{+3} and Er^{+3} have equal radii and Y occurs with lanthanides (heavier).
- d) Density of lanthanides increases from La to Lu (Eu and Yb exceptions due to difference in crystal structure)

COMPLEX FORMATION

The complex formation of lanthanide are lesser in comparison to transition element due to –

- i) f orbitals are not able to hybridization and covalent bonding in these elements.
- ii) The ionic radii of lanthanide are larger than those of metals of 1st transition series which shows the decrease in ionization potential i.e. lower the electrostatic force of attraction.

The bonding complexes are also rare in these case. It is occur due to residual in positive (highly +ve 10 vs) Acetyl acetone **dibentoyl wethare** for us complexes.

COMPARISION BETWEEN D BLOCK AND LANTHANIDE

- 1) Lanthanide are more reactive than d-block elements. The reactivity of lanthanide resembles with that of alkaline earth metals.
- 2) The lanthanide are soluble in NH_3 ... giving deep blue colour while transition metals rarely dissolve in it.
- 3) The lanthanide show nearly **oxidat** state +3 with a very few exceptions of +2 and +4 while d-block elements are famous for their variable values. In some cases it varies from +2 to +7.
- 4) The magnetic property depends upon the ground term only in d- block elements while in lanthanides, it is very much susceptibility to ground state i.e. M. J. value in d- block elements than
- 5) Due to non participation of f electron lanthanide form a fewer complexes while in transition metals d- electrons participate in bonding and forms a large no. of complexes.
- 6) The d- d- transitions give rise to broad bands in transition elements while in lanthanide bonds are very sharp.
- 7) Due to lanthanide contraction the property of lanthanide are very similar of and their separation is very much difficult but d-block elements can be separated without

The magnetic property of lanthanide are due to unpaired f electrons present in it. The 5S and 5P orbitals remain in between of orbitals. Therefore $4f$ orbitals are well shielded from such external species.

Therefore there is a small variation in magnetic properties among the lanthanide complex and salts. It generally depends upon the nature of metal ions.

The ground state is well isolated and well populated. S o J values are significant in determining magnetic properties and magnetic moment may be given by -

$$g \sqrt{J(J+1)} \quad \text{BM}$$

Where g = gyro magnetic

The various ground state and expected magnetic properties are as follows :- lanthanide.

$$g \sqrt{J(J+1)} \quad \text{BM}$$

<u>ION</u>	<u>GROUND STATE</u>	
La ⁺³	ISo	0.00
Ce ⁺³	2F5/2	2.54
Pr ⁺³	3H4	3.58
Nd ⁺³	4I 9/4	3.62
Pm ⁺³	5I4	2.70
Sm ⁺³	6H 3/2	0.84
Eu ⁺³	7 F o	0.00
Gd ⁺³	85 7/2	7.94
Lu ⁺³	ISo	0.00
Yb ⁺³	2 F 7/2	7.94
Tm ⁺³	3H6	7.60
Fr ⁺³	4I 5/2	9.60

10.60

f orbitals are well shielded from external field. In the *f f* transition the absorption are very sharp i.e. live like nature. However *fⁿ* & *f¹⁴⁻ⁿ* have identical ground term splitting and identical absorption spectra. The colour are also identical in such cases.

<u>ION</u>	<u>GR.STATE</u>	<u>COLOUR</u>	<u>ION</u>	<u>G.S.</u>
La ⁺³	ISo	Color less	lu ⁺³	ISo
Ce ⁺³	2F8/2	„ „	yb ⁺³	2F 7/
Pr ⁺³	3H4	Green	Tm ⁺³	3H6
Nd ⁺³	4I 9/2	reddish	Er ⁺³	4I 5/
Pm ⁺³	5I 1/4	Pink yellow	HO ⁺³	5I8
Sm ⁺³	6H 5/2	yellow	Dy ⁺³	6HI8
Eu ⁺³	7 FO	Pink	Tb ⁺³	7F6
Gd ⁺³	85 5/2	Color less	Gd ⁺³	857

It may be showed that *f_o*, *f₇*, *f_{lut}*, Ions i.e. Gd⁺³, La⁺³ and lu⁺³ are colour less. In some cases transition from *u_f* to *5d*, give deep pink colour.

CHEMISTRY OF LANTHANIDES CONTRACTION

The continuous decrease in the size of lanthanides ions from La^{+3} to Lu^{+3} is known as lanthanide – contraction. It has very significant effect on post lanthanides elements and among the lanthanides also. The contraction observed in the series is larger than the similar contraction in transition elements i.e. ionic radii of La^{+3} 1.061 Å ionic radii of Lu^{+3} 0.848 Å i.e. a contraction of 0.213 Å takes place. It may be observed that the size first decreases slowly and then rapidly with the increasing atomic no.

<u>SYMBOL</u>	<u>RADII OF M^{+3} (in Å)</u>
La -----	1.061
Ce -----	1.034
Pr -----	1.013
Nd -----	0.995
Pm -----	0.976
Sm -----	0.964
E4 -----	0.950
Gd -----	0.938
Tb -----	0.923
Dy -----	0.908
Ho -----	0.884
Er -----	0.881
Tm -----	0.867
Yb -----	0.859
Lu -----	0.848

Reason :-

In this series nuclear charge of increasing from 57 to 71 with similar increase in the $4f$ electrons.

As we know that the shielding of $4f$ electrons is very poor. The effective nuclear charge experienced in these cases increases rapidly. Therefore size also decreases regularly.

EFFECT OF LANTHANIDE CONTRACTION

The continuous variation in the physical and chemical properties of lanthanides are due to lanthanide contraction. However the elements are very similar to each other. This is often evident from the variation in size.

(1) The radius of lanthanum (La^{+3}) ion is 1.061 Å and it decreases to Lu^{+3} (0.848). The size of Y^{+3} ion is (0.88). It is obvious that it lies between La^{+3} and Lu^{+3} . Therefore its properties are very close to lanthanides and so is always found in lanthanide ore and it is very difficult to separate Y from lanthanides. A closer look indicates that Y^{+3} resembled Dy^{+3} and Ho^{+3} .

(2) In IIIB group of periodic table lanthanide is larger than Y . Moving to IVB group Zr is smaller than Y and from Zr , Hf should be larger.

But due to the inclusion of?

- (a) Stability of oxidation state.
- (b) Effective nuclear charge
- (c) Variation of ionic radius
- (d) Magnetic properties of M^{+n} compounds.

- (e) Intensity of colour of compounds.
 (f) M. P. of Metals.

(a) Stability of oxidation states :-

Generally lower oxidation states are more stable than higher oxidation states for first series and for second and third series the reverse is true i.e. higher oxidation state is more stable than lower oxidation states. The stability of oxidation state is reflected by nature of bonds.

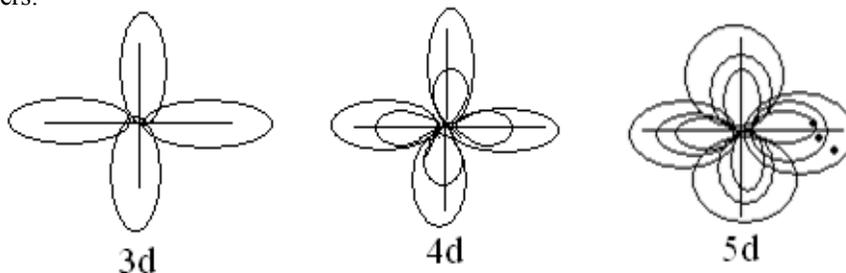
Example : CrCl₆ is unstable whereas WCl₆ is stable compound.

(b) Effective nuclear charge :-

The order of effective nuclear charge (Z^*) of transition metals of different series is

$Z^* \text{ I Series} < Z^* \text{ II Series} < Z^* \text{ III - Series}$

This is so due to greater extension of orbitals in space for the outer most configuration orbitals of third members.



Due to greater extension, orbitals of 5^n converge and extend closer to the nucleus and electrons are more attracted by the nucleus.

(c) Variation of ionic radius :-

The ionic radius increases with increase in outer most orbit in three series from top to bottom. This trend is valid for first two series members but the third series members have nearly equal ionic radius to the second series member e.g. $Ti^{+3} < Zr^{+3} \approx Hf^{+3}$

The third member comes after lanthanides [Ce (58) to Lu (71)], due to lanthanide contraction, increase in radius due to increase in the outer most orbit is balanced and so third member of the group has nearly equal radius to the second member.

(d) Magnetic properties of M^{+n} compounds :-

$$\text{All } M^{+n} \text{ cat ions are para magnetic - } \mu_{\text{eff}} = \mu_s \left(1 - \frac{K\lambda}{10Dq} \right)$$

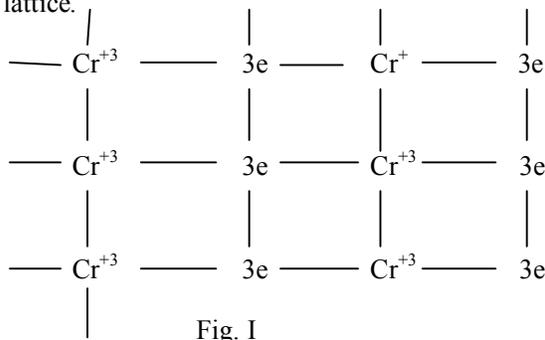
As value of λ increases from 1st to 3rd series, μ_{eff} decreases from 1st to 3rd series for a system having same number of unpaired electron.

Metals exist in the solid states as M^{+u} and μ_e , M^{+u} contains unpaired electrons and hence metals are para magnetic

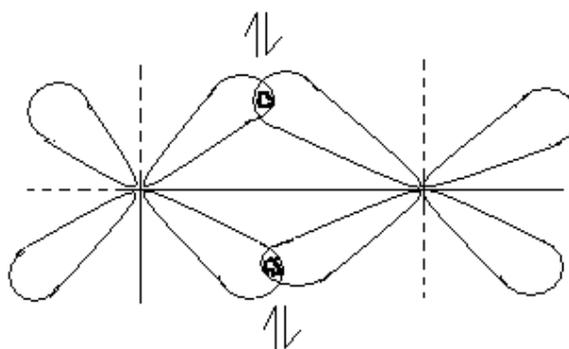
(e) M. P. of metals :- Melting point of transition metals is high. High melting point is due to covalent bonds in addition to electronic attraction between M^{+u} , μe in the lattice.

With the exception of Zn group all transition metals have high melting point. All melt above $900^{\circ}C$. High melting point of transition metals is due to involvement of $(n - 1) d$ electrons in covalent bonding.

Melting point in a group increases with increase in atomic no. Ex.: $Cr^{+3} (- 3d^3)$ exists as Cr^{+3} , $3e$ in the lattice.



$Cr^{+3} (- 3d^3)$ has 3 unpaired electrons and forms three covalent bonds (Fig. II) due to $d - d$ overlap with other Cr^{+3} ions in the lattice.



Chemistry of Lanthanides.....to the following :-

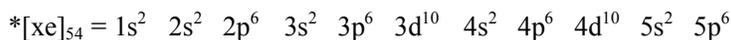
- (a) Electronic configuration
- (b) Oxidation states and their stabilities
- (c) Magnetic property of M^{+3} compounds
- (d) Spectra and colour of M^{+3} compounds
- (e) Principle of separation of M^{+3} compounds

The elements in which the additional electron enters $(n - 2) f$ orbitals are called inner transition elements. The valence shell electronic configuration of these elements can be represented as $(n - 2) f^{0, 2, \dots, 14} (n - 1) d^{0, 1, 2}, ns^2$. These are also called f - block elements because the extra electron goes to f orbitals which belong to $(n - 2)$ th main shell. f block elements have been classified as uf and sf block elements corresponding to the filling of $4f$ and $5f$ orbitals of $(n - 2)$ th main shell.

uf block elements are also called lanthanides or lanthanones because of their strong resemblance to lanthanum atomic number 57. The complete electronic configurations of all the lanthanides are shown below:-

Atomic Number	Name	Symbol	Complete configurations
57	Lanthanum	La	$*[xe] 4f^0 5d^1 6s^2$
58	Cerium	Ce	$[xe] 4f^2 5d^0 6s^2$
59	Praseodymium	Pr	$[xe] 4f^3 5d^0 6s^2$
60	Neodymium	Nd	$[xe] 4f^4 5d^0 6s^2$

61	Promethium	Pm	$[\text{xe}] 4f^5 5d^0 6s^2$
62	Samarium	Sm	$[\text{xe}] 4f^6 5d^0 6s^2$
63	Europium	Eu	$[\text{xe}] 4f^7 5d^0 6s^2$
**64	Gadolinium	Gd	$[\text{xe}] 4f^7 5d^1 6s^2$
65	Terbium	Tb	$[\text{xe}] 4f^9 5d^0 6s^2$
atomic Number	Name	Symbol	Complete configurations
66	Dysprosium	Dy	$[\text{xe}] 4f^{10} 5d^0 6s^2$
67	Holmium	Ho	$[\text{xe}] 4f^{11} 5d^0 6s^2$
68	Erbium	Er	$[\text{xe}] 4f^{12} 5d^0 6s^2$
69	Thulium	Tm	$[\text{xe}] 4f^{13} 5d^0 6s^2$
70	Ytterbium	Yb	$[\text{xe}] 4f^{14} 5d^0 6s^2$
**71	Lutetium	Lu	$[\text{xe}] 4f^{14} 5d^1 6s^2$



** = Anomaly in configurations due to half filled and fulfilled 4f - orbitals which are relatively more stable.

(b) Oxidation states and their stabilities :-

All of the lanthanides form the Tri-positive lanthanide cations. It is actually due to the fact that the magnitudes of the energy required to remove an electron from the gaseous ion in its lower oxidation states (i.e., ionization energy) and of that released when two gaseous ions combine with water to form the aquated species (i. e. hydration energy) are such that all the tetra positive species (except Ce^{4+}) and all the dispositive species (except Eu^{2+}) revert to the tri positive species are more stable than the di and tetra positive species in aqueous solutions.

In the solid state the combination of ionization energy and the lattice energy is more negative for the tri positive lanthanides for di and tetra positive species. Consequently the tri positive lanthanides are also the most common in the solid compounds.

Stability of various oxidation states :-

On the basis of general rule that empty, half filled and completely filled 4f orbitals are highly stable the formation of Ce^{4+} , La^{3+} ($4f^0$) Tb^{4+} , Eu^{2+} , Gd^{3+} ($4f^7$) and yb^{2+} , Lu^{3+} ($4f^{14}$) ions can be explained. In addition to the special stability associated with $4f^0$, $4f^7$ and $4f^{14}$ configurations there may be other factors such as thermodynamic and kinetic in determining the stability of various oxidation state of lanthanides.

The stability order of +2 state is $\text{Eu} > \text{yb} \gg \text{Sm} > \text{Tm} \sim \text{Nd}$.

The stability order of +4 state is $\text{Ce} \gg \text{Tb} \sim \text{Pr} > (\text{Nd} \sim \text{Dy})$

(c) Magnetic property of M^{+3} compounds :-

The paramagnetic property of an ion or an atom is due to the presence of unpaired electrons in it. Thus since both La^{+3} ($4f^0, 4f^0, 5d^0, 6s^0$) and Lu^{+3} ($4f^{14}, 5d^0, 6s^0$) ions have no unpaired electrons, there are not paramagnetic. All other Lu^{+3} ions show paramagnetic property.

Since for most of Lu^{+3} ions the energy difference between the two successive J levels of a multiplet (i. e. multilet width is large compared to KT, K = Boltzmann constant and T = absolute temperature there is a strong L-S coupling. In these ions the unpaired electrons in (n - 2)f orbitals are quite deeply seated and hence are well shielded by 5S and 5P electrons from the effects of other atoms in their compounds (crystal field effect). Consequently, the effective magnetic moments of Lu^{+3} ions with exception of Sm^{+3} and Eu^{+3} ions are given by the following equation :-

$$\mu_{\text{eff}} = \mu_j = g \sqrt{J(J+1)} \quad \text{BM} \quad \text{---- (1)}$$

where g is the l and c splitting factor and is given by – $g = \frac{1+J(J+1)+s(S+1)-L(L+1)}{2J(J+1)}$ ---(2)

S = resultant spin quantum number L = resultant orbital quantum number and J = resultant inner quantum number which is obtained by coupling L and S .

Although for most Ln^{3+} ions there is an almost fool agreement between the calculated and experimental μ_{eff} values, for Sm^{3+} and Eu^{3+} ions the agreement is poor. Thus due to the fact that in case of Sm^{3+} and Eu^{3+} ions

The energy difference (i.e. multiplied width) between the successive J energy levels is comparable to KT and the J levels above the lowest energy J level are populated by atoms to some extent.

We know that for Ln^{3+} ions like La^{3+} ($4f^0$), Gd^{3+} ($4f^7$) and Lu^{3+} ($4f^{14}$) which have S term symbol, $L = 0$ I C, no orbit effect ($L = 0$ shows S term symbol) For these ions when $L = 0$, $J = S$ and hence $g = 2$, thus equation (1) reduces to

$$\mu_{\text{eff}} = \mu_s = 2\sqrt{S(S+1)}$$

$$\begin{aligned} \text{Or } \mu_{\text{eff}} = \mu_{\text{spin only}} &= 2\sqrt{n/2 \left(\frac{n}{2} + 1 \right)} \\ &= \sqrt{n(n+2)} \end{aligned}$$

(d) Spectra and colour of M^{+3} compounds :-

Colours of lanthanide's (III) compounds are due to laporte forbidden $f - f$ transitions i.e. transitions between the J states of $4f^n$ configuration. Hence the absorption bands of Ln^{3+} ions (except Ce^{3+} and Yb^{3+} ions) are very weak but sharp when compared to these of d- block elements. Many of these **bands** are live – live and become even narrower as the temperature is lowered These narrow **bands** appear due to $f - f$ transition and are independent of the nature of the anion present. As $4f$ electrons lie deep inside the atom the colours of Ln^{3+} ions are not affected by changing the anion.

Laporte permitted **bands** due to the transitions of $4f^n \rightarrow 5d^1$ type have been observed in Ce^{3+} , Tb^{3+} , Sm^{2+} , Eu^{2+} and Yb^{2+} . These **bands** are strong and broader. Since the transition is considerably influenced by the chemical environment. A charge transfer phenomena is also observed in certain lanthanide ions e. g. the orange – red colour of Ce^{4+} is due to the electronic transition from the legend orbital to the f - orbital of cerium. Compounds of Eu^{3+} with reducing anions are yellow due to electron transfer from the metal.

(e) Principle of separation of M^{+3} compounds :-

The separation of the individual rare earths may broadly be divided into two classes :-

(1) Old classical method :- The following classical methods were not only used by the early workers in the port but still remain as very important methods for economical production of rare – earths on commercial scale.

(i) Fractional crystallization :- This procedure depends upon slight differences in the solubility of various salts.

(ii) Fractional precipitation method :- This is based on the fact that the basic character of the hydroxides of lanthanide elements decreases from La 57 to Lu 71. Thus when PH of the solution containing mixture of lanthanide elements is gradually increased by adding NH_3 , amines or alkali etc. the hydroxides of YH erbium group lanthanides (Gd 64 – Lu 71) being less basic get preferentially ppted while those of the cerium group lanthanides (La 57 – Eu 63) which are more basic are left behind in the solution. From a

given sub-group individual lanthanides are then separated by the further fractional precipitation of the hydroxides.

(iii) Fractional thermal decomposition of oxy salts :- This method is based on the fact that the rate of thermal decomposition of oxy salts such as nitrates, sulphates and acetates of lanthanide elements at a given temperature decrease from La 57 to Lu 71.

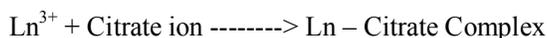
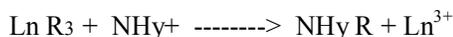
(iv) Change of oxidation states by selection oxidation or reduction procedure :- Some of the lanthanides show +2 and + oxidation states in addition to +3 state which is the most characteristic of all the elements of lanthanide series. The properties of Ln^{2+} and Ln^{4+} ions are different from those of the usual Ln^{3+} ions. Selective oxidation or reduction therefore, provides a very effective methods of separating specific lanthanides.

(2) Modern Methods :-

(i) Ion – Exchange method :- This is the most effective method now available for the separation of lanthanide elements. This method utilizes synthetic cation exchange resins which are usually organic compounds containing sulphonic (- SO_3H) or carboxylic acid (- COOH) groups, the hydrogens of which are replaced by other cations. Thus, if an aqueous solution containing a mixture of tripositive lanthanide ions Ln^{3+} (aq) is allowed to pass down a column packed with a cation – exchange resin [HR (Solid)] the Ln^{3+} (aq) ions replace H^+ ions of $-\text{SO}_3\text{H}$ or $-\text{COOH}$ group of the resin and thus get fixed on the resin –



Since Ln^{3+} (aq) is largest in size, is attached to the resin in the column with minimum firmness. In order to remove Ln^{3+} ions fixed as LnR_3 (Solid) on the resin, column is eluted (i.e. bleached) with a complexing agent in aqueous solution a buffer solution of ammonium citrate – citric acid (pH – 4 to 7). Such complexing agents are called eluants or eluates or eluting agents. During elution process NH_4^+ ions of the eluting agent replace Ln^{3+} ions from LnR_3 (Solid) to give Ln^{3+} ions which react with citrate ion to form the Ln – Citrate Complex.



The process of elution is to be repeated several times.

(ii) Solvent (liquid – liquid) extraction method :-
First reported by Fisher the method is based on the differences in the solubility of lanthanide salts in water and an immiscible or partially miscible organic solvent.

(iii) Paper Chromatography :-

Cerrai and Testa separated some rare earths by ascending paper chromatography. This is based on the fact that an increase in R_F value is noted with decreasing atomic number of the rare earths.

The other methods of separation are gas chromatography, thin layer chromatography and the complex formation.

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Q. In what way Lanthanides and Actinides resemble and differ in properties ?

Ans.:- Resemblance :-

- (i) The decrease in atomic radii in lanthanides and elements from Ac onwards is similar.
- (ii) Many compounds of lanthanides and Ac onwards are isomorphous.
- (iii) The absorption spectra of Ce^{+3} , $\text{Pu}^{+4}(f^1)$, Nd^{+3} , $\text{U}^{+3}(f^3)$ and Gd^{+3} , $\text{Cm}^{+3}(f^7)$ are comparable.

- (iv) μ values of both lanthanides Ce(III) to Gd(III) show similar trend and depend on J.
- (v) Lanthanides and NP onwards compounds are separated by ion – exchange. The elution curve is similar.
- (vi) Lanthanides as well as Ac onwards elements are reactive.
- (vii) Gd^{+3} and Cm^{+3} are stable (f^7).
- (viii) +3 State is common for lanthanides and Ac onwards.

Differences :-

- (a) $5f$ orbital is influenced by legends $5f$ orbitals split in crystal field.
- (b) The properties of actinides are intermediate between lanthanides and
- (c) Actinides form complexes curving f - electrons but not lanthanides.
- (d) pu onwards several oxidation states pu (+3, +4, +5, +6) are available, which is not the case with lanthanides.
- (e) U, NP, Pu, Am form NO^{+2} and Mo^{+2} which are not found with lanthanides.

Q. 9 (b) – Explain d – block contraction, lanthanide contraction and Actinide contraction.

Ans. :- d – block contraction :- The atomic and ionic radii for the elements of 3rd series decrease generally,

on moving from left to right in period. This is due to the fact that an increase in the nuclear charge tends to attract the electron cloud inwards. The atomic radii for the elements from Cr to Cu are however, very close to one another. This is due to d- block contraction. The simultaneous addition of electron to 3d – level exercise the reverse effect by screening the outer 4 s – electrons from the inward pull of the nuclear. As a result of these two opposing effects, the atomic radii do not alter much on moving from Cr to Cu.

Lanthanide contraction :-

As we move along the lanthanide series there is a decrease in the atomic and ionic radii. This steady decrease in the atomic and ionic radii is called lanthanide contraction. In lanthanides, the additional electron enters $4f$ sub shell but not in the valence – shell namely sixth shell. The shielding effect of one electron in $4f$ sub shell by another in the same sub shell is very little, being even smaller than that of d – electrons because the shape of f sub-shell is very much diffused. The nuclear charge however increases by unity of each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of $4f$ - electrons. This results in that electrons in the outer most shell experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic radii go on decreasing as we move from $L a 57$ to $Lu 71$.

Actinides contraction :-

There is an actinide contraction (i.e decrease in ionic radii of An^{3+} and An^{4+} ions) analogous to the lanthanide contraction with increasing positive charge on the nucleus. Thus actinide contraction is due to the addition of successive electrons to an inner f - shell (i.e. $5f$ shell, so that the imperfect screening of the increasing nuclear charge by the additional $5f$ electrons results in a contraction of the outer or valence orbital.

The gimp in contraction between the consecutive elements in the actinides is greater than in the lanthanides. The greater contraction is due to the lesser shielding of $5f$ electrons which are therefore pulled more strongly by the nucleus. This contraction leads to a decrease in the basicity of the elements with increasing atomic number.

-----X-----

Magnetic moments of Eu^{+3} and Sm^{+3} deviate from μ_j value

In case of Eu^{+3} and Sm^{+3} ions the energy difference (i.e. multiplet width) between the successive J energy levels is comparable to KT and the J value levels above the lowest energy level are populated by atoms to some extent. Whereas in all the other Ln^{+3} ions multiplet width is large compared to KT (K = Boltamann

constant and $T =$ absolute temperature). So in all of these Ln^{3+} ions there is strong L-S coupling and the magnetic moments of these Ln^{3+} ions is given by the equation :

$$\mu_{\text{eff}} = \mu_j = g \sqrt{J(J+1)} \text{ BM}$$

Where g is the lamb splitting factor and is given by –

$$G = \frac{1 + J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

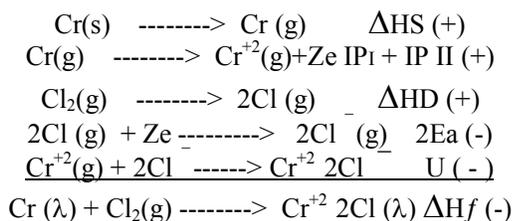
But μ_{eff} value for Eu^{3+} and Sm^{3+} ions deviate from μ_j value for the above mentioned reasons.
-----X-----

Differentiate between $d-d$ and $f-f$ transition.

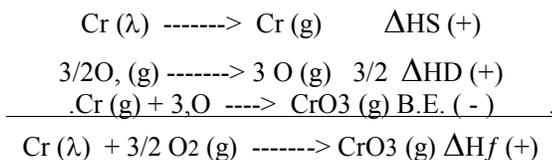
(a) Cr^{+3} is more stable than $Cr(VI)$ where as reverse is for Mo .

Ans.:- Lower oxidation states are generally more stable for transition metals of – 3d series where as for 4d and -5d series higher oxidation states are more stable.

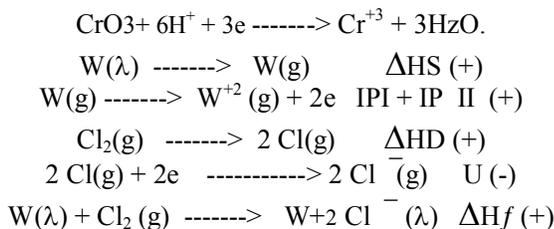
Lower oxidation state of transition metals is electrovalent but higher oxidation state is covalent :-



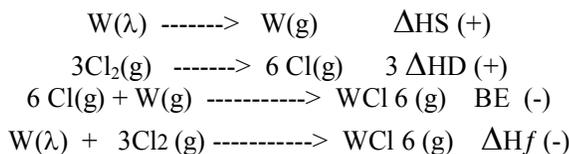
Lattice energy and E_a compensate more than $\Delta H_S + \text{IP I} + \text{IP II} + \Delta H_D$ and $CrCl_2$ has negative ΔH_f and is stable. In solution Cr^{+2} is oxidation to Cr^{+3} and λ_o Cr^{+3} is more stable than Cr^{+2} .



Bond energy does not compensate for $\Delta H_S + 3/2 \Delta H_D$ and so ΔH_f for CrO_3 is less negative and CrO_3 is instable.



U does not compensate for $\Delta H_S + \text{IPI} + \text{IPII} + \Delta H_D$ and hence ΔH_f is less negative and WCl_2 is unstable.



B.E. of $6W-cl$ bonds compensates more than $\Delta H_S + \Delta H_D$ and ΔH_f is negative and WCl_6 is stable.

Effective nuclear charge has the order $Cr^{+3} < Mo^{+3} \gg W^{+3}$.

Cr, Mo and W all the three metals are from three different transition series. Cr comes from 1st, Mo from 2nd and W comes from 3rd transition series.

Due to greater extension of orbitals in space for the outer most configuration orbitals of third members effective nuclear charge (Z^*) has the order :

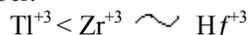
$$Z^* \text{ 1st series} < Z^* \text{ 2nd series} \ll Z^* \text{ third series} -$$

Hence,

$$Z^* \text{ Cr}^{+3} < Z^* \text{ Mo}^{+3} \ll Z^* \text{ W}^{+3}$$

Ionic radius has the order

In a group the ionic radii increase with increase in atomic number (i.e. increase in outermost orbit). This trend is valid for first two members but the third member has nearly equal ionic radius to the second member.



Third member comes after lanthanides [Ce (58) to Lu (71)], due to lanthanide contraction. Increase in radius due to increase in the outer most orbit is balanced by lanthanide contraction and so third member of the group has nearly equal radius to the second member.

(d) Intensity of colour of second and third series compounds is much less than of first series compounds.

Properties of actinides are intermediate between lanthanides and transition metals.

(i) : Electronic configuration of lanthanides is $4f^x 5d^0 6s^2$, of actinides is $5f^x 6d 7s^2$ and of transition metals is $(n-1)d^x ns^2$. Due to presence of electron in $6d^1$ actinides show similarity in properties to transition metals and due to presence of electrons in $5f^x$ actinides show similarity in properties to lanthanides. Thus actinides have properties intermediate between lanthanides and transition metals.

(ii) : Transition metal cations as well as actinide cations are affected by crystal field of ligands, but not the lanthanide cations. Thus on actinides, there is effect of both crystal field and L – s coupling.

(iii) : Absorption band for transition metal compounds (d – d transition) is much broader and of actinides is less broader due to interaction with the surrounding, but of lanthanide compounds is sharper because $4f$ is buried inside and has effect of the surrounding.

(iv) : Lanthanide contraction type contraction occurs in actinides also, but the effect is less pronounced but more pronounced.

CHAPTER -05

SOLID STATE - PART I

INTRODUCTION :-

Solids are characterised by the compressibility, rigidity and mechanical strength, Some solids like sodium chloride, sulphur and sugar besides being incompressible and rigid, have also characteristic geometrical forms. Such substances are said to be crystalline solids. Another category of solids such as glass, rubber and plastics, which possess properties of incompressibility and rigidity to a certain extent, but do not have definite geometrical forms. Such substances are called amorphous solids.

TYPES OF CRYSTALS:-

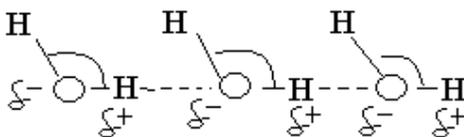
The solid crystals are classified into four types depending upon the nature of the units which occupy the lattice points .

1. Molecular crystals.
 2. Covalent crystals.
 3. Metallic crystals.
 4. Ionic crystals.
1. Molecular crystals:- (e-g, water molecules)

Molecular crystals in which the units occupying the lattice points are molecules i.e the lattice points is molecular crystals consists of specific molecules which do not carry any charge. The binding forces between the molecules are of two types.

- i. Dipole- Dipole forces.
- ii. Vanderwaal's forces.

Dipole - Dipole forces occur in solids which consists of polar molecules for example in water molecules, (ice or in liquid) the negative end of one molecule attracts the positive end of a neighbouring molecules,



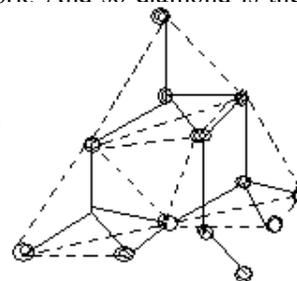
Vanderwaal's forces are more general and occur in all kinds of molecular solids, The bonding within a non- metal molecule is largely covalent in character and yet the individual molecules are held to each other by same forces are called Vanelerwaal's forces , As a result non- metallic solids usually exists as aggregations of molecule.

Both types of molecular forces mentioned above and much weaker than the coulombic forces of attraction between oppositely charged ions existing in ionic crystals. Due to the less binding energy in molecular crystals heat of evaporation is very low in comparison to the ionic crystals therefore molecular crystals are more volatile and have lower melting and boiling points on account of weak forces binding the molecules together , molecular crystals are usually soft, easily compressible and can be easily distorted due to the absence of charged particles molecular crystals are bad conductor of electricity in solid, liquid as well as in dissolved state.

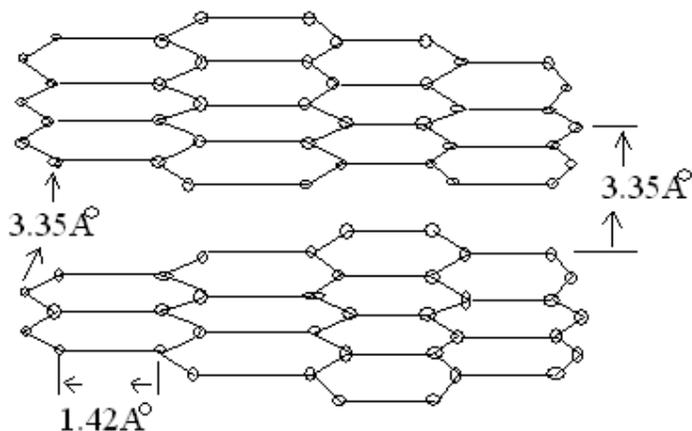
1. Covalent- crystals (e.g.- Diamond):-

In which the units are atoms. The lattice is covalent crystals consists of atoms linked together by a continuous system of covalent bonds. Diamond & graphite are important example of covalent crystals. Each carbon atom is covalently bonded by sharing of electrons to four other atoms . Each carbon atoms is surrounded by four other carbon atoms to the corners of a regular tetrahedron Thus every atom is allowed to complete its out is electron octet. This gives rise to a rigid three dimensional network. And so diamond is the hardest substance known with a high density and melting point.

(Structure of diamond)



Structure of Graphite :-

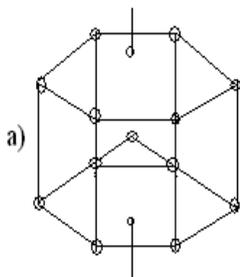


Graphite has a layered or layer lattice structure in which the atoms in a layer are joined up as hexagons similar to those in benzene ring, naphthalene, anthracene etc.. The bond length in these hexagons is of 1.42 \AA . The distance between layers is larger. It is 3.35 \AA between layers which is much more than normally expected for covalent bonds. This explains the possibility of covalent bonding between the layers.

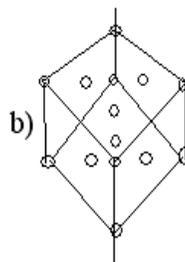
Since, as discussed above a chemical bond is not possible between carbon atoms in different layers the fourth valency remains unsatisfied i.e. some electrons are free or unpaired. This permits the passage of electricity through graphite and makes it a good conductor of electricity. Due to the feeble forces between the different layers, rupture between the various layers can occur easily. Such substances therefore are soft. They are used as lubricants because one plane of atoms can readily slip over another.

3. METALLIC CRYSTALS e.g. METALS :- In which the units are positive metallic ions surrounded by a 'Sea' of electrons. In metallic elements the co-ordination number is either 8 or 12. This means that each atom in an element is held to 8 or 12 more atoms. It is evident therefore that atoms in metallic elements can't be held by covalent bonds because they don't have so many electrons in their valence shells. The atoms in a metallic element therefore are believed to be held together by means of a special type of bond known as metallic bond. The force that binds a metal ion to a number of electrons within its sphere of influence is known as a metallic bond. On account of low ionisation energies of metals, some of the atoms lose one or more of their valence electrons and change into positive ions. The electrons emitted from the atom in this manner are not localised. These in fact are mobile and thus keep the positively charged ions held together. Thus a metal behaves as an assemblage of positive ions immersed in a 'sea' of mobile electrons. Due to attraction between positive ions and surrounding electrons there is some fall of energy in the case of metallic bonding. According to the definition of metallic bond in metallic aggregates each atom may share the electrons of many nearest neighbouring atoms in a manner which permits requisite fall in energy without of course, violating Pauli's exclusion principle.

An important characteristic of metallic crystals is that the atoms have a high coordination number e.g. 8 in body centred cubic lattice as for lithium, caesium, Barium, vanadium & molybdenum and 12 in hexagonal for Beryllium, magnesium etc. and 12 in cubic close packed str. For copper, calcium & Aluminium etc.



Hexagonal close packing



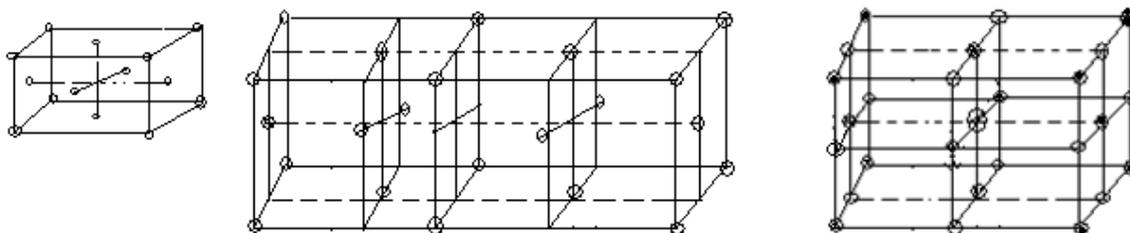
Cubic close packing

This in spite of high C N the no. of electrons around each single atom does not exceed twice the no. of valence orbitals.

4. Ionic crystals e. G. NaCl :- In which the units are positively and negatively charged ions. In ionic crystals the units occupying lattice points are positive and negative ions. In sodium chloride for example the units are Na^+ ions and Cl^- ions. Each ion of a given sign is held by coulombic forces of attraction to all ions of opposite sign. These forces are very strong, and therefore, the amount of energy required to separate ions from one another is very high. Accordingly the ionic crystals have the following characteristics.

- (i) The latent heat of fusion & vaporisation of ionic crystals are very high.
- (ii) The vapour pressures of ionic crystals at ordinary temperatures are very low.
- (iii) The melting & boiling points of ionic crystals are very high.
- (iv) Ionic crystals are hard and brittle.
- (v) Ionic crystals do not conduct electricity as ions cannot migrate from their lattice positions and free electrons are not available.
- (vi) Ionic solids are soluble in water and also in other polar solvents. But in non polar solvents the solubility may be very low or absent.
- (viii) In dissolved and molten states ions acquire freedom of migration under applied fields and thus the ionic crystals can conduct electricity.

X-ray studies of NaCl crystals, which belong to the cubic system have shown that these crystals have interpenetrating face centred cubic arrangements of sodium & chloride ions.



In ionic crystal structure of NaCl each sodium ion is octahedrally surrounded by six chloride ions. Chloride ions have a similar situation. As the unit cells shown above for NaCl crystal, it has 14 – sodium ions and 13 – chloride ions. Their distribution and effective contributions to the unit cell are as follows :-

8 Na^+ ions at the corners, each is shared between 8 unit cells. Net contribution $8 \times \frac{1}{8} = 1$, 6 Na^+ ions in the six faces, each shared between two unit cells. Net contribution $6 \times \frac{1}{2} = 3$ ions effective no of Na^+ ions in the unit cell = 1 + 3 = 4 ions.

12 NaCl^- ions at the 12 edges. Each shared between 4 unit cells.

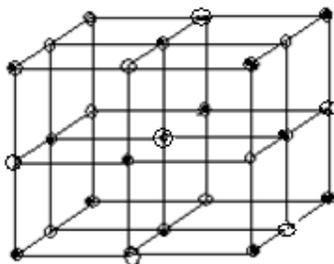
Net Contribution = 3 ions ($12 \times \frac{1}{4}$),

One Cl^- ion at the centre of the unit cell

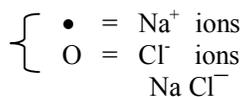
\therefore Net Contribution = 3 + 1 = 4 ions

Or { effective no. of Cl^- ions in the unit cell }

$\therefore \text{Na}^+ \text{Cl}^- = 4 : 4 = 1 : 1$



[14 – Na^+ ions,
13 – Cl^- ions]



BORN HABER CYCLE & LATTICE ENERGY :-

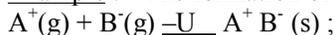
Ques.:- Explain the term lattice energy. How would you proceed to calculate the lattice energy of ionic solids or,

Describe how with the help of Born Haber cycle you would calculate the lattice energy of NaCl .

The lattice energy of an ionic solid is defined as the energy released during the formation of one mole of a crystal of the solid from the constituent gaseous ions separated from each other by infinite distances.

It is generally denoted by U .

Example :- The formation of a mole of a crystal from the constituent gaseous ions.



{ Here in the equation $-U$ has a negatively sign since energy is released in the process } with the coming together of positive and negative ions, there is a considerable decrease in potential energy of the system. Hence in the formation of an ionic solid from the constituent gaseous ions, as in the above example, there is a considerable, release i.e. evolution of energy. Hence U has a negative sign. According to the first law of thermo dynamics, the energy that is released in the formation of one mole of an ionic solid from the constituent gaseous ions is numerically equal to the energy that will be needed to convert one mole of the same ionic solid into the gaseous ions. Thus –



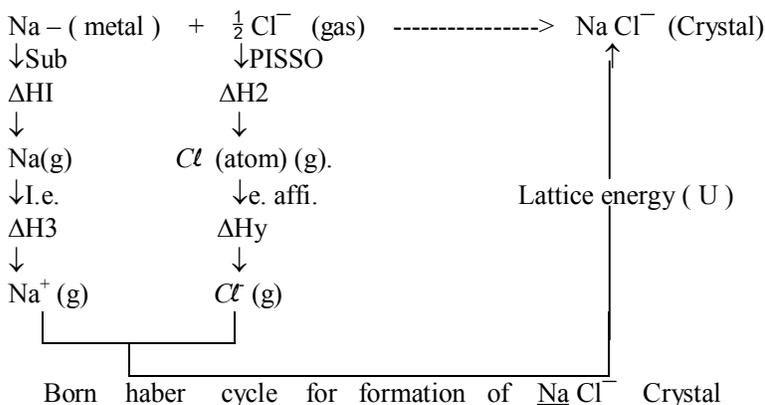
U = Lattice energy with the reversed sign.

[Here U has positive sign which shows the absorption of energy in the process]

It is obvious, therefore that the higher lattice energy of an ionic solid the greater will be its stability. This is on account of strong electrostatic attraction between oppositely charged ions present in the solid. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the valency (charge of the ions, the greater would be the lattice energy of the ionic solid. Thus lattice energy increases as we move from uni-univalent ionic solid to uni-bivalent ionic solids and then to bi-bivalent ionic solids.

BORN HABER CYCLE :- The cycle was devised by Born & Haber in 1919 relates the lattice energy of a crystal to other thermodynamic data. This approach is based on the assumption that formation of ionic crystal may occur either by direct combination of the elements or by alternative process in which –

- The reactants are vaporised and converted into gaseous atoms.
- The gaseous atoms converted into ions and
- The gaseous ions are combined to give product.



CALCULATION OF LATTICE ENERGY BY BORN HABER CYCLE :-

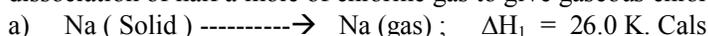
Let us consider the formation of one mole of crystalline Sodium Chloride NaCl , from its elements i.e. Sodium Solid and Chlorine gas. The heat change involved in the reaction is -98.21 K.cal .

The reaction therefore, may be represented as, $\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$;

$$\Delta H = - 98.21 \text{ K.cal} \text{ ----- (1)}$$

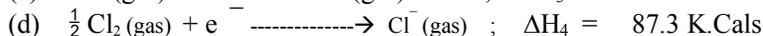
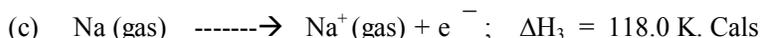
The above reaction may be considered to take place through the following three hypothetical steps –

I. The first step involves the sublimation of one mole of solid metallic sodium into gaseous state and dissociation of half a mole of chlorine gas to give gaseous chlorine atoms i.e. -



II. In the second step, the gaseous atoms of sodium and chlorine are converted to gaseous ions.

Energy of ionisation is required for converting Na (gas) into Na^+ (gas) and the energy of electron affinity is evolved in the conversion of Cl (gas) into Cl^- (gas), i.e.



III. The third and final step involves combination of gaseous Na^+ ions and Cl^- ions to give one mole of NaCl crystal lattice. The energy released in this process evidently is equal to the crystal lattice energy of NaCl .

According to Hess law, the heat of formation of one mole of NaCl should be the same irrespective of the fact whether it takes place directly as in eq (1), above or through the three hypothetical steps. Hence,

$$- 98.21 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

$$\text{Or } - 98.21 = 26.0 + 28.09 + 118.0 - 87.3 + U$$

$$U = 26.0 + 28.9 + 118.0 - 87.3 + 98.21$$

\therefore Lattice energy – 183.81 K.cals.

The negative sign indicates that energy is released.

THEORETICAL VALUE OF LATTICE ENERGY :-

The theoretical value of lattice energy may be calculated using the Born landle equation

$$U = \frac{NO AZ + Z^- e^2 \left(1 - \frac{1}{n}\right)}{r} = \frac{NO A Z^+ Z^- e^2 \left(1 - \frac{1}{n}\right)}{r}$$

Where,

NO = Avogadro constant = $6.023 \times 10^{23} \text{ mole}^{-1}$

A = Medulong constant which depends upon the geometry of crystals.

Z^+ & Z^- = are the charges on the positive and negative ions.

C = Charge on an electron

r = Inter ionic distances

n = Constant called the Born exponent

APPLICATION OF BORN – HABER CYCLE :-

- (i) The most important application is in the determination of electron affinities which are difficult to determine by other method.
- (ii) The Born Haber cycle also provides an explanation for why most metals fail to form stable ionic compounds in low valance states such as AlO , MgCl .
- (iii) It is useful in determination of size of atoms.

Conclusion drawn from Born – landle equation :-

- (i) The lattice energy varies directly as the product of the charges on the ions of the ionic crystal.
- (ii) Lattice energy varies inversely as the inter nuclear distance r_0 between the oppositely charged ions in an ionic crystal.

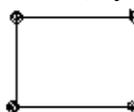
Application of Lattice energy :-

With the help of lattice energy we can estimate electron affinities, proton affinities and heats of formation. Further applications found.

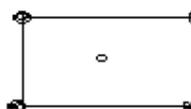
- In the discussion of the special properties of fluorine in relation to other halogens.
- In the account of stabilities of metal hydrides poly halides and peroxides & super oxides.
- In the derivation of crystal field stabilisation energies.
- In the discussion of the characterising of high oxidation states of metals as fluorides and of their low oxidation states as sodides.

The fourteen Bravais lattice & the unit cell diagram for each.

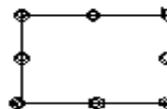
If the unit cell has points only at the corner then it is called a primitive lattice, symbolised P. A Primitive Lattice has only one point per unit cell.



A unit cell may have a point as its body centre in addition to those at corners. Such a cell is doubly primitive because it contains two points. Its symbol is 'I'. addition



A unit cell may have points on the centre of its six faces, in addition to those at the corners. Such a unit cell contains four points per unit cell and is quadruple primitive. It's symbol is 'F' (face centred)

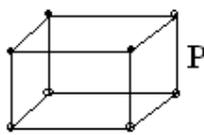


In monoclinic and orthorhombic system there is a possibility of one pair faces having additional points at the centre in addition to those at corners. Such lattice are doubly primitive and are called end-centred or (A⁻ or B⁻ or C⁻ entered).

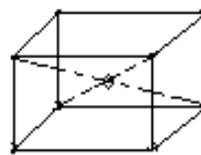
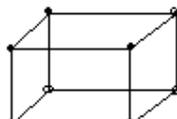
Based on the above definitions of different unit cell we may tabulated the 14 Bravais Lattice type as follows-

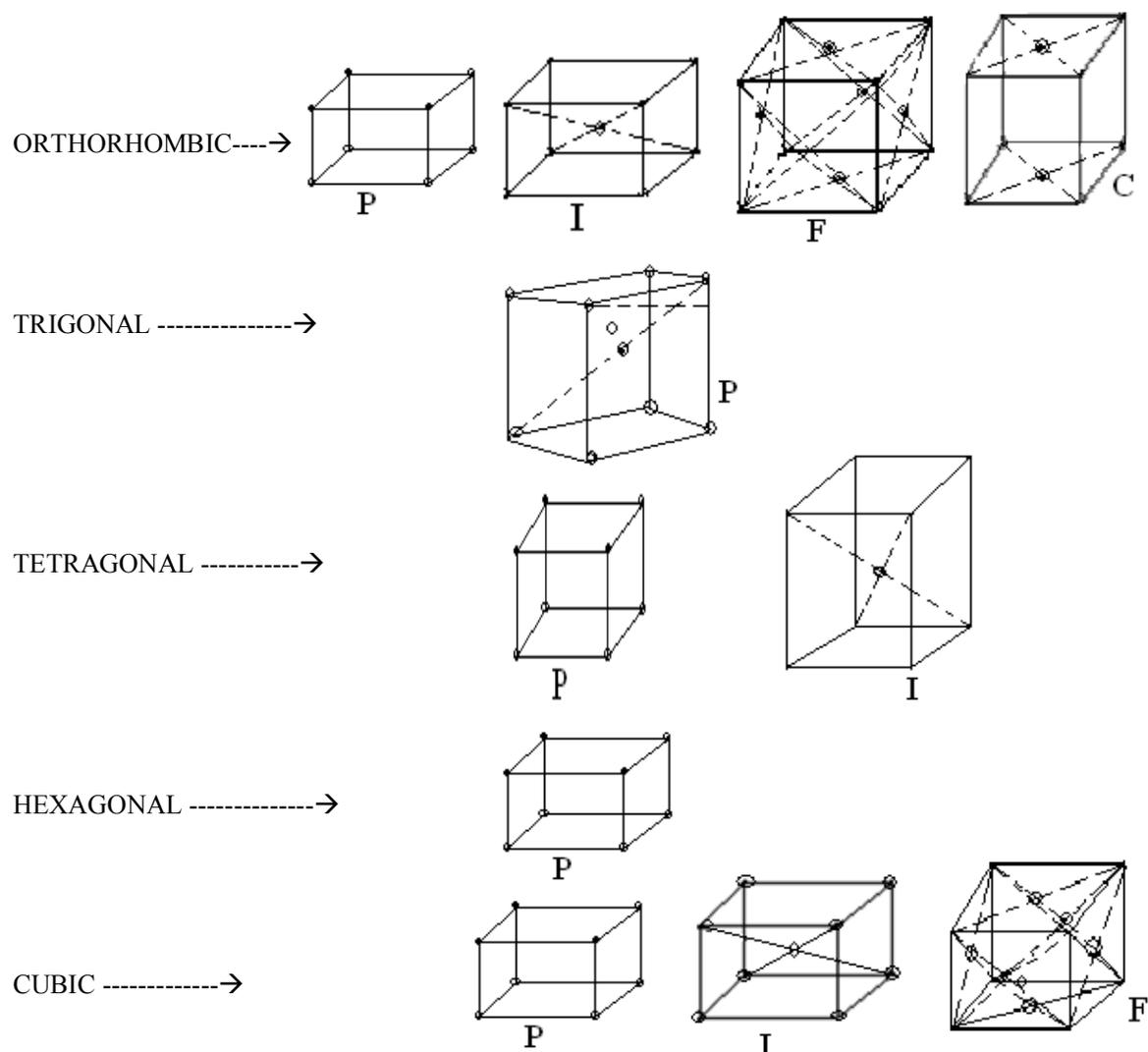
NAME OF SYSTEM	POSSIBLE LATTICE TYPE SYMBOL	NUMBER	TOTAL
TRICLINIC	P	1	14 TYPE
MONOCLINIC	P } C }	2	
ORTHORHOMBIC	P } C } I } F }	4	
TRIGONAL	P or R	1	
TETRAGONAL	P } I }	2	
HEXAGONAL	P	1	
CUBIC	P } I } F }	3	

TRICLINIC ----->

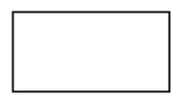
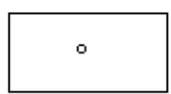


MONOCLINIC ----->





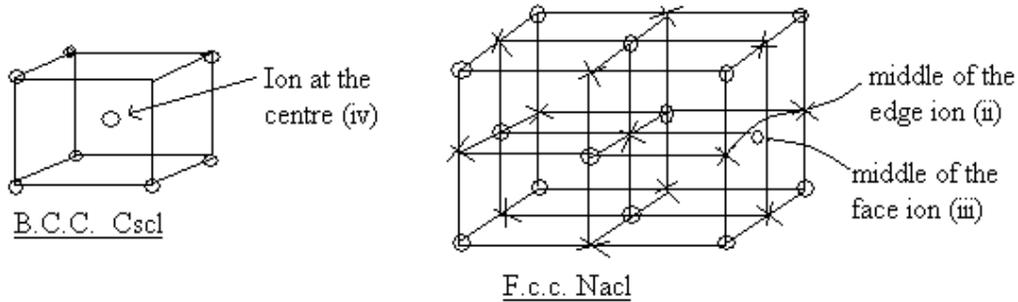
Two dimensional Lattice types are five in number. They are :-

- (i) Square -----  $a = b$
 $\theta = 90^\circ$
- (ii) Rectangle -----  $a \neq b$
 $\theta = 90^\circ$
- (iii) Centred rectangle ----  $a \neq b$
 $\theta = 90^\circ$
- (iv) Parallelogram -----  $a \neq b$
 $\theta \neq 90^\circ$
- (v) Rhombus -----  $a = b$
 $\theta = 120^\circ$

Effective Atomic No. :-

An atom in unit cell, all the time do not contribute totally to the unit cell and hence there is difference in the effective atomic no. For a unit cell of cubic lattice following points are to be followed in order to predict or calculate the effective atomic number.

- (i) An atom at the corner of the cubic cell will contribute 1/8 to the unit cell.
- (ii) An atom or ion at the middle of the face of the cube will contribute 1/2 to the unit cell.
- (iii) An atom or ion at the middle of the edge of the cube will contribute 1/4 to the unit cell.
- (iv) An atom or ion at the centre of the cube will contribute 1/1 to the unit cell.

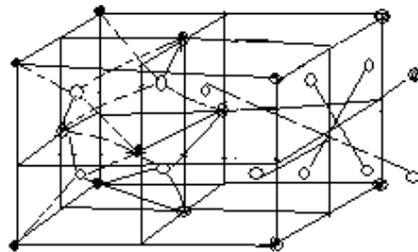


For e.g. if we want to calculate the effective atomic no. of a face centred cubic lattice, we proceed as follows :-

- (i) As the no. of points at the corner of the cubic is 8 therefore -
- contribution of point per unit cell = $8 \times \frac{1}{8} = 1$



Crystal structure of CaF₂ :-

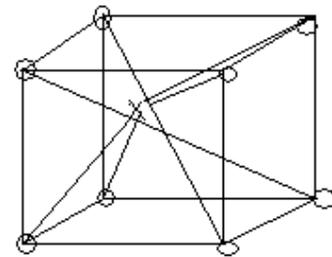


● = Calcium
○ = Fluorine

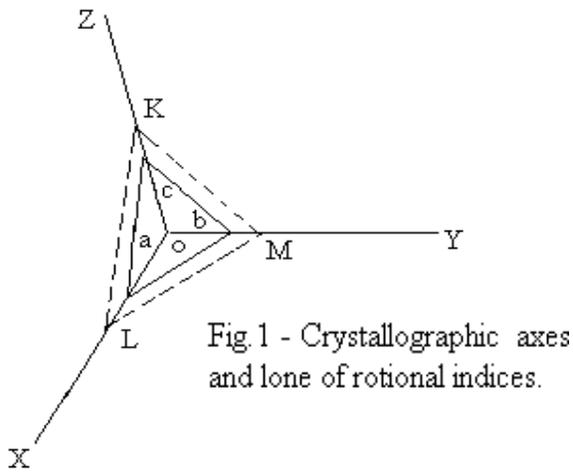
Ca = 8 Coordination no. Cubic
F = 4 Tetrahedral

Structure of CsCl :-

In this structure CS^+ ions are represented by 'O' and Cl^- ion By. The Cl^- ion is surrounded by eight CS^+ ions. In the Structure of CsCl, corner of unit cell is occupied by CS^+ ions and inside the body cl^- is present at the centre. In this way Cl^- ion is surrounded by 8 CS^+ ions. Therefore co-ordination no. of CS^+ ion is 8. Each CS^+ ion is attached with one Cl^- ion which is present at the centre of the cell. Since it is common to 8 unit cells.



MILLER INDICES :- For denoting faces of crystal three co-ordinate axes are chosen. These three axes are either intercept faces of the crystal or be parallel to same of the faces, in which case intercept will be infinitive. For denoting faces of crystal unit plane as shown in figure is selected. The intercept of this plane on the three axes are chosen as unit distance. These unit distance should be such that intercept of the faces will be represented as ma, nb and pc. This m, n & p may be whole number – infinitive or fraction.



The multiple of unit distance i.e. m, n & p are called Weiss indices. In stead of Weiss indices it is more andvantage to use Miller indices Weiss is defined as follows :-

The reciprocal of Weiss indices and multiplying through out by the smallest no. so that ratio become whole number or zero is called Miller indices. For example if Weiss indices of a face is $2a, \frac{2}{3}b$ and ∞c then Miller indices will be $1/2, \frac{1}{2/3}, 1/\infty$ or $1/2, 3/2$ and 0 .

Multiplying by smallest no. 2, we get :-

Thus Miller indices of this plane will be 130 and is written as (130).

Problems :- How will you express Miller indices of the four faces of topaz.

Ans. : Weiss indices of the topaz will be written as (i) $(1, 1, \infty)$ (ii) $(1, 1, 1)$, (iii) $(1, 1, 2/3)$, (iv) $(2, 1, \infty)$

The reciprocal of Weiss indices of the four faces of the topaz are –

- (i) $1/1, 1/1, 1/\infty = 1, 1, 0$
- (ii) $1/1, 1/1, 1/1 = 1, 1, 1$
- (iii) $1/1, 1/1, \frac{1}{2/3} = 1, 1, 3/2$
- (iv) $\frac{1}{2}, 1/1, 1/\infty = \frac{1}{2}, 1, 0$ respectively

Now multiplying by smallest no. where necessary we get –

- (i) $(1, 1, 0)$, (ii) $(1, 1, 1)$, (iii) $(2, 2, 3)$, (iv) $(1, 2, 0)$

Thus the Miller indices of four faces of topaz will be –

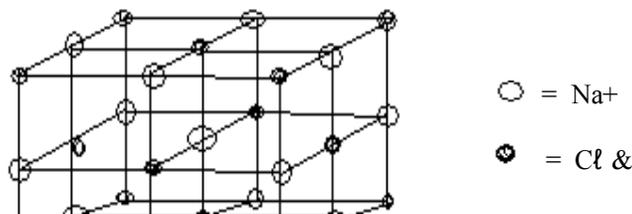
- (i) (110) , (ii) (111) , (iii) (223) , (iv) (120) respectively

Note : a) The reciprocal values of (i) and (ii) is multiplied by 1 to have whole no.
 b) The reciprocal values of (iii) and (iv) are multiplied by 2 to have whole no.

Unit Cell :- The smallest unit of Lattice which on extending in three dimension in space forms space lattice is called unit cell. For example we know that each CS^+ ion is surrounded by eight chloride ions and vice versa. The unit cell of caesium chloride can be shown as above given in figure (i) and (ii).

In case of sodium chloride each sodium ion is surrounded by six chloride ion and vice-versa. X-rays examination reveals that structure of sodium chloride is face centred cube. It is unit cell can be denoted as follows :-

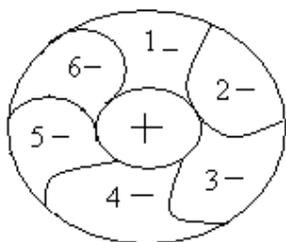
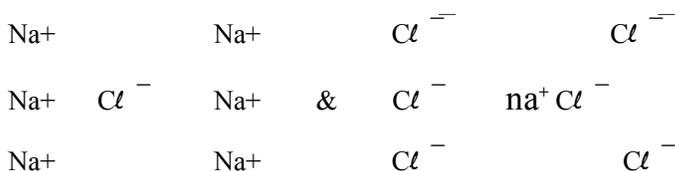
Face centered cube



Inter facial face :- Each unit of solid is bounded by a plane which is called face of the crystal. These faces intersect each other. The angle at which two faces intersect is called inter facial angle, e.g. each cube is bonded by six plane known as face of the cube. Two faces of the cube intersect at 90° , So the inter facial angle of the cube is 90° .

Edge length :- Two faces of a solid meet at a certain line known as edge of the crystal e.g. There are six faces in cube. Two faces of a cube meet at a line known as edge of the cube. There are twelve edge in cube.

Co-ordination number :- Number of opposite ions – immediate contact with an ion in a crystal is known as co-ordination number. For example in sodium chloride crystal each sodium ion is surrounded by six chloride ion and each chloride ion is surrounded by six sodium ion. Thus the co-ordination number of sodium chloride ion is six. Similarly in caesium chloride crystal each caesium ion is surrounded by eight chloride ion and each chloride ion is surrounded by eight caesium ion. So the co-ordination no. of CS^{+} and Cl^{-} ion is eight in a caesium chloride crystal. The co-ordination no. of an ion in a crystal depends upon relative size of the ion. It can be proved geometrically that of the ratio of size of cation and anion in a crystal is 0.155 - 0.225 than the co-ordination no. will be 3.



The co-ordination no. of the atom or ions (marked as +) is 6. It means there are six nearest neighbour. In simple cubic system. In BCC system the C.N = 8 and in F.C.C. system C.N = 12.

Radius ratio :- The ratio of radii of cation and anion of an ionic crystal is called radius ratio.

$$\text{Thus radius ratio} = \frac{\text{Size of cation } (r^{+})}{\text{Size of anion } (r^{-})}$$

The radius ratio has great effect on the size and shape of an ionic crystal. The effect of radius ratio on the size and shape of the crystal is known as radius ratio effect. For maximum stability of an ionic crystal, it is essential that an ion should be in contact with opposite ions and opposite ion should touch each other. This will be minimum distance between ion in case of stable crystal. The radius ratio in such case is known as limiting radius ratio. It can be proved geometrically that co-ordination number of an ion in ionic crystal can be determined on the value of radius ratio as given below.

(Limiting Radius Ratio in Crystals)

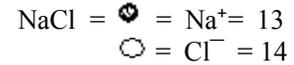
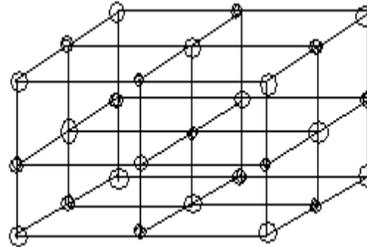
Limiting Radius Ratio	Co-ordination number	Shape of crystal
0.155 - 0.225	3	Plane triangular
0.225 - 0.414	4	Tetrahedral
0.414 - 0.732	4	Square planar
0.414 - 0.732	6	Octahedral
0.732 - 1.000	8	Cubic

Crystal structure of sodium chloride (NaCl) :- The radius of Na^+ ion is 0.95 \AA and that of Cl^- ion is 1.81 \AA . Hence radius ratio of NaCl is 0.524 which lies between 0.732 and 0.414. Hence the co-ordination number should be 6 or 4 and shape should be either octahedral or square planar.

The x-ray study of crystal shows that sodium chloride has octahedral structure which suggest that each sodium ion is surrounded by six chloride ion and in a regular octahedron. Each chloride ion is surrounded by 6 sodium ions at the corners of regular octahedron.

The x-ray examination has shown that the distance between the centres of two adjacent ions 2.814 \AA . On adding the radius of Na^+ & Cl^- ions the result is $0.95 + 1.81 = 2.76 \text{ \AA}$ which is quite close to 2.814 \AA . This confirms that there is little or no space between the adjacent ions. The crystal structure of NaCl is as follows :

In this structure chloride ion Cl^- are arranged in face centred cubic (CCP) type of symmetry.



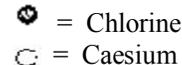
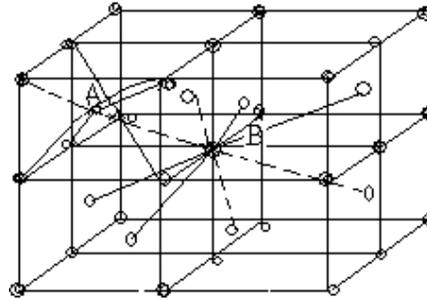
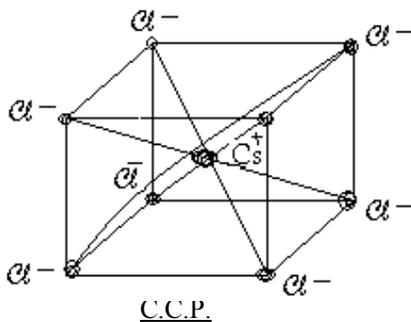
The Na^+ ions occupy all the octahedral sites (holes) constituted by the packing of Cl^- ion. Thus it is clear that there is one octahedral hole for each sphere packed in this manner. Thus for each Cl^- ion there is one Na^+ ion. It may be noted that neither Cl^- ions are touching one another or Na^+ ions, because in that case crystal structure would not be stable. The Na^+ ion occupying the octahedral sites are sufficiently large to keep the Cl^- ions apart from one another and similarly Cl^- ions are sufficiently large to the Na^+ ions apart from one another.



Crystal structure of cesium chloride (CSCI) :- In cesium chloride the radius ratio r^+/r^- is equal to $1.69 / 1.81 = 0.93$ which lies between 0.732 – 1.00.

Hence the co-ordination no. should be 8 and a cubic structure. The Cl^- ions from the simple cubic arrangement and Cs^+ ions are present in interstitial sites. Thus Cl^- ions may be regarded as lying at the corners of cube and Cs^+ ion at the body centre of the cube. Each Cs^+ ion is seen to have eight chloride ions as nearest neighbours. If the structure is extended it can be seen that each Cl^- ion is also surrounded by eight Cs^+ ions.

The x-ray photographic suggested that $\text{Ca}^{2+} * \text{Cl}^-$ ions are packed in cubic closed packed arrangement. Their unit cell can be shown as given below :-



Problem :- The caesium chloride lattice is one percent more stable than Sodium Chloride lattice.

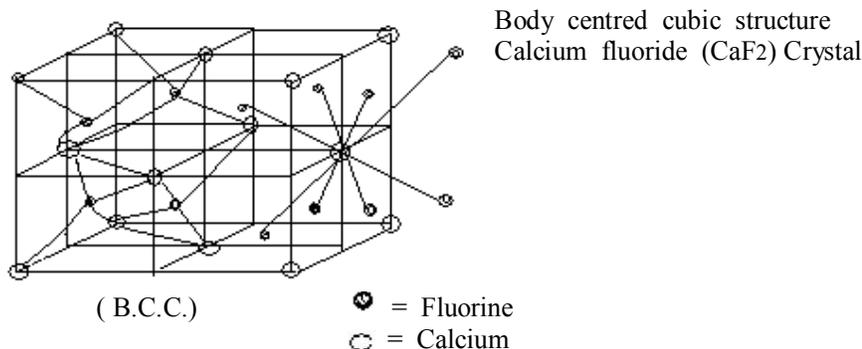
Ans.:- This is due to difference in Co-ordination number. It is found that Co-ordination no. of CSCI is higher than NaCl and it is expected that each ion of caesium chloride would have more ions of opposite charge as its neighbours which arises the extra stability of caesium chloride than sodium chloride. Thus caesium chloride lattice is one percent more stable than the sodium chloride lattice.

Calcium Fluoride Structure :- Calcium Fluoride possess fluorite type of structure. The radius ratio of calcium fluoride is 0.73 and so, co-ordination no. is 8. It means that each calcium ion is surrounded by eight fluoride ions. As the valency of fluoride ion is half of the valency of calcium ion, so each fluoride ion is

surrounded by four calcium ions. In this way in calcium fluoride each calcium ion is surrounded by eight fluoride ion in body centred cubic arrangement and each fluoride ion is surrounded by four calcium ions in tetrahedral arrangement. Such arrangement is called 8:4 arrangement.

Calcium ions in fluorite structure are arranged in face centred cubic close packed (ccp) type of arrangement. All the eight octahedral sites constituted by four Ca^{+2} ions are occupied by eight F^{-} ions.

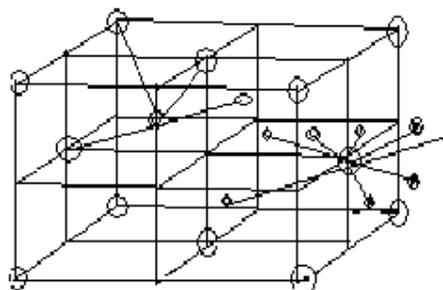
The structure of calcium fluoride can be shown by following figure :-



Crystal Structure of Lithium Dioxide :- Lithium oxide consists a lithium ion oxide ion. The valency of oxide ion is double the valency lithium ion which is the reverse of calcium fluoride. The structure of lithium oxide is anti fluorite type of structure. In this structure each lithium ion is surrounded by four oxide ion in tetrahedral arrangement. Each oxide ion is surrounded by eight lithium ion in body centred cubic arrangement. In this structure oxide ions are packed in face centred cubic closed packed arrangement. C.C.P.

The structure of lithium oxide can be shown by the

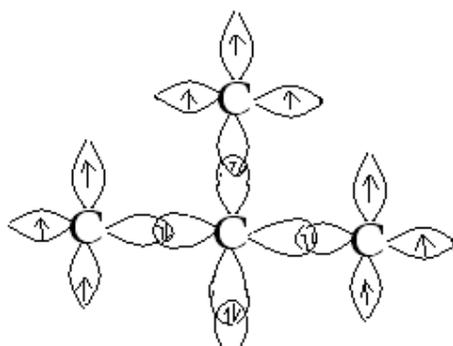
Given diagram where $Li^{+} = \bullet$
 $O_2^{-} = \circ$



Li₂O

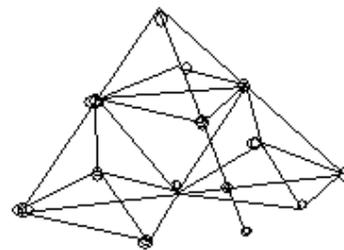
Structure of Diamond :- In diamond each carbon atom is constantly bonded by sharing of electrons to four other atoms each carbon is surrounded by four others at the four corners of regular tetrahedron atom. Thus orbital by each carbon atom in diamond contains a pair of electrons of opposite spin. In this way each of orbital and orbital of carbon atom in diamond are strongly bonded with four carbon atoms in continuous chain of regular tetrahedron manner. Due to this reason diamond is the hardest substance. As no carbon atom in diamond contains unpaired electron so it is a band conductor of electricity.

In diamond entire crystal is regarded as one large carbon molecule and it is called Macro molecule. The structure of diamond is represented as give below :-



Or

Structure of diamond



Zinc Sulphide Structure :-

Zinc sulphide also belongs to the category of AX type of ionic solid . It has two types of structures known as :

- (i) Zinc blende Structure and
- (ii) Wurtzite Structure

(i) Zinc blende structure :- In zinc sulphide, the radius ratio $\frac{r^+}{r^-}$, is 0.40. This suggests that the co-ordination number is 4 and that the crystal has tetrahedral structure. Thus each Zn^{2+} ion (represented by a plane circle) is surrounded by four S^{2-} ions (represented by shaded circle) disposed towards the corners of a regular tetrahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions, as shown in Fig.-A. A more convenient description of Zinc Sulphide Structure is to regard the four sulphide ions as present in a cubic close packed (ccp) type of arrangement. Since there are two tetrahedral sites for each sphere packed in this manner, there would be 8 tetrahedral sites. However, since **stoichiometry** of ZnS is 1:1, there are only four zinc ions for four sulphide ions. Hence only half of the tetrahedral sites (holes) are occupied by Zn^{2+} ions. The remaining tetrahedral sites remain empty, it is believed that the tetrahedral sites are occupied in a regular way. Thus alternate sites are left vacant.

(ii) The Wurtzite Structure :- In the Wurtzite Structure (Fig. B) sulphide ions are present in a hexagonal close packed (hcp) type of arrangement. In this type of arrangement also as has been shown before. There are two tetrahedral sites per sphere. Thus there would be eight tetrahedral sites constituted by S^{2-} ions and only half of these will be occupied by Zn^{2+} ions.

It will be noted that the only difference between zinc blende and wurtzite structures is that whereas in the former case the sulphide ions are arranged in ccp type of packing (i.e. there is ABC ABCsequence of layers), in the later case they are arranged in hcp type of packing (i.e. there is ABABA sequence of layers). The co-ordination in each case is 4:4.

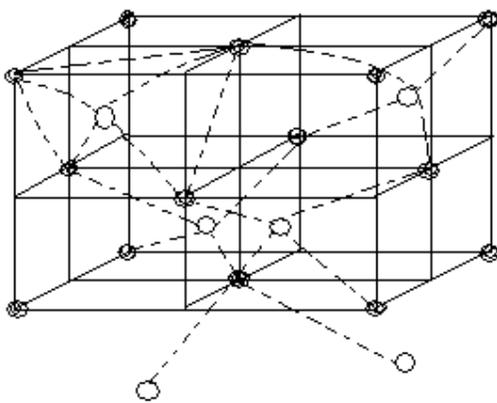


Fig. A

Zinc blende Structure
Plane circles represents Zn^{+2} ions while shaded Circles represents S^{2-} ions

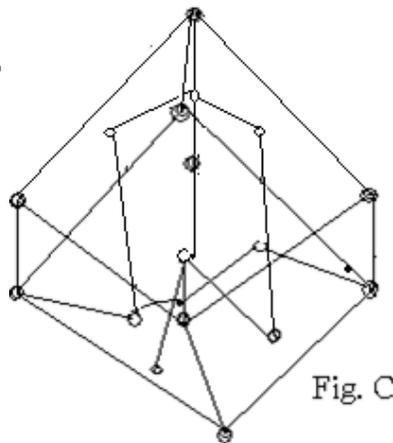


Fig. C

Re-oriented structure of Zinc Blende

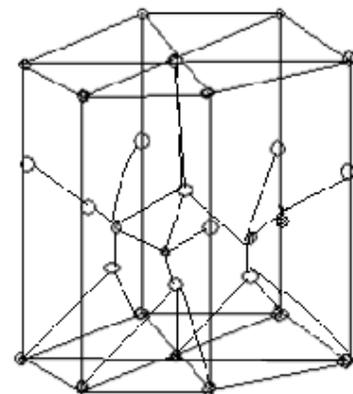


Fig. B

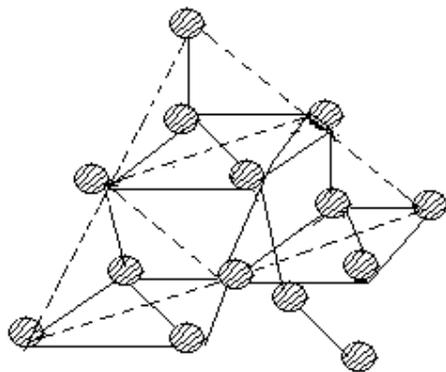
The Wurtzite Structure
plane circles represents Zn^{+2} ions while shaded circles represents S^{2-} ions

- ⊙ Sulphide
- Zinc

In order to illustrate the similarity between the structures of zinc Blende and Wurtzite, the structure of Zinc Blende is shown in a re-oriented manner in Fig. C.

Diamond is the hardest,

In diamond each carbon atom is Sp^3 – hybridised. Thus in diamond, each carbon atom is surrounded by other four carbon – atoms tetrahedrally and bonded to them. This gives a “giant structure” shown as -

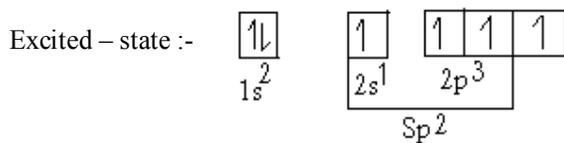
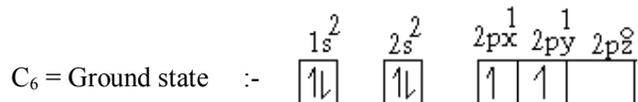


● = C - atoms

Also the bonding between them is very strong. Thus diamond is the hardest.

Graphite is a good conductor of electricity though it is a covalent crystal.

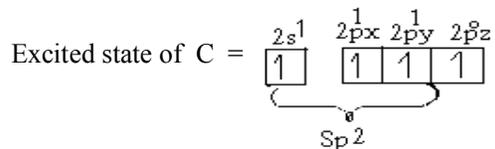
Graphite is a covalent crystal. In graphite each carbon atom is Sp^2 hybridised - shown as :-



Thus each carbon- atom in graphite is surrounded by three other carbon- atom s and each carbon atom has unhybridised p_z – orbital which contains one unpaired electron. Thus free electrons are available to move in graphite crystal. Hence it conducts electricity.

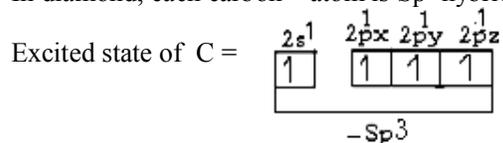
Graphite is a good conductor of electricity while diamond is a non conductor of electricity.

In graphite each carbon atom is Sp^2 – hybridised shown as



Thus in graphite each carbon – atom is joined to other three carbon – atoms and each carbon atom has one unhybridised orbital containing one unpaired electron. Thus free electrons are available to move in graphite crystal. Hence graphite is good conductor of electricity.

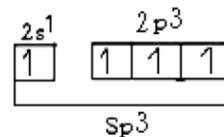
In diamond, each carbon – atom is Sp^3 hybridised, shown as :-



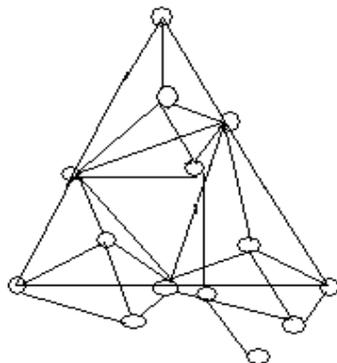
Thus free electron is not available in diamond. Hence it is non conductor of electricity.

Diamond is hard while graphite is soft :-

In diamond each carbon atom has Sp^3 hybridisation shown as -



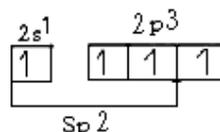
Thus in diamond each carbon atom is surrounded by four other carbon – atoms tetrahedrally and bonded to them. The bonding between carbon atom is very strong. This gives a giant structure of diamond shown as –



o = C atom

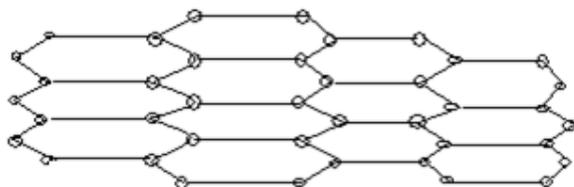
Thus diamond is hard.

In graphite each carbon atom is Sp^2 hybridised shown as :-



Thus each carbon – atom in graphite is bonded by three other carbon atoms forming a planar sheets of fused eye be hexagonal rings and each carbon – atom has an unhybridised pz – orbital containing one unpaired electron.

These occurs a poor interaction between neighbouring planes through pz – orbital.

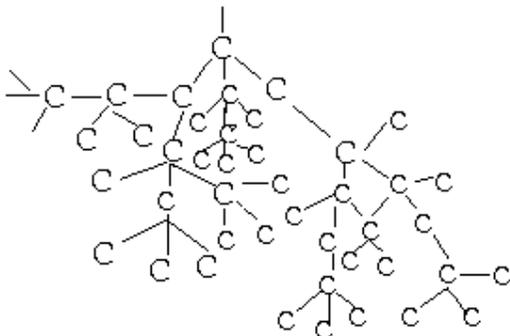


o = C atom

Thus graphite is soft

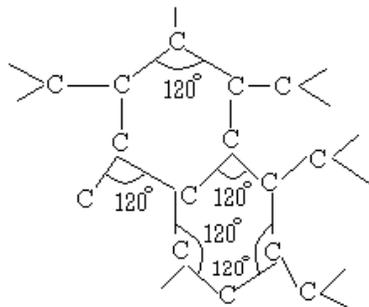
Diamond has higher melting point than graphite.

In diamond each carbon atom is Sp^3 hybridised. Thus each carbon – atom is strongly bonded to three other carbon atoms tetrahedrally. This makes diamond a giant and inter locked molecule, shown as -



Hence Diamond has high melting point.

In graphite each carbon atom is Sp^2 hybridised. Thus each carbon atom is bonded to three other carbon – atom trigonally. Each carbon atom containing one unpaired electron in its unhybridised Pz – orbital through which a poor interaction between neighbouring planes occur. It can be shown as -



Hence graphite has low melting point.
This diamond has higher melting point than graphite.

Graphite has lower density than diamond.

The bond length in graphite is greater than the bond length in diamond. This is because the each carbon – atom in graphite is Sp^2 hybridised while each carbon – atom in diamond is Sp^3 hybridised. Due to Sp^2 hybridisation, each carbon atom in graphite contains one unpaired electron in its unhybridised p_z – orbital. Thus a poor interaction between neighbouring planes also occur through this unhybridised p_z orbital. Thus if same number of graphite and diamond molecules are taken then graphite molecules cover more place than diamond molecules.
It means graphite has low density in comparison to diamond.

Na is softer than Mg.

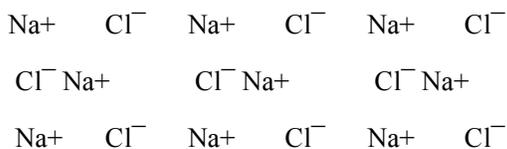
Metals are characterised by low ionisation potentials. Thus metals easily loose electrons and form cat ions. In case of Na, the formation of Na^+ ion is shown as :- $Na(g) \rightarrow Na^+(g) + e^-$
In the case of Mg :- $Mg(g) \rightarrow Mg^{++}(g) + 2e^-$
The bonding between cation i.e. Na^+ and Mg^{++} and electron is metallic in nature. Since the strength of metallic bonding increases with increase in number of available electrons for bonding.

In case of Na each Na^+ ion is bonded to only one electron while in Mg, each Mg^{++} ion is bonded to two electrons. Thus Mg has strong metallic bonding then Na. Hence Na is softer than Mg.

NaCl is harder than Na and have high melting point.

Na has low ionisation potential. Thus it easily loses one electron and forms Na^+ ion shown as –
 $Na(g) \rightarrow Na^+(g) + e^-$

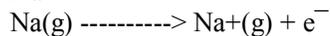
The bonding in Na between $Na^+(g)$ and e^- is very weak. In NaCl crystal points are occupied by Na^+ and Cl^- ions. It is an ionic solid.



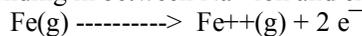
The bonding between Na^+ & Cl^- is purely electrostatic in nature. The electrostatic bonding between NaCl is stronger than metallic bonding in Na. Thus NaCl is harder than Na and also have high melting point than Na.

Na is softer than Fe.

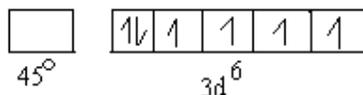
Metals are characterised by low ionisation potential. Thus they easily loses electrons to form cat ions. In case of Na^+



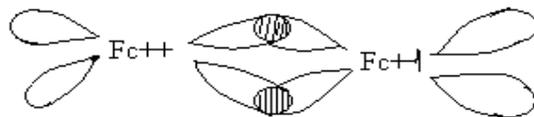
The bonding in between Na^+ ion and electron. In the case of Fe :



The bonding in between Fe^{++} ion and two electrons. Thus in Fe, metallic bonding occurs. Since Fe^{++} ion has outer electronic configuration $3d^6$ shown as –



Since unpaired electron is present in 3d orbital. Thus d-d overlap takes place. Due to this overlap, π bond is formed called $d\pi - d\pi$ bond. Thus in Fe, a $d\pi - d\pi$ bond is formed in addition to metallic bonding, shown as



Therefore, Fe is harder than Na. Fe also has higher melting point than Na Fe also has higher melting point yhan Na.

NaCl is non-conductor of electricity but on melting it becomes conductor of electricity.

Ans. :- NaCl is an ionic solid. In solid state the ions i.e. Na^+ ion and Cl^- ion have fixed places. When the electric field is applied the ions can not move. Hence NaCl is non-conductor of electricity.

When solid NaCl is converted into molten state or fused state, the well arranged order of ions is destroyed. In this case ions have no fixed places. They can easily move in whole crystal by applying electric field. Hence fused NaCl becomes conductor of electricity.

Q. 11 :- Ionic solids are soluble in water ?

Ans. :- In ionic solids the points are occupied by oppositely charged ions. The bonding between them is electrostatic in nature. The force of attraction between the ions is given as ;

Where Q_1 and Q_2 are the oppositely charge on points, r is distance between them and K is dielectric constant of medium.

For air, dielectric constant $K = 1$

Thus force of attraction between ions is great. Hence ionic solids exist in air. But for water, dielectric constant $K = 80$. Thus force of attraction between ions is 80 times less in water than in air. Hence ionic solids are soluble in water.

At ordinary temperature the vapour pressures of ionic solids are low.

In ionic solids points are occupied by oppositely charged ions. The bonding between oppositely charged ions is purely electrostatic i.e. very strong bonding between ions. Due to strong bonding in solids, they are not easily vaporised. High temperature is required for vaporisation of ionic solids. Thus at ordinary temperature the ionic solids are not more vapourated. Hence they have low vapour pressure at ordinary temperatures.

NOTE :-

The heat of hydration of ionic solids i. e. energy required for breaking the solids is also high due to strong bonding between solids.

SOLID STATE - PART- II

Define Miller indices of a crystallographic plane and find the structure of CsCl, cscu and diamond.

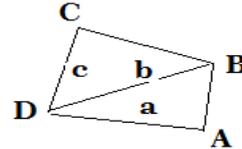
A plane passing through at least two lattices points is called a crystallographic plane.

Miller indices of a family of parallel crystallographic plane is a set of three rational numbers divide of common divisors. Symbolized hkl. To find the miller indices of crystal plane we

- (1) Take the intercepts on the crystallographic axes.
- (2) Clear of function, if any, without common divisor.

For example:- The plane ABC which cuts the crystallographic axes at the ends of three unit vectors the law says .

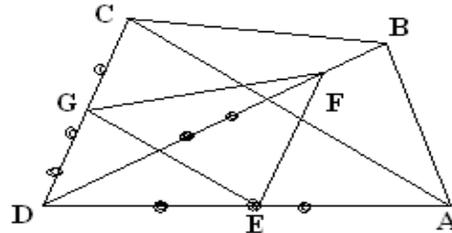
- (1) 1,1,1
- (2) 1,1,1
- (3) Not needed



Since Miller indices of plane ABC is (111) it is known as the unit plane or parametral plane.

For plane EFG

- (1) Intercepts are 2/10, 3/4, 3/5



opposite ions e.g. each Na⁺ ions in NaCl surrounded by six (6) Cl⁻ ions and vice versa.

- (2) Reciprocal are 10/2, 4/3, 5/3

- (3) 30, 8, 10

hkl = (15, 4, 5)

Miller indices of the faces of a cube:-

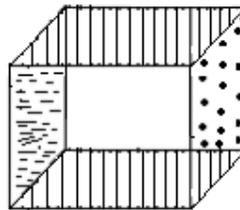
Face FCBG

- (1) Intercepts are a, b, c

Impurity 1 ∞

- (2) Reciprocal are 010

- (3) Not needed - hkl = (010)



Face AHDE has miller indices 0 0

" AHGB " " " 00

" EFCD " " " 00

" EFGH " " " 100

" DABC " " " 00

Cube face are (00) (T00) (0 0) (0T0) (00) and (001)

Structure of simple type :-

- (1) Primitive cubic -----> CsCl

Atoms (.) -----> 000

Cl (o) -----> 1/2,1/2,1/2

One formula unit per cell.

- (2) q Cubic :- Cs metal

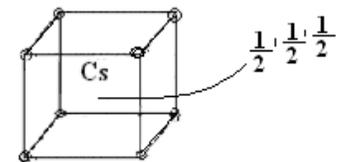
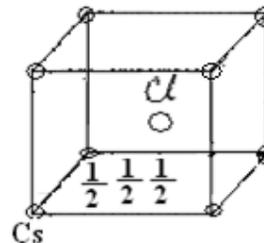
Atoms Cs ----- 000

Cs ----- 1/2 1/2 1/2

Face centred Cu, Au, Ag, Pt, Fe, Cu, Four Cu are needed.

Coordinates of the atoms are (000, 1/2 1/2 1/2, 1/2 01/2, 01/2, 1/2)

4. F.C.C. NaCl (Alkali halides 4 formula unit is needed) .



Na -----> 000, 1/2 1/2, 0, 1/2 0 1/2, 0 1/2 1/2 -----



$\alpha(o) \rightarrow 1/2, 1/2, 1/2, 0, 0, 1/2, 0, 1/2, 0, 1/2, 0, 0$

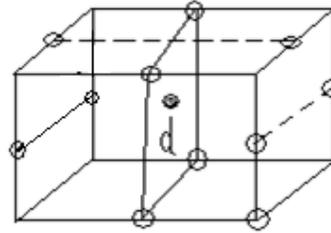
5:- F.C.C (Special)

Diamond

lattice is F.C.C

the two identical C-atoms at (0,0,0), (1/4,1/4,1/4)

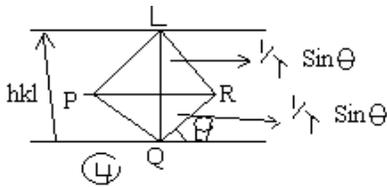
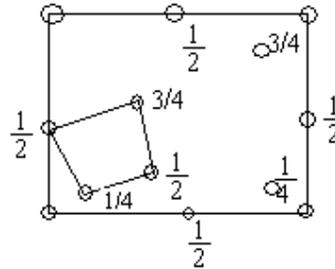
Because of (1/4,1/4,1/4)



Lattices point Diamond is hard and (10B) gives

$$\vec{S} \perp \vec{BC}$$

Hence \vec{S} is \perp to the miller plane hkl.



Hence with PQ as the incident ray and QR as diffracted, we find from Fig. (4) that -

$$2d \sin \theta = \lambda$$

$$\text{Or } \lambda = 2d_{hkl} \sin \theta$$

Which is Bragg's law. The Bragg's

law reduces the law e.g. n to

simple reflection condition. The difference from ordinary reflection is that how many orders of reflection are possible due to the presence of the Miller plane. In the case of ordinary reflection for a given angle of incidence, there is a single reflection possible.

-----X-----

Q- 82. Finding of the symmetry elements of cube melting.

Ans:- CRYSTAL--- Crystal are homogeneous solid, bonded by plane faces, meeting in sharp edges and having a regular geometrical shape which they acquire during their formation.

OR,

Crystal are homogeneous solids bound by naturally formed plane faces.

Crystal possesses symmetry. This symmetry of crystals is related to the internal atomic arrangement inside it.

External symmetry elements of a crystal are :-

[1] CENTRE OF SYMMETRY :- A crystal is said to possess a centre of symmetry when each face has a face parallel to it. In other words parallel faces must occur in pairs.

[2] PLANE OF REFLECTION SYMMETRY :- A crystal is said to possess a plane of symmetry when one half of it is the mirror image of the other half across the plane.

[3] ROTATION AXES :- A crystal is said to possess an axis of symmetry when after a rotation of $360^\circ/n$ about the axis it attains a congruent position. The value of n may be 1, 2, 3, 4, or 6 only.

Axis with $n = 5$ or greater than 6 are not possible. The axes are named as :-

$n = 1$ --- Identity axes --- symbol --- congruent position

$n = 2$ --- Diad ---  --- 180°

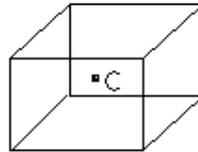


n = 3	----	Triand	----	-----	120 ⁰	
n = 4	----	Tetrand	----		-----	90 ⁰
n = 6	----	Hexad	----		-----	60 ⁰

Axis with n = 5 leaves vacant site and n = 7 or more gives a super position of material . In either cases homogeneity is violated . Hence n = 5 or greater than 6 are not possible axis.

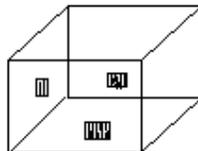
SYMMETRY ELEMENTS OF A CUBE :-

(i) A centre :--

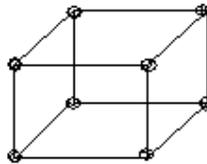


(ii) ROTATION AXES : ---

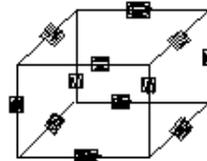
[a] Tetrads -- 3



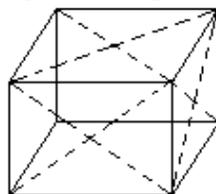
[b] Traids --- 4 (corresponding to eight corners or the four body diagonals)



[c] Diads -- 6 (corresponding to twelve edges)



(iii) Plane of symmetry --- Three planes along with the three tetrads .

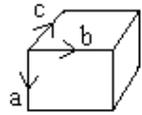


Six planes along the diads .

A total of 23 (1+13+9) external symmetry elements are in cube . This is maximum number which a crystal can have.

Q . :-- Explain unit cell , Lattice , Crystallographic axis and seven crystal system .

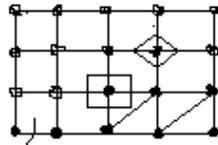
Ans.:-- UNIT CELL --- The smallest pattern unit whose repetition in three dimension builds a crystal is called unit cell . A unit cell is represented as the volume occupied by three unit translation vectors \vec{a} , \vec{b} and \vec{c} . In three dimensions \vec{a} , \vec{b} , \vec{c} , describe a parallelepiped which serves as the unit cell .



A unit cell is the smallest unit of a crystal lattice .

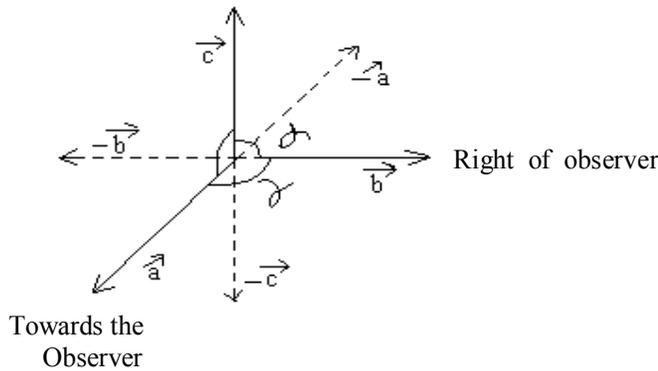
LATTICE --- A periodic array of points in space is called a lattice . Each point is a site of an atom of the crystal .

A structure = A Lattice + A Basis

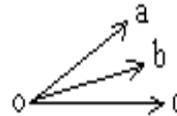


Unit Cell

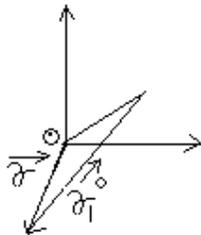
CRYSTALLOGRAPHIC AXES ---



Conventional choice for crystallographic measurement is



Any lattice point with r reference to O origin is defined by position vector



$$\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$$

Where u, v, w are arbitrary integers

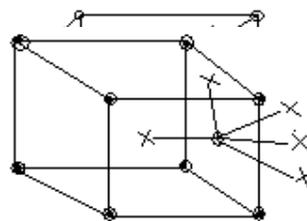
$$\text{Here, } \vec{r}_1 = \vec{r} + u\vec{a} + v\vec{b} + w\vec{c}$$

SEVEN CRYSTAL SYSTEM :--

Based on the minimum rotation symmetry crystals can be classified into seven head know n as Seven Crystal Systems.

crystal structure of Li_2O .

Lithium oxide has anti fluorite structure. Each oxide ion (O^{2-}) is surrounded by 8 Li^+ ion (Li^+) in a body centred cubic crystal . Since there is twice as many Li^+ ion as O^{2-} so the C.No of Li^+ is 4 and that of O^{2-} is 8. Thus the structure of Li_2O may be described at approximately c c p arrangement of O^{2-} ion with Li^+ ion in tetrahedral holes .



- $\times = \text{Li}^+$
- $\times = \text{Li}^+$
- $\bullet = \text{O}^{2-}$

type of solids

(a) Ionic Solid (b) Molecular Solid (c) Metallic Solid (d) Covalent Solid.

Ans.:- Ionic Solid:-

i) Constituent particles (i.e. units that occupy lattice points) :- An ionic solid is made up of cations and anions e.g. NaCl (Na⁺ Cl⁻), CuSO₄ (Cu⁺⁺ SO₄^{&&}).

ii) Binding force :- Each ion is held together by coulombic forces of attraction to all ions of opposite sign. Each ion in ionic solid is surrounded by certain no. of opposite ions e. g. Each Na⁺ ion in NaCl is surrounded by Six (6) Cl⁻ ions and vice versa.

iii) Physical properties :- A constituent ion in ionic solid is held together by very strong coulombic forces of attraction. So,

a) its heat of vaporisation is very high.

b) its vapour pressure of ordinary temp is very high.

c) its m.pt & b.pt is very high.

d) it is hard and brittle.

e) Ionic solids are insulator in the solid state but good conductor in liquid state or when dissolved in water or solvent of high dielectric constant.

In the solid state constituent ions of ionic crystals are entrapped in the fixed places and held together by very strong coulombic forces of attraction. As a result they can not move from their fixed position when electric field is applied.

In the molten state or in solid well ordered arrangement of ions in the crystal is destroyed and coulombic force of attraction between ions of opposite charges becomes very weak. In this condition ions are in a position to move about where an electric field is applied. Due to this reason ionic solid in molten state or when dissolved in water or solvent of high dielectric constant is good conductor of electricity.

f) Ionic solids are soluble in water or in other polar solvent but insoluble in non polar solvent.

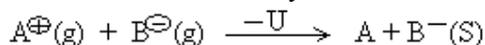
(ii) Melting point :- (Crystal) :- It has sharp m.p. i.e. it changes abruptly into liquid state.

Amorphous :- does not have m.p.

(a) Lattice energy (b) Space lattice & unit cell. (c) Co-ordination nos. (d) Crystal system (e) Bravais Lattice.

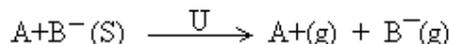
(a) Lattice Energy :- The lattice energy of an ionic solid is defined as the energy released during the formation of one mole of a crystal of the solid from the constituent gaseous ions separated from each other by infinite distance.

The formation of one mole of a crystal from the constituent ions may be represented as under :-



(U has a ⁻ve sign since energy is released in this process).

According to the first law of Thermo – dynamics the energy i.e. released in the formation of one mole of an ionic solid from the constituents gaseous ions is numerically equal to the energy that will be needed to convert one mole of the same ionic solid into the gaseous ions thus,



U = lattice energy with sign reversed [U has new the sign as energy is observed in this process]. It is clear that the higher the energy of an ionic solid the greater will be its stability.

Lattice energy of ionic solids are quite high. This is on account of strong electrostatic attractions between oppositely charged ions present in the solid. Since coulombic forces of attraction vary directly as the product of charge. It follows that higher the valency (charges) of the ions in the ionic solid. Thus lattice energy increases as we move from univalent ionic solids to bivalent ionic solids & then to divalent - divalent ionic solids.

Lattice energy increases with decrease in size of ions.

This lattice energy can be determined by experimentally by Born – Haber cycle. It can be calculated theoretically by Born- landle can.

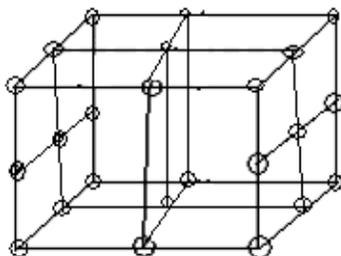
$$-U = \frac{ANZ^+ Z^- e^2}{r_0} \left(1 - \frac{1}{n}\right)$$

Where A = modulongconst. (the value of modulong const depends upon type of ionic solid & geometrical arrangement).

- n = Born - exponent
- n = 7 9 10 12
- Ne Ar Kr Xe
- C = Charge of an electron
- N = Avogandro's number
- Zⁿ⁺ = Charge on cat ion
- Zⁿ⁻ = Charge on anion
- r₀ = Sum of randii of cat ion & anion.

Space Lattice & Unit Cell :- The position of atoms molecules ions in a crystal relative to one another in space are designated usually by points such a representation is called space lattice. A space lattice is an arrangement of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.

UNIT CELL :- A unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance. the example of space lattice and unit cell can be given by the following diagram. Each point represents an identical atoms or group of atoms.



Space Lattice & Unit Cell

Coordination number :- The no. of oppositely charged ions surrounding a particular ion in the structure of ionic solid is known as co-ordination number of the ion. There are Six Cl⁻ around Na⁺ and vice versa in NaCl crystal, thus the co-ordination no. of both Na⁺ & Cl⁻ is 6.

For an ionic solid of the formula M_x the co-ordination no. of both Cat ion & anion is the same. For an ionic solid of the formula, M_x2 the co-ordination no. of M⁺⁺ is twice as that of X⁻. The co-ordination no. of an ion in ionic solid is determined by Radius ratio i. e. Limiting radius ratio.

$$\left(\frac{r^+}{r^-} = \frac{\text{radius of cation}}{\text{radius of anion}} \right)$$

The limiting radius ratio & corresponding co-ordination nos are given below :-

$\frac{r^+}{r^-}$	Co-ord. No.	Shape
0.155 to 0.225	3	Plane triangular
0.225 to 0.414	4	Tetrahedral
0.414 to 0.732	6	Octahedral
0.732 to 1.00	8	Cubic

Crystal System :- It can be shown from geometrical consideration that there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 point group or 32 system. As some

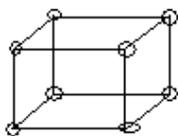
of the system have been grouped together. Some have only seven basic crystal systems. These are cubic tetrahedral, hexagonal, orthorhombic, monoclinic, triclinic and rhombohedral.

These systems together with the unit cell parameters i.e. the intercepts a, b, c & the crystal angles α, β & γ between three imaginary axis are given below :-

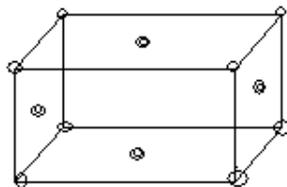
Crystal Systems	Parameters of intercepts	Crystal angles
(1) Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
(2) Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
(3) Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
(4) Monoclinic	$a \neq b \neq c$	$\alpha = \gamma \neq \beta \neq 90^\circ$
(5) Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
(6) Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
(7) Rhombohedral	$a = b = c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

Bravais Lattice :- Bravais shows from geometrical consideration that there can only be 14 different ways in which similar points can be arranged in three dimensional space i.e. Bravais divided 7 systems of crystal into 14 parts. Thus the total no. of space lattice belonging to all the seven crystal system is only 14. For example the crystal belonging to cubic system have three kinds of Bravais lattices depending upon the shape of the unit cell.

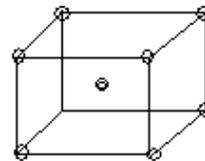
- (i) The simple cube of lattice in which there are points at the corner of each unit.
- (ii) The face centred cubic lattice in which there are points at the corners of as well as at the centre of each of the six faces of the cube.
- (iii) The body centred cubic lattice in which there are points at the corners as well as in the centre of each cube.



Simple Cubic Lattice



Face Centred Cubic Lattice



Body Centred Cubic Lattice

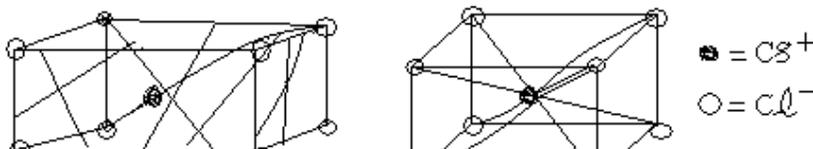
Crystal Systems	Bravais Lattice
1. Cubic Systems	3 - Primitive FCC, BCC
2. Orthorhombic	4 - Primitive FCC, BCC and Cubic
3. Tetrahedral	2 - Primitive & BCC
4. Monoclinic	2 - Primitive & end centred
5. Triclinic	1 - Primitive ,, ,,
6. Hexagonal	1 - Primitive ,, ,,
7. Rhombohedral	1 - Primitive ,, ,,
	14

CRYSTAL STRUCTURE of Caesium Chloride :-

The radius ratio of CS^+ & Cl^- ions is 0.93 (i.e. $\frac{r_{CS^+}}{r_{Cl^-}} = \frac{1.69}{1.81} = 0.93$). It suggests that the

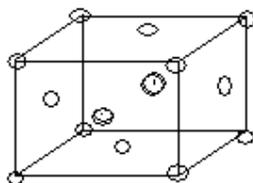
co-ordination no. of either CS^+ ion of Cl^- is 8. Thus each CS^+ ions form the simple cubic arrangement and caesium ions CS^+ are present interstitial sites. Thus Cl^- may be regarded as lying at the body centre of the cube. If the structure is extended as shown. It can be seen that each Cl^- ion is also surrounded by 8 Cl^- ion.

Thus the structure is body centred cubic type of arrangement. CsBr & CsI have also such structure



STRUCTURE OF LITHIUM OXIDE (Li₂O) :-

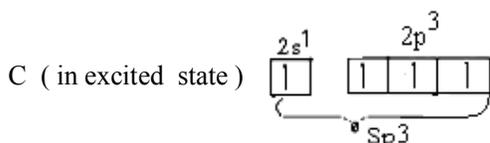
Lithium oxide has antifluorite structure each oxide ion (O²⁻) is surrounded by eight Li⁺ ions in a body centred cubic arrangement. Since there are twice as many Li⁺ ions as O²⁻ ions, so the co-ordination no. of 4 O²⁻ ions are tetrahedrally arranged round each Li⁺ ion. Thus the structure of lithium oxide may be desirable as an approximately c p arrangement of O²⁻ & ions with Li⁺ ions in the tetrahedral holes. The structure can be shown by following diagrams :-



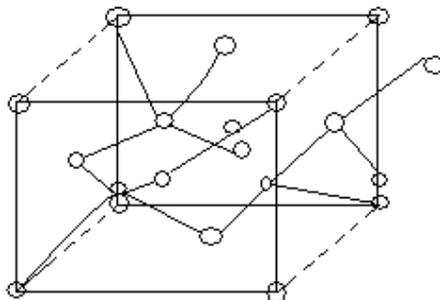
Anti fluorite Str. of Li₂O

This structure is and adopted by the oxides M₂O & Sulphides M₂S of Li, Na, K & Rb.

STRUCTURE OF DIAMOND :- In diamond each carbon is Sp³ hybridised.



Each carbon in diamond is covalently bonded to four other carbon atoms by overlapping of its four Sp³ hybridised orbitals to four other atoms. Thus each carbon atom in diamond is surrounded by 4 others at a distance of 1.54 Å. This is three dimensional structure & extends through out the whole lattice, thus each structure is giant molecules can be represented by following diagram.



Crystal Structure of diamond

This structure accounts for many other properties of diamond. It's m.pt & b.pt are unknown but presumably extra ordinary high. It is also conductor of electricity. Since all the electricity are firmly held in the C- C bond.

RADIUS RATIO :- The limiting case of arrangement of ions in ionic solids are, (a) the anion around the cation should touch each other. So that sum of radius of two anions should be equal to their inter nuclear distance. (b) Anion should touch cat ion so that the internuclear distance should be equal to sum of radii of cat ions and anion. The limiting case of an ionic solid of the formulae MX having co-ordination no. 3 can be shown as below :-

Radius Ratio or Limiting Ratio

The co-ordination of an ion depends on the size of both cation and anion. The ratio of size of cat ion (r⁺) to size of anion (r⁻) is known as limiting radius ratio. Thus caution Limiting radius ratio = $\frac{r^+}{r^-}$

SOLID STATE-PART-III

Crystal or Solids are classify on the basis of its bonding.

(i) IONIC SOLID :- In the ionic crystals the crystals points are occupied by cat ions and anions. The bonding between them is electrostatic in nature.

e.g. NaCl, NaF, Na₂O etc.

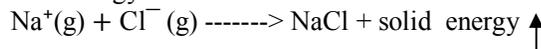
In NaCl the units are Na⁺ ion and Cl⁻ ions. These are held together by electrostatic force of attraction. The electrostatic force between oppositely charged ions are very strong.

Characteristics of ionic crystal :-

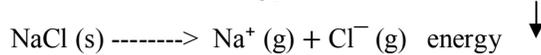
- (1) In ionic crystals its heat of vaporisation is high.
- (2) It has high melting and boiling point.
- (3) It is soluble in water and other polar liquid but insoluble in non polar liquid.
- (4) They are generally brittle in nature.
- (5) It does not conduct electricity in solid state but conducts electricity quite well when molten
- (6) Their electrical conductivity is very low at ordinary temperature.
- (7) These are generally transparent and insulators.
- (8) It has dielectric constant which changes with frequency of A-C applied.

Lattice Energy :-

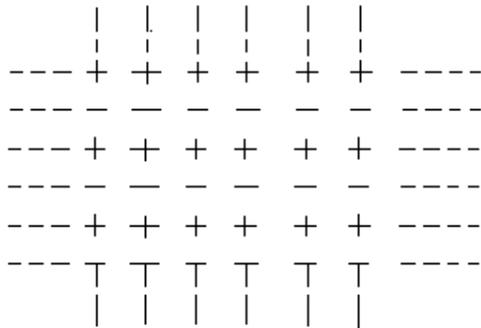
The energy released when gaseous cation and anions are held together and form ionic solid is called lattice energy, or the energy absorbed when ionic solids is converted into cations and anions.



Or



Ionic Solids show lattice structure and the energy associated with the lattice is called lattice energy. The ions are arranged at lattice point as -



There is attraction occurs between the cations and anions and also repulsion between cations and cations and anions and anions.

$$\text{Energy due to attraction} = \frac{-e^2}{r} \times 2 + \frac{-e^2}{3r} \times 2 + \frac{-e^2}{5r} \times 2$$

$$\text{Energy due to repulsion} = \frac{e^2}{2r} \times 2 + \frac{e^2}{4r} \times 2 + \frac{e^2}{6r} \times 2$$

Thus effective energy :-

$$\frac{-e^2}{r} \times 2 + \frac{e^2}{2r} \times 2 - \frac{e^2}{3r} \times 2 + \frac{e^2}{4r} \times 2 - \frac{e^2}{5r} \times 2 + \frac{e^2}{6r} \times 2$$

Or

$$= \frac{-2e^2}{r} + \frac{e^2}{r} - \frac{2e^2}{3r} + \frac{e^2}{2r} - \frac{2e^2}{5r} + \frac{e^2}{3r}$$

Or

$$= -\frac{2e^2}{r} \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \dots \right]$$

$$= -\frac{Ae^2}{r}$$

r

Where A is Madelung constant and depends upon the nature of lattice structure.

$$\text{Lattice energy } U = Nz^+z^- \frac{Ae^2}{r^0} \left(1 - \frac{1}{n} \right)$$

Where N = Avogadro's no.

Z^+ = Charge on cation

Z^- = Charge on anion

r^0 = Inter nuclear distance ($r^+ + r^-$)

n = another constant

The value of n depends upon the inert gas configuration of the ion.

(Cont) (n)

He - ----- 5

Ne - ----- 7

Ar - ----- 9

Kr - ----- 10

Xe - ----- 12

The lattice energy depends upon –

(1) The charge of the ion.

(2) Radius of the ion.

(1) The Charge of the Ion :- The lattice energy increases with the charge of the ion.

(2) Radius of the ion :- The lattice energy decreases with decrease in the radius of the ion.

Application of Lattice Energy :

(1) In the discussion of special properties of fluorine in relation to other halogens.

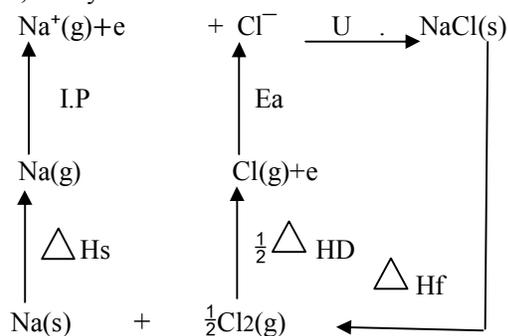
(2) In the accent of stabilities of metal hydrides, poly hydrides, peroxide and super oxide.

(3) In the derivation of crystal field stabilization energy,

(4) To determine the born haber cycle.

Born Haber Cycle :-

Born haber cycle shows the energetic involved in the formation of ionic (electrovalent) compound with reference to NaCl, the cycle can be shown as follow :-



$$\text{Thus } \Delta H_f = \Delta H_s + \text{I.P.} + \frac{1}{2} \Delta H_D + E_2 + U$$

$$U = \Delta H_f - \Delta H_s - \text{I.P.} - \frac{1}{2} \Delta H_D - E_2$$

$$U = \frac{A Z^+ Z^-}{r^0} \left(1 - \frac{1}{n} \right)$$

USES OF BORN – HABER CYCLE :-

Born haber cycle can be used for the determination of electron affinity of various substances which are difficult to determine by other methods. Born haber cycle helps rationalise the existence of certain compounds and the non existence of other. Born Haber Cycle provides interesting insights into the energy factors operating in ionic compounds.

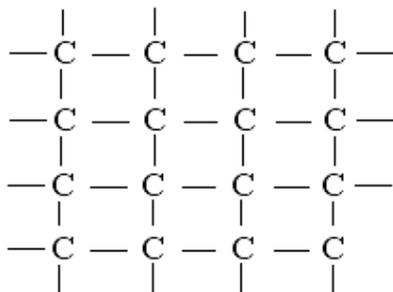
(2) COVALENT CRYSTAL :-

Covalent solids are formed by covalent bonding. This type of bonding resulting from sharing of one or more electron by the atoms. The crystal points of covalent crystal are occupied by atoms. The bonding force between the crystal points are covalent e. g. Diamond, Silicon, Carbide, Zinc Sulphide, Silver iodide, graphite.

Characteristics of Covalent Solids :-

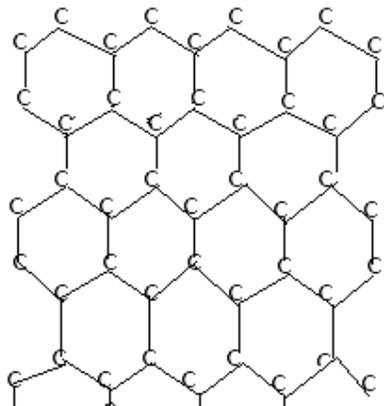
- (i) There is continuous network of covalent bonds forming a giant three dimensional structure.
- (ii) Due to three dimensional network covalent crystals have generally high melting and boiling point.
- (iii) Covalent solids are very hard since the bond is very strong e.g. diamond, exceptionally graphite is soft.
- (iv) The conductivity of covalent solids varies over a wide range.
- (v) They are insoluble in polar solvents but soluble in ether and benzene etc.
- (vi) They generally exhibit structural and space isomerism due to their dimensional nature.

STRUCTURE OF DIAMOND :- Diamond is hardest substance known. In diamond each carbon atom is covalently bonded by sharing of electrons from other atom at the four corners of a regular tetrahedron. Thus every atom is allowed to complete its octet. This gives rise to a rigid three dimensional net work.



Structure of Graphite :- In graphite each Sp^2 carbon atom is bonded and surrounded with three another Sp^2 carbon atom making a six – membered fixed ring system forming a plane of carbon atoms. On each carbon atom there is a unhybrid p^z orbital.

The bond distance between c – c is 1.48\AA



Structure of Graphite

3. Metallic Solid :- The crystal point of metallic crystal are occupied by metals ions. Bonding in such crystal are metallic bonding e.g. sodium, iron, chromium, magnesium metallic crystals of an assemblage of positive ions (Kernols) immersel in sea of electron (mobile). Thus each electron belongs to a number of positive ions and each positive ions belongs to number of electron. The force that binds a metal ion (Kernel) to a number of a electron within its sphere of influence is known as metallic bond.

Characteristics of metallic crystals :-

- (i) It is weaker than ionic and covalent crystal.
- (ii) Metallic crystals are good conductor of heat and electricity.
- (iii) Most of metals are quite hard and rough.
- (iv) Metals are Malleable and ductile.
- (v) Metals also possess electricity.
- (vi) Metals have high tensile strength.
- (vii) Except alkali metals they have very high melting and boiling point.

4. Molecular crystals :- The crystal points are occupied by molecules. In molecular crystals the bonding capacity of both atoms are saturated and the molecule has no residual capacity for further bonding. It is because of weak forces of attraction present in them, that they possess low melting and boiling points. These weak forces originate from dipole. Dipole interaction and London dispersion forces are called Vander Waals forces. The examples of molecular crystals are mica, ice, carbon, dioxide, Argon etc.

Characteristics of molecular crystals :-

- (i) Molecular crystals are generally soft.
 - (ii) They have low melting and boiling point.
 - (iii) They are bad conductor of electricity because they consists of neutral molecules in solid as well as in molten or dissolve state.
-

SOLID STATE-PART-IV

Classification of crystals on the basis of bonding :-

(i) Ionic Solid :- In ionic crystal the crystal points are occupied by cations, anions. The bonding between them is electrostatic in nature e.g. ----- NaCl, CsCl, NaF, CoF₂, Na₂O, TiO₂ etc. In NaCl for example the units are Na⁺ ions and Cl⁻ ions. These ions are held together by coulombic force of attraction each Na⁺ ion is surrounded by six Cl⁻ ion and Cl⁻ is surrounded by six Na⁺ ion. The Coulombic force of attraction between oppositely charged ions are very strong.

Characteristics of ionic crystal :-

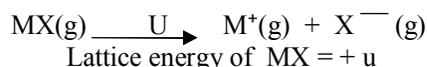
- (i) The heat of vaporisation of ionic crystal is high.
- (ii) It does not conduct electricity in solid state but conducts electricity quite well when molten.
- (iii) These are soluble in water and other polar liquid but insoluble in non-polar liquid due to low value of di-electric content.
- (iv) They are generally brittle in nature and can not be drawn into sheets or wires.
- (v) They are strong and hard having high melting and bolting point.
- (vi) Their electrical conductivity is very low at ordinary temperatures but increases with increase of temperatures. Thus they are generally transparent and insulators.
- (vii) The di electric constant changes with frequency of A.C. applied.

Lattice Energy :- The lattice energy of an ionic solid is defined as quantity of energy released when constituent gaseous ions brought from an infinite distances to form one mole of an ionic solid. If Na⁺ and Cl⁻ are taken as constituent ions then the equation for the formation of one mole of ionic solid NaCl can be represented as follows.



Here -U is called as lattice energy of ionic solid NaCl. The value of lattice energy is here negative, because energy is released in this process.

Lattice energy may be defined as quantity of energy absorbed when one mole of an ionic solid is converted into its gaseous constituent ions. This can be represented as -



Here u is positive because energy is absorbed in this process.

Lattice energy of a solid depends on ----> (i) Size of the Ion ----> As the size of ion having the same unit of charge increases lattice energy decrease. For example, lattice energy decreases from NaF to NaI because size increases from F⁻ - I⁻.

When the size of the ion is increases Lattice energy will be decreased.

(ii) Charge on an ion -----> Lattice energy increases as charge on ion increases. For example, lattice energy of CaO is greater than CaCl₂ because oxide (O⁼) ion has greater charge than Cl⁻ ion. Thus lattice energy increases from univalent to uni-divalent ionic solid and then to divalent - divalent solid i.e.



Lattice energy of an ionic solid is also determined by Born Haber Cycle. It can be determined also by direct method, using Born equation given as ---->

$$u = \frac{ANZ^+Z^-e^2}{\gamma_0} \left(1 - \frac{1}{n} \right)$$

Where - u = lattice energy of ionic crystal, A = Madung constant its value depends on the type of space lattice of ionic solid and arrangement of ions in ionic solid.

N = Avogadro's number

Z⁺ = Charge on Cat ion, Z⁻ = Charge on anion.

γ₀ = Sum of radii of cation and anion

n = Born constant or Born exponent

Its values depends on electronic cloud density on an ion.

Average value for Born exponent

Elect. Str. of ion	n.	Example
He	5	Li ⁺ , Be ⁺²
Ne	7	Na ⁺ , Mg ⁺² , O ⁻² , F ⁻
Ar	9	K ⁺ , Ca ⁺² , S ⁻² , Cl ⁻
Kr	10	Rb ⁺ , Br ⁻ ,
XE	12	CS ⁺ ,

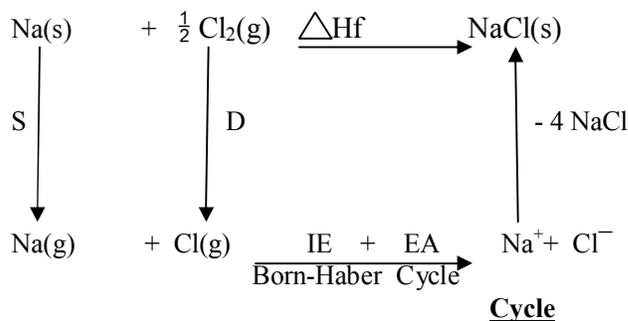
e = Electronic charge.

APPLICATION OF LATTICE ENERGY

Lattice energy finds numerous applications. Some of them are as under:-

- (i) In the discussion of special properties of fluorine in relation to other halogens.
- (ii) In the account of stabilities of metal hydrides polyhalides, peroxides and superoxide.
- (iii) In the derivation of crystal field stabilisation energy.
- (vi) In the discussion of characterisation of high oxidation states of metals as fluorides and their low oxidation states as iodides.

Born – Haber Cycle :- The direct determination of the lattice energy of an ionic crystal has been carried out for only a few compounds. In the majority of cases it is not possible to measure. This energy directly, however a cyclic process has been derived by Born and Haber which relates the crystal energy to other thermo chemical quantities where the energy of formation of a crystal from its component element is known as it is possible to dissect this value into the energies of a number of process which may be postulated as constituting the intermediate steps in the formation of crystal. By the means of this cyclic procedure it is possible to calculate algebraically the theoretical lattice energy of crystal. For example formation of sodium chloride from Elementary gaseous chlorine and solid sodium metal. It may be assumed that sodium metal. It may evaporated and the diatomic chlorine is dissociated ; then the alkali atoms are ionized and the electron so obtained is transferred to chlorine atom so that positive sodium ions and negative chlorine ions are left in the gaseous phase. As indicated diagrammatically :-



Here the energy of sublimation of metallic sodium is S, The ionization energy of gaseous sodium is IE The energy of **dissociation** of Cl₂ is D. The electron affinity of chlorine atom is EA and the lattice energy of solid NaCl is - U NaCl . The heat of formation of crystals from its elementary elements is designated as Q.

The total energy of formation of the crystal from its elementary compounds is given as :-

$$-Q = S + D + \text{IE} - \text{EA} - \text{UD}$$

The value of Q is accurately known experimentally for many substances and where the other thermochemical value also determined experimentally. Now resulting the aforesaid equation we can calculate lattice energy of the crystal.

$$U_0 = Q + S + D + IE - EA$$

Uses of Born – Haber cycle :-

Born –Haber cycle can be used for the determination of electron – affinity of various substances which are difficult to determine by other methods. Born- Haber cycle helps rationalise the existence of certain compounds and the non-existence of other. Born – Haber cycle provides interesting insights into the energy factors operating in ionic compounds.

2. Covalent Crystal :-

Covalent Solids are formed by covalent bonding. This type of bonding resulting from sharing of one or more electron by the atoms. The crystal pt of covalent crystal are occupied by atoms. The bonding force between the crystal points are covalent e.g. Diamond, Silicon Carbide, Zinc Sulphide, Silver iodine, graphite,, sulphur phosphorus etc.

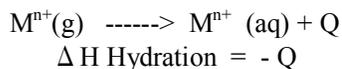
Characteristics of Covalent Solids :-

- (i) There is continuous network of covalent bonds forming a giant three dimensional structure.
 - (ii) Due to three dimensional network covalent crystals have generally high melting and boiling point.
-

SOLID STATE PART-V

Q. :- hydration energy and give the factors which influence hydration energy ?

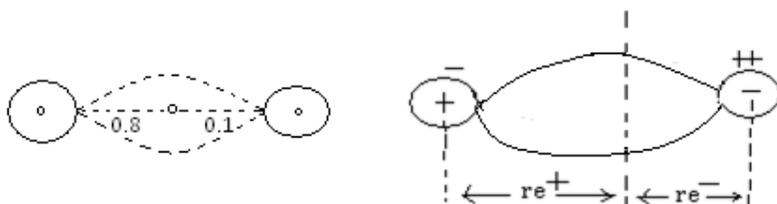
Ans.:- The enthalpy change in the conversion of mole of a gaseous ions to aqueous ions is called hydration energy.



Heat is released in hydration of ion. Hydration energy is given by the expression.

$$\Delta H_{\text{hydr.}} = \frac{ze^2}{2e} \left(1 - \frac{1}{D} \right)$$

Where, $\Delta H_{\text{hydr.}}$ = Hydration energy
 e = Charge on the electron
 D = Dielectric constant of the **medium**
 e = Distance between the Centre of gravity of the polar solvent molecule (water) -



In presence of ion H_2O is polarised as shown in the above figures.

$$\left. \begin{aligned} r_{e^+} &= r^+ + 0.8 A^0 \\ r_{e^-} &= r^- + 0.1 A^0 \end{aligned} \right\} \begin{array}{l} \text{for Cat ion} \\ \text{for anion} \end{array}$$

Thus, $r_{e^-} < r_{e^+}$

For cat ions and anions having the same radius, r_{e^-} is greater for the cat ions than the anions since,

$$\Delta H_{\text{hydr.}} = \frac{Ze^2}{2r_e} \left[1 - \frac{1}{D} \right] \left[1 - \frac{1}{d} \right]$$

(a) Radius of the ion :- According to the above expression of hydration energy :

$$\Delta H_{\text{hydr.}} \propto \frac{1}{r^{\pm}}$$

Thus greater the value of radii of the ion, lower will be its hydration energy, hence

$\Delta H_{\text{hyd}}(\text{Cation}) > \Delta H_{\text{hyd}}(\text{anion})$

$\Delta H_{\text{hyd}} Na^+ > \Delta H_{\text{hyd}} K^+$ [since $r_{K^+} > r_{Na^+}$]

$\Delta H_{\text{hyd}} F^- > \Delta H_{\text{hyd}} Cl^-$ [since $r_{Cl^-} > r_{F^-}$]

(b) Change of the ions :-

Since, $\Delta H_{\text{hyd}} \propto Z$

Therefore, hydration energy will increase from Na^+ to Al^{3+}

(c) Effective nuclear charge :- If r^+ and charge of the ion remains the same, greater is the value of Z^*
 Greater is the hydration energy

Since, 1 & electron ion has higher Z^* value than that of $>$ electron ion

$\therefore \Delta H_{\text{hydr.}} Ag^+ > K^+$
 (18 e^-) (8 e^-)

$$\Delta H_{\text{hyd}} \text{ Cd}^{2+} > \text{Ca}^{2+}$$

$$(18 e^-) \quad (8 e^-)$$

(d) When radius and charge ion similar both for cat ion and anion. Anion has higher hydration energy

$$\Delta H_{\text{hyd}} \text{ F}^- > \Delta H_{\text{hyd}} \text{ K}^+$$

$$\text{Here } r_{\text{F}^-} = r^- \text{ \& } = 1.36$$

$$r_{\text{K}^+} = r^+ = 1.33$$

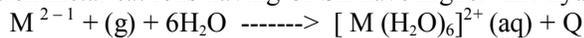
$$\therefore \text{re } r_{\text{F}^-} = r^- + 0.1 = 1.36 + 0.1 = 1.46$$

$$\text{re } r_{\text{K}^+} = r^+ + 0.8 = 1.33 + 0.8 = 2.13$$

$$\therefore \Delta H_{\text{hyd}} \text{ F}^- > \Delta H_{\text{hyd}} \text{ K}^+$$

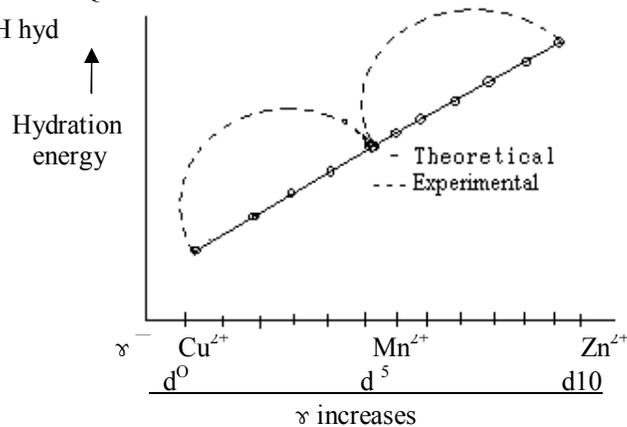
(e) CFSE :-

Transition metal cat ions having CFSE have higher ΔH_{hyd} than expected



$$\Delta H_{\text{hyd}} = -Q$$

$$\text{CFSE} \propto \Delta H_{\text{hyd}}$$



System	CFSE (Zq)	System	CFSE (Zq)
Ca ²⁺ d ⁰	0	Fe ²⁺ d ⁶	-4Zq
Sc ²⁺ d ¹	-4Dq	Co ²⁺ d ⁷	-8
Ti ²⁺ d ²	-8	Ni ²⁺ d ⁸	-12
V ²⁺ d ³	-12	Cu ²⁺ d ⁹	-6
Cr ²⁺ d ⁴	-6	Zn ²⁺ d ¹⁰	0
Mn ²⁺ d ⁵	0		

As SC²⁺ to Cr²⁺ and Fe²⁺ to Cu²⁺ have CFSE this experimental value of hydration energy is greater than theoretically expected value. Ca²⁺, Mn²⁺ and Zn²⁺ have no CFSE and so their experimental and theoretical values are the same.

=====X:=====

Electrode potential Strength of oxidising and reducing agent is influenced by the value of electrode potential ?

When a metal is immersed in a solution containing its own ions and electric potential is set up between the two.

The size of the potential E for the electrode reaction.



is given by the Nernst equation

$$E = \dots + \dots - \dots$$

Where R = Gas constant

T	=	Absolute temp
n	=	Valency of ions
F	=	Faraday
E	=	Oxidation potential
E ⁰	=	Standard Oxidation Potential
a	=	activity

for the most purposes, the activity (a) may be replaced by the concentration of the ions in solution. Thus,

$$E = E^0 + \frac{RT}{nF} \ln [Mn^{+}]$$

$$= E^0 + \frac{0.059}{n} \log [Mn^{+}] \text{ at } 25^{\circ}C.$$

A/C to IUPAC recommendation only reduction potential should be called electrode potential..

Oxidation potential is equal to reduction potential but opposite in sign .

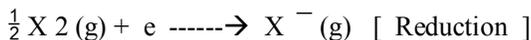
$$E_{ox} = - E_{red}$$

Thus, $E = E^0 - \frac{RT}{nF} \ln [Mn^{+}]$

$$= E^0 - \frac{0.059}{n} \log [Mn^{+}]$$

Electrode potential is used in predicting the strength of an oxidising agent and reducing agent. We know,
 $M \rightarrow Mn^{+} + ne$ [Oxid.]

The more +ve value of oxidation potential or the more -ve value of reduction potential the greater is the reducing power of M.



Hence the more +ve value of reduction potential or more -ve value of oxidation potential, the greater is the oxidising power of X₂.

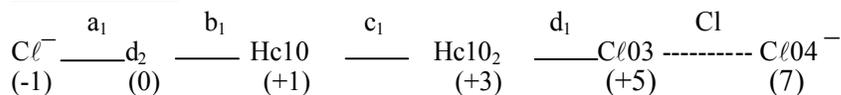
-----X:-----

(C) Cl shows variousoxidation.....states show the potentialdiagram.....for Cl in

(i) acidic medium (ii) Basic medium

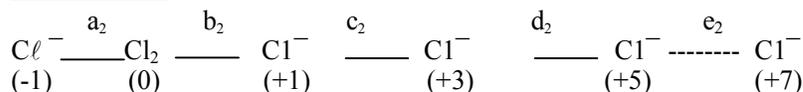
Ans - diagram showing the potential b/w the various oxidation state of an element is called inertial diagram it shwown -1, 0, +1, +3, and +7. The potential diagram in acidic and baic medium for Cl can shown as.

Acidic medium :-



- (i) $Cl^{-} \rightarrow \frac{1}{2} Cl_2 + e$; E = a₁
- (ii) $\frac{1}{2} Cl_2 + H_2O \rightarrow HClO + H^{+} + e$; E = b₁
- (iii) $HClO + H_2O \rightarrow HClO_2 + 2H^{+} + 2e$; E = c₁
- (iv) $HClO_2 + H_2O \rightarrow ClO_3^{-} + 3H^{+} + 2e$; E = d₁
- (v) $ClO_3^{-} + H_2O \rightarrow ClO_4^{-} + 2H^{+} + 2e$; E = e₁

Basic medium :-

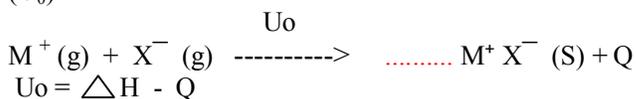


- (i) $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$; $E = a_1$
 (ii) $\frac{1}{2} \text{Cl}_2 + \text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + e^-$; $E = b_1$
 (iii) $\text{ClO}^- + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{H}_2\text{O} + 2e^-$; $E = c_1$
 (iv) $\text{ClO}_2^- + 2\text{OH}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O} + 2e^-$; $E = d_1$
 (v) $\text{ClO}_3^- + 2\text{OH}^- \rightarrow \text{ClO}_4^- + \text{H}_2\text{O} + 2e^-$; $E = e_1$

As step (1) does not depend on H^+ or OH^- concentration, $E = a_1 = a_2$ but for others, value of E are different in acid or basic medium.

Lattice Energy Give the factors which influence lattice energy ?

The enthalpy change in the formation of one mole ionic solid from its gaseous ions is called lattice energy (U_0)



Heat is released in the formation of ionic solid from its gaseous ions. The lattice energy is given by the –

$$U_0 = \frac{Z^+ Z^- A N_0 e^2}{r_0} [1 - \frac{1}{N}]$$

Where, U_0 = Lattice Energy

Z^+ = Effective charge of cat ion

Z^- = Effective charge of anion

N_0 = Avogadro number

$r_0 = r_0^+ + r_0^-$ = Intumnuclear distance

A = Madulong constant

Which depends on the geometry of the crystal.

N = Born exponent (it is related to the repulsion between the electron clouds of oppositely charged ions; often assumed to be equal to 1).

The value of n depends on the inert gas configuration of ions.

Ion configuration		n
He	-	5
Ne	-	7
Ar	-	9
Kr	-	10
Xe	-	11

For NaCl [Na^+ , Ne, Cl^- = Ar] the value of $n = \frac{6+7}{2} = 6.5$

Factors influencing the Lattice Energy :-

(A) Radius of the ions :-

From the expressionwe know...that $U_0 \propto 1/r_0$; therefore the down the radius of the ion ..lonch. is the r_0 and have higher than the lattice energy.

For NaCl and KCl

$r_{\text{Na}^+} < r_{\text{K}^+}$

$U_0 \text{ NaCl} > U_0 \text{ KCl}$

(B) Charge of the ion :

Since from the expression $U_o \propto \frac{z}{r}$. Therefore greater is the charge of the ions, greater is the lattice energy.

For example, CaCl_2 and NaCl ,

$$Z_{\text{Ca}^{2+}} > Z_{\text{Na}^+}$$

$$\therefore U_o \text{ Ca Cl}_2 > \text{Cl}$$

(C) Effective nuclear charge :

Greater in the effective nuclear charge greater is the lattice energy.

18 electrons system has higher Z^* than 8 electrons system. For example CdCl_2 and CaCl_2

$$\frac{Z^* \text{ Cd}}{18 e} > \frac{Z^* \text{ Ca}}{e}$$

This is so because 18 e structure is more polarising than 8 e structure and so Z^* for 18e structure is greater than 8 electron structure even when they have same radius and charge on the ion.

$$U_o \text{ CdCl}_2 > U_o \text{ CaCl}_2$$

(D) CFSE : Transition metal cations having CFSE value have higher lattice energy.

System	CFSE (Dq)	System	CFSE (Dq)
$\text{Ca}^{2+}d^0$	6	$\text{Fe}^{2+}d^6 \longrightarrow$	-4Dq
$\text{Sc}^{2+}d^1$	4	$\text{Co}^{2+}d^7 \longrightarrow$	- 8
$\text{Ti}^{2+}d^2$	8	$\text{Ni}^{2+}d^8 \longrightarrow$	-12
$\text{V}^{2+}d^3$	12	$\text{Cu}^{2+}d^9 \longrightarrow$	- 6
$\text{Cr}^{2+}d^4$	6	$\text{Zn}^{2+}d^{10} \longrightarrow$	0
$\text{Mn}^{2+}d^5$	0		

As Sc^{2+} to Cr^{2+} and Fe^{2+} to Cu^{2+} have CFSE their experimental value of lattice energy is greater than theoretically expected value. Mn^{2+} and Zn^{2+} have no CFSE and their experimental and theoretical values of lattice energy are same.

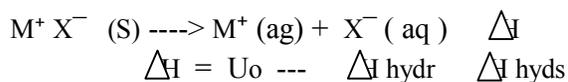
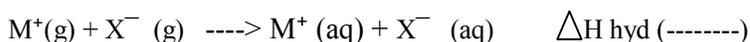
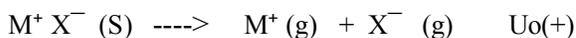
Explain how lattice energy and hydration energy ...influence.... solubility of ionic compounds

Apart from lattice energy and hydration energy, entropy act of heat, complex formation and common ion effect also influence solubility of a salt solubility of a substance can be represented as :



Lattice Energy and Hydration Energy :-

Equation (1) can be shown in two steps :



From the above reaction it is clear that if $U_o > \Delta H_{\text{hydr}}$, Salt is in soluble due to the ΔH_{Soln} .

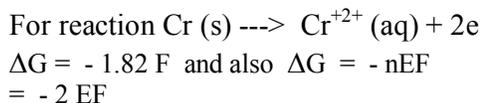
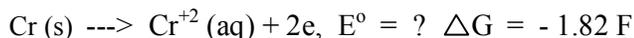
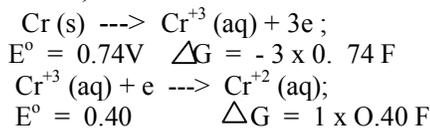
$U_o < \Delta H_{\text{hydr}}$, Salt is soluble due to -ve ΔH_{Soln} . Thus Na_2SO_4 is soluble in water because $U_o < \Delta H_{\text{hydr}}$

△

BaSO₄ is insoluble in water because $U_o > H_{\text{hydra}}$.

Q.3.(c) :- Calculate E° for $\text{Cr}(s) \rightarrow \text{Cr}^{2+}(\text{aq}) + 2e$ using the following data :-
 Cr/Cr^{3+} , $E^{\circ} = 0.74\text{V}$; $\text{Cr}^{3+}/\text{Cr}^{2+}$, $E^{\circ} = 0.40\text{V}$

Ans. :- Since,



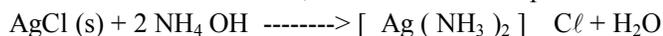
$$\begin{aligned} \therefore -2EF &= -1.82 F \\ \therefore E^{\circ} &= 0.91 \text{ Volt} \end{aligned}$$

-----X-----

AgCl is insoluble in water but soluble in dil NH₄ OH. in water but soluble in dil NH₄ OH.

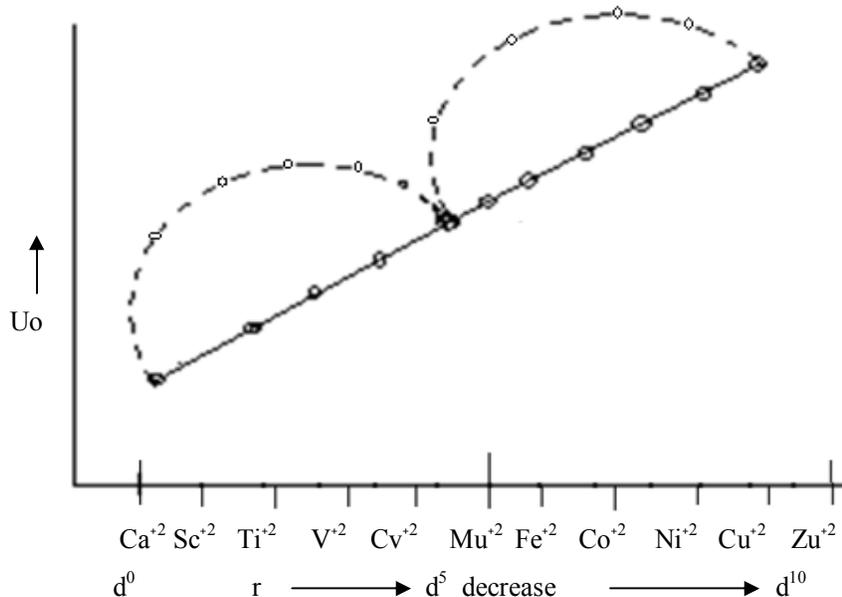
AgCl is insoluble in water due to its abnormal high lattice energy. This high lattice energy is due to the strong vanderwaals attraction between Silver and chloride ions in addition to the usual electrostatic attraction between the oppositely charge ion.

But it is soluble in dil NH₄ OH due to the complex formation



Complex plot of experimental hydration energy for Ca⁺² to Zn⁺² or of lattice energy for CaO to ZnO and the abnormality .

Experimental graph of lattice energy for thedivalent ions (Ca⁺² to Zn⁺²) can be plotted as follows :-



From the above graph it is clear that transition metal cations having CFSE having higher lattice energy CFSE for these cations can be summarised as follows :-

<u>System</u>	<u>CFSE (Dq)</u>	<u>System</u>	<u>CFSE (Dq)</u>
---------------	------------------	---------------	------------------

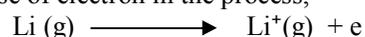
Ca ⁺²	d ⁰	0	Fe ⁺²	d ⁶	- 4
Sc ⁺²	d ¹	4	Co ⁺²	d ⁷	- 8
Ti ⁺²	d ²	8	Ni ⁺²	d ⁸	- 12
V ⁺²	d ³	12	Cu ⁺²	d ⁹	- 6
Cv ⁺²	d ⁴	6	Zu ⁺²	d ¹⁰	- 0
Mu ⁺²	d ⁵	0			

As Sc⁺² to Cv⁺² and Fe⁺² to Cr⁺² have CFSE their experimental value of lattice energy is great than theoretically (i.e. from charge and consideration) expected value Ca⁺², Mn⁺² and Zn⁺² have no CFSE so their experimental and theoretical value of lattice energy is same.

I.P. of lithium is greater than of Na, yet the former is stronger reducing agent than the latter.

Lithium has the highest value of oxidation (electrode) potential so it is a powerful reducing agent.

The oxidation (electrode) potential value shows lithium to be the best reducing agent while its IP value suggests that release of electron in the process,



Should not be easy as it would require large energy. The anomaly is explained on the basis of the highest

Hydration energy of Li⁺ ion due to its small radius . The high hydration energy value offsets the value of I.P. and the net effect is -ve i.e.

$$(\text{HS} + \Delta P.) (\text{H hy } \Delta) < \Delta H \text{ Hydration}$$

Therefore, lithium is a strong reducing agent.

Solubility of M(OH)₂ and MSO₄ has different trend M(OH)₂ alkaline with metal)

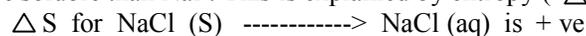
The reverse trend in solubilities of hydroids [M (BH)₂] and sulphates (MSO₄) of alkaline earth metals is due to the collective effect of lattice energy and hydration energy. The hydration energy of the cations decreases down the group. As size of the sulphate is much larger the ro (r⁺+ r⁻) is almost constant and so the lattice energy of the sulphates are almost constant. The effects of these two energies are such that - ΔH hyd + U i.e. ΔH solution becomes more and more positive i.e. energy released in dissolution gradually decreases and so the solubility of the sulphates decreases.

In the hydroxides [M (OH)₂] as the size of the O H[⊖] is smaller the lattice energies of hydroxides are not constant rather they also decrease progressively down the group. It is so happen that lattice energies

Δ H solution for NaCl is more positive than of NaF, the former is more soluble in water.

On the basis of lattice energy and hydration energy NaCl should be less soluble than NaF because U ΔH hyd i.e. Δ H solution is more +ve for NaCl.

However experimentally NaCl is found to be more soluble than NaF. This reverse trend is found to be more soluble than NaF. This is explained by entropy (Δ S)



From the relation,

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

Since ΔS is +ve for NaCl, TΔS is -ve hence ΔH - TΔS i.e. ΔG = -ve. Hence, ΔG (or NaCl is more -ve than that of Na (s) -----> NaF (aq). Therefore, NaCl is more soluble in water.,

Decrease more than the hydration energy and the net effect becomes gradually - ve and thus - ve value i.e. the heat released from Be to Ra (..alkaline... earth metals) and so solubility of hydroxides increases.

For solubility the hydration energy (heat released) must be enough to supply the energy required to break the salts into their constituent ions i.e. $\Delta H_{\text{hyd}} > U_0$.

Hydration energy for K^+ is lower than F^-

Radius and charge of both K^+ and F^- are similar as follows :-

$$F^- = r^- = 1.36 \text{ \AA}$$

$$K^+ = r^+ = 1.33 \text{ \AA}$$

Therefore, distance between C G of the polar solvent molecule for

$$veF^+ = r^- + 0.1 = 1.36 + 0.1 = 1.46 \text{ \AA}$$

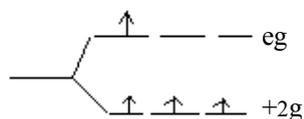
$$veK^+ = r^+ + 0.8 = 1.33 + 0.8 = 2.13 \text{ \AA}$$

Since, $\Delta H_{\text{hydration}} \propto 1/r_c$

So, hydration energy of F^- ion will be greater than K^+ ion.

Lattice energy for Cr is greater than expected from charge and radius consideration.

Cr (Cr^{2+}) is d^4 system.



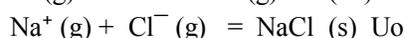
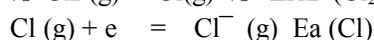
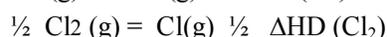
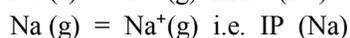
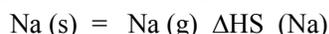
$$\begin{aligned} \text{CFSE} &= [- 4 \times 3 + 6 \times 1] Dq \\ &= - 12 + 6 = - 6 Dq \end{aligned}$$

Those transition metal ions which have CFSE, their experimental value of lattice energy is greater than theoretically expected value. Here Cr^{2+} (Cr) has CFSE value $- 6 Dq$. Therefore its experimental value of lattice energy is greater than theoretically expected (i.e. from charge and radius consideration)

Lattice energy of an ionic solid can be estimated with help of Born Haber cycle.

The formation of an ionic compound can be studied with the help of a thermo dynamical cycle called Born Haber cycle.

In order to construct the Born Haber cycle, we consider the following thermo chemical equations, using NaCl as an example –

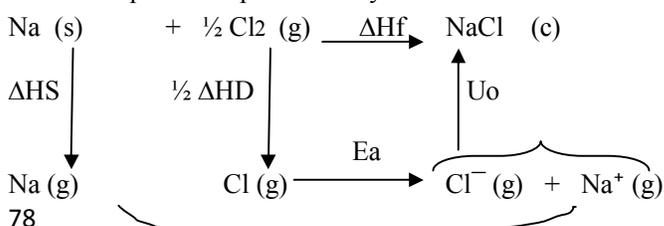


Thus formation of NaCl from Na and $\frac{1}{2} Cl_2$ depends on (i) sublimation energy (+), (ii) IP(+), (iii) Dissociation energy(+), (iv) Electron affinity (-) and (v) lattice energy (-).

The energies are inter related by the equation (A/c to Hess law)

$$\Delta H_f = \Delta H_S + IP + \frac{1}{2} \Delta H_D + E_a + U_0$$

The above process represents a cycle as :



I.P. ↗

Using +ve sign for energies absorbed and – ve sign for energies released we have

Heat of sublimation of Na (ΔH_S)	=	108.5 KJ mol ⁻¹
Dissociation energy of Cl ₂ ($\frac{1}{2} \Delta H_D$)	=	243.0 „
I. P. of Na (IP)	=	495.2 „
Ea of Cl ₂ (Ea)	=	- 348.3 „
Lattice energy of NaCl (Uo)	=	- 7587 „

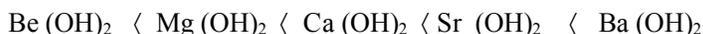
$$\text{Putting these elements we get } -\Delta H_f = 108.5 - \frac{1}{2}(243.0) + 495.2 - 348.3 - 755.7$$

$$= -381.8 \text{ kJ mol}^{-1}$$

Thus there is a net decrease of energy with formation of NaCl which is responsible for the formation of this compound.

Solubility of M(OH) and MSO₄ has different trend (M alkaline earth metal).

The hydration energy of M(OH)⁺² decreases from Be⁺² to Ba⁺² due to increase in radius from Be⁺² to Ba⁺². Lattice energy of M(OH)₂ also decrease from Be(OH)₂ to Ba(OH)₂ due to increase in radius from Be⁺² to Ba⁺². The difference in lattice energy and hydration energy becomes less and less positive from Be(OH)₂ to Ba(OH)₂ due to increase in radius from Be⁺² to Ba⁺², and so solubility increases from Be(OH)₂ to Ba(OH)₂. [The decrease in lattice energy is more relative to the hydration energy from Be(OH)₂ to Ba(OH)₂]. Therefore solubility trend of M(OH)₂ in alkaline earth is



In case of sulphate due to large size of SO₄²⁻, lattice energy of all MSO₄ is nearly same, hydration energy decreases from Be⁺² to Ba⁺² and hence difference of lattice energy and hydration energy becomes more and more positive from Be SO₄ to Ba SO₄ and unsequently solubility decreases from Be SO₄ to Ba SO₄.

Therefore, solubility of sulphate has the order :



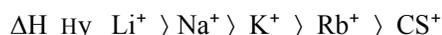
Hydration energy for K⁺ is lower than of F⁻

Ans.:- Hydration energy can be expressed as :- $\Delta H_{Hy} = Zre (1 - 1/D)$

Where ΔH_{Hy} = Hydration energy
 Z^* = effective nuclear charge
 e = Charge of electron
 D = Dielectric constant
 re = radius of ion

* I.P. of Li is greater than of Na, yet the former is stronger reducing agent than the later.

Ans. :- Due to smaller size of li⁺ the order of hydration energy in alkali metal is as follows :-



Because the expression for hydration energy (ΔH_{Hy}) is :

$$\Delta H_{Hy} = - \frac{Z^* e^2}{re} (1 - 1/D)$$

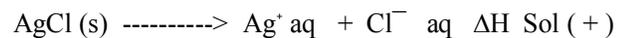
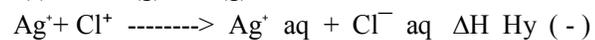
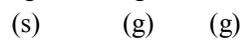
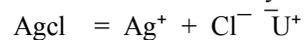
Where, Z^* = effective nuclear charge
 e = Charge of electron
 D = Dielectric constant
 re = Ionic radius + 0.8 i.e. $r^+ + 0.8$

Here, Z^* is constant and r^+ increases from Li⁺ to CS⁺ hydration energy decreases from Li⁺ to CS⁺.

Therefore, though I. P. Of Li is greater than of Na, its reducing power is greater than Na due to high hydration energy of Li^+ which compensates for high I. P.

Agcl is insoluble in water but soluble in dil NH_4OH .

The reason behind the insolubility of Agcl in water can be given as –



As $U^+ \Delta H \text{ Hy}$ is positive Agcl is insoluble in water.

AgCl is soluble in dil NH_4OH due to formation of soluble complex :-



SOLID STATE PART-VI

Defects in Solids

In an ideal crystal the same unit cells containing the same lattice points occur in the whole of the crystal. Crystal defects arise when the lattice sites remain unoccupied by the constituting ions. At absolute zero, crystals possess perfectly ordered arrangements of ions. So there is no defects. As the temperature increase the chance that a lattice sites may be unoccupied by ion increases and defect arises.

The crystal defect is evidenced from the following observations :

- (i) The chaotic limit of crystal and the shearing stress necessary to displace one plane of atomic relative to other in crystal is less than that expected from an idealised structure.
- (ii) The observed electrical conductivity of crystals at temperature much below their melting point is many times higher as compared to the theoretical conductivity.

TYPE OF DEFECTS :

The defects are classified as :-

- (a) Point defects, (b) Line defects, (c) Plane defects.

(a) POINT DEFECTS : These defects are mainly of two types :

- (i) Stoichiometric defects
- (ii) Non Stoichiometric defects

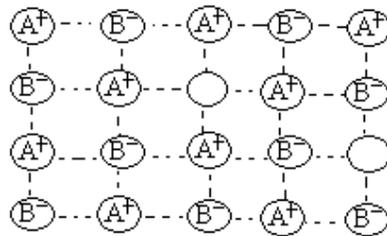
Stoichiometric defects

These are those in which the number of +ve and -ve ions are exactly in the ratio indicated by their chemical formula. In crystals of such compounds two defects are very common which are :

- [a] Schottky defects [b] Frenkel defects

[a] Schottky defects :- In a pair of holes (unoccupied lattice point) exist in the crystal lattice due to absent of one +ve and one -ve ions. Such defects are called Schottky defects

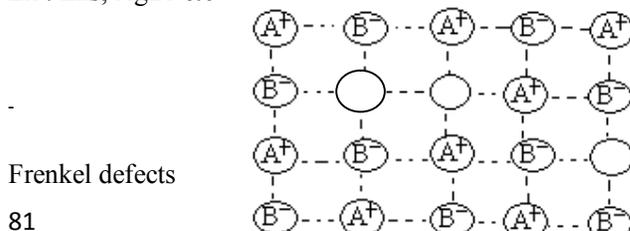
Ex.: CSCI, NaCl



Figure; represents the Schottky defects

[b] Frenkel defects :- When a hole is formed in the lattice because the cation or anions occupy an interstitial position instead of its correct lattice position but, stoichiometric remains unchanged. This defect is called Frenkel defect. The given figure represents this defect.

Ex : Zns, AgBr etc



Non, stoichiometric defects:

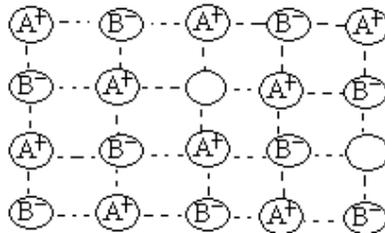
In non stoichiometric compounds the ratio of +ve and -ve ions present in the compound from the ratio indicated by their chemical formula.

In such compounds either the +ve or -ve present in excess and the balance is maintained either having extra electrons or extra +ve charge. These defects are two types:

- (a) Metal excess defects
- (b) Metal deficiency defects

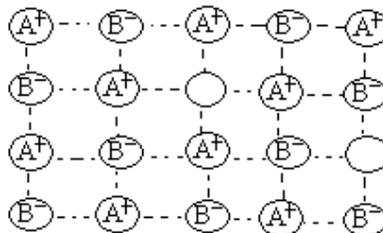
Metal excess defects: In this defect, +ve charge in excess in the crystal lattice and may be formed in two ways:

- (a) It may be formed when a -ve ion is missing from its lattice leaving a hole which is occupied by an extra electron to maintain the electrical balance. This defect is represented in the following figure. Ex. KCl.



(Metal excess due to absence of anion)

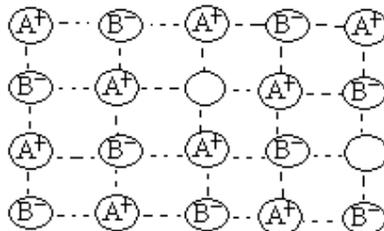
- (b) The metal excess defects may also appear if a +ve ion may occupy interstitial position in the lattice to maintain electrical neutrality, the electron is also in the interstitial space as shown in the figure. Ex-Zinc



(Metal excess defect caused by interstitial cations)

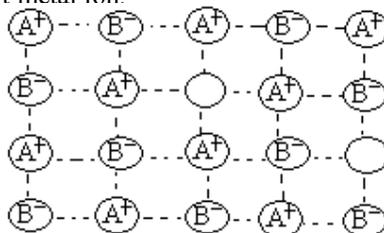
Metal deficiency defects : This defect occurs in a crystal in two ways:

- (a) In the first way a +ve ion may be missing from its lattice site and the extra -ve charge is balanced by adjacent metal ions having two charges instead of one as shown in the figure. Ex- FeO, FeS, NiO etc.



(Metal deficiency caused by missing +ve ion.)

- (b) In the second way an extra -ve ion may find an interstitial position and the charges are below by means of an extra charge on an adjacent metal ion.



(Metal deficiency caused by interstitial -ve ion.)

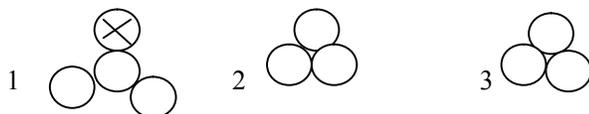
Radius ratio and co-ordination number

Radius ratio : In ionic solid the co-ordination number of ions as well as the geometrical shapes of crystals depends upon very largely in the relative size of ions. The ratio of the radii of cation and anion called radius ratio. When we take the minimum value radius ratio, it is called limiting radius ratio.

$$\text{Radius ratio} = \frac{r^+}{r^-}$$

The effect of this ratio in determining the co-ordination number and the shape of the ionic is known as the radius ratio decides the packing of solids.

Let us consider an ionic compound AX in the CN of A^+ cation is 3 i.e. there X^- ions will be in contact with the A^+ cation.



In the above three figures, I represents the completely stable molecule while the structure II shows the molecules, AX is completely unstable as the anion is in contact with each other but cations do not touch any of the anions i.e. totally repulsive force acts there.

In figure III cation (A^+) touches all three anions as well as anions are also in contact with each other. Therefore attractive force and repulsive force act simultaneously, however attractive force is strong.

In such a case the radius ratio is found to be 0.155 ($r^+/r^- = 0.155$).

If the radius ratio falls below this value this component will be destroyed or will not exist.

Therefore, for co-ordination number the limiting (lowest) radius ratio is 0.155 ($r^+/r^- = 0.155$).

Limiting radius ratio for different co-ordination numbers can be worked out.

Co-ordination number	shape	limiting
3	planar triangular	0.155 to 0
4	Tetrahedral	0.225 to 0
4	square planar	0.414 to 0
6	octahedral (Fcc)	0.414 to 0
8	cubic (Bcc)	0.732 to 0

As the lower limiting ratio is reached geometrical arrangement changes. Thus if radius ratio is less than 0.732 the cubic structure can not occur.

Similarly, if the ratio r^+/r^- is less than 0.414 octahedral and square planar arrangement will not occur.

Co-ordination number : [Goldschmidt co-ordination number] :- the number of nearest neighbours of an ion or molecule in a lattice system is called the co-ordination number of corresponding atom, ion or molecule.

For a compound formed by M^+ and X^- if the co-ordination number of M^+ is 6. This means that cation is surrounded by 6 anions(X^-). In order to have the compound neutral the C.N of X^- should also be 6. For a compound formed by M^{+2} and X^- if the C.N. of M^{+2} is 6 C.N. of anion should be 3.

$$\text{Each cation attributes the charge} = \frac{\text{total charge or cation}}{\text{C.N}} = \frac{1}{3}$$

Hence, in this case formula should be Mx_2 and then neutrality of lattice structure is maintained.

In general, the co-ordination of cation is equal to the C.N. of anion in the lattice of compound AX type. And the C.N. of cation is double of the C.N. of anion in the lattice of Ax_2 type (A is metal x is number)

System	C.N.
Simple cubic system	6
Body centred cubic System	8
Hexagonal or face centred Cubic system	12

Spinel Structure

Mixed oxides of the general formula $A^{+2} B_2^{+3} O_4$ are called spinel after the name of the mineral, spinel $Mg Al_2 O_4$. A^{+2} and B^{+3} are divalent and trivalent metallic cation. In spinel structure the oxygens are arranged in cubic close packed lattice. Such lattice, each o-atom has 12 other o-atoms equidistant from it and the holes between o-atoms of two types:

- (1) Octahedral holes : As these are surrounded by six o-atoms, there is one of such holes for each o-atom
- (2) Tetrahedral Holes : As these are surrounded by four o-atoms, there are two such holes for each o-atom. These are smaller than the octahedral holes.

There are twice as many tetrahedral holes as there are octahedral holes. The cations occupy the octahedral holes and tetrahedral holes since these are large enough to be filled by cations.

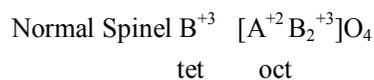
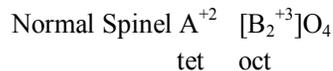
There are two types of cations and corresponding two types of spinel structure:

- (a) Normal spinel
- (b) Inverse spinel.

Normal Spinel : in normal spinel, all the A^{+2} cations occupy the tetrahedral holes and the B^{+3} cation occupies the octahedral holes.

Inverse Spinel : In inverse spinel, all the A^{+2} cations and half of B^{+3} cations are in octahedral holes and the remaining half of B^{+3} cations are in tetrahedral holes.

Thus the normal and inverse spinel can be represented as,



(1) As the lower limiting ratio is reached geometrical arrangement is changes. Thus if radius ratio is less than 0.752 the cubic structure can not occur. Similarly, if the ratio r^+ / r^- is less than 0.414 octahedral and square planar arrangement will not occur.

Co-ordination number :- [Gold Schmidt Co-ordination number] :- The number of nearest neighbours of an atom, ion or molecule in a lattice system is called the co-ordination number of corresponding atom, ion or molecule.

For a compound formed by M^+ and X^- if the Co-ordination number of M^+ is 6. This means that cation is surrounded by 6 anions (X^-). In order to have the compound neutral the C. N. of X^- should also be 6. For a compound formed by M^{+2} and X^- if the C. N. of M^{+2} is 6 then C.N. of anion should be....3 each cation attributes the charge

$$= \frac{\text{total charge or cation}}{\text{C.N.}} = \frac{-1}{3}$$

.....
.....

(ii) Tetrahedral holes :- As these are surrounded by four O – atoms, there are two such holes for each) – atom. These smaller than the octahedral holes.

There are twice as many tetrahedral holes as these are octahedral holes. The cations occupy the octahedral holes and tetrahedral holes since there are large enough to be filled by cations.

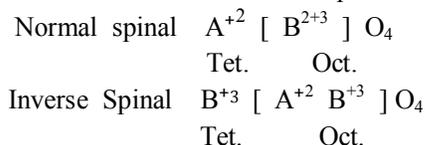
There are two types of cations and corresponding two types of spinal structure :-

- (a) Normal spinal (b) Inverse spinal

Normal spinal :- In normal spinal, all the A+2 cations occupy the tetrahedral holes and the B+3 cations occupy the octahedral holes.

Inverse spinal :- In inverse spinal, all the A+2 cation and half of B=3 cations are in octahedral holes and the remaining half of B+3 cations are in tetrahedral holes.

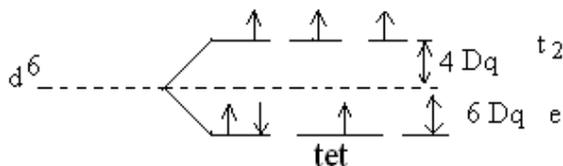
Thus the normal and inverse spinal can be represented as -



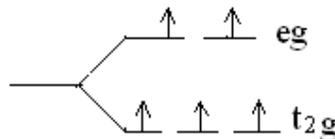
The species enclosed in square brackets occupy the octahedral holes. By calculating CFSE value it can be shown that why some spinal are normal while others are inverse. For which CFSE is large, is the structure of inverse spinal. For calculating CFSE value it is assumed that the oxide ion (O^{2-}) produces weak field.

Actually spinal crystal structure is same as **antirutile** structure. Examples :

- (1) $Fe_3 O_4 \rightarrow Fe^{II} Fe_2^{III} O_4$
 (a) Normal spinal $\rightarrow Fe^{II} [Fe^{III} Fe^{III}] O_4$
 (b) Inverse spinal $\rightarrow Fe^{III} [Fe^{II} Fe^{III}] O_4$
 CFSE for normal spinal
 $Fe^{II} [Fe^{III} Fe^{III}] O_4$



CFSE \Rightarrow
 $= [4 \times 3 + 3 (-6)] Dq$
 $= 12 - 18 = 6 Dq$ (in text)



$$= - \quad -$$

$$=$$

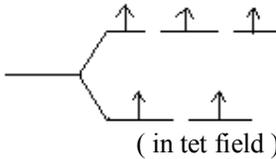
CFSE in weak oct. Field

$$= (-4 \times 3 + 2 \times 6) Dq = -12 + 12 = 0$$

...for $2Fe^{+3} \dots = 0 \times 0 = 0$

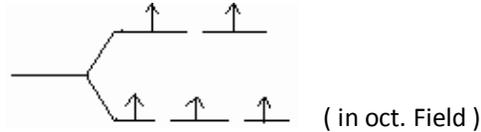
Total CFSE = $\frac{-8}{3} + 0 = - \quad Dq$ ----- (i)

CFSE for inverse spined
 $Fe^{III} [Fe^{II} Fe^{III}] O_4$
 $Fe^{+3} \dots \rightarrow 3d^5$ system



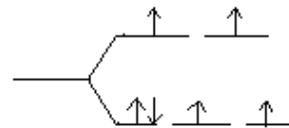
CFSE in weak tet field
 $= (-6 \times 2 + 3 \times 4) = 0$

$Fe^{+3} \dots \rightarrow 3d^5$ system



CFSE = $(-4 \times 3 + 6 \times 2) Dq = 0$

$Fe^{+2} \dots \rightarrow 3d^6$ system



CFSE in weak oct field

$$= (4 \times -4 + 6 \times 2) = -16 + 12 = -4 Dq$$

Total CFSE calculated for inverse spinel

$$= 0 + 0 - 4 Dq = -4 Dq$$
 ----- (ii)

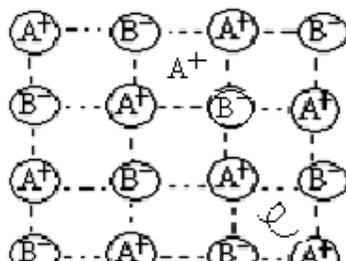
Since CFSE is greater for inverse spinel hence Fe_3O_4 exists in inverse spinel crystal structure.

Or Explain

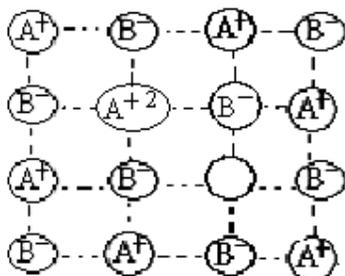
*(a) CdO and ZnO are n - type whereas Cu_2O and NiO are p - type semi conductors.

Ans.:- All the above compound is stoichiometric compounds because the ratio of +ve and -ve ions present in the compound differs from the ratio indicated by their chemical formula.

CdO and ZnO metal excess defect due to an extra +ve ion may occupy interstitial position in the lattice and to maintain electrical neutrality, the electron e^- , also present in the interstitial space as shown in the figure:



Crystal with metal excess defects contain free electrons and these migrate when electric field is applied. As a consequence of this the crystal conducts electricity but the conduction is poor, such crystals are generally called n – type semiconductor. U_2O and NiO show metal deficiency defects because Cu and Ni show variable valency.



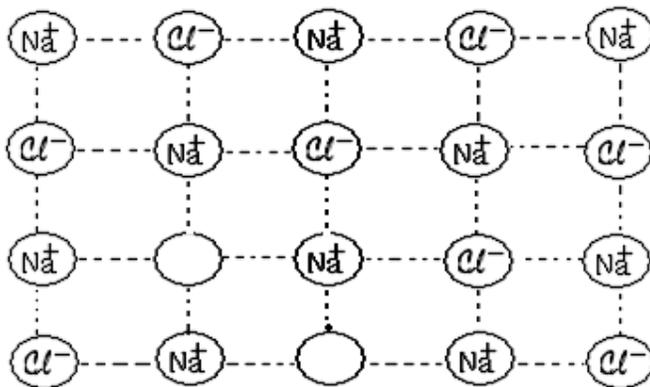
Crystals with metal deficiency defect contain positive holes, when electric field is applied electrons from adjacent atoms flow to fill this site in the process making another positive hole. Thus current is carried in opposite direction of migration of positive hole. This type of conduction is known as p – type semiconductor.

Thus CdO and ZnO are n – type whereas Cu_2O and NiO are p-type semiconductor.

(c) NaCl shows Schottky defect whereas AgBr shows Frenkel defect.

(d) Ans.:– In Schottky defect, a pair of holes (unoccupied lattice points) exists in the crystal lattice due to the absence of one +ve and one –ve ion.

Such defects are intrinsic defects. Ionic compounds with high coordination number and where positive and negative ions are of similar size show such defects. NaCl fulfills the above condition for Schottky defect so it shows Schottky defect as shown below :-

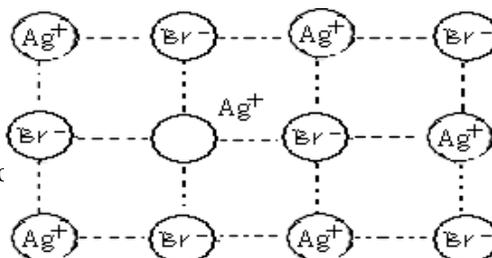


In Frenkel defect a hole is formed in the lattice because the cations or anions occupy an interstitial position instead of their correct lattice position but the stoichiometry remains unchanged.

These defects are easily formed

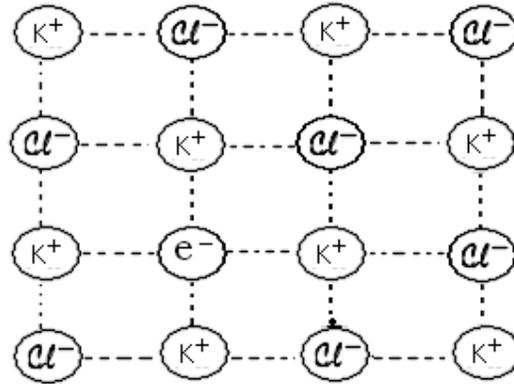
(a) when the difference in size between the positive and negative ions is large. Since positive ions are generally smaller than –ve ions, it is more common to find the +ve ions occupying interstitial positions.

(b) The compounds bearing low coordination number. AgBr fulfills the condition of Frenkel defect ...so, it shows Frenkel defect as shown below :-



KCl is colourless but when it is heated in K-vapour

Ans:- KCl shows metal excess defect which is formed by missing of $-ve$ ion from its lattice site leaving a hole which is occupied by an extra electron to maintain the electrical balance so when KCl is heated in vac vapour it turns blue. The blue colour is due to excess of K^+ ion in lattice. The $-ve$ ion may be absent from its lattice site leaving a hole which is occupied by an electron as shown below :



$NaCl$ has FCC and $CsCl$ has BCC structure.

$NaCl$ has FCC structure . In this structure the co-ordination number of both the cation and the anion is as because the ratio of the ...radius of cation and anion [i.e. Na^+ and Cl^-] = 0.529 ($Na^+=0.952$ and $Cl^- = 1.9$ which fall to 0.732 each ion has face central.....cubic arrangement.

In the crystal of $NaCl$ every Na^+ ion is surrounded by six chloride ions which occupy the corner of an octahedron. Similarly every chloride ion is surrounded by six Na^+ ions.

Two F.C.C. with respect to Na^+ and with respect to Cl^- are interlocked with each other so that 50% of the cube is common.

Each corner will be shared by eight. Hence Na^+ belonging to one unit cell is $= 8 \times \frac{1}{8} = 1$

Due to face $= 6 \times \frac{1}{2} = 3$

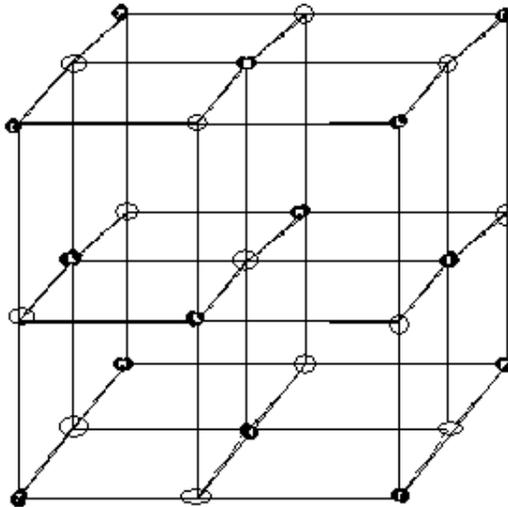
So, total no. of $Na^+ = 3 + 1 = 4$

Similarly, total no. of Cl^- occupying edge $= 12$

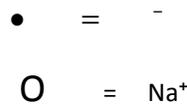
Each will shared with 4 unit cells So for one unit $= 12 \times \frac{1}{4} = 3$

Due to middle $= 1$

Total no. of $Cl^- = 4$



$NaCl$ Structure

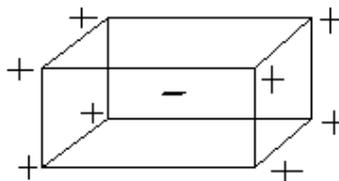
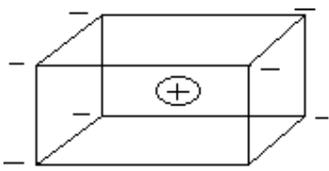


Identical $\rightarrow CaO, MgO, AgCl, AgBr$

$CsCl$ has BCC structure. In this structure, the radius ratio for $CsCl$ is 0.93 which lies between0.732 to 1.00 i. e. The structure of $CsCl$ must be cubic (BCC).

As the Cs^+ ions and C^- ions are present in Cs in same proportion so the co-ordination number of both the ions are equal and is eight (8). It is not close packed arrangement and so it is not strictly body centred cubic. In a body centred cubic arrangement the atoms of the centre of the cube is identical to those at corners. In this the ions at the corners and body centre are different and the structure must be described as a body centred cubic type of arrangement.

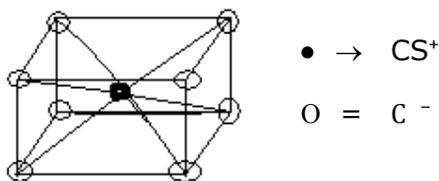
It is formed by interpenetration of simple cubic structure of C^- and simple cubic structure of Cs^+ .



$$\text{CS}^+ = 8 \times \frac{1}{8} = 1$$

$$\text{C}^- = 1$$

Identical CsBr, CsI, CsCN, NH_4^+ , NH_4Br



(e) CaF_2 and Li_2O differ in crystal structure.

Ans.:- CaF_2 and Li_2O differ in crystal structure, the reason behind it can be formulated as follows :-

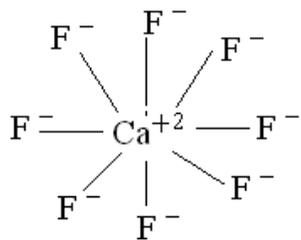
CaF_2 shows fluorite structure :

Since there are twice as many Fluorite as Ca^{+2} ions. The co-ordination number of both ions is not the same. As the C.N. of Ca^{+2} ion is eight (8). The co-ordination number of F^- ion must be four.

The numerical value of C.N. suggests that in fluorite structure each Ca^{+2} ion issurrounded.....by eight F^- ion occupying the corners ofcube...(BCC..... arrangement) and each F^- ion is surrounded tetrahedrally by four calcium ions.

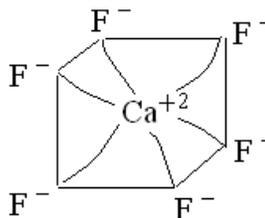
The co-ordination numbers are eight (8) and four (4) and this is called an 8:4 arrangement. The fluorite structure is found when the radius ratio is 0.73 or above.

It may be related to the close packed structures. Though the Ca^{+2} ions are too small lto touch each other (so the structure is not strictly close packed), their relative positions are like those in a cubic close packed structure and the F^- ions occupy all of the tetrahedral holes.



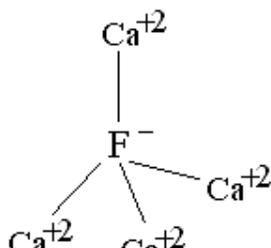
(B.C.C. arrangement)

Or,

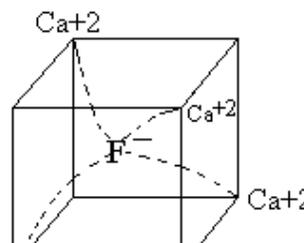


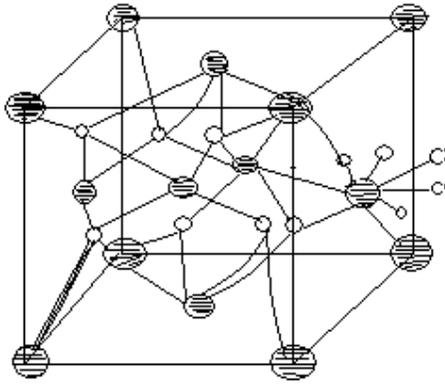
(B.C.C. arrangement)

Each F^- ion is tetrahedrally surrounded.



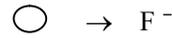
Or,





$$\text{Tetrahedral } r_{\text{Ca}^{+2}} = \frac{0.99}{1.37} = 0.74$$

$$r_{\text{F}^-} = 1.37$$



(Fluorite Structure)

[Identical $\rightarrow \text{BaCl}_2, \text{SrCl}_2, \text{BaF}_2, \text{SrF}_2, \text{PbF}_2, \text{VO}_2, \text{ThO}_2, \text{CdF}_2, \text{HgF}_2$]

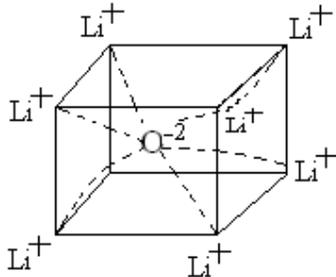
Li_2O shows antifluorite structure \rightarrow

Many of the ionic compounds of M_2X type show antifluorite structure. Here M. Denotes to metal and X to non-metal.

Antifluorite structure is similar to the fluorite structure in all respect except that the position of cations are now taken up by anion and vice – versa. So co-ordination number of anion is eight (8) and of cation is four (4).

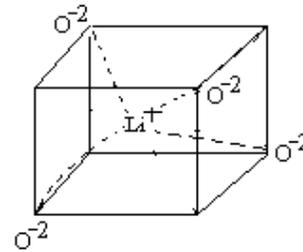
Let us take up the structure of Li_2O , C.N. of Li^+ is 4 and that of O^{2-} is 8. Structure of Li_2O is similar to CaF_2 - except ;in manner that position of Li_2 and O^{2-} are just reverse to that of Ca^{+2} and F^- .

O^{2-} are close packed in B.C.C. fashion and all tetrahedral holes are occupied by Li^+ . Li^+ ions are arranged in simple cubic fashion and the central position is occupied by O^{2-} in B.C.C. fashion.



Octahedrally (B.C.C.)

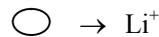
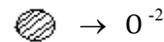
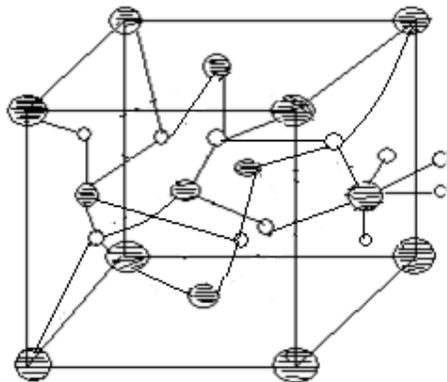
Arrangement Li^+ around O^{2-}



Tetrahedrally

arranged O^{2-} around Li^{+2}

Collectively, the antifluorite structure of Li_2O can be shown as below :-



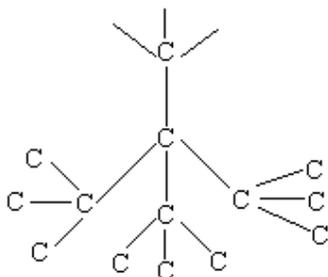
Li_2O

Identical $\rightarrow \text{K}_2\text{O}, \text{Na}_2\text{S}, \text{K}_2\text{S}$

Diamond is hard and non-conductor of electricity but graphite is soft and conducts electricity.

Diamond is a covalent crystal of carbon in which each carbon is covalently bonded to four other carbon by utilizing sp^3 hybrid orbital..

Each is surrounded by others at the four corners of a regular tetrahedron. Thus the ...octet.. of each atom is completed and it gives rise to rigid three dimensional network. Due to this structure, diamond is the hardest substance known with a high density and melting point. The entire crystal is regarded as one large carbon molecule and is called a macro molecule which is shown below :-



Diamond crystal structure

Crystal structure of Diamond

The effective number of atoms per unit cell in diamond -

$$\begin{aligned}
 &= 8 \times \frac{1}{8} + \frac{6}{3} + 4 \\
 &= 1 + \frac{6}{3} + 4 \\
 &= \frac{3 + 6 + 12}{3} = \frac{21}{3} = 7.
 \end{aligned}$$

Graphite is also a crystal of carbon but in this case each carbon is covalently bonded to only three others using sp^2 hybrid orbitals. The remaining fourth electron forms a π - bond.

Thus all atoms in a single plane are linked to give flat hexagons. The hexagons are held together in sheet like structure, parallel to one another. Each sheet may be regarded as fused system of benzene rings. The layers are held together by relatively weak Vander Waals Forces and are about 3.35 \AA apart which is more than twice the covalent radius of carbon (1.54 \AA).

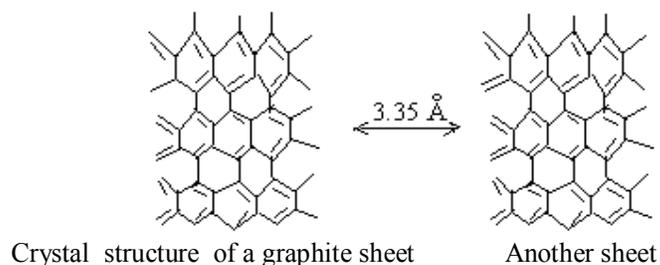
The wide separation accounts for density of graphite being much lower than diamond (graphite 2.22 gm / cc).

Diamond -----> 3.51 gm / cc

Therefore, graphite is comparatively soft.

Because π electrons are mobile, graphite can conduct electricity. As force between the different layers or sheets (Vander Waals Forces) are relatively feeble, rupture between the various layers can occur easily.

Graphite is used as lubricant because are place of atoms can readily slip over another.



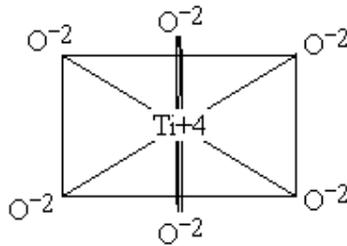
Graphite is thermodynamically stable form of carbon by 1.9 KJ mol⁻¹ at room temperature and ordinary pressure.

Rutile and antirutile structure

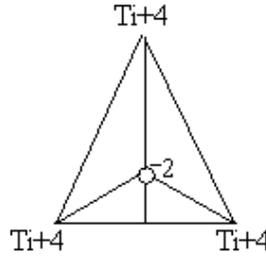
Rutile structure [TiO₂] -----> The rutile structure is found where the radius ratio is between 0.73 and 0.41. The coordination numbers are six (6) and three (3) for the cation and anion respectively.

In case of TiO₂, the radius ratio is between 0.73 and 0.41.

In this structure each Ti⁺⁴ is octahedrally surrounded by six O⁻² ions and each O⁻² by three Ti⁺⁴ ions arranged triangularly.

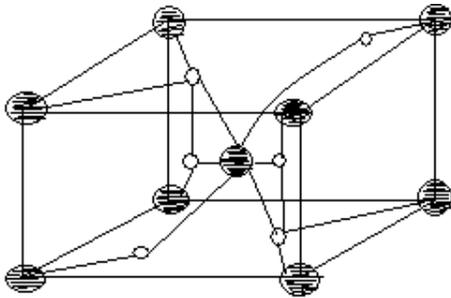


Octahedrally



Triangularly

The rutile structure is not close packed but the Ti⁺⁴ ions may be considered as forming a considerably distorted body centred cubic lattice.



Rutile structure

Identical :

[CaCl₂, SnO₂, PbO₂, GeO₂, ZnF₂,
MnF₂, NiF₂, CaF₂, MnO₂, MgO₂,]

In anti rutile structure a positions of cations are taken up by anions and vice – versa, So, C.N. of anion is 6 and that of cat ion is 3. O₂

There are only a few cases in rutile structure that the radius ratio is below 0.41, e. g., Silica (SiO₂) and B
Role of defects in producing semi conductor properties in ionic solid.

Stoichiometric defect produces semi conductor properties in ionic solid.

Crystals with metal excess defects are n – type semi conductor . This defect contain free electrons and these migrate when electric field is applied. As a consequence of this the crystals conduct electricity but the conduction is poor such crystals are generally called n type semi conductors. Ex- CdO, ZnO.

Crystals with metal deficiency defects are p- type semi-conductor - This defect contains positive hole when electric field is applied. Electrons from adjacent atoms flow to fill this site in the process making another positive hole. Thus current is carried in opposite direction of migration of positive hole.

This type of conduction is known as p – type semi-conductor. Ex.- Cu₂O, NiO

eF₂. These have (N. of 4 and 2 but radius ratio predictions are uncertain as they are appreciably covalent.).

(e) α , β , γ and ϵ phase of brass.

Ans.: - Cu Crystallises in F.C.C. form whereas Zn is close packed hexagonal. About 32% Zn will dissolve in Cu (α - Brass). About 5% of Cu in Zn (η - brass) without change of the respective Lattice structure.

Between these limits however three different solid form called β , γ , ϵ phase exist.

$$\left[\begin{array}{l} \text{Cu} = 1.28 \text{ \AA} \\ \text{Zn} = 1.38 \text{ \AA} \end{array} \right]$$

$$\text{Diff.} = 7.2\%$$

Phase	Composition	Stoichiometric	Structure
α	Zn 0-32%		Random
/	Cu 100 – 68%		Substitutional solu. Of Zn in Cu
β	Zn 45 – 50% Cu 55 – 50%	CuZn	Body centre cubic arrangement
γ	Zn 60-65% Cu 40-35%	$\text{Cu}_5 \text{Zn}_8$	Complete cubic structure with 5^2 atom per unit cell
ϵ	Zn 82 – 88% Cu 18 – 12%	CuZn_3	Close packed hexagonal lattice having dimension different 
η	Zn 97 – 100% Cu ³		Random substitutional solid solu. of Cu in Zn

The relation between various phase can be shown in following phase diagram.

[Fig.- ID Lee page 88]

CHAPTER-06 SOLVENT SYSTEM- NON AQUEOUS SOLVENT

It was observed by Humic – Rothery that various phase β , γ and ϵ always occurred when the Ratio of sum of the valences electrons to the number of atoms is 3 : 2, 21:3 and 7:4 irrespective of particular metal involved e.g. –

Ideal formula	<u>No. of valences electron</u>	Phase
	No. of atom	
CuZn	3/2	β
Cu ₅ Zn ₈	21/3	γ
CuZn ₃	7/4	ϵ

-----x x x -----

Calculate the limiting radius ratio for C.N. 4 or 6

Square planar or octahedral $\left\{ \begin{array}{l} \text{C N} = 4 \text{ or} \\ \text{C N} = 6 \end{array} \right\}$

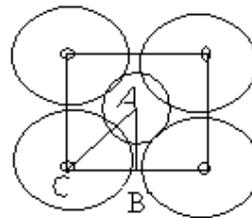
The crystal structure for C N = 6 can also be represented by the same figure as that of square planar. One sphere will above and other below the plane .

BC = r^-

AC = $r^+ + r^-$

Cos 45° = $\frac{BC}{AC} = \frac{r^-}{r^+ + r^-}$

AC = $r^+ + r^-$



Or, $\frac{1}{\sqrt{2}} = \frac{r^-}{r^+ + r^-}$

Or $r^+ + r^- = \sqrt{2} r^-$

Or, $\frac{r^+}{r^-} = \sqrt{2} - 1$

$\frac{r^+}{r^-} = 0.414$

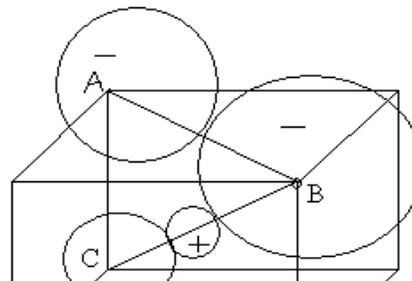
$\frac{r^+}{r^-} > 0.414$ -----> Square Planar

For tetrahedral (C.N = 4), Let each side be a

AB = $r^- + r^- = 2r^-$

= $\frac{a}{\sqrt{2}}$ = $\frac{a}{\sqrt{2}}$

Or, $r^- = \frac{1}{\sqrt{2}} a$ -----> (i)



$$BC = 2r^+ + 2r^-$$

In ΔABC ,

$$\begin{aligned} BC^2 &= AC^2 + AB^2 \\ &= a^2 + (\sqrt{2} a)^2 = 3a^2 \end{aligned}$$

$$\text{Or, } (2r^+ + 2r^-)^2 = 3a^2$$

$$2(r^+ + r^-) = \sqrt{3} a$$

$$\text{Or, } r^+ + r^- = \frac{\sqrt{3}}{2} a$$

$$\text{Or, } r^+ + r^- = \frac{\sqrt{3}}{2} \cdot 2r^- \text{ From relation (i)}$$

$$= \frac{1.732}{1.414} r^-$$

$$\frac{r^+ + r^-}{r^-} = \frac{1.732}{1.414}$$

$$\frac{r^+}{r^-} = \frac{1.732}{1.414} - 1$$

$$= \frac{0.318}{1.414} = 0.225$$

Thus minimum limiting radius ratio for tetrahedral arrangement is 0.225

i. e. when $r^+ / r^- \geq 0.225$ arrangement is tetrahedral.

Explain (i) FCC (ii) BCC (iii) HCP (iv) CCP

Though pure Ge is non-conductor of electricity but when it is doped with Gr III A or IV A elements, it conducts electricity, Explain.

When Ge is doped with III A elements such as In which contains three electrons in the valence shell. By adding the In covalent structure is not completed.

Thus some sites normally occupied by electrons are left empty and so constitute, "positive holes". Electrons from adjacent atoms flow to fill this site in the process making another "positive hole". Thus current is carried in opposite direction of migration of positive hole. This type of conductor is known as p - type of semi conductor. On the other hand if some atoms with five electrons in its valence shell such as "As" be introduced in the crystal of Ge, four of them will form bonds while fifth will conduct electricity. This is extrinsic conduction and as it is caused by excess of electrons it is n - type semi conductor.

structure of Brass :-

Brass is an alloy of Cu and Zn. Copper has face centred cubic form where as zinc has hexagonal close packed structure. About 32% of zinc will dissolved in copper (α - Brass) and about 5% of copper in zinc (β Brass)

without change of the respective lattice structures. Between these units, however three different solid forms called β , α and ϵ phases respectively exist. The first of these is BCC, the second has a complex cubic structure containing 52 atoms in the unit cell and the third has a closed packed hexagonal lattice but its dimension differ appreciably from those of zinc. Although the three solids do not necessarily separate out as pure substances. It has been generally occupied for various reason that they are inter metallic compounds of compositions α - Zn, Cu_5Zn_8 and Cu_3Zn_3 respectively.

Thus when molten Cu the following phases occur Zinc is added to matter Cu, the following phases occur

α	$\alpha + \beta$	β	$\beta +$		$+ \epsilon$	ϵ	$\epsilon +$	
Cu 1083				Zn 419				

The phase diagram is given as (J.D. lee page 88)

Q:- Why liquid ammonia is a solvent? Compare liquid ammonia as a solvent with water or aqueous medium.

Ans.: - Liquid ammonia is a best solvent following specific characters are given below . Since water is also best solvent therefore a comparative study between them is taken which is mentioned below.

- 1) Protic Solvent:-Water provides H^+ to the substance similarly liq. NH_3 provides protons. Hence both are Protic Solvent.
- 2) Hydrogen bonding:-Hydrogen bond exists in water and so water is capable of forming hydrogen bond Similarly hydrogen bonding exists in liq. NH_3 too. Hence liq. NH_3 is also capable forming H- bond. This capability is lesser in NH_3 than that of water. Hence both forms hydrogen bonding.
- 3) Ionising Solvent:-When ionic compounds dissolve in water it becomes readily ionized. Thus water is called a ionizing solvent. It is done due to the high dielectric constant about 85.0 in water at 25°C . When ionic compounds dissolve in liq. NH_3 it also dissolves but it is less ionizing than water and solubility is also poorer than water due to low dielectric constant 22 at -33.5°C .
- 4) Polar Solvent:-Water is good solvent for ionic and polar compounds because it has dipole moment 1.84D. While liq. NH_3 is too good solvent for ionic and polar compounds but it is less polar than water because it has dipole moment 1.47D. And solubility is lesser in liquid NH_3 than that is H_2O .
- 5) Auto ionization:-
Both shows auto ionization

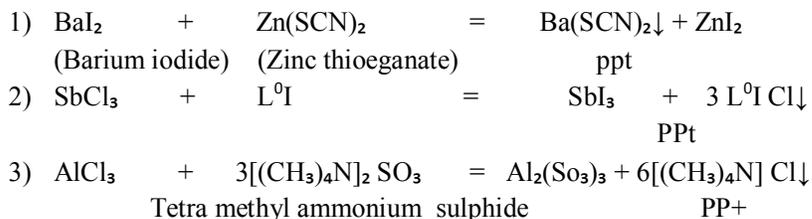
$$\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$$
 Ionization constant, $K = 1.0 \times 10^{-14}$ at 25°C .

$$\text{NH}_3 + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$$
 Ionization constant $K = 1.9 \times 10^{-33}$ at -50°C
 But liquid NH_3 has lesser extent of ionization constant.
- 6) Temperature raved:-Water acts as a solvent between 0°C and 100°C while liq. NH_3 acts as a solvent between -33°C and -78°C .
- 7) Redox reaction:- Oxidizing agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, and reducing agents like KI , SnCl_2 etc are fairly stable in water. Therefore
 (Page 11 ka hai) In liq. Ammonia strong oxidizing agents do not exist, therefore, it is a poor solvent for them. However the species like alkali metals (strong redoxing agents) which does not exist in water can exist in liq. Ammonia. Therefore liquid ammonia is a better solvent for them than water.

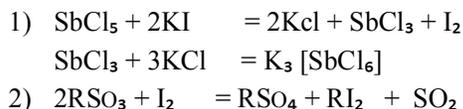
LIQUID (SO_2)

IMPORTANT REACTIONS

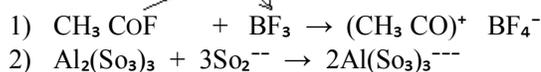
A. Precipitation reaction:-



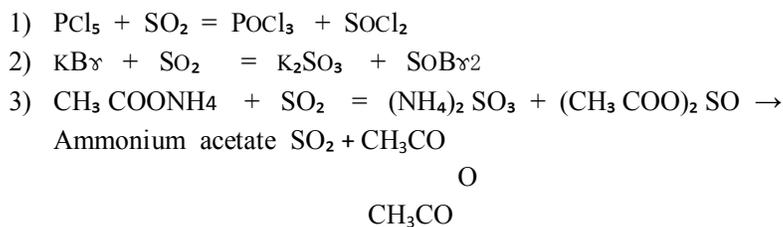
B. Redox reaction:-



C. Complex Formation Reaction:-

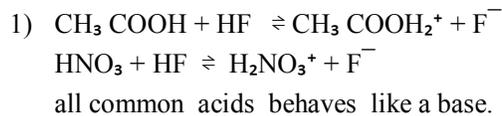


D. Solvolysis reaction:-

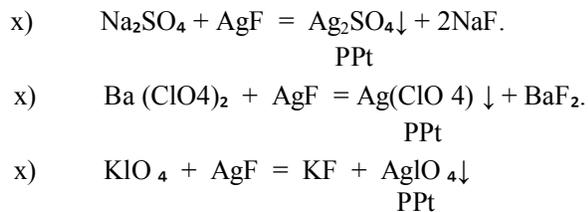


Properties:- B.P = 19.4⁰C
 F.P = -83⁰C | HF – (Liq. Hydrogen Fluoride)
 Dielectric constant = 83.6 (0⁰ C)
 Dipole moment = 1.9 D

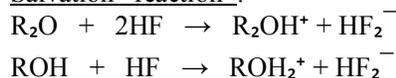
CHEMICAL REACTION:-



2) Precipitation reaction:-



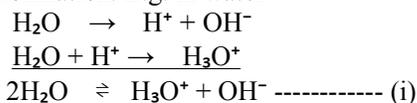
3) Salvation reaction:-



1.

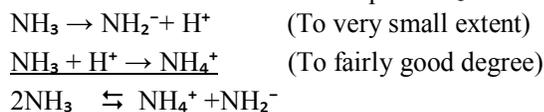
Auto- ionization acid base concept in non-aqueous solvent like (i) HF (ii) NH₃ (liq.), (iii) SO₂ (liq).

Auto ionization:-When two molecules of the same solvent establishes an equilibrium producing cations and anions. The phenomena is known as auto ionization. E.g. in water

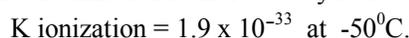


Water acts as H⁺ donor as well as H⁺ acceptor in solution there by producing OH⁻ and H₃O⁺ ions respectively. Therefore it is said that water under goes auto ionisation.

K ionisation = 1.0 x 10⁻¹⁴ at room temperature (25⁰C). This indicates the extent of ionization in H₂O. This phenomenon i.e. auto ionisation also occurs in liquid NH₃ but to a lesser extent.



The lesser extent of ionization is indicated by its lower value of ionization constant.



The lower value of the ionization constant is explained on the basis of the fact that NH₃ is a better H⁺ acceptor than H⁺ donor (since it is a base).

The lower specific conductivity value of liq. NH₃ than that of H₂O is also due to lesser extent of auto ionization.

In liq. SO₂, the auto ionization can be shown as:-



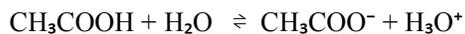
And that in liq. HF it can be shown as



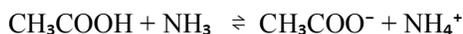
However the extent of auto ionization in liq. SO₂ and in liq. HF is very poor, as their conductivity in solution is extremely low.

Acid-Base concept ion (NH₃) Liquid

In liq. NH₃, as i) clear from the reaction equilibrium (ii) any species which provides NH₄⁺ (analogous to H₃O⁺ in H₂O) is acid and the species which provides NH₂⁻, NH⁻ or N⁻ (analogous to OH⁻ or O⁻) is base i.e. NH₄ Cl or NH₄⁺ salts are acids in liquid NH₃ while KNH₂, PbNH and BiN are bases in liquid ammonia . Since NH₃ is a stronger base than water, therefore the behaviour of acetic acid and Urea in the two solvents i.e. H₂O and liq. NH₃ can be compared as follows :-

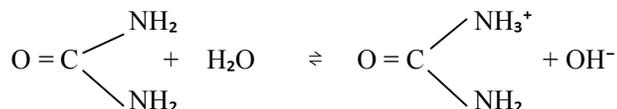


This reaction has low equilibrium constant value i.e. acetic acid is a weak acid in water but in liq. NH₃.



K ionization is high i.e. CH₃COOH is a stronger acid in liq. NH₃.

Similarly,



i.e. Urea is a base in water but in liq. NH₃.

Acid-base concept in SO₂ (Liquid)

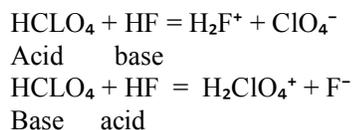
According to auto ionization in liq. SO₂ as shown in reaction (iii) any species which provides SO⁺⁺ i.e. thionyl ion in liq. SO₂ and those which provide SO₃⁻⁻ ions in liq. SO₂ (analogous to OH⁻) are acids and bases respectively in liq. SO₂.

e.g. thionyl chloride SOCl_2 and $\text{SO}(\text{SCN})_2$ thionyl and thiocyanate behave as acids in liq. SO_2 while potassium Sulphate K_2SO_3 or cesium Sulphate are bases in liq. SO_2 .

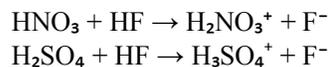
Acid-Base concept in HF (liquid)

According to eqn. (iv) any species which give HF^-_2 or F^- in solution acts as basis and a substance which yield H_2F^+ acts as acid in hydrogen fluorid.

Since HF it-self is a strong acid therefore, only those which are stronger acids than HF can behave as acids in liq. HF- e.g. perchloric acid HClO_4 which is the strongest acid in aqueous solution act as a poor acid (rather amphoteric) in HF.



Other acids like HNO_3 , H_2SO_4 etc. which are stronger acids in water acts as a base in HF since they provide F^- The respective reaction are as follows:-



Physical properties of liq. NH_3 :-

- 1) Liquid NH_3 has low viscosity than water.
- 2) It has low dielectric constant value than water.
- 3) It does exist in acids and bases.
- 4) It is hygroscopic. It absorbs water readily.
- 5) Metal dissolves in liq. NH_3 dissolving metal having low I.P low sublimation. Dissolving metal is liq. NH_3 e.g. a) Alkali metal
b) Alkaline earth metal
c) Lanthanides
They are all dissolves in liq. NH_3 .
- 6) Dissolution is purely physical in nature.
- 7) Liquid NH_3 is good conductor of electricity.
- 8) Conduction is electrolytic in nature.
- 9) It is good reducing agent.
- 10) Liq. NH_3 gives identical absorption spectra.
- 11) This Sol^n is paramagnetic in nature.
- 12) In the concentration Sol^n of liq. NH_3 having blue colour which associated with bronze colour.
a) Its conduction becomes metallic.
b) Its paramagnetism characters decreases.

[Liquid Ammonia (NH_3)]

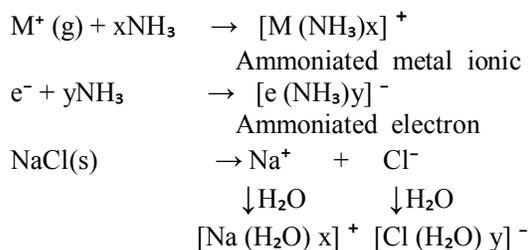
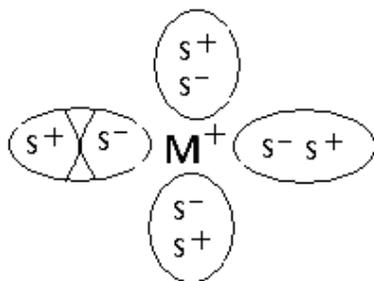
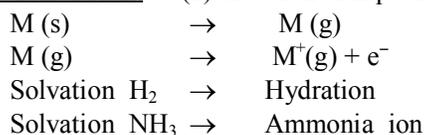
CHARACTERISATION OF LIQUID NH_3 :-

PHYSICAL CHARACTERS :-

- 1) Liquid NH_3 has low viscosity than water.
- 2) Liquid NH_3 has low electric constant than water.
- 3) Liquid NH_3 do exist in Acids and Bases.
- 4) It is hygroscopic. It absorbs water readily.

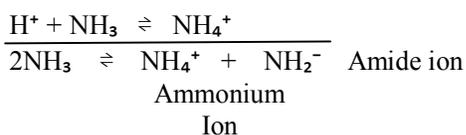
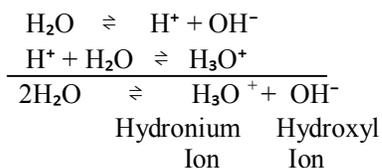
- 5) Metal dissolves in liquid NH₃ dissolving metal having low I.P. low sublimation dissolving metals in liquid NH₃ are e.g.
- Alkali metals
 - Alkaline earth metals
 - Lanthanides, they are all dissolve in liquid NH₃
- Dissolution is purely physical in nature.
 - Liquid NH₃ is good conductor of electricity
 - Conduction is electrolytic in nature.
 - Liquid NH₃'s solution is good reducing agent.
 - Liquid NH₃ gives identical absorption spectrum.
 - This solution is paramagnetic in nature.
 - In the concentration solution of liquid NH₃ having blue colour which associated with bronze colour.
 - Its conduction becomes metallic.
 - Its para magnetism characters decreases.

Chemical characters :- (1) Reaction of liq. NH₃ with metals :-



- Colour is due to ammoniated electron.
- Absorption spectra due to transition of electron from one energy level to another energy level.

2) Auto-ionization:-Both water and ammonia display comparable auto ionization equilibrium represented as below.



Due to its high ionizing capacity, low dielectric constant at about 22.
It is as a solvent.

Explain the behaviour of metals in liq. Ammonia.

- In dilute solution
- In concentrated solution

When a small piece of alkali metal (e.g. Na) is dissolved in dilute ammonia, it dissolves and the solution attains blue colouration. The Solⁿ is paramagnetic and good conductor of electricity. The conductivity is in the range of electrolytes dissolved in liq NH₃.

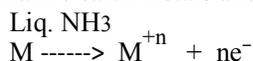
The density of Solⁿ resembles the density of pure ammonia.

However, when more alkali metals is dissolved (i.e. in concentration Solⁿ of liquid ammonia gives) a bronze colour which phase floats on the blue Solⁿ. Finally blue colour disappears and bronze Solⁿ is obtained.

This bronze coloured phase shows conductivity in the metallic range. The density decreases and magnetic susceptibility also resembles to that of metals. The metal however can be recovered by evaporating the Solⁿ. Alkaline earth metals and lanthanides do not dissolve in liq ammonia.

The properties or behaviour of metal can be explained in the liquid ammonia on the basis of dissolving metal in liq. NH₃.

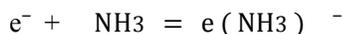
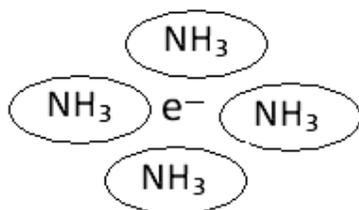
Alkali metals :- alkaline earth metals and lanthanides dissolve in liq ammonia as –



The NH₃ molecules surround the electron in the same way as anions are surrounded by solvent molecules.

The ammoniated Ammoniated Ammo

The ammoniated electron is surrounded by NH₃ molecules -



It is similarly like analogous to H₂O.

(a) The properties of metal liquid ammonia system in dilute Solⁿ are explained by the above postulates.

i) Conductivity :- Since the Solution contains ammoniated metal ion i.e. cation and ammoniated electron i.e. anion due this, it is a good conductor of electricity and conduction is electrolytic in nature.

ii) Para magnetism :- Due to the presence of free i.e. mobile ammoniated electron which is unpaired. The Solution is Para magnetic.

iii) Colour :- The ammoniated mobile electrons absorb energies of certain frequency which becomes different in the nature of metal atom. This is to be possible due to the transition of electron from ground state to the excited state. Thus all the metal in the dilute Solution of liq. NH₃ gives blue colouration and shows identical absorption spectra.

iv) Density :- The density of metal liquid ammonia in dilute system resembles that of pure ammonia because the Solution does not bring about any change in the liq. System.

v) Reducing agent :- Due to presence of free electrons they are reducing agent.

(b) Behaviour of metal in concentration system of liq. NH₃.

In case Solution the behaviour of metal is metallic because non ammoniated electron. Its ions metal ions and some electron remain un ammoniated and behaves as metals.

i) Conductivity :- Conductivity decreases and approaches towards metallic conductivity.

ii) Para magnetism also decreases due to the pairing of un ammoniated electron and thus magnetic susceptibility of solution resembles that of metals

iii) The absence of ammoniated electrons are responsible for the disappearance of blue colour and bronze colour appears due to metallic nature of concentration solution.

Ques. :- List out the advantages and disadvantages of using liquid ammonia.

Ans.:- Advantages of using liquid ammonia as solvent :-

- One of the greatest advantages of using liq NH₃ as a solvent is that, Liquid NH₃ without reacting dissolves alkali metal. The dissolved alkali metal can be recovered by the evaporating the alkali metal ammonia Solution.
- In alkali metal ammonia Solution which contain mobile ammoniated electron e⁻ (am). It can be used for reducing the materials which is soluble in liq NH₃. Hence liq NH₃ is a good reducing agent solution.
- Liq NH₃ has lesser tendency than water undergoes solvolysis reaction with dissolved solutes.

DISADVANTAGES OF USING Liq. NH₃ AS A SOLVENT.

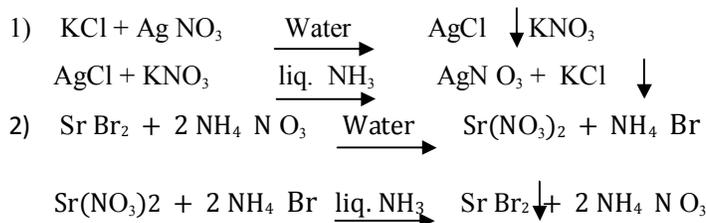
- At normal temperature and pressure NH₃ is a gas. It can be liquified at - 33.5⁰C or by increasing pressure. Therefore for liquification of NH₃, high pressure and low temperature are essential condition.
- Special techniques are required to use liquid nh3 as a solvent.
- Since it is hygroscopic, the reaction may not be done in open. It is done in sealed tube because moistures are not come in contact of ammonia.

Explain the following reaction in liq. NH₃

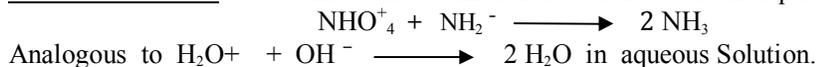
- Metathetical or PPT reaction.
- Acid base reaction
- Auto ionization
- Redox reaction
- Solvolysis

(i) Metathetical or PPT reaction in liq NH₃ :-

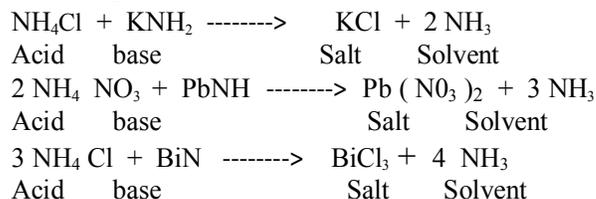
The solubility of compounds in water and liquid ammonia differs and hence some reactions which are not possible in water occurs in liq NH₃. In some cases the direction of reaction gets changed. All the reaction are double decomposition and compound & resolvable in liq. NH₃ get ppted. Few examples are :



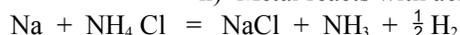
(ii) Acid base reaction :- We know neutralization reaction occurs in liq. NH₃.



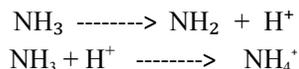
i) Thus following are neutralization reaction :-

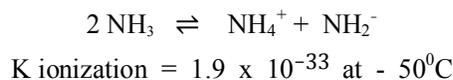


ii) Metal reacts with acid to give H₂ analogous to the reaction :



(iii) Auto ionization :- When two molecules n of the same solvent establishes an equilibrium producing cations and anions, the phenomenon is called auto ionization.





(iv) Redox reaction :-

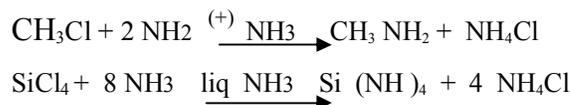
- i) When air is passed in the Solution of Na in liq NH₃ we get sodium per oxide. This is a redox reaction.
- ii) When S & Na in liq NH₃ is dissolved and crystallized then poly sulphur separates out.

(v) Solvolysis or Solvolytic reaction :-

Solvolysis reactions or solvolytic reactions are those in which the solvent is split into two parts and one or both parts get attached to a solute molecule or ion.

In solvolysis reaction the concentration of either cation or anion is increased which is characteristics of auto ionization of the solvent. The solvolysis reaction taking place in water liq NH₃ and alcohol are called hydrolysis, ammonolysis and alcoholysis.

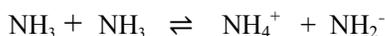
Similar to hydrolysis in aqueous medium ammonolysis occurs in liq NH₃. Some examples are given below :-



Here NH₄⁺ and NH₂⁻ attached on two parts are just like the attachment of H⁺ and OH⁻ in aqueous medium.

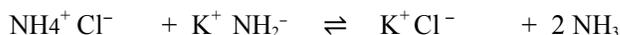
NH₄Cl is acidic but KNH₂ is basic in liquid ammonia.

NH₃ exhibits autoionization.



That substance which gives NH₄⁺ ion in liq. NH₃ is an ammono acid e. g. NH₄Cl While these substance which gives KNH₂ (NH₂⁻, NH⁻², N⁻³) in liq NH₃ called ammono base e.g. NaNH₂, PbNH, BIN.

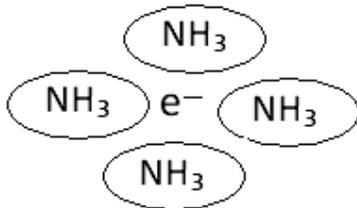
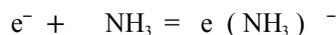
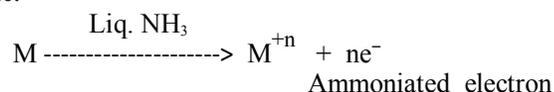
The interaction of an ammono acid and an ammono base gives a salt called ammono salt and also a solvent.



Ammono acid ammono base ammono salt solvent

Metals in liquid NH₃ are paramagnetic and reducing agent.

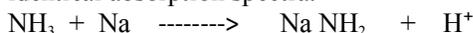
When metal like sodium dissolves in dilute liq NH₃, Metal ammonia Solution forms ammoniated electron which is surrounded by liq. NH₃. Due to presence of free ammoniated electron which is unpaired the Solution is paramagnetic.



due to electron it is reducing agent.

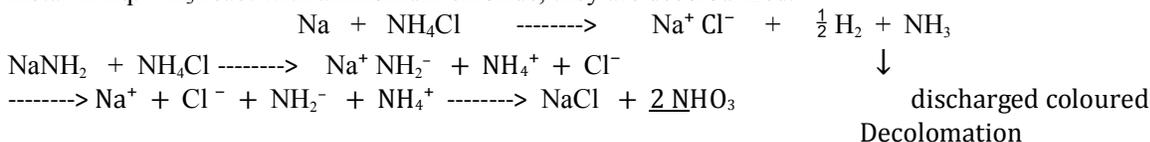
Sodium metal in dilute liquid ammonia give blue colour.

When dissolves in dilute liq NH₃ sodium ammonia Solution gives ammoniated electron which is surrounded by liq. NH₃. For its blue colouration – The ammoniated electron absorbs energies of certain frequencies and it is free of the nature of metal atom. It is done due to the transition of electron from ground state to the excited state. Thus all the metal ammonia Solution are blue in colour in dilute liq NH₃ and shows identical absorption spectra.



Why blue colour is discharged by adding NH_4Cl in it.

Liq. NH_3 Solution of ammonia chloride react with metal to give hydrogen. Thus when blue Solution of alkali metal in liq. NH_3 react with ammonium chloride, they are decolourized.



Show the variation of conductivity of metals liq NH_3 system, if the Solution is concentrated.

Metal in concentration Solution of liquid NH_3 gives metallic nature because non ammoniated electron. These un ammoniated electron behaves as metals.

Conductivity in it decreases and approaches towards metallic conductivity.

Para magnetism also decreases due to the pairing of un ammoniated electron.

The behaviour of metals in liquid ammonia:

- a) Dilute solution
- b) In concentration Solution .

Give the reasons for such behaviours.

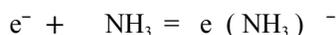
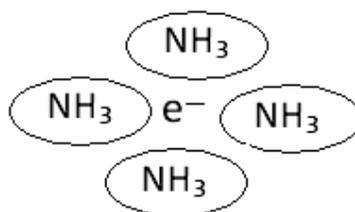
When a small piece of alkali metal e. g. Na is dissolved in dil liq ammonia. It dissolves and the Solution obtains blue colouration. the Solution is paramagnetic and good conductor of electricity. The conductivity is in the range of electrolytes dissolved in liq. NH_3 .

The density of Solution resembles the density of pure ammonia.

However, when more alkali metal is dissolved in concentration Solution of liquid ammonia gives bronze colours which floats on the blue Solution. At last blue colour disappears and bronze Solution is obtained.

This bronze coloured phase shows conductivity in the metallic range. The density decreases and magnetic susceptibility also resembles to that of metals. The metal however can be recovered by evaporating the Solution. Alkaline earth metals and lanthanides do dissolve in liq. ammonia.

The properties of the behaviour of metal can be in the liquid ammonia on the of dissolving in liq. NH_3 and dissolves NH_3 metal in liq. NH_3



Similarly metal ion is also surrounded by NH_3 molecules, analogous to hydrated cation in aqueous solution of an electrolyte. The properties of metal liquid ammonia system in dilute Solution are explained by the above postulates.

- i) Conductivity :- Since the Solution contains ammoniated metal ion (cation) and ammoniated electron (anion), it is a good conductor of electricity and conduction is electrolytic in nature.
- ii) Para magnetism :- Due to the presence of free ammoniated electron which is unpaired the Solution is para magnetic.
- iii) Colour :- the ammoniated mobile electron absorbs energies of certain frequency which becomes different in the nature of metal atom. This is to be possible due to the transition of electron from ground state the excited state. Thus all the metal in the dilute solution of liq. NH_3 gives blue colouration and shows identical absorption spectra.

- iv) Density :- The density of metal liquid ammonia in dilute system resembles that of system of pure ammonia because the solution does not bring about any change in the liq. System.
- v) Reducing agents :- Due to available electrons they are reducing agents.
- (a) Behaviour of metal in concentrated System of liq. NH_3
 In case Solution the behaviour of metal is metallic because of non ammoniated electron. Its ions metal ions and some electron remain un-ammoniated and behaves as metals.
- Conductivity decreases and approaches towards metallic conductivity.
 - Para magnetism also decreases due to the pairing of unammoniated electron and thus magnetic susceptibility of Solution resembles that of metals.
 - The absence of ammoniated electrons are responsible for the disappearance of blue colour and bronze colour appears due to metallic nature of concentrated Solution.

List out the advantages and disadvantages of using liquid ammonia.

Followings are the specific advantages of using liquid ammonia over water.

- Alkali metals react readily with water due to its highly reactive nature which there occurs no chemical reaction between alkali metals and liq NH_3 . Hence alkali metals cannot be used in aqueous Solution while liquid ammonia can be used as a solvent for alkali metals.
- Weak oxidizing agents which are difficult to be reduced in other solvents can be reduced by metal liquid ammonia system. Since it is strong reducing agent.
- Water becomes a poor solvent due to hydrolysis of salts. The ammonolysis occurs to a lesser extent if liquid ammonia is used. Hence liq. Ammonia is a better solvent than water in this regard.
- Many compounds which are not possible to be isolated in water can be isolated in liq. ammonia e. g. metal carba metals, metal sulphides etc. are easily precipitated in liq. ammonia.
- Ammonia has a lower dielectric constant value therefore it is a poorer solvent for ionic compounds. Consequently it is a good solvent for covalent compounds.
- Reactions taking place below 0°C can not be performed in liquid ammonia.

Following are the disadvantages of using liquid ammonia as a solvent over water :-

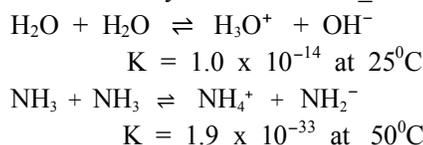
- At normal temperature and pressure NH_3 is a gas. However it can be liquefied at -33°C or by increasing pressure. Therefore in order to use liquid ammonia high pressure and low temperature are essential conditions.
- Special techniques are required to use liquid NH_3 as a solvent.

Compare water and liquid ammonia as solvent.

Water in addition to its readily or abundantly availability is a cheaper medium which contains some specific characters due to which it is termed as the 'best Solvent'. Such characters are present in liq. Ammonia too, to a certain extent. A comparative study between their properties is mentioned below :-

- Protic Solvent :- Water provides H^+ to the substance. Similarly protons can also be derived from liquid NH_3 . Hence both are protic solvents.
- Hydrogen – bonding :- There exists hydrogen bonding in water and water is capable of forming hydrogen bond. Therefore any substance which can form hydrogen bond with water are water soluble like alcohols, sugars, glucose etc.
 Similarly, hydrogen bonding exists in liq. NH_3 too. Hence liq. Ammonia is also capable of forming H – bond though this ability is lesser in NH_3 than that in water. Thus such substances are soluble in liq. Ammonia. Though solubility of such substances in liq. NH_3 is poorer than that in water.
- Ionizing solvent :- Ionic compounds dissolve in water and they get readily ionized. Thus water is called a ionizing solvent. It is due to the high dielectric constant value of water.
 $K = 82.0$ for water at 25°C . Hence ionic compounds are water soluble.
 The dielectric constant for liquid NH_3 (KNH_3) is 22.0 at -33.5°C . This indicates that liquid ammonia is also an ionizing solvent, but it is less ionizing than water. Thus ionic compounds do dissolve in liquid NH_3 but solubility is poorer than water.
- Polar Solvent :- Water has a dipole moment 1.84 D . hence after ionization, solvation (hydration) occurs and therefore, water is a good solvent for ionic and polar compounds. The dipole moment of liquid NH_3 is 1.47 D . Hence it is less polar than water. However ionic and polar compounds dissolve in liquid ammonia as well but the solubility is lesser in liquid NH_3 than that in H_2O .

- 5) Auto ionization :- As indicated by their ionization constants –



acids and bases both exist in water, therefore neutralization and other acid base reactions can occur in water.

In liq NH_3 even weaker acids in water behaves as stronger acids. Hence they react effectively while such reaction are different in water.

- 6) Temperature – range :- Water acts as a solvent between 0°C and 100°C while liq. NH_3 acts as a solvent between -33°C and 78°C
- 7) Redox reaction :- Oxidizing agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and reducing agents like KI , SnCl_2 etc are fairly stable in water. Therefore redox reactions occur readily in water.

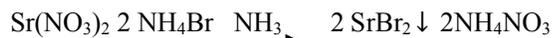
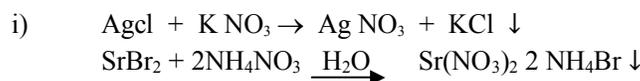
In liq. Ammonia strong oxidizing agents do not exist, therefore it is a poor solvent for them. However the species like alkali metals (strong reducing agents) which does not exist in water can exist in liq. Ammonia. Therefore liquid ammonia is a better solvent for them than water.

(A) Reactions in liquid ammonia :-

- a) Precipitation reaction :- The solubility of compounds in water and liquid ammonia differs and hence some reactions which are not possible in water occurs in liq NH_3 . In some cases the direction of reaction gets changed. All the reactions are double decomposition and compound insoluble in liq NH_3 get ppted. A few examples are :-



Similarly in liquid NH_3



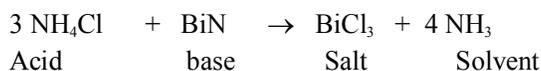
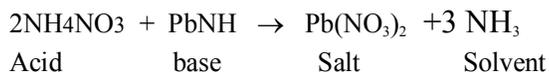
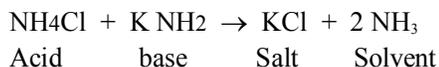
- b) Acid base reaction :- As we knew ammonia salts are acidic in liq. NH_3 and amides etc. are base in liq. NH_3 , neutralization reaction occurs in liq. NH_3 .



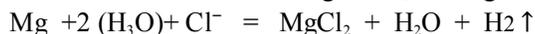
Analogous to $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ in aq Solution

Thus,

- i) Following are neutralization reactions :-



- ii) Metal reacts with acid to give H_2 analogous to the reaction.



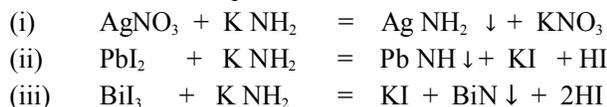
In liq NH_3 medium, we have $\text{Na} + \text{NH}_4\text{Cl} = \text{NaCl} + \text{NH}_3 + \frac{1}{2}\text{H}_2$

Thus the blue colour of Na and liquid NH_3 solution is discharged by adding NH_4Cl in it.

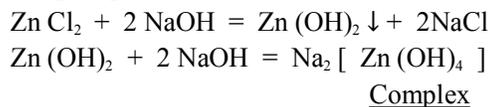
- c) Analogous to the precipitation of hydroxide in aqueous medium, metal amides are precipitated in liq NH_3 solution.



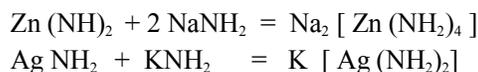
Following are the reactions in liq NH₃



d) In some cases the precipitate of the hydroxide dissolves in liquid forming complexes e.g. –



Similarly in liq NH₃



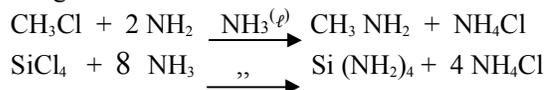
These reactions may be quoted as complex formation & reactions.

e) Redox reactions :-

i) When air is passed in the Solution of Na in liq. NH₃ we get sodium peroxide. This is a redox reaction.

ii) When S & Na in liq. NH₃ is dissolved and crystallized then poly-sulphur separates out.

f) Ammonolysis reactions :- Similar to hydrolysis in aqueous medium ammonolysis occurs in liq NH₃. Some examples are given below :-

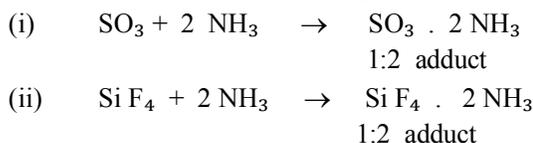


Here NH₄⁺ and NH₂⁻ attached on two parts are just like the attachment of H⁺ and OH⁻ in aqueous medium.



g) Ammoniation reaction :- Hydration occurs in aq medium in which water molecules associated with salt or ion exactly in the same way attachment of NH₃ is called ammoniation. It results in the formation of ammoniates.

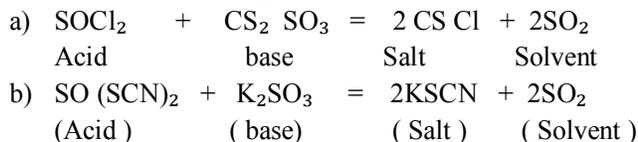
In liq. NH₃



Above reactions are analogous to $\text{CuSO}_4 + 5 \text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

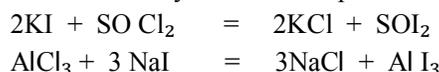
(A) Reactions in liquid Sulphur dioxide :-

1) Acid – base reactions :- Typical neutralization reaction in liq SO₂ is given as below :-

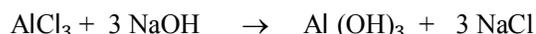


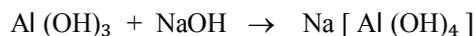
SO Cl₂ and SO (SCN)₂ are acids and CS₂ SO₃ & K₂ SO₃ are bases in liquid SO₂.

2) Precipitation reactions :- Liquid SO₂ is a poor solvent for ionic compounds. Such compounds may be synthesized in a well crystallized and pure form in this medium.

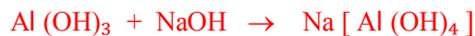


3) Amphoteric reactions :- In aqueous medium the following reactions show amphoteric behaviour of Al Salt –

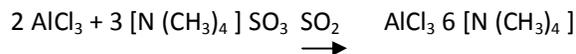




Similar reaction in liq SO₂ can be -

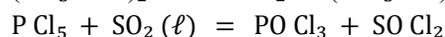
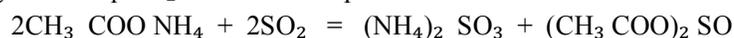


Similar reaction in liq. SO₂ can be shown as,



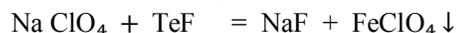
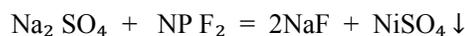
This may be quoted as complex formation reaction also.

- 4) Solvolytic reaction :- Analogous to hydrolysis in aqueous medium and ammonolysis in liq NH₃, we have solvolysis in liq SO₂ as well. Examples of such reactions are –

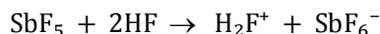


- e) Reactions in liquid hydrogen Fluoride :-

(1) Precipitation reaction :- Alkali metals parachutes, sulphates etc. are precipitated in liq HF medium as follow :-



(2) Acid base reaction :- In liq HF, lewis acids like BF₃, SbF₅ acts as acid and reacts with HF, Lewis acid like BF₃, SbF₅ acts as acid and reacts with HF as follows :



Other acids in HF behave as bases



- 3) Adduct formation :- Some adducts are formed as the ammoniation and hydration reaction in liq NH₃ and H₂O medium respectively, e.g. KF HF, NH₄F, 2HF etc.

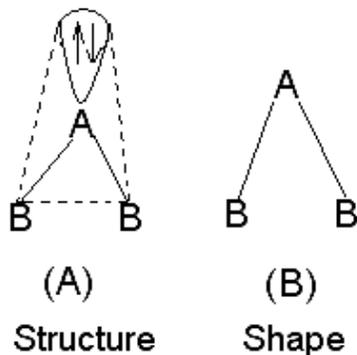
- 4) Protonation :- Organic solvents like benzene undergo protonation in HF as follows :-



(up to Page 35)

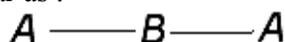
CHAPTER-07 THEORY OF CHEMICAL BOND- HYBRIDISATION

In the chapter of chemical bond, hybridization and structures derived from different hybridization have been discussed. While discussing the structure, only σ bonds are considered. The shape of molecule is derived from the structure. Electrons cannot be seen and hence, if there is lone pair of electron on AB_2 type molecule its structure will be triangular as in (A), but its shape will be angular as in (B).

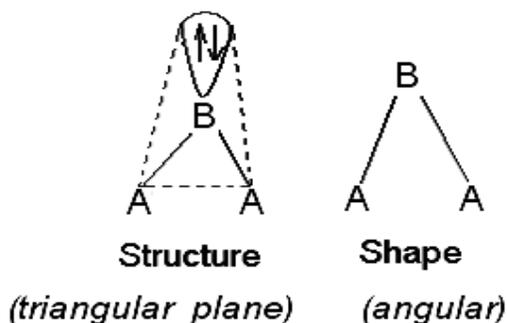


All diatomic molecules have linear structure and shape

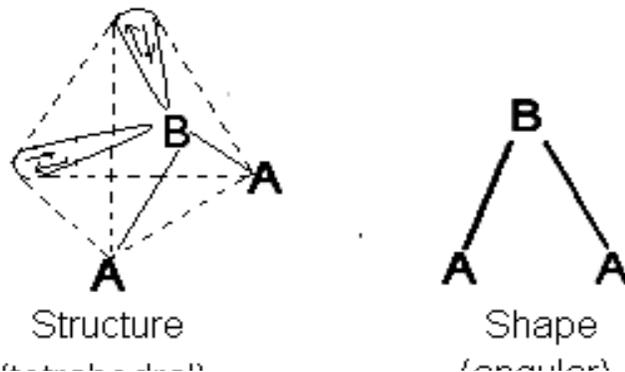
Hybridization, structure and shape of AB_2 type : AB_2 type molecules may have (a) no lone pair electron on the central atom, (b) one or one pair electron on central atom, (c) three or two lone pair electron on central atom and (d) five or three lone pair electron on the central atom. In (a) two orbitals for the bond pair orbital is needed and so the hybridization of central atom is sp and structure as well as shape is linear as :



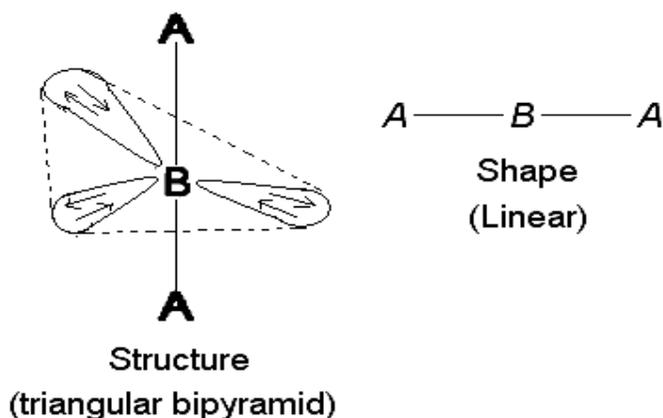
In (b), two orbitals for bond pair and one orbital for the lone pair is needed. Thus three orbitals are needed. The hybridization is sp^2 the structure is triangular plane and the shape is angular as :



In (c) four orbitals are needed (two for bond pair and two for lone pair, the hybridization is sp^3 , structure is tetrahedral and shape is angular.



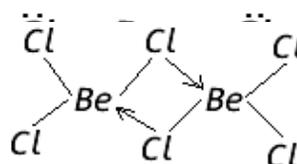
In (d) five orbitals are needed (two for bond pair and three for lone pair), the hybridization is sp^3d , structure is trigonal bipyramid and the shape is linear.



H_2O , CO_2 , NO_2 , NO_2^+ , NO_2^- , ClO_2 , ClO_2^- , SO_2 , O_3 , I_3^- , XeF_2 , $BeCl_2$, N_3^- are typical examples of AB_2 type.

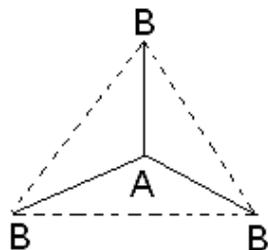
Molecule	Total valence electron	Minimum number of bonds	Electrons with octet or duet	Lone pair electron	Orbital needed	Hybridization	Structure	Shape
(i)	(ii)	(iii)	(iv)	(ii) – (iv)	(iii)+(iv)			
H_2O	8	2	4	4=2 pair	4	sp^2	tetrahedral	angular
CO_2	16	2	16	0	2	sp	Linear	Linear
NO_2	17	2	16	1	3	sp^2	tetrahedral plane	angular
NO_2^+	16	isoelectronic with CO_2			structure shape		similar to CO_2	
NO_2^-	18	2	16	2=1 pair	3	sp^2	triangular	angular
ClO_2	19	2	16	3=1 pair+1e	4	sp^3	tetrahedral	angular
ClO_2^-	20	2	16	4=2 pair	4	sp^3	tetrahedral	angular
SO_2	18	isoelectronic with NO_2^- ,			structure, shape similar to NO_2			
O_8	18	„	„	„	„	„	„	„
I_8^-	22	2	16	6=3 pair	5	sp^3d	trigonal bipyramid	linear
XeF_2	22	isoelectronic with I_8^-			structure, shape similar to I_8^-			
$BeCl_2^*$	16	isoelectronic with CO_2			structure, shape similar to CO_2			
N_3^-	16	isoelectronic with CO_2			structure, shape similar to CO_2			

* $BeCl_2$ has linear structure :
dimerizes

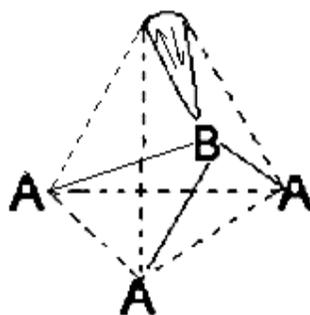


as there are only 4 electrons around Be, it
:

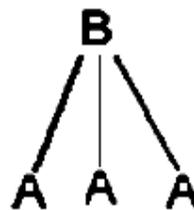
Hybridization, structure and shape of AB_3 type : AB_2 type molecules may have (a) no lone pair electron on central atom A and (b) one or one pair on A (c) three two pair electron on A . In (a), three orbitals are needed for the bond pair electrons, hybridization is sp^2 and the structure as well as shape is triangular plane as :



In (b) four orbitals are needed (three for bond pair and one for lone pair), hybridization is sp^3 , structure is tetrahedral and shape is pyramidal as :

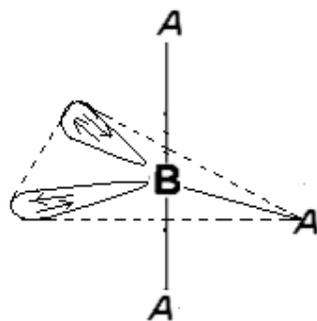


Tetrahedral structure

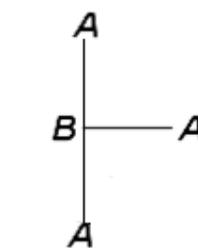


Pyramidal shape

In (c), five orbitals are needed (three for bond pair and two for lone pair), hybridization is sp^3d , structure is trigonal bi-pyramid and shape is T-shaped as :



Trigonal
bipyramid structure



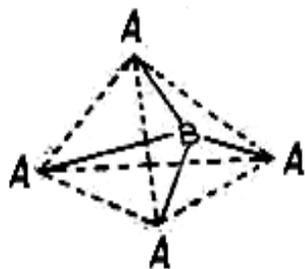
T-shaped

NH_3 , BF_3 , BrF_3 , PCl_3 , SO_3 , NO_2^- , CO_3^{2-} , BO_3^{3-} , ClO_3^- , etc. are typical examples of AB_3 .

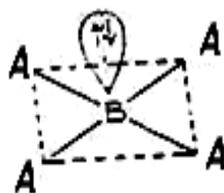
Molecule	Total valence electron	Minimum number of bonds	Electrons with octet or duet	Lone pair electron	Orbital needed	Hybridization	Structure	Shape
(i)	(ii)	(iii)	(iv)	(ii) - (iv)	(iii) + (iv)			
NH ₃	8	3	6	2=1 pair	4	sp ³		tetrahedral pyramidal
BF ₃ triangular	24	3	24	0	3	sp ²	triangular plane	plane
PCl ₃ pyramidal	26	3	24	2=1 pair	4	sp ³		tetrahedral
BrF ₃	28	3	24	4=2 pair	5	sp ³ d	trigonal bipyramid	T-shaped
SO ₃ ⁻	24	isoelectronic with BF ₃			structure similar to BF ₃			
NO ₃ ⁻	24	„	„	„	„	„	„	„
CO ₃ ⁻²	24	„	„	„	„	„	„	„
BO ₃ ⁻³	24	„	„	„	„	„	„	„
ClO ₃ ⁻	26	„	„	PCl ₃	„	„	„	PCl ₃

Hybridization, structure and shape of AB₄ type : SO₄⁻², CH₄, ClO₄⁻, PO₄⁻³, MnO₄⁻,

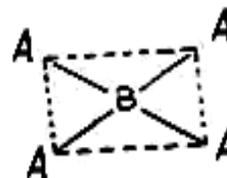
CrO₄⁻², SiO₄⁻³, XeF₄, ICl₄⁻ etc. are typical examples of AB₄ there may be (a) no lone pair electrons on A, (b) one or two electrons on A and (c) three or four electrons on A. In (a) four orbitals are needed, hybridization is sp³, structure as well as shape is tetrahedral. In (b) five orbitals are needed the hybridization is sp³d, structure is square pyramid and shape is square planar. In (c) six orbitals are needed, hybridization is sp³d², structure is octahedral and shape is square planar.



Tetrahedral structure



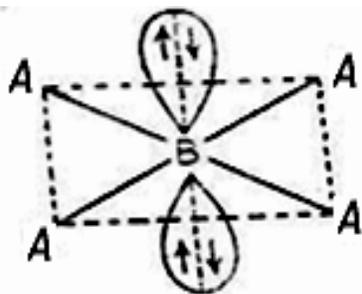
Square pyramid



Square planar

and shape

(a)

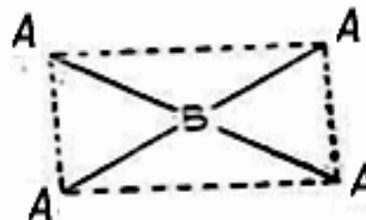


Structure octahedral

(c)

structure

(b)



Shape square planar

(c)

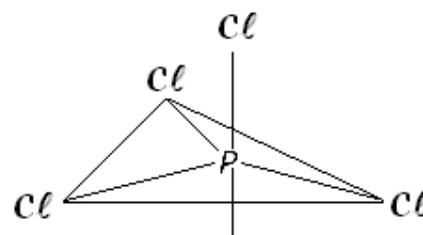
Molecule	Total valence electron	Minimum number of bonds	Electrons with octet or duet	Lone pair electron	Orbital needed	Hybridization	Structure	Shape
(i)	(ii)	(iii)	(iv)	(ii) – (iv)	(iii)+(iv)			
SO ₄ ⁻²	32	4	32	0	4	sp ³		tetrahedral
CH ₄	8	4	8	0	4	sp ³	„	„
PO ₄ ⁻³	32	isoelectronic with SO ₄ ⁻²					structure shape similar to SO ₄ ⁻²	
ClO ₄ ⁻	32	„	„ „	„	„	„	„	„
SiO ₄ ⁻⁴	32	„	„ „	„	„	„	„	„
MnO ₄ ⁼	32	„	„ „	„	„	„	„	„
CrO ₄ ⁻²	32	„	„ „	„	„	„	„	„
XeF ₄	36	4	32	4=2 pair	6	sp ³ d ²	octahedral	square planar
ICl ₄	86	isoelectronic with XeF ₄					structure similar to	shape XeF ₄

Hybridization structure and shape of AB₅ type : PCI₅ , BrF₅ etc. are typical examples of AB₅.

PCI₅ :

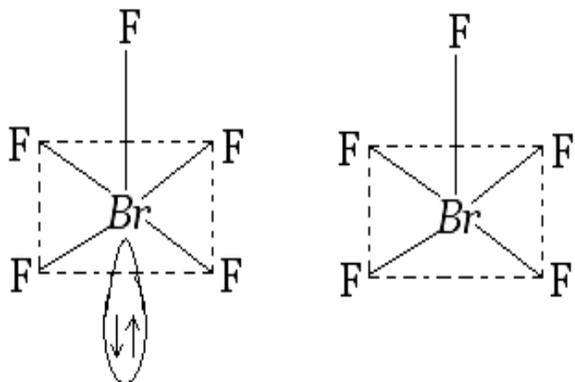
- Total valence electrons = 5 + 5 x 7 = 40
- Minimum number of bonds = 5
- Electrons with octets = 5 x 8 = 40
- Lone pair electron = 0
- Number of orbitals needed = 5
- Hybridization = sp³d
- Structure = trigonal bipyramid
- Shape = trigonal bipyramid

Structure and shape (pentagonal bipyramid)



BrF_5 : Total valence electrons = $7 + 5 \times 7 = 42$

Minimum bonds	= 5
Electrons with octets	= $5 \times 8 = 40$
Lone pair electron	= 2 i. e., 1 pair
Total orbitals needed	= 6
Hybridization	= sp^3d^2
Structure	= octahedral
Shape	= square pyramid

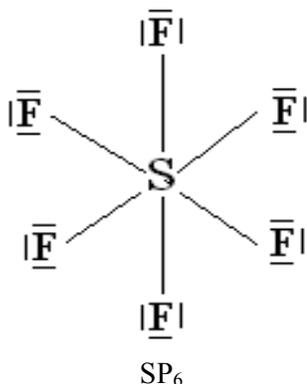


Octahedral structure

Square pyramid shape

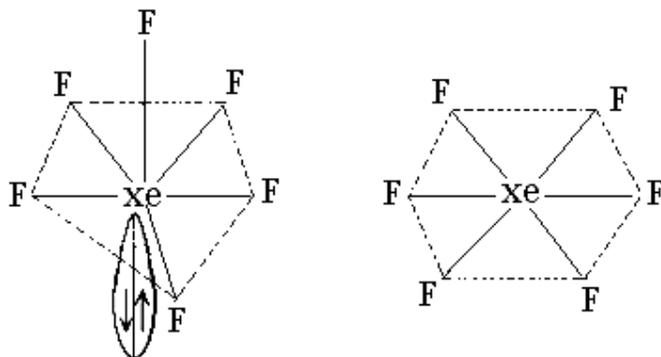
Hybridization, structure and shape of AB_6 type : SF_6 and XeF_6 are typical examples of AB_6 .

SF_6 :	Total valence electrons = $6 + 6 \times 7 = 48$
	Minimum bonds = 6
	Electrons with octets = $6 \times 8 = 48$
	Lone pair electron = 0
	Orbitals needed = 6
	Hybridization = sp^3d^2
	Structure = octahedral
	Shape = octahedral



XeF_6 :	Total valence electrons = $8 + 6 \times 7 = 50$
	Minimum bonds = 6
	Electrons with octets = $6 \times 8 = 48$
	Lone pair electron = 2, I.E., 1 pair

Orbitals needed = 7
 Hybridization = sp^3d^3
 Structure = pentagonal bipyramid
 Shape = octahedral

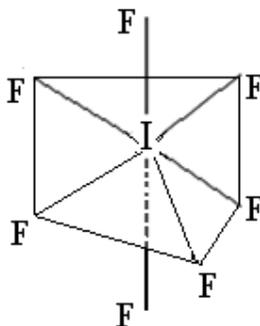


Structure

Shape Hybridization, structure and shape

of AB_7 type : IF_7 is the typical examples of AB_7 .

IF_7 : Total valence electrons = $7 + 7 \times 7 = 56$
 Minimum bonds = 7
 Electrons with octets = $8 \times 7 = 56$
 Lone pair electron = 0
 Orbitals needed = 7
 Hybridization = sp^3d^3
 Structure = pentagonal bipyramid
 Shape = pentagonal bipyramid



Hybridization, structure and shape from electronic dot structures : Hybridization, structure and shape can be predicted from electronic dot structure.

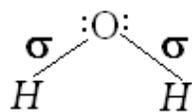


C has two σ bonds hence two equivalent orbitals of C are involved. Two equivalent orbitals are obtained by sp hybridization, hence C is sp hybridized, the structure of CO_2 is linear and its shape is also linear.



S has three σ -bonds and hence sp^2 hybridization of *S*, the structure as well as shape is triangular planar.

H_2O :



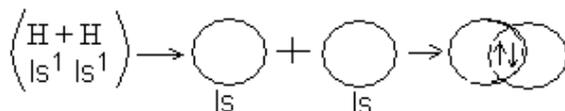
O has two σ bonds and two lone pairs. Hence 4 orbitals are needed. The hybridization of *O* is sp^3 , structure of H_2O is tetrahedral and shape is angular.

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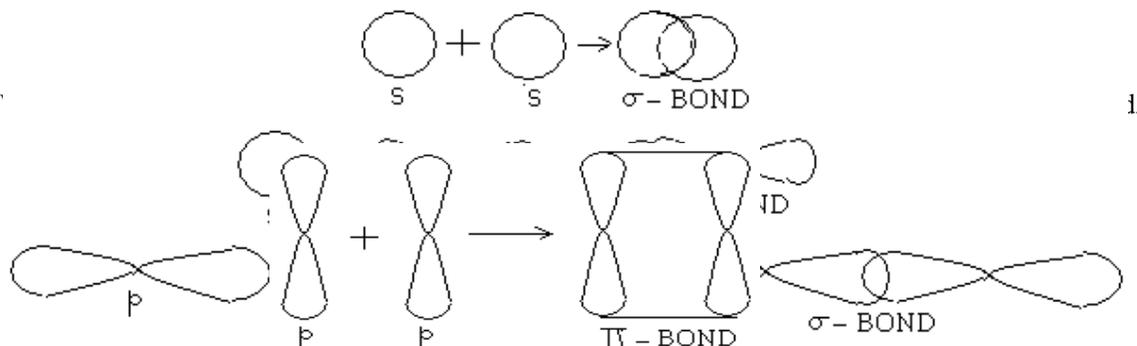
CHAPTER -08

THEORY OF CHEMICAL BONDS

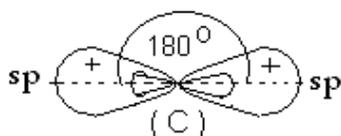
As we know Sigma and Pi bonds when Covalent bonds are formed by the overlap of orbitals.



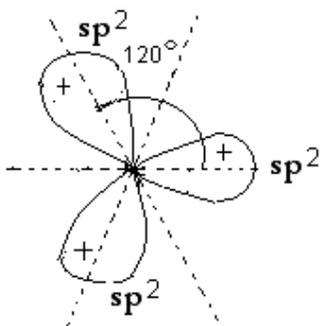
When the orbital overlap is end-on (diagonal), the overlap is called σ (sigma) overlap and the bond is σ - bond.



Hybridization : The process of mixing different orbitals of the same atom to give equivalent orbitals is called hybridization. When two different orbitals are mixed, two equivalent orbitals are obtained. The orientation of the equivalent orbitals is different from the orientation of the original orbitals. The equivalent orbitals are called Hybrid orbitals. If s and p are mixed, two equivalent hybrid orbitals sp are obtained. The hybrid orbitals are oriented as :



If s , p , p are mixed, three sp^2 hybrid orbitals are obtained with the following orientation :

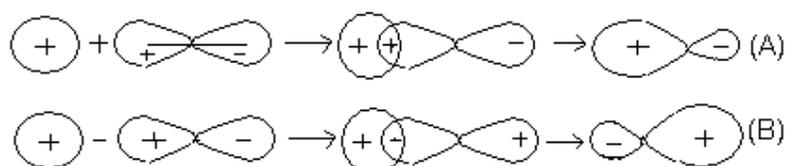


If s , p , p , p are mixed, four sp^3 hybrid orbitals are obtained with the following orientation :

<i>B</i>	(ground state)	$\uparrow\downarrow$	\uparrow \square \square	1 unpaired electron
<i>B</i>	(excited state)	\uparrow	\uparrow \uparrow \square	3 unpaired electron
<i>C</i>	(ground state)	$\uparrow\downarrow$	\uparrow \uparrow \square	2 unpaired electron
<i>C</i>	(excited state)	\uparrow	\uparrow \uparrow \uparrow	4 unpaired electron

As there are 2, 3 and 4 unpaired electrons in the excited state of Be, B and C, they can form 2, 3 and 4 bonds, but one of the orbital is *S* while the others are *p* and so it is expected that one bond will have different characteristic from the others. Experimentally it is observed that in $BeCl_2$ both the Be-Cl bond, in BF_3 all the three B-F bonds and in CH_4 all the four C-H bonds are similar. This means that all the orbitals are identical in bond formation. Thus in Be, *S* and 2*p* orbitals mix and give three equivalent orbitals and in carbon *S* and 3*p* orbitals mix and give four equivalent orbitals. The mixing of different orbitals of the same atom to give equivalent orbital is called hybridization and the equivalent orbitals are called hybrid orbitals. If two orbitals *S* and *P_x* are mixed, two hybrid orbitals are obtained and they are called '*SP* hybrid orbitals'. If *S*, *P_x* and *P_y* are mixed they give *SP²* hybrid orbitals and the number of hybrid orbitals is 3. Similarly *S*, *P_x*, *P_y*, *P_z* give four *SP³* hybrid orbitals.

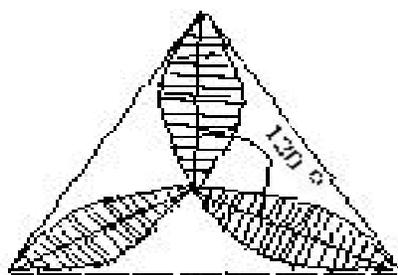
The formation of *SP* hybrid orbitals from *S* and *P* can be illustrated as follows :



When A and B are superimposed equivalent orbitals are obtained as shown in first diagram of page 112. Thus two equivalent *SP* hybrid orbitals are obtained. The orbitals are inclined at an angle of 180° and are linear.

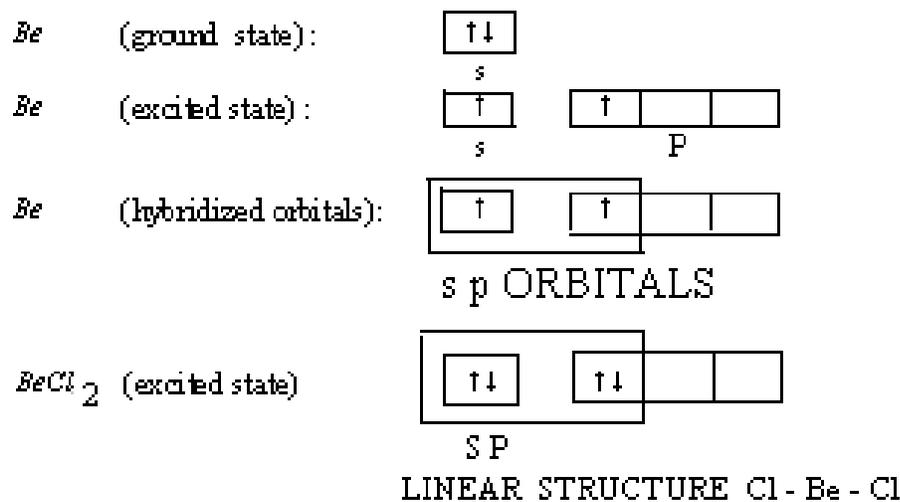
Similarly *S*, *P_x* and *P_y* give three *SP²* hybrid orbitals inclined at an angle of 120° as shown in the middle diagram of page 112.

These orbitals give triangular planar shape :

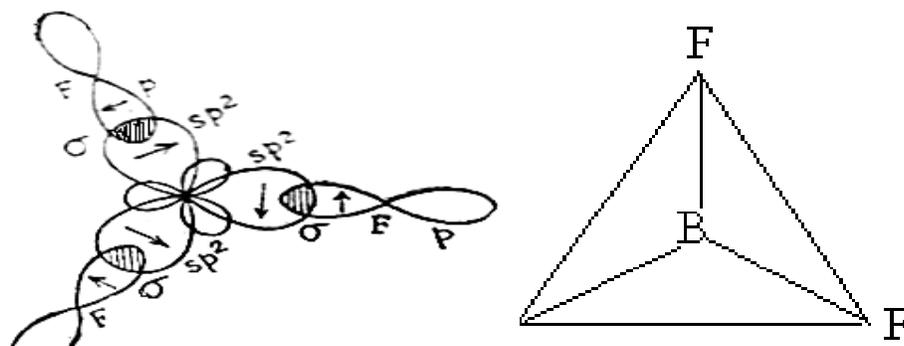
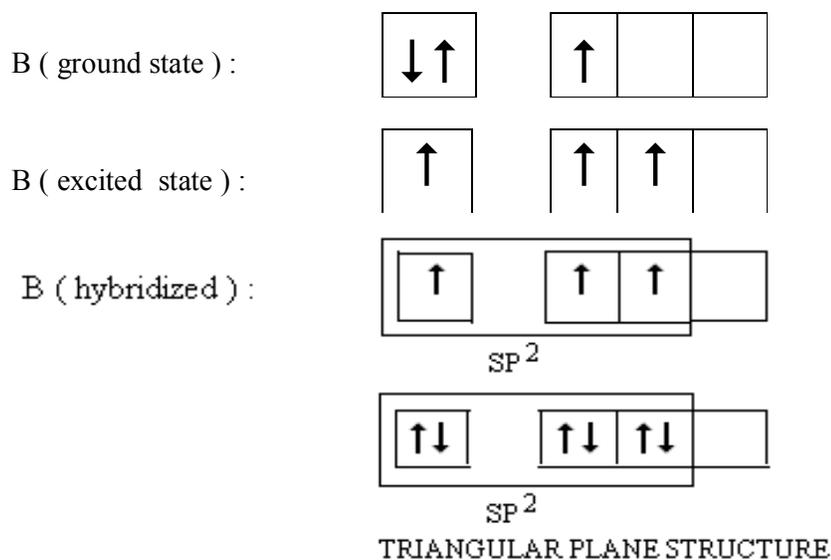
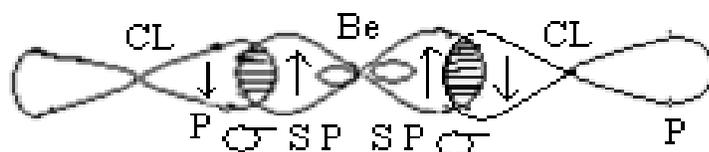


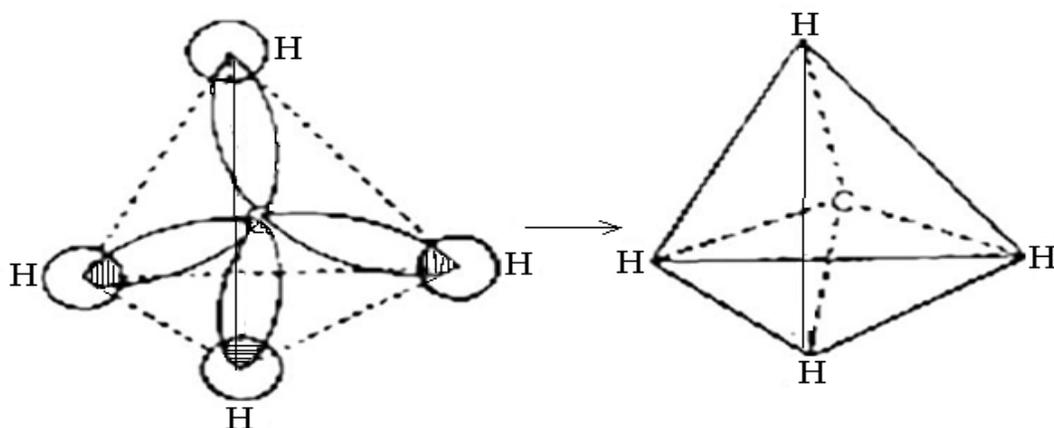
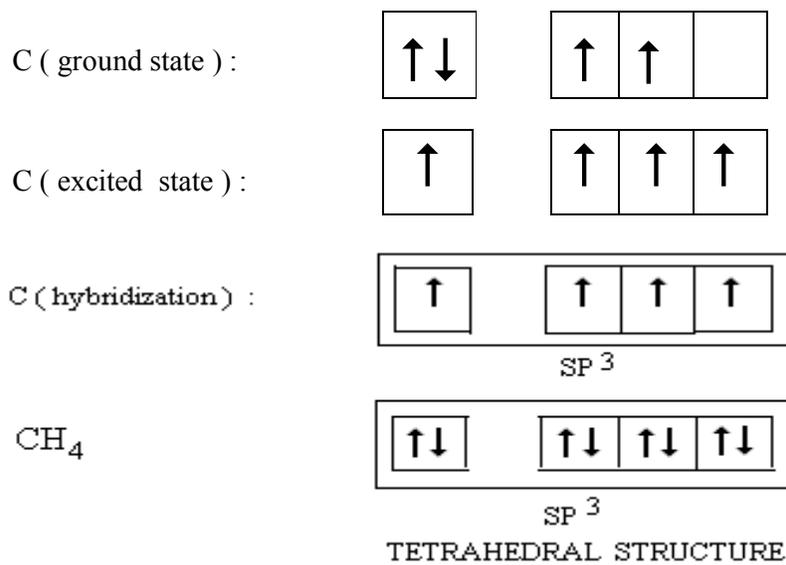
S, *P_x*, *P_y*, *P_z*, give 4 *SP³* hybrid orbitals inclined at an angle of $109^\circ 28'$ and give tetrahedral shape as shown in last diagram of page 112.

Now when Be forms two bonds, the formation can be illustrated as follows :

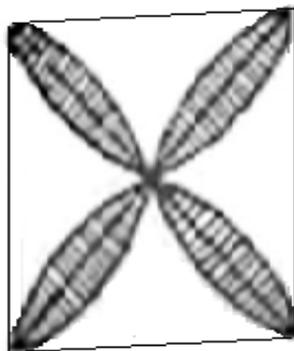


In terms of orbital overlap it can be shown as :

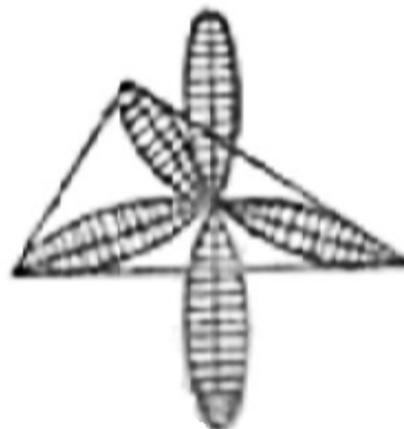




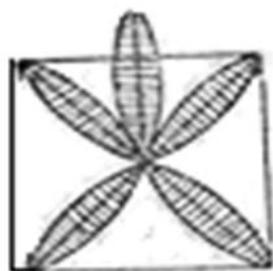
There are other types of hybridization such as dsp^2 (square planar, 4 bonds), dsp^3 (trigonal bipyramid, 5 bonds), dsp^3 (square pyramid, 5 bonds), d^2sp^3 (octahedral, 6 bonds) d^2sp^3 (Pentagonal bipyramid).



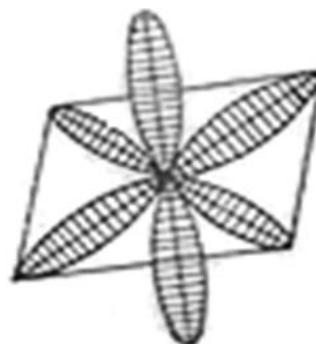
S, P_x, P_y, $dx^2 - y^2$
SQUARE PLANAR



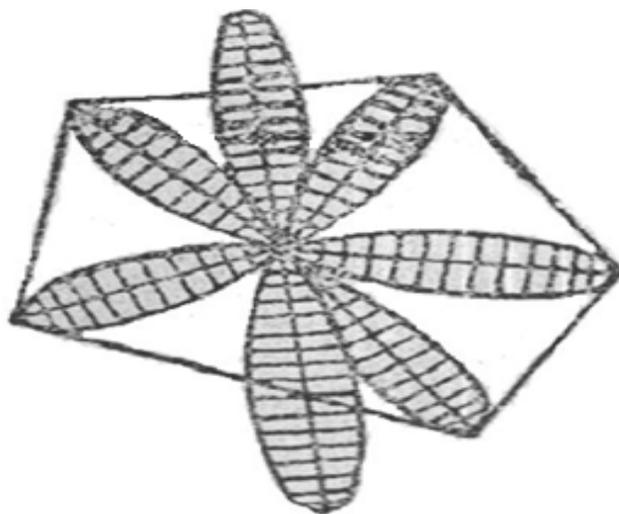
S, P_x, P_y, P_z, dz^2
TRIGONAL BIPYRAMID



S, P_x, P_y, P_z, dx² - y²
SQUARE PYRAMID



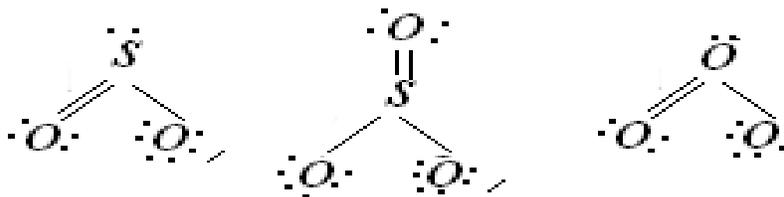
S, P_x, P_y, P_z, dx² - y², dz²
OCTAHEDRAL



S, P_x, P_y, P_z, dx² - y², dz², dxy
PENTAGONAL BIPYRAMID

THUS S, P_x, P_y, P_z, dx² - y², dxy, dxz, dx² etc. are pure orbitals and SP, SP², SP³, dsp², d²SP², dsp³, d³SP³ etc. are hybrid orbitals.

Covalent bond radii : In case of covalent bonds, there may be single, double or triple bond. If one electron is shared by both element the bond is single bond, if two electrons are shared then the bond is double bond and if three electrons are shared then the bond is triple bond. In diatomic molecules such as H₂, Cl₂, Br₂, F₂, I₂, HCl, HBr, HI, HF there is a single bond (A - B). In molecules O₂, N₂ there are multiple bond i.e. O₂, a double bond (approximately) and in N₂ a triple bond. In polyatomic molecules like CH₄, CCl₄, NH₃, H₂O etc. there is single bond, CH₄ has 4 C - H bond, CCl₄ has 4 C - Cl bond, NH₃ has 3 N - H bond and H₂O has 2 O - H bond. In molecules like SO₂, SO₃, O₃ etc. there are single and double bonds.



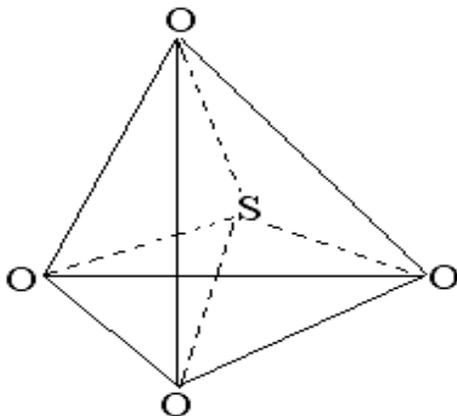
Bond lengths of simple diatomic molecules is the sum of their covalent radii. For multiple bonds, the bond lengths can be calculated as follows :

In $\text{C} \equiv \text{C} = 0.60 + 0.55 = 1.15 \text{ \AA}$

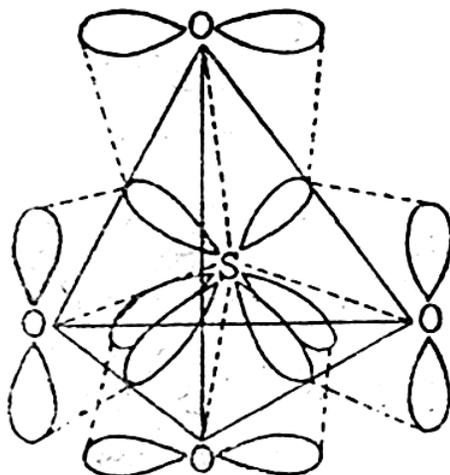
Higher the number of bonds between the two elements, shorter is the bond length. Thus C-C=1.54, C=C=1.33 and C≡C=1.21 Å. The hybridization in C-C, C=C and C≡C are sp^3 , sp^2 and sp . C-C bond for sp^2 is 0.77, sp^2 is 0.74 and sp is 0.70 Å for single bond. Thus there is decrease in distance due to nature of hybridization. In $(\text{CN})_2$, is 1.3 Å. If C(r) is taken, then $2 \times 0.77 = 1.54 \text{ \AA}$ should have been the distance. If sp is taken, then $2 \times 0.70 = 1.40$ should be the distance.

dπ - pπ overlap : We have discussed earlier that σ bond is formed by diagonal overlap of orbitals and π bonds are formed by sideways overlap of orbitals. Thus s-s, s-p, px-px, s-d overlap give rise to σ bonds and py-py, pz-pz, dxy-dxy, d-p etc. give rise to π bonds.

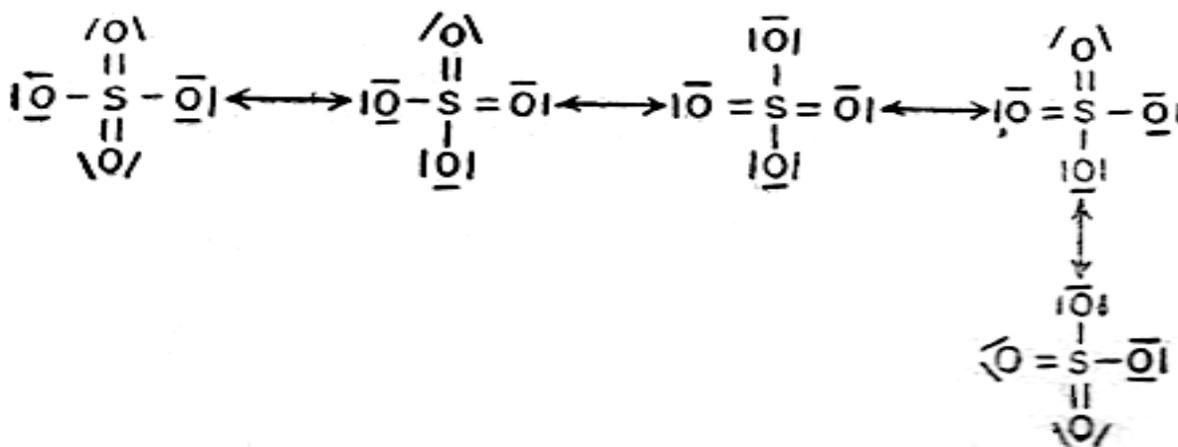
In case of SO_4^{--2} ion the structure is tetrahedral and hybridization of S is sp^3 .



The S-O bond length is shorter than expected. Calculated bond length is 1.76 Å whereas experimental bond length is 1.63 Å. The shortening of bond length is due to π-bonding. pπ - pπ bonding is not possible since p-orbitals of S are used up in sp^3 hybridization. S has empty d-orbitals and so π-bond is formed due to dπ - pπ overlap. $d_{x^2-y^2}$ and d_{z^2} orbitals are used in dπ - pπ.



Similarly d_z^2 overlap with p-orbital of O can occur.

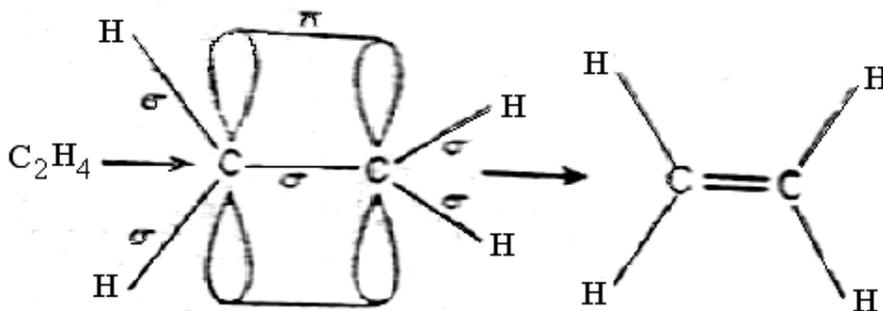


Similarly, in case of ClO_4^- , PO_4^{3-} , SiO_4^{4-} there is $d\pi - p\pi$ bonding. The oxidation state in ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} are +7, +6, +5, +4 for Cl, S, P and Si and so the size of the element increases from Cl to Si. Due to increasing size the extent of $d\pi - p\pi$ overlap becomes less effective and so shortening of bond decreases from ClO_4^- to SiO_4^{4-} . This is illustrated below :-

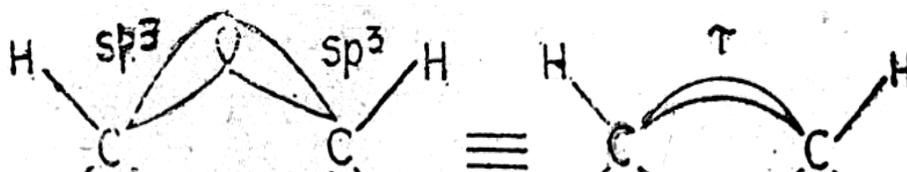
	Calculated	Experimental	Shortening	
	X-O	X-O		
ClO_4^-	1.68	1.46	0.22	decreases
SO_4^{2-}	1.69	1.49	0.20	
PO_4^{3-}	1.71	1.54	0.17	
SiO_4^{4-}	1.76	1.63	0.13	

(τ tau) bond : C_2H_4 $\left(\begin{array}{c} H & \pi & H \\ & C=C & \\ H & \sigma & H \end{array} \right)$ has one σ and one π

bond in $>C=C<$. The hybridization of C is sp^2 and σ and π overlaps can be shown as :

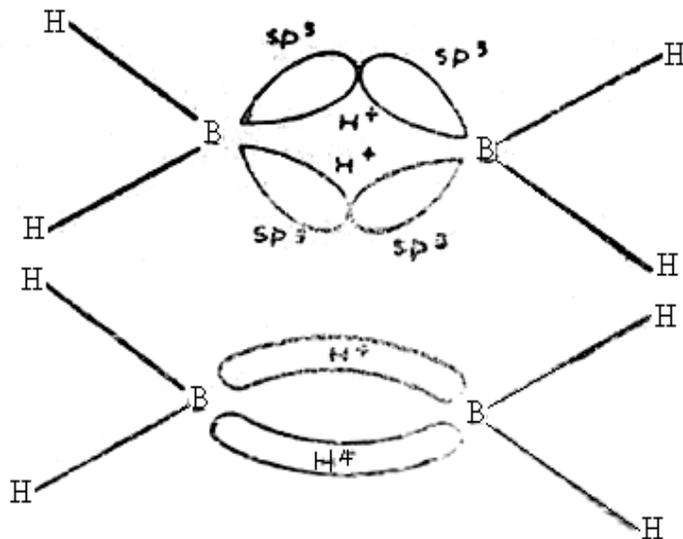


The formation of C_2H_4 can also be explained on the basis of sp^3 hybridization of carbon as shown in next page.



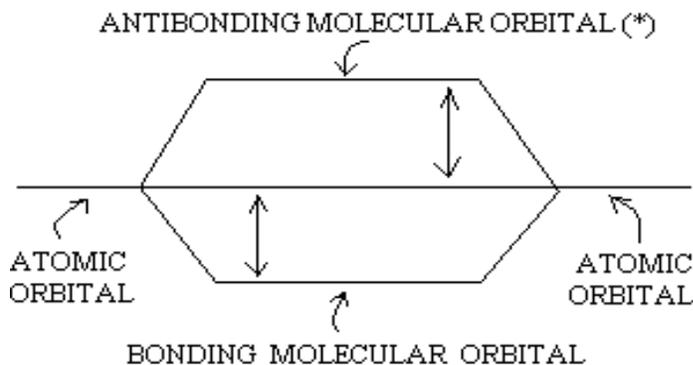
The overlap of $sp^3 - sp^3$ gives tau-bond (τ). Thus in C_2H_4 there are two tau-bonds between the carbon atoms.

The shape of tau-bond is like banana and so it is also called banana π bond. Thus tau-bond is a special case of π -bond. Tau-bond is also found in B_2H_6 .



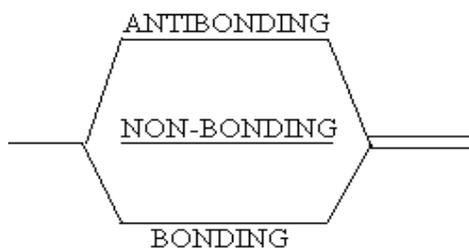
As H^+ is present in the charge cloud, the bond is also called protonated π bond.

Molecular orbital : When atomic orbitals of two atoms are combined (say for example 1 orbital on each atom), two molecular orbitals are obtained. One of the molecular orbital is bonding and the other is anti-bonding. The energy of the atomic orbitals and the energy of the anti-bonding molecular orbital is higher in energy than the atomic orbitals. This can be illustrated as :

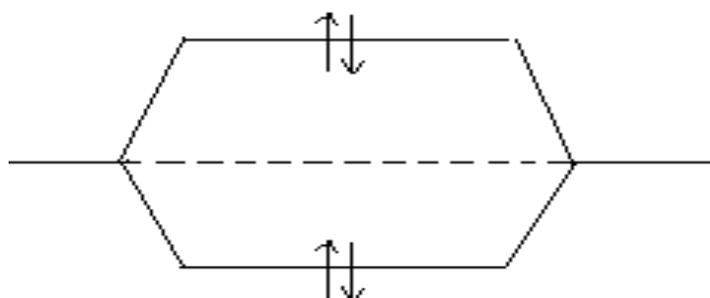


Thus the number of molecular orbital is equal to the number of atomic orbitals combined to form molecular orbitals.

The molecular orbital which does not participate in bond formation is called non-bonding molecular orbital. Its energy is similar to the energy of atomic orbitals. This can be illustrated as :



If equal number of electrons are present in bonding and antibonding molecular orbitals, then the molecular orbitals taken together are non-bonding molecular orbital since net energy change is = 0. This can be seen from the diagram below :

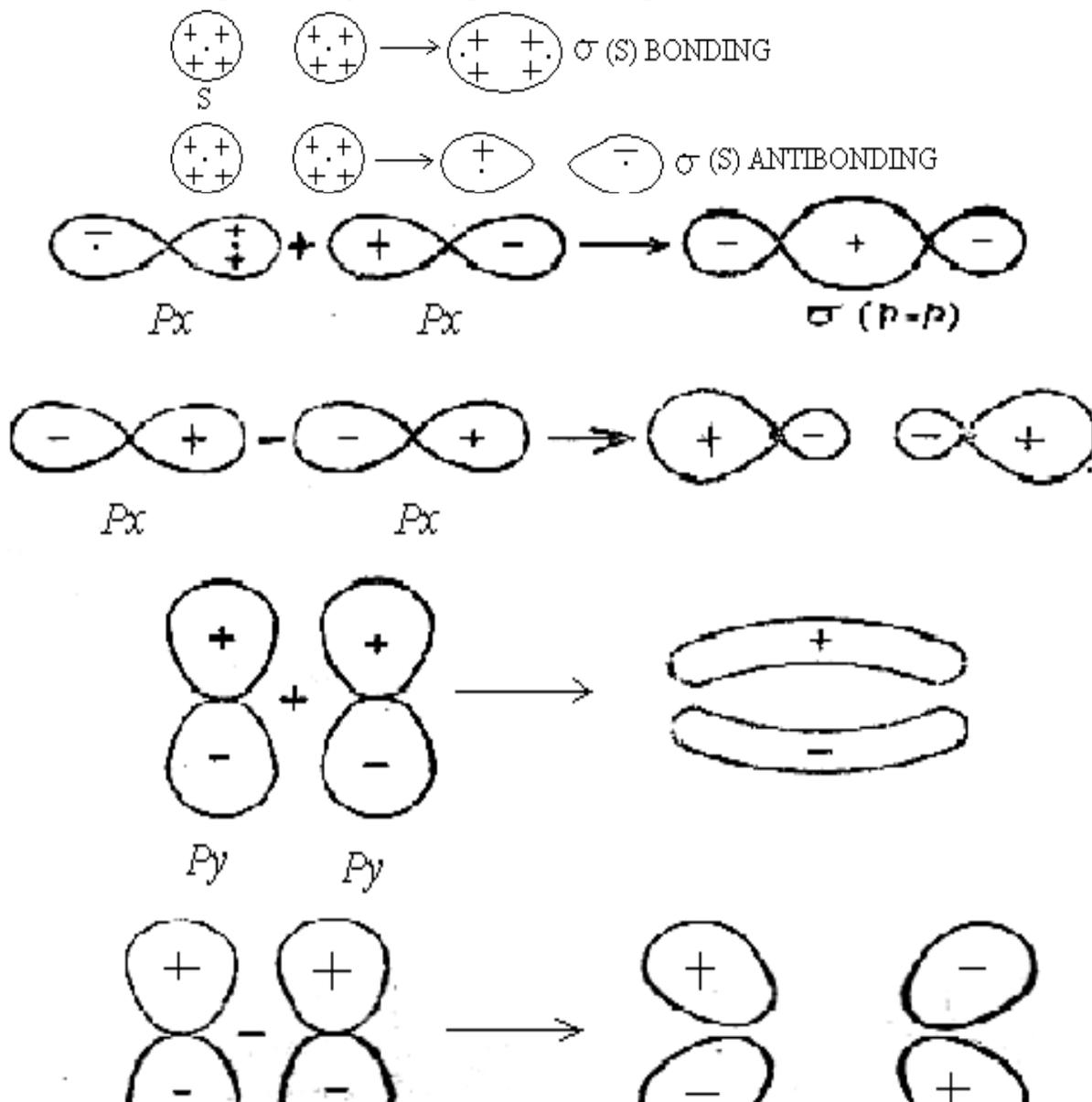


Gain in energy = $2E$

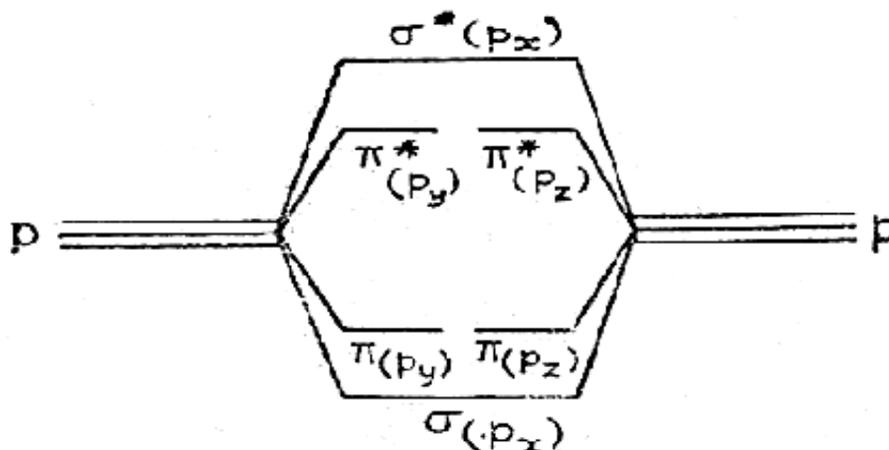
Loss in energy = $2E$

Net change = $2E - 2E = 0$

Shape of molecular orbitals : The shapes of bonding and antibonding molecular orbitals obtained by $S + S$ and $S - S$ ($S + S$ gives bonding and $S - S$ gives anti-bonding) are as shown below :

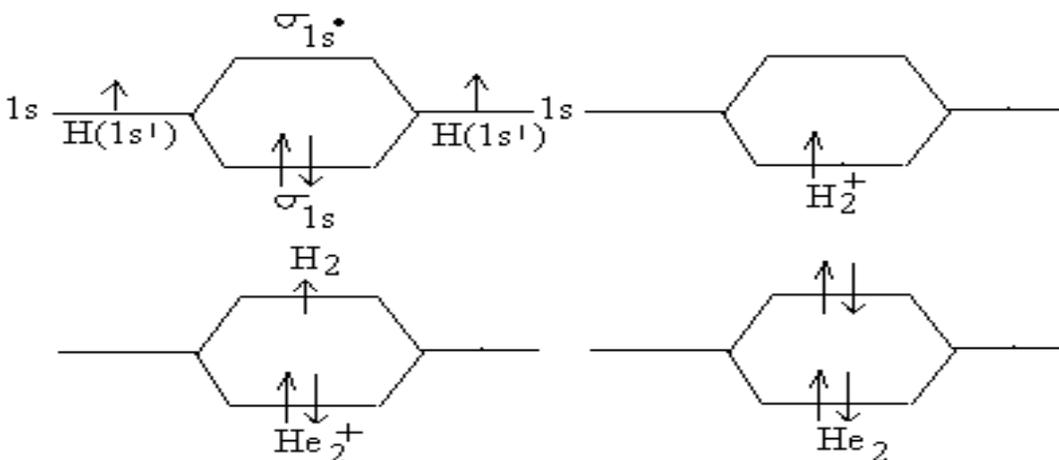


Similarly, $P_z - P_z$ gives π and π^* . It must be remembered that $P_x \pm P_x$ gives rise to σ type molecular orbitals and $P_y \pm P_y$ and $P_z \pm P_z$ gives π type of molecular orbitals (if σ and π -bonds).



Bond order : Bond order is given by the expression : $x = \frac{n_b - n_a}{2}$, where x is the bond order, n_b = number of electrons in bonding orbital and n_a = number of electrons in the anti-bonding molecular orbital (electrons present in non-bonding orbital do not participate in bond formation). Bond order is the effective number of bonds between two atoms in a compound. If there are 4 electrons in bonding molecular orbitals and 2 electrons in anti-bonding molecular orbital, then bond order is 1. If there are 2 electrons in bonding and two electrons in anti-bonding molecular orbitals the bond order is zero i. e. no bond formation occurs.

Molecular orbital diagrams for H_2 , H_2^+ , He_2 , He_2^+ :



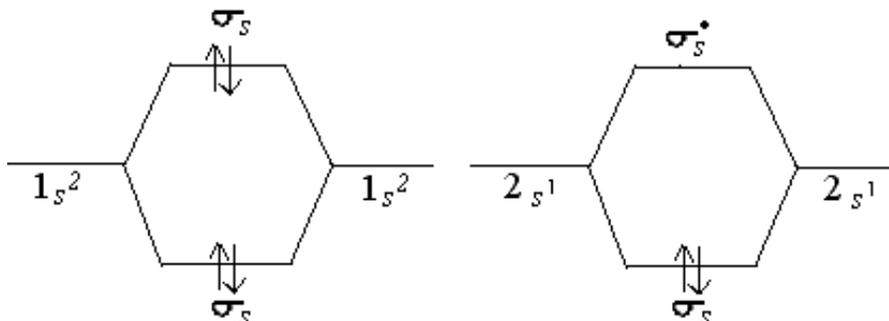
H_2 : Bond order = $\frac{n_b - n_a}{2} = \frac{2 - 0}{2} = 1$. The molecular orbital is σ type ($s - s$ overlap) and so there is one sigma bond (σ -bond) in H_2 . The bond energy is 103 Kcal.

H_2^+ : Bond order = $\frac{n_b - n_a}{2} = \frac{1 - 0}{2} = \frac{1}{2}$. Thus there is one electron σ -bond in H_2^+ . The strength of one electron bond is half of two electron bond.

He_2 : Bond order = $\frac{n_b - n_a}{2} = \frac{2 - 2}{2} = 0$.

Thus there is no bond in He_2 i. e. helium does not exist as diatomic molecule.

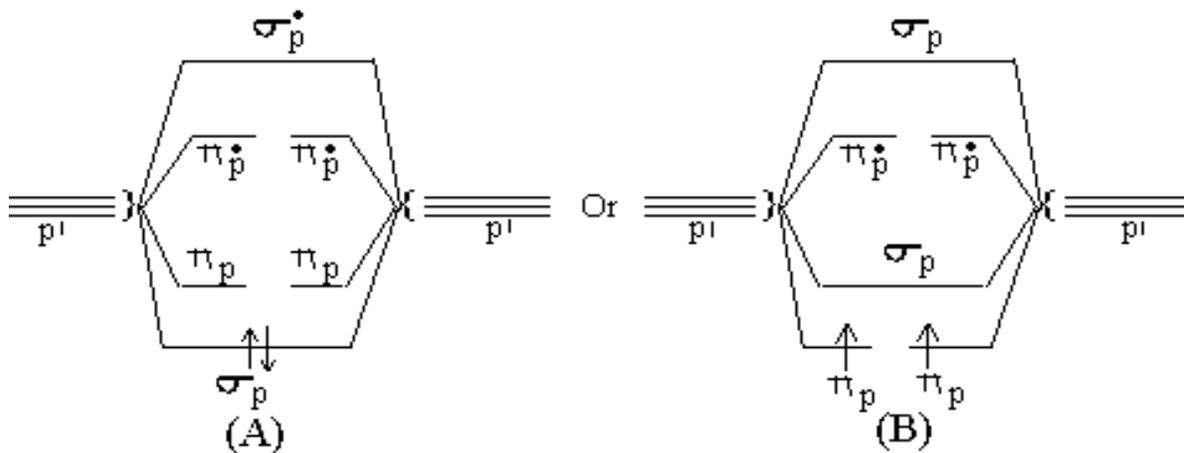
He_2^+ : Bond Order = $\frac{n_b - n_a}{2} = \frac{2-1}{2} = \frac{1}{2}$. Thus there is one electron bond in He_2^+
Molecular orbital diagram of Li_2 : Electronic configuration of $\text{Li}(3)$ is $1s^2 2s^1$.



σ_{1s} and σ^*_{1s} contain equal number of electrons and hence the molecular orbitals due to $1s - 1s$ are non-bonding. Bond order is due to σ_{2s} only and it is one. Thus there is one σ bond in Li_2 and one pair of non-bonding electrons on each Li i.e. Li_2 can be shown as : $\text{Li} - \text{Li}$:

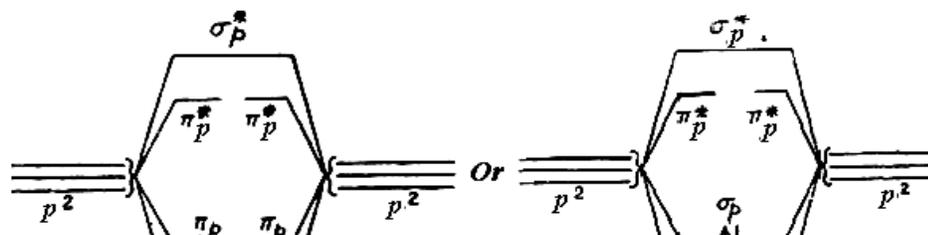
Molecular orbital of Be_2 : Electronic configuration of $\text{Be}(4)$ is $1s^2 2s^2$. The molecular orbital will contain 2 electrons in σ_{1s} , 2 electrons in σ^*_{1s} , 2 electrons in σ_{2s} and 2 electrons in σ^*_{2s} (see the diagram for Li_2). Thus the bond order will be zero and Be_2 will not exist i.e. Be does not exist as diatomic molecule.

Molecular orbital diagram of B_2 : $\text{B}(5)$ $1s^2 2s^2 2p^1$. In B_2 , $1s^2$ and $2s^2$ will be non-bonding (cf. Be). The bonding molecular orbital will be due to p^1 .



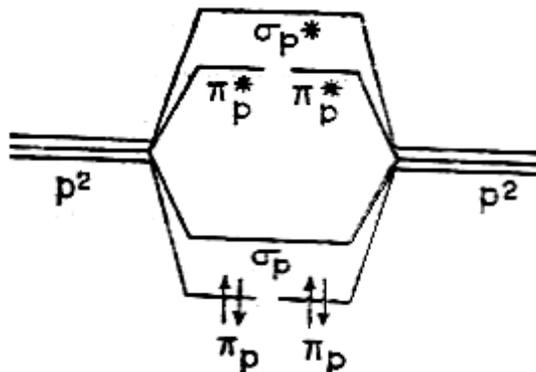
In (A) σ_p is lower in energy than the π_p and in (B) π_p is lower in energy than σ_p . Experimentally, it has been found that B_2 molecule contains two unpaired electrons. Hence B_2 can be shown by (B) and has two π bonds of one electron each and the bond order is 1.

Molecular orbital of C_2 : $\text{C}(6)$ $1s^2 2s^2 2p^2$. In C_2 , $1s^2$ and $2s^2$ will be non-bonding (cf. Be_2). The bonding molecular orbitals will be due to p^2 .



It has been found that the molecule does not contain unpaired electron and hence neither of the distribution given above accounts for this. The only possible distribution will be when the four of electrons are in π .

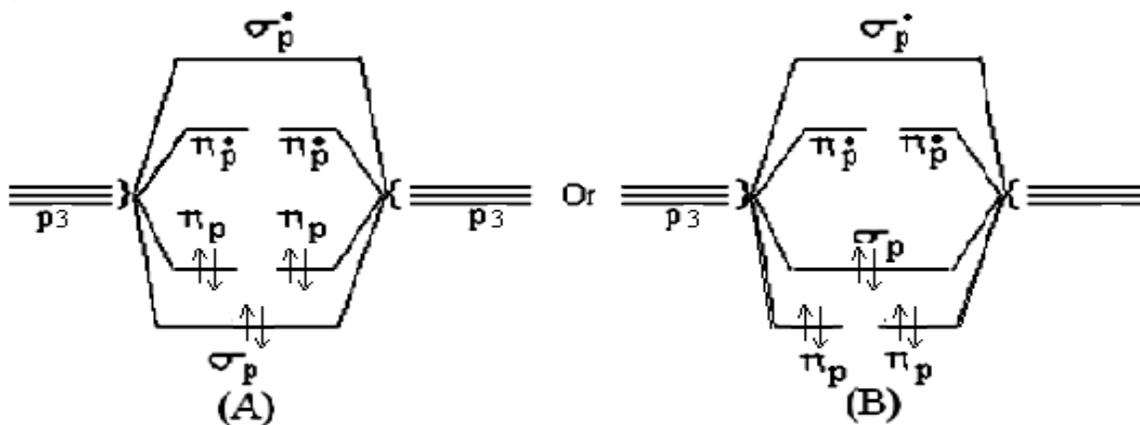
The distribution can, therefore, be shown as in figure :



$$\text{Bond order} = \frac{n_b - n_a}{2} = \frac{4 - 0}{2} = 2 \text{ hus, there are two } \pi \text{ bonds in } C_2.$$

Molecular orbital diagram for N_2 : $N(7) 1s^2 2s^2 2p^3$. $1s^2$ and $2s^2$ give non-bonding molecular orbitals. Bonding molecular orbitals are due to p^3 .

N_2 molecule :



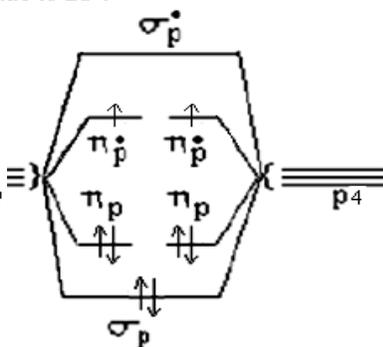
Either in (A) or in (B), the situation is the same. Bond order is 3 and N_2 contains 1 σ and 2 π bonds.

Molecular orbital diagram of O_2 : $O(8) 1s^2 2s^2 2p^2$. In O_2 , $1s^2$ and $2s^2$ give non-bonding molecular orbital. Bonding orbitals arise due to $2p^4$.

Thus O_2 contains 1 σ bond of two electron bonds. The

$$\frac{n_b - n_a}{2} \left(\frac{6 - 2}{2} = 2 \right)$$

Molecular orbital diagram electrons in bond in F_2 .



\therefore strength of three electron bond is half $2 + \frac{1}{2} = 2$, which is found from σ vs that O_2 contains two unpaired electrons. Thus O_2 can be shown $2s^2 2p^6$. There are 2 electrons in σ_p , 4 orbitals are non-bonding there is 1 σ

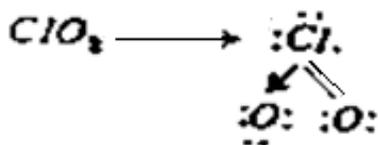
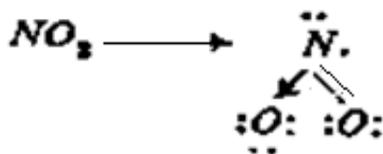
Molecular orbital diagram of(10) $1s^2 2s^2 2p^6$. There are 2 electrons in σ_p , 4 in πand 2 in σ_p^* and hence bond order is zero i.e. Ne_2 does diatomic molecule.

Molecular orbital diagram for CO, NO+ :

Molecule	Total valence electron			
N_2	$5 + 5 = 10$	N(7)	$1s^2$	V.E. 5
CO	$4 + 6 = 10$	C(6)	$1s^2$	V.E. 4
NO^+	$5 + 6 - 1 = 10$	O(8)	$1s^2$	V.E. 6
CN^-	$4 + 5 + 1 = 10$			

The molecular orbital diagram for NO^+ and CN^- is similar to N_2 .

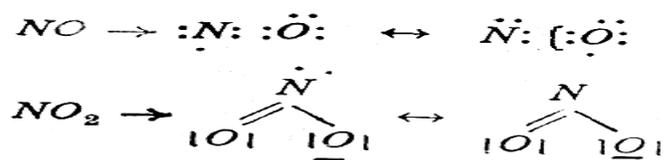
One and three electron bonds : H_2^+ has one electron bond (see M. O. diagram for H_2^+), B_2 has two bonds of one electron each (see M. O. diagram for B_2). He_2^+ has three electron bonds (see M. O. diagram for He_2^+) and O_2 has two π -bonds of three electron each (see M. O. diagram for O_2). NO , NO_2 , ClO_2 etc. also have three electron bonds. Generally, molecules or ions having odd number of valence electrons have one or three electron bonds. The strength of one or three electron bond is half of two electron bonds.



Odd, electron molecules : Molecules having odd number of valence electrons are called odd electron molecules. NO , NO_2 , and ClO_2 are odd electron molecules.

Molecule	Valence Electron
NO	$5 + 6 = 11$
NO_2	$5 + 12 = 17$
ClO_2	$7 + 12 = 19$

Such molecules have unpaired electrons and so they are paramagnetic. They also tend to dimerise $2NO_2 \rightarrow N_2O_4$ and have resonance structures.



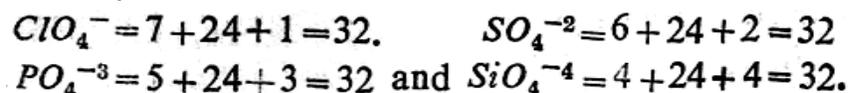
Due to unpaired electron, they are also coloured.

It may be remembered that though O_2 molecule has even number of valence electrons ($6 + 6 = 12$), it is paramagnetic because it contains two unpaired electrons, O_2 also gives blue colour when heated. (see M. O. diagram of O_2).

Iso-electronic species : Species having same number of electrons are called iso-electronic.

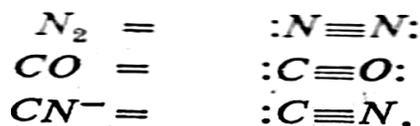
Na^+ [Total electrons = 10]
 F^- [Total electrons = 10]
 Ne [Total electrons = 10]

Thus Na^+ , F^- and Ne are iso-electronic. If the total number of valence electrons in a molecule or ion is equal, they are also called iso-electronic with reference to valence electrons, ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} are iso-electronic because they contain the same number of valence electrons :



Similarly CO , N_2 , CN^- are iso-electronic.

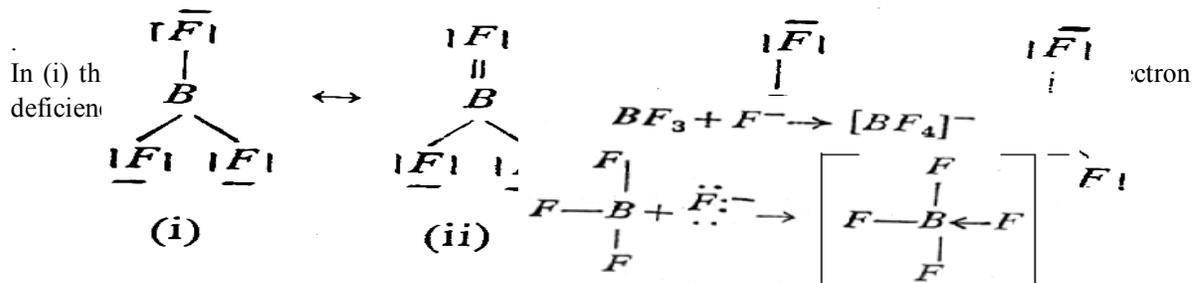
Iso-electronic species have similar structure. Thus ClO_4^- , SO_4^{2-} , PO_4^{3-} and SiO_4^{4-} are all tetrahedral. CO , N_2 , CN^- have similar electronic dot structures :



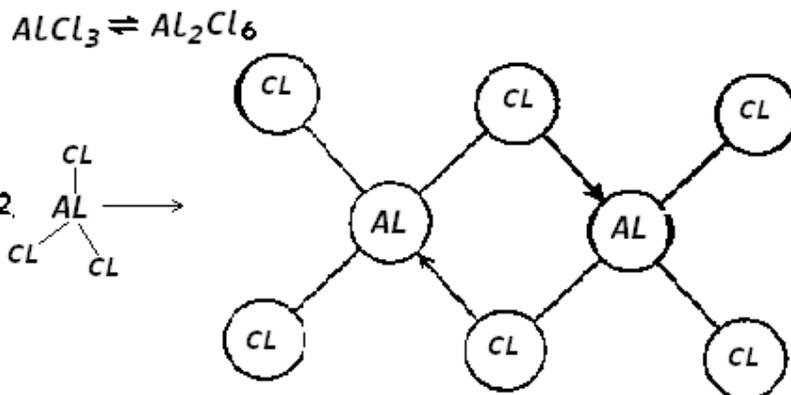
Some iso-electronic molecular or molecules ions are given below (with reference to valence electrons)

- (i) SO_2 , O_3
- (ii) CO_2 , NO_2^+
- (iii) N_2 , NO^+ , CN^- , CO
- (iv) ClO_4^- , SO_4^{2-} , PO_4^{3-} , SiO_4^{4-}
- (v) XeF_2 , I_3^-
- (vi) XeF_4 , ICl_4^- .

Electron deficient compounds : Compounds such as BF_3 , $AlCl_3$ do not have octet of electron around the central atom and may be called electron deficient compounds. However, these compounds do not represent true electron deficient compounds, because they remove the electron deficiency by π bonding, complex formation, or by dimerization

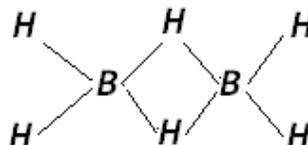


The electron deficiency is removed by the formation of co-ordinate bond,



Thus there are 8 electrons around each Al in Al_2Cl_6 and electron deficiency is removed by dimerization.

True electron deficient compounds are those which have insufficient number of electrons than the number of two electron bonds. B_2H_6 is an example of electron deficient compound. The structure is given as :



Number of bonds in $B_2H_6 = 8$

Electrons needed $- 2 \times 8 = 16$ (For two electron bond)

Electrons in $B_2H_6 = 2 \times 3 + 6 = 12$ (each B has 3 V. E. and each H has 1 V. E.)

Thus there are 12 valence electrons sufficient to form 6 bonds, but B_2H_6 has 8 bonds as shown in the structure. As a matter of fact each B_2H_6 has two electron - three centered bond i.e., there is one

electron bond for

Stable ionic structures :

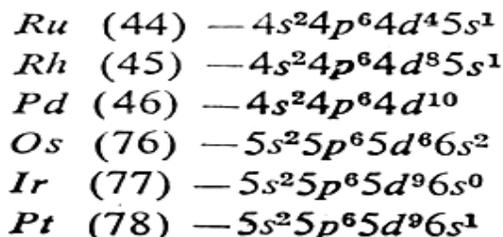
- 2 electron :** $H^-, Li^+, Be^{+2}, B^{+3}$
- 8 electron :** $O^{-2}, F^-, Cl^-, Br^-, I^-, Na^+, Ca^{+2}, Al^{+3}$
- 18 electron :** $Zn^{+2}, Cd^{+2}, Hg^{+2}, Cu^+, Ag^+, Au^{+3}$
 $Tl^{+3}, As^{+5}, Sb^{+5}, Bi^{+5}, Pb^{+4}, Sn^{+4}$
- 18+2 electron :** Pb^{+2}, Sn^{+2}

Transition metal cations do not have above ionic structures, yet they form stable compounds.

Cation	Electron configuration	Electrons	Structure	Compound
Cr^{+2}	$3s^2 3p^6 3d^4$	12	electron structure	$CrCl_2$
Cr^{+3}	$3s^2 3p^6 3d^3$	11	„ „	$CrCl_3$
Fe^{+2}	$3s^2 3p^6 3d^6$	14	„ „	$FeCl_2$
Fe^{+3}	$3s^2 3p^6 3d^5$	13	„ „	$FeCl_3$
Mn^{+2}	$3s^2 3p^6 3d^5$	13	„ „	MnF_2
Ni^{+2}	$3s^2 3p^6 3d^8$	16	„ „	$NiCl_2$
Co^{+2}	$3s^2 3p^6 3d^7$	15	„ „	$CoCl_2$

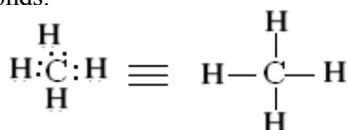
All the compounds are stable.

Electronic configuration of Pd(46) is $4s^2 4p^6 4d^{10} 5s^0$. This is due to the fact that 18 electron structure is stable. Thus in order to get 18 electron structure Pd had $4s^2 4p^6 4d^{10}$ and not $4s^2 4p^6 4d^8 5s^2$:-

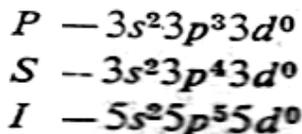


All these are due to the tendency to get closer to 18 electron structure.

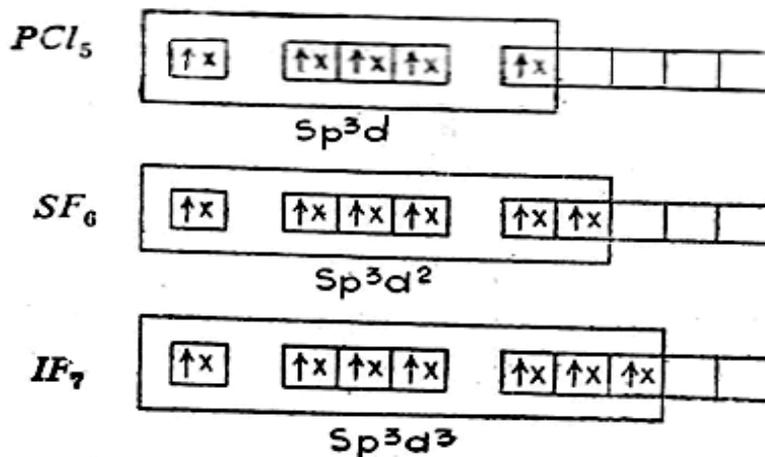
Maximum covalency : As per octet rule, there should be 8 electrons around the central atom for stability. Thus there should be 4 covalent bonds.



In PCl_5 , SF_6 and IF_7 there are 5, 6 and 7 bonds i.e., 10, 12 and 14 electrons around the central atoms P, S and I respectively. Thus in these compounds the covalency of the central atom is 5, 6 and 7 respectively. Even though they violate octet rule, they are stable. The central atoms have d-orbital in their configuration.



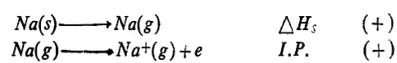
Due to availability of empty d-orbitals, electrons excess over 8 are accommodated in d-orbitals.



↑ is central atom electron and x is F electron

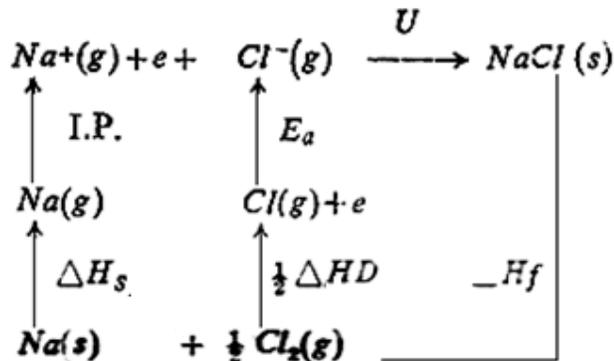
Thus elements which have empty d-orbitals can have covalency greater than 4. Covalency of P, S and I is 5, 6 and 8 respectively. Due to covalency maxima N forms NCl_3 , but not NCl_5 , but P forms both PCl_3 and PCl_5 .

Factors favouring ionic bond : Let us consider the formation of NaCl from Na and Cl_2 .



The formation of ionic bond is controlled by ΔH_s (sublimation energy), I. P. (ionization potential), ΔH_D (dissociation energy), E_a (electron affinity) and U (lattice energy). Lower value of ΔH_s , I. P., ΔH_D and higher value of E_a and U favours the formation of ionic bond.

Born-Haber Cycle : Born – Haber Cycle shows the energetic involved in the formation of ionic (electrovalent) compound. With reference to NaCl, the cycle can be shown as follows :



$$\text{Thus } \Delta H_f = \Delta H_s + I.P. + \frac{1}{2} \Delta H_D + E_a + U$$

From Born-Haber Cycle, any one of the energetic can be estimated, provided others are known.

Estimation of ionization potential :

$$\begin{aligned}
 \Delta H_f &= \Delta H_s + I.P. + \frac{1}{2} \Delta H_D + E_a + U \\
 \therefore I.P. &= \Delta H_f - \Delta H_s - \frac{1}{2} \Delta H_D - E_a - U
 \end{aligned}$$

Estimation of E_a :

$$\begin{aligned}
 \Delta H_f &= \Delta H_s + I.P. + \frac{1}{2} \Delta H_D + E_a + U \\
 \therefore E_a &= \Delta H_f - \Delta H_s - I.P. - \frac{1}{2} \Delta H_D - U
 \end{aligned}$$

Estimation of ionic radius :

$$\begin{aligned}
 \Delta H_f &= \Delta H_s + I.P. + \frac{1}{2} \Delta H_D + E_a + U \\
 U &= \Delta H_f - \Delta H_s - I.P. - \frac{1}{2} \Delta H_D - E_a \\
 U &= \frac{AZ^+Z^-}{r_0} \left(1 - \frac{1}{n} \right)
 \end{aligned}$$

Knowing Z^+ , Z^- , U , A and n , $r^0 = r^+ + r^-$ can be calculated -

$$\begin{aligned}
 r^+ &= \frac{Z^- \text{anion}}{Z^+ \text{cation}} \\
 r^- &= \frac{Z^+ \text{cation}}{Z^- \text{anion}}
 \end{aligned}$$

Thus from $r^+ + r^-$ and r^+ / r^- , the value of r^+ can be calculated.

Kapustinskii equation : The expression for lattice energy is given as :

$$U = \frac{ANZ^+Z^-e^2}{r^0} \left(1 - \frac{1}{n} \right)$$

Where A is Madelung constant, N is Avogadro's number, Z^+ is charge of cation, Z^- is charge of anion $r^0 = r^+ + r^-$ (internuclear distance), and n is constant.

Kapustinskii found that ratio of Madelung constant and number of ions in the structure is nearly constant and is 0.874.

$$\frac{A}{N} = 0.874$$

$$A = 0.874 \chi N$$

Substituting the value of A , the equation obtained is called Kapustinskii equation.

$$U = \frac{0.874 N v Z^+ Z^- e^2}{r^+ + r^-} \left(1 - \frac{1}{n} \right)$$

v is the number of ions in the formula of the compound. If $n = 9$, then,

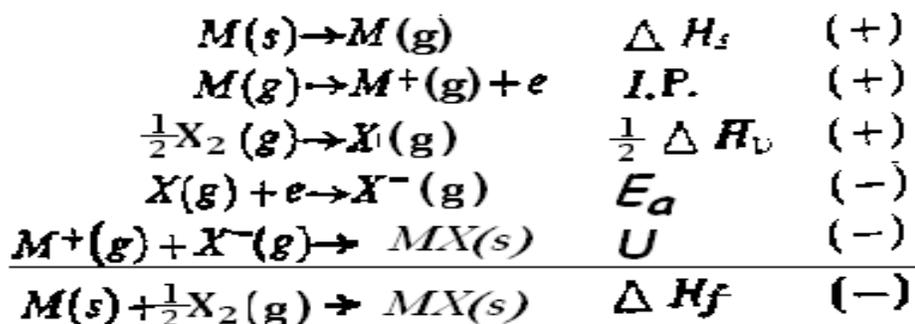
$$U = \frac{256 v Z^+ Z^-}{r^+ + r^-} \text{ K cal.}$$

The equation has been used to estimate lattice energy of ionic compounds and ionic radius.

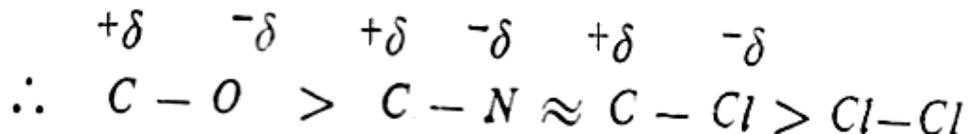
The lattice energy is estimated by putting the value of $r^+ + r^-$, v , Z^+ , Z^- .

The ionic radius is estimated as follows:

Let us consider the formation of NaF and KF.



Higher the electronegativity difference, greater is the value of δ i.e., larger is the polarity



10. How does electronegativity determine the nature of bond?

Ans. If the electronegativity difference is large, the bond is electrovalent. This happens in the case of the combination of metals and non-metals.

Na + Cl: difference is 2.2

0.8 3.0

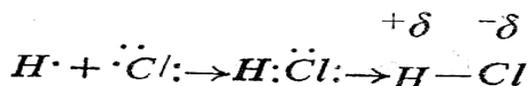
\therefore Bond is electrovalent i.e., Na+Cl⁻.

If the electronegativity difference is small, the bond is polar covalent. This happens when two different non-metals combine :

H + Cl, difference is 0.9

2.1 3.0

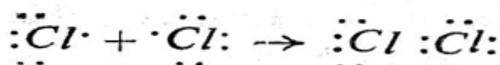
∴ Bond is polar covalent.



If the electronegativity difference is 0, the bond is non-polar covalent. This happens when atoms of the same element combine (or elements having same electronegativity combine)

Na \cdot + \cdot Na difference is 0
0.8 0.8

∴ Bond is non-polar covalent.

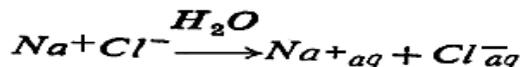


11. Comment on the properties of chemical compounds based on the nature of bonds.

Ans. Electrovalent Compounds : Contain electrovalent bond i.e., cations and anions,



1. In water the electrovalent compounds dissociate and become aqueous ions



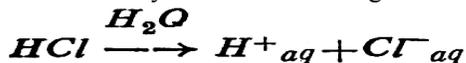
2. In aq. Solution the compounds conduct electricity. The ions act as carrier for electricity.
3. Due to electrostatic attraction, the melting point of the compounds are high.

Covalent compounds : (Non-polar-covalent) -

1. Insoluble in water.
2. Do not conduct electricity in solution.
3. Melting point is low.

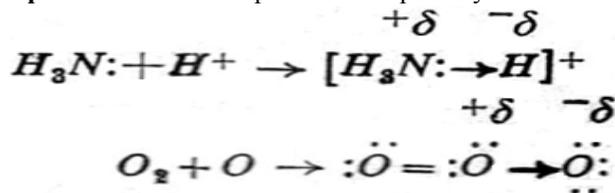
Covalent compounds : (Polar-covalent) -

1. Soluble in water. They ionize in water to give ions :



2. Conduct electricity in aqueous solution.
3. Melting point lies intermediate between electrovalent and non-polar covalent compounds.

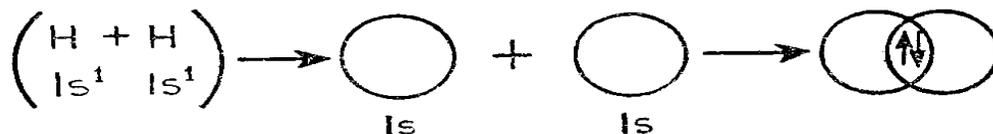
Co-ordinate compounds : These compounds have polarity :



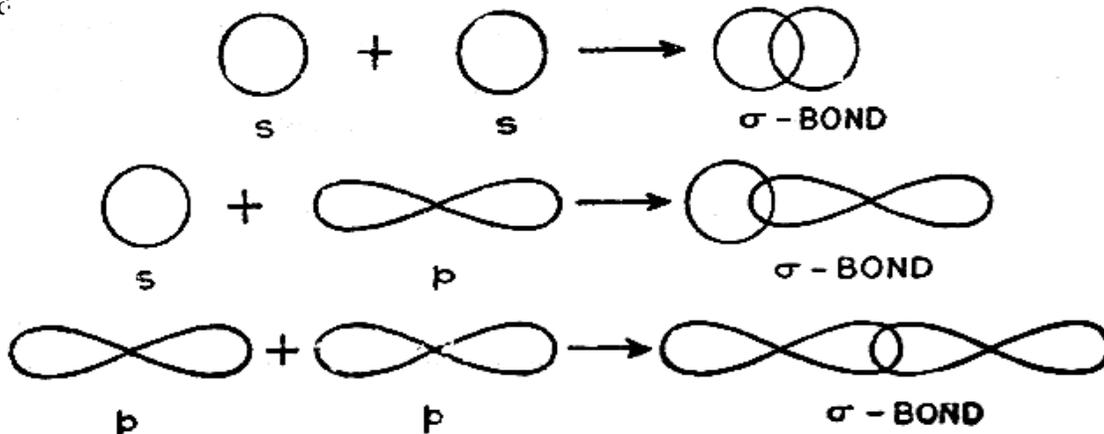
and hence behave as polar covalent compounds.

12. What do you mean by σ and π bonds ?

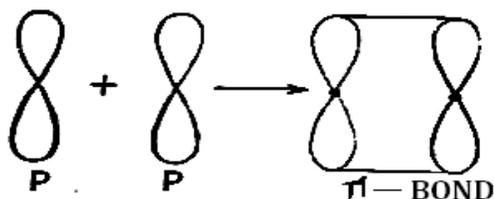
Ans. Bonds are formed by the overlap of orbitals.



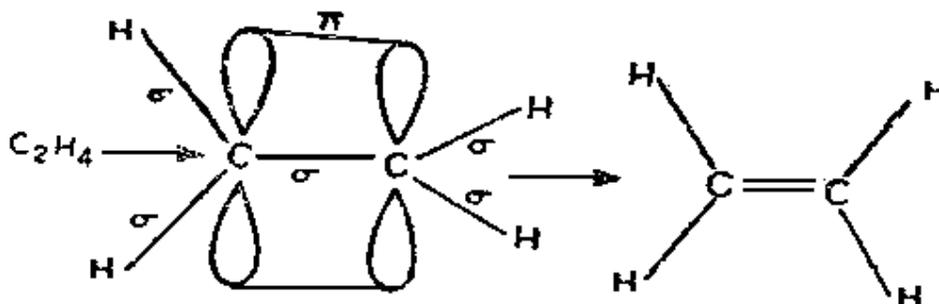
When the orbital overlap is end-on (diagonal), the overlap is called σ (sigma) overlap and the bond is σ - bond.



When the orbital overlaps side ways, the overlap is called π (Pai) overlap and the bond is called π bond.



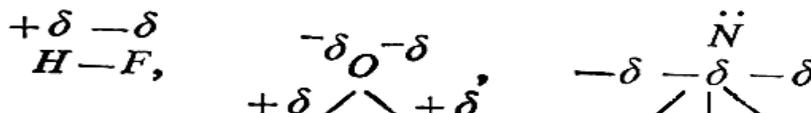
σ and π bond can be illustrated with C_2H_4



Thus in >C=C< there is 1 σ -bond and 1 π -bond between the two carbons. Similarly in $\text{-C}\equiv\text{C-}$ there is 1 σ and 2 π - bonds between the two carbon atoms.

13. What is hydrogen bond ? What type of elements exhibit H-bond ? What is the effect of H-bond on properties of compounds ?

Ans. Molecules formed by two different not-metals are polar due to difference in electro negativity. HF, H_2O , NH_3 are polar molecules.



and hence there is delocalized orbital overlap over the whole molecule.

In case of normal metals like *Na, K, Ca, Mg* etc. the attractive forces are between M^{+n} and ne , but in the case of transition metals in addition to M^{+n} and ne , attraction, there are covalent bonding due to incompletely filled d -orbitals. As for example Fe can be in the lattice as Fe^{+2} , $2e^-$; each Fe^{+2} has $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.



The unpaired electrons on Fe^{+2} can pair up with unpaired electrons on other atoms forming covalent bonds. Due to larger number of bonds in transition metals, the m. p. of transition metals are higher than the normal metals.

15. What is bond energy and how is it related to dissociation energy ?

Ans. Energy required to break a bond is called bond energy.



The energy needed to dissociate a molecule into the constituent atoms is dissociation energy.

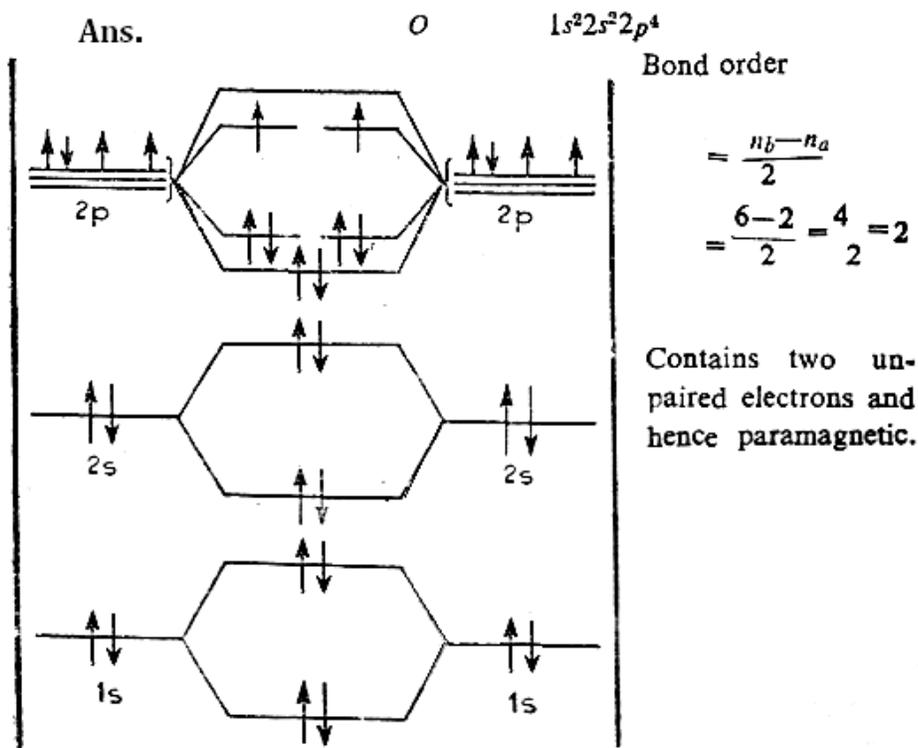


For diatomic molecules bond energy = dissociation energy.

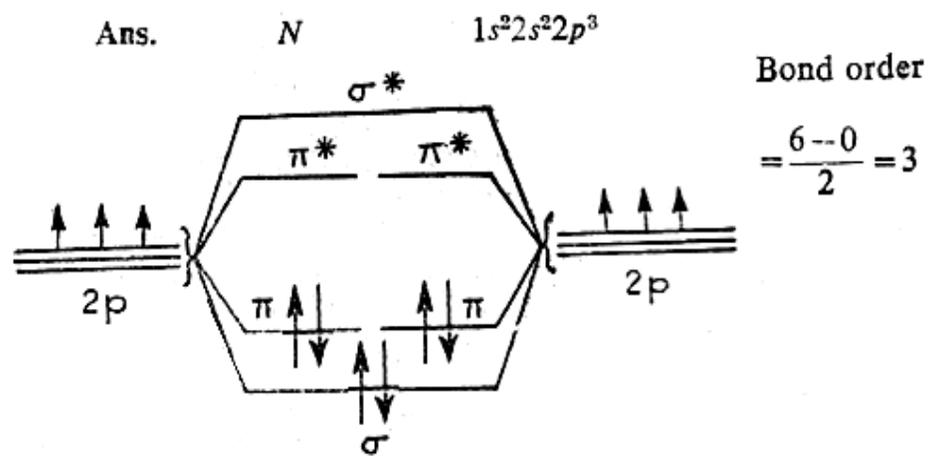
For polyatomic molecules, bond energy = $\frac{\text{dissociation energy}}{\text{number of bonds}}$

The C – H bond energy in CH_4 is dissociation energy of CH_4

16. Draw the molecular orbital diagram for O_2 and comment on bond order and magnetic property.



17. Draw the molecular orbital diagram for N_2



NOTE : Molecular orbital corresponding to 1s and 2s similar to O_2 .

Bonding in Organic Compound Bonds weaker than covalent :-

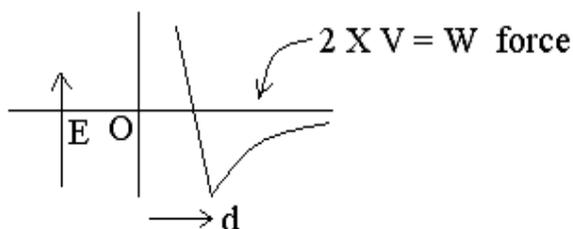
Organic compounds are outcome of aggregation of atoms leading to specific three dimensional arrangements. These atoms are of the order of 50 – 100 Kcal / mol. However in addition to this, there are certain forces which can hold atoms & molecules but these forces are much weaker than covalent bonds. Often these weak forces have values some tenth of Kcal / mol. It is noted that most of the physical properties of compounds are dependent upon their molecular weight e.g. the melting point or the boiling point of the compounds are directly related to molecular weight. Generally it is formed that the melting point & boiling point rise with rise in molecular weight. Sometimes it is noticed that compounds are comparable molecular weight differ to great degree in melting point and boiling point. Such findings can be explained through certain forces which are quite weak but strong enough to have their influence on the properties of the molecules.

Among these forces, following are quite important –

- (i) Vander Waals Force
- (ii) Dipole attraction
- (iii) Hydrogen bonding

I :- VANDER WAALS FORCE :- Electrons move around the nuclear but during the motion of the electrons the centre of gravity of the –ve charge may not coincide continuously with the centre of gravity of the charge. As a result of this dipole is created (area covering + ve & - ve charges) when two such dipoles happen to come close to one another they are kept by electro static force of attraction. This electro-static force of attraction is quite weak but has significant influence in certain cases.

In order to have full application of this force let us study the plots of energy as a function of distance between two He – atoms.



When two He – atoms are far – apart so that these do not influence one another, the energy of the system is taken as zero, when the two atoms are gradually brought closer, there is drop in the energy – content due to Vander Waals force of attraction operating between the two He atom. After reaching energy minimum, any attempt to bring the two atoms still closer results in abrupt rise in energy content. It is due to Vander Waals force of repulsion. This happens because on coming very close to each other, the electron cloud of one seriously interpenetrated the electron clouds of the other. This means the electron clouds of the two atoms try to remain in the same position at a time. This results in repulsion between the –vely charged electron clouds. Due to this an energy rises. In addition to this there is also internuclear repulsion, which also causes increase in energy. The motion of electrons around the nucleus of an atom is not independent of the motion of electrons in the adjacent atoms to explain it, let us consider two atoms of He. If during the course of motion electrons of an atom is on the right side of the nucleus, then the electrons in the adjacent atom will be on the right side of the

adjacent nucleus. Similarly if the electrons are on the left side of the nucleus of an atom, then the electrons belonging to the adjacent atoms will be on the left side of its nucleus.

Schematic diagram showing co-ordination of motion of an electrons of an atom or that of the other - Whatever may be the mode of co-relation of electron movement, the electrons belonging to one atom is nearer to the nucleus of the other atom. Thus force of attraction is established. Since the electrons of the two atoms are not of the same size. So interelectronic repulsion is ruled out. At a certain distance the internuclear repulsion is also not operating. This results in attraction between the two atoms and this is called Vander Waals force of attraction.

This interaction can take place between any two atoms or group of atoms. Even inert gas molecules have this sort of interaction.

Vander Waals interaction can be of two types :-

1. **Vander Waals force of attraction** :- As described above that can be Vander Waals force of attraction between two atoms or molecules. This force of attraction is inversely proportioned to seventh power of distance separating the two atoms. Thus for a short change in the distance, there is much change in Vander Waals force of attraction. Hence Vander Waals force of attraction is a short range force.

2. **Vander Waals force of repulsion** :- When two atoms are brought very close together & the orbitals do not calla-see to form bond between the two atoms, there is increase in energy – content of the system due to interelectronic repulsion between two atoms. This is called Vander Waals force of repulsion (repulsion is also due to internuclear repulsion). Vander Waals force of repulsion $\propto \frac{1}{d^{1000}}$ with change in the distance of two atoms the change in Vander Waals

force of repulsion is abrupt while the change in Vander Waals force of attraction is gradual.

FACTORS ON WHICH VANDER WAALS INTERACTION DEPENDS :-

Vander Waals interaction is greatly dependent the polarisability factor. [Polarisability is deformation of atoms of great molecules (i.e. deformation of electron cloud) under the influence of electric field]

- (a) Vander Waals interaction is dependent upon electrons so higher the number of electrons, greater shall be Vander Waals interaction. Thus atom with higher atomic number has greater Vander Waals interaction than atom having lower atomic number.
- (b) Polarisability affects the bonding electrons as well as the non-bonding electron. Bonding electrons are much more firmly held than non-bonding electron, therefore the degree of polarisability experienced by non-bonding electrons is much greater. This is the reason of greater Vander Waals interaction experienced by molecules having atoms with lone pair of electrons (N S O halogens).
- (c) The degree of polarisability is also dependent upon the size of the atom. Greater is size, greater is the polarisability. Hence such atoms e. g. S, Br, I etc.
- (d)

Area of touch :- V. W. interaction is greatly dependent upon the area of touch. Thus greater the surface of contact between two atoms or two molecules, greater is the V. W. interaction. Therefore

molecules with spherical shapes have little V. W. interaction because (in case of spheres the area of touch is very small)

Thus it is observed that the straight chain molecules have much greater V.W. interaction than branched chain molecules.

IMPACT :- V. W. interaction has it's influence on the physical properties of molecules.

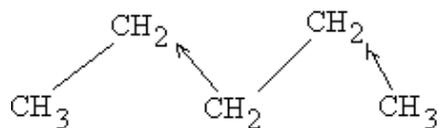
(1) Such as melting point, boiling point and viscosity.

Generally m pt & b pt are depending upon the molecular weight with increase in the molecular weight, there is increase in the value of each of these properties. But it has been found that in isomeric compounds with comparable molecular weight, the melting point and boiling point are different. This fact can be explained in certain cases by the application of V. W. interaction. For, Ex. In case of two isomeric hydrocarbons the straight chain hydrocarbon has higher melting point and boiling point as these experienced greater V. W. interaction (force of attraction between moles, this is on account of the greater area of contact between molecules). As a result of this the molecules ad-hire and greater thermal energy is required to bring about the melting & boiling of the molecules.

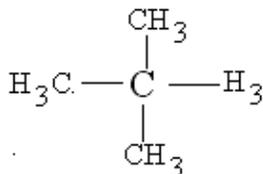
In case of branched chain isomers, the area of contact is small. So they experienced weak V. W. interaction.

Consequently lesser thermal energy is given for melting & boiling :-

Ex. :-

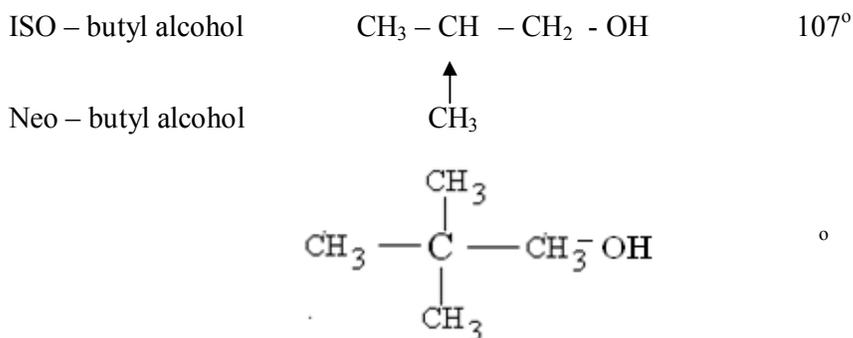


n - Pentane (otright chain greater interaction)



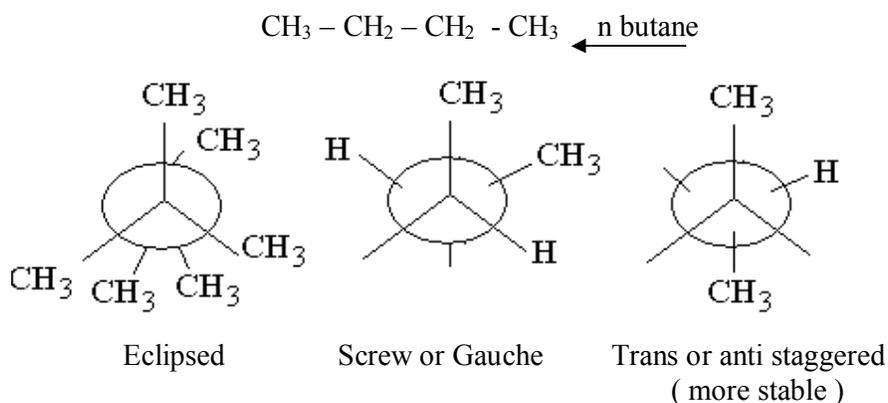
(Neo -Pentane (Highly branched much lesser interaction)

(1) <u>Compounds</u>	<u>Structure</u>	<u>M.P.</u>
n - pentane	CH ₃ - CH ₂ - CH ₂ - CH ₂ - CH ₃	36°
ISO - pentane	CH ₃ - CH - CH ₂ - CH ₃	28°
Neo - pentane		9.3°
(2) <u>Compounds</u>		<u>M.P.</u>
n - butyl alcohol	CH ₃ - CH ₂ - CH ₂ - CH ₂ OH	117°



In case of solids crystals the molecules are firmly packed close to one another to give symmetrical shaped. Thus much thermal energy is required to disarrange this arrangement. As a consequence of this it is difficult to observe and study the influence of V.W. interaction on the melting point of crystalline solids.

(2) The impact of V.W. interaction is sizable in the establishment of confirmation of certain molecules. For Ex. The greater stability of the (trans or anti) staggered confirmation over the Gouache confirmation of n – butane can be explained on the basis of greater V. W. force of repulsion experienced by Gouache confirmation.

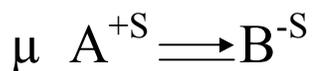


II Dipole Association :-

When two atoms are bounded together by a covalent bond and due to unequal sharing of bonded pair of electrons charges affirm on the two atoms and bond dipole is created. When two molecules having such bond dipoles get near each other, they are hold by the force of attraction called dipole association. The magnitude of the varies inversely as the fourth power of the distance between the two dipoles. This is a short range force but operates over greater distance than V.W. force.

Dipole association has influence on the properties of molecules, Dipole when the centre of gravity of electrons and nucleus present in a molecule do not coincide, there is a charge separation as a consequences of this a permanent dipole is arises. The magnitude of this is given in terms of dipole moment which is equal to $a \times d$, where 'a' is the magnitude of charge & 'd' is the distance between two poles, 'a' is of the order of 10^{-8} cm whereas 'd' is of the order of 10^{-10} e.s.u. Thus the dipole moment (π) is of the order of 10^{-18} e.s.u. It is called 1 Debye or I(D).

Dipole moment is a vector quantity (has got both magnitude & direction). The presence of π is indicated by an arrow which points towards the centre of (-v e) charge.



Factor which are responsible for the μ & its's magnitude :-

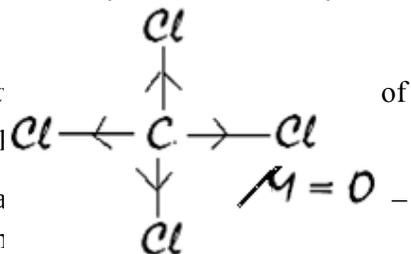
- (1) When two atoms with different electro-negativity are joined together by a covalent bond the more electro-negative atom pulls the bonded pair of electrons towards it self. As a consequence of which the partial (- v e) charge on the more electro-negative atom & corresponding (+ s) charge resides the lesser electro-negative atom. The extent of this depends upon the difference in the electro-negativity of the two atoms, greater the difference, greater is the magnitude of charge appearing & greater is the resulting bond dipole moment.
- (2) If the covalent bond is between two atoms which have significant difference in their atomic sizes, the centre of gravity of the (- ve) charge & the (+ve) charge (which generally is inside the molecules) may not be at mid point between the two atoms. This results a charge – separation & consequently π .

Features of dipole moment (π)

- (1) Dipole moment is the outcome of a permanent displacement of the bonded pair of electrons towards a particular atom. It is not an induced momentary charge – separation (this momentary induced charge – separation gives rise to V.W. forces).
- (2) Dipole moment arises not due to a presence of charge, but it is the result of charge separation. Ions are polarisable but do not have dipole moments.
- (3) If there is a covalent bond between a H – atom and any other atom excluding H – then a – v e charge centre around that atom H $\xrightarrow{\quad}$
- (4) If there is a covalent bond between a C- atom and any other atom excluding H & C then a – v e charge centre around that atom C $\xrightarrow{\quad}$
- (5) If a molecule has more than one polar bond the net dipole moment of the molecule between vectorial addition of the component moments.

If the molecule is symmetrical the π of the molecule may be zero provided the component moments are equal in magnitude but opposite in direction e. g. *ccl₄*

- (6) If a molecule has got two polar covalent bond constituting t equal magnitude, the net π of the molecule will be zero only if a com



- (7) If the key atom present in a group is joined to a C in a moment will be linear otherwise it will be non-linear, e. g. group with



Group with non-linear bond moment :- OH - OR

(8) If a molecule is put in an electric field the $-ve$ charge present in the molecule gets displaced towards the $+ve$ end of the field and the nucleus gets displaced towards the $-ve$ end of the field. The displacement of the $+ve$ charge (i.e. nucleus) is considerably less as compared to the displacement of the electrons. This momentary displacement leads to momentary polarisability and consequently π . This is called induced dipole moment. The magnitude of this π depends upon the force of the electric field (F) and polarisability α (* displacibility of charge centre in electric field)

This is momentary μ and operates only during the appliance of external electric field.

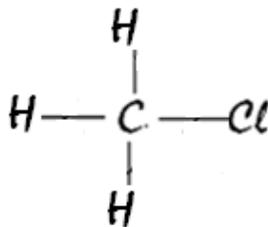
Victorial additions :-

Victorial additions have been found to be of wide application and used in organic chemistry.

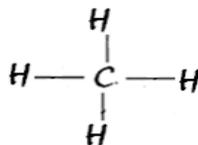
(1) If a molecule has more than one polar covalent bond which leads to component bond moments, then the μ of the moles will be victorial addition of these component moment. Thus if the values of the component moments are known the μ of the molecule can be known.

Similarly if the μ of the molecule is known and the bond moments of all but one is known then the bond moment of the missing one can be calculated.

Illustration :- Dipole moment of CH_3Cl . The μ of this molecule will be victorial addition of three component moments of C-H and the bond moment of C-cl.



If the tetrahedral angle is not distorted, a net effect of the three C – H bond moments will be the bond moment of one C – atom [Since μ of CH_4 is zero] therefore



$$\mu_{\text{CH}_3\text{Cl}} = \mu_{\text{C-H}} + \mu_{\text{C-Cl}}$$

Thus if component moments are known μ of CH_3Cl can be known. Similarly, if $\mu_{\text{CH}_3\text{Cl}}$ & $\mu_{\text{C-H}}$ are known, we can know the value of $\mu_{\text{C-Cl}}$.

$$\mu_{\text{C-Cl}} = \mu_{\text{CH}_3-\text{Cl}} - \mu_{\text{C-H}}$$

(2) Dipole moment of $\text{CH}_3 - \text{OH}$

The μ of the molecule can be computed on the basis of the geometrical shape of a molecule and the component bond moments for e-g. the μ of $\text{CH}_3 - \text{OH}$ can be calculated by applying the law of the Science for parallelogram.

$$\begin{aligned} \mu_{\text{CH}_3-\text{OH}} &= \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 108^\circ} \\ &= \sqrt{1.53^2 + 1.16^2 + 2 \times 1.53 \times 1.16 \times \cos 108^\circ} \\ &= 1.64 \text{ D} \end{aligned}$$

This value is in agreement with the observed value which is 1.67 D.

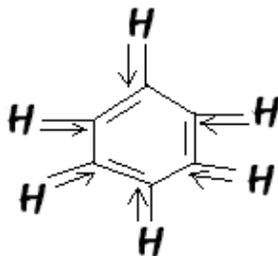
(3) The dipole moment associated with C-C-bond is highly dependent upon the nature of hybridization of carbon.

- (i) Sp^2C^+ -- CSp $\mu = 1.15 \text{ D}$
- (ii) $\text{Sp}^3\text{C}^{\ominus}$ -- CSp² $\mu = 0.68 \text{ D}$
- (iii) $\text{Sp}^3\text{C}^{\ominus}$ -- CSp $\mu = 1.48 \text{ D}$

(4) Dipole moment of Benzene :-

In the aromatic compound benzene the six - H atoms are oriented in such a way that the moment associated with one C-H bond is opposed by another C-H bond moment (the two bond moments are equal in magnitude and operating in diagonally opposite direction)

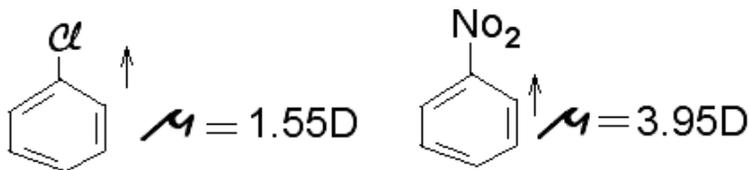
$\therefore \mu$ for benzene is zero



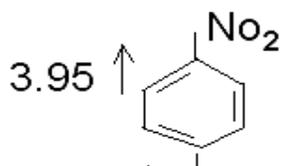
(5) Assessment of μ on L p - disubstituted benzene :-

In case of p - disubstituted benzene, the μ of the molecule will be approximately algebraic sum of the component moments associated with mono substituted benzene.

ILLUSTRATION :- Let us consider p-diloro sutro benzene, its μ is to be determined, given $\mu_{\text{Cl}} = 1.55 \text{ D}$, $\mu_{\text{NO}_2} = 3.95 \text{ D}$



Both - Cl and - NO₂ groups are electron withdrawing in nature. Therefore the moments in both chloro-benzene and nitro benzene are directed away from the ring.



In case of p - chloro nitro benzene the two components moments are opposing one another. Therefore the μ of p - nitro chloro benzene will be -

$$\mu = (3.95 - 1.55) \text{ D} = 2.4 \text{ D}$$

This calculated value is in agreement with the observed value.

(6) Assessment of μ of -O and m - disubstituted benzene :-

The μ of o - & m - disubstituted benzene can be determined if the moments associated with the corresponding mono substituted benzene are known. The effect of hyper conjugation on μ can be from following illustration.

<u>Compounds</u>	<u>μ</u>
1. $\text{CH}_2 = \text{CH}_2$ (Ethylene)	0.0.D
2. $\text{CH}_3 - \text{CH} = \text{CH}_2$ (Propylene)	0.4.D
3. $\begin{array}{c} \text{H} - \text{C} = \text{O} \\ \uparrow \\ \text{H} \end{array}$ (Paraldehyde)	2-7 D
4. $\begin{array}{c} \text{CH}_3 - \text{C} = \text{O} \\ \uparrow \\ \text{H} \end{array}$ (Acetaldehyde)	2-8 D
5. $\text{CH}_3 - \text{CH}_2 - \text{C} = \text{O}$ (Propionaldehyde)	2-72 D
6. $\begin{array}{c} \text{CH}_3 - \text{CH} = \text{CH} - \text{C} = \text{O} \\ \uparrow \\ \text{H} \end{array}$	3.67 D due to resonance

Ethylene molecule is non polar & so $\mu = 0$. Propylene has got μ value 0.4D. This can be only due to some polarity present on the molecule. This can be explained only through hyper conjugation.

Let us consider the dipole moment value of acetaldehyde and formaldehyde. Acetaldehyde has got higher μ . It can be argued that this increase in μ is due to electron releasing (+I) effect of $-\text{CH}_3$ gr. Now let us consider the μ of acetaldehyde and propionaldehyde. Acetaldehyde has got higher μ value. It is noted that ethyl has greater +I effect than $-\text{CH}_3$ gr. So if inductive effect would have been real factor, the μ of propionaldehyde should have been higher. But it is hyper conjugative effect which is dominating.

In acetaldehyde, there are three α -H atoms are present on propionaldehyde in acetaldehyde there are greater hyper-conjugative effect and consequently the value of μ .

NOTE :- The high value of μ of α -F unsaturated aldehyde is due to resonance effect & we know that resonance has a powerful electron releasing effect.

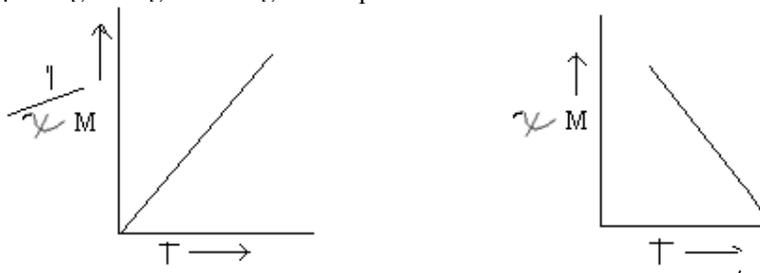


Expression for (i) Curie Law (ii) Curie Weiss law and, explanation variation of magnetic susceptibility with $1/T$ and T .

Curie Law :- Curie found that the molar magnetic susceptibility (χ_M) of a paramagnetic substance is inversely proportional to absolute temperature (T).

$\chi_M \propto 1/T$ (Curie - law) or $\chi_M = C/T$ where 'C' is constant and is known as Curie-Constant.

This is an equation of straight line passing through the origin. The plot of $1/\chi_M$ versus T is shown below :-



From the slope of straight line curie constant 'C' can be known. The equation holds good for many paramagnetic substances. This equation does not hold good for many other substances.

Curie Weiss law :- There are the substances which do not obey curie law i.e. $\chi_M = C/T$ such substance straight line obtained by the plot of $1/\chi_M$ versus T does not pass through the origin but cuts the temperature axis. This indicates that curie law needs slight modification. This modified form of curie law is known as Curie-Weiss law. Curie Weiss law is defined by the following equation

$$\chi_M = \frac{C_{\text{Corr}}}{T-Q} \quad \text{Or,} \quad \chi_M = \frac{C_{\text{Corr}}}{T+Q}$$

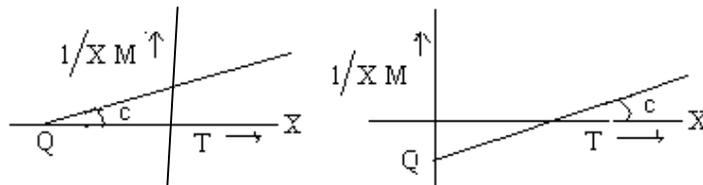
Where χ_M = Commuted molar susceptibility

T = absolute temperature

C = Curie constant

Q = Weiss constant

When $1/\chi_M$ is plotted against T , a straight line is observed which cuts the temperature axis. The slope of this straight line is equal to C and the temperature at which the line cuts the X-axis is equal to Q .

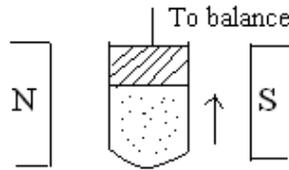


The value of Q may be $+ve$ or $-ve$. If Q is $+ve$ (i.e. about $0^\circ K$) the substance is said to be ferromagnetic and if Q is $-ve$ (i.e., below $0^\circ K$) the substance is said to be anti ferromagnetic. The value of μ_{eff} for the substance which obey Curie-Weiss law is given by

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_m \text{ con}(T-Q) \text{ B.M.}}$$

Determination of magnetic susceptibility by Gouy method.

Ans. -



The Gouy's method for the determination of magnetic susceptibility :-

- (1) A thin cylinder containing the sample is suspended by non-magnetic wire in magnetic field.
- (2) The cylinder is center balanced by placing weight in the pan attached to the other end of the arm of the balance.

Let us suppose that, the weight of sample in air = m

Weight of sample in magnetic field = m

Loss in weight by applying magnetic field = $m - m_1 = \Delta m$

Then, the magnetic susceptibility (χ_M) of that substance is given by

$$\chi_M = \frac{2gl}{H^2} \cdot \frac{\Delta m}{m} \quad \chi_M$$

Where g = gravitational acceleration

l = length of the tube

M = molecular weight of the sample $2gl/H^2$ is constant, i.e. for any unknown sample if some current

is used for some tube the constant remain same and then χ_M is determined.

Proof:- The small force dF experienced by the sample of volume susceptibility and small volume du in a magnetic field H is given by - $dF = H \cdot \chi \cdot du$, $\frac{dH}{dx}$

Where, $\frac{dH}{dx}$ is the field gradient,

Now, if A is the cross-sectional area and $d\chi$ is the small height of the sample,

Then $A d\chi = du$

Hence, $dF = H \cdot \chi \cdot A \frac{d\chi}{d\chi} \frac{dH}{dx}$

On integration, we get - =

$$\text{Or, } F = A \chi \frac{1}{2} (H^2 - H_0^2)$$

Where H and H_0 are the lower and upper limits of magnetic field.

Since, $\chi_g = \frac{\text{Volume susceptibility}}{\text{Density}} = \frac{\chi}{d}$

$$F = A \chi_g d \frac{1}{2} (H^2 - H_0^2)$$

$$d = \frac{\text{Mass (m)}}{\text{Volume}}$$

$$d = \frac{m}{A \times l} \text{ or, } Ad = \frac{m}{l}$$

$$\text{So, } F = \chi_g \frac{m}{l} \frac{1}{2} (H^2 - H_0^2)$$

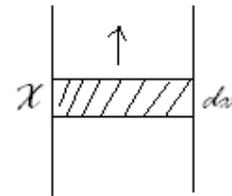
H_0 is neglected, then

$$\chi_g = \frac{2lF}{H^2, m} \quad \text{Since, } F = \Delta m \times g$$

$$\text{So, } \chi_g = \frac{2l - \Delta m \cdot g}{H^2 \times m}$$

$$\chi_g = \frac{2l \times \text{Change in weight of the sample} \times g}{H^2 \times \text{wt of the sample}}$$

$$\text{Or, } \chi_m = \frac{2l - \Delta m \cdot g}{H^2, m} \quad M$$



M = mol wt of the substance

The quantity $2 \ell g / H^2$ is called tube calibration constant. Thus constant is first determined by taking a measurement on a standard substance. Such as $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$,

Then the effective magnetic moment, μ_{eff} is calculated as,

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_m^{\text{con}} (T - Q) B. M.}$$

Relation between magnetic susceptibility, magnetic moment and temperature.

Let us suppose that one mole of magnetic dipole in a system, when the magnetic moment of each magnetic dipole is μ . The average magnetic moment at any temperature may be given by Maxwell Boltzmann distribution as, -

$$\bar{\mu} = \frac{\mu^2}{3KT} \cdot H \quad \text{Thus the total magnetic moment of one mole will be } \bar{\mu} N = \frac{\mu^2 N}{3KT} \cdot H$$

The molar magnetic susceptibility χ_m can be given as :-

$\chi_m = \chi_g M$ (where χ_g is gram – susceptibility)

$$= \frac{\chi}{\rho} M \quad (\text{Where } \chi \text{ is volume susceptibility),}$$

$$\chi M = \frac{\chi}{\rho}, \quad M = \frac{I}{H \rho} M,$$

Where I = molar magnetic moment per unit volume and H is applied magnetic field.

$$= \frac{\bar{\mu} N}{H \rho} \cdot \frac{M}{V}$$

$$= \frac{\mu^2 N}{3KT} \cdot \frac{H}{N} \cdot \frac{M}{\rho} \cdot \frac{I}{V} = \frac{\mu^2 N}{3KT}$$

$$\text{i.e. } \frac{3K}{N} \chi M \cdot T = \mu^2$$

$$\sqrt{\frac{3K \chi M \cdot T}{N}} = \mu$$

$$\mu \text{ in } \beta M = \sqrt{\frac{3K}{N \beta^2}} \sqrt{\chi M T}$$

$$\mu = 2.84 \sqrt{\chi M T}$$

Difference between temperature independent and temperature dependent magnetic moment.

When a system is placed in magnetic field it splits the non-degenerate lands, The effect may be considered in two steps.

- (1) First order Zeeman effect
- (2) Second order Zeeman effect

(1) Temperature dependent paramagnetism :- If the effect of II order Zeeman effect is ignored the expression of magnetic susceptibility contains T, i. e. it varies inversely proportional to the absolute temperature (as stated by Curie), this paramagnetism is called temperature dependent paramagnetism,

$\chi M \propto 1/T$ It arises due to I order Zeeman effect.

(2) Temperature independent paramagnetism (van Vleck paramagnetism) or Residuals paramagnetism :-

It arises due to the II order Zeeman effect. The value of magnetic susceptibility due to second order Zeeman effect = $N \alpha^2$

$$\text{Where, } \alpha^2 = \frac{2}{2J+1} L$$

Where, w_i is second order Zeeman effect. This does not contain any temperature term. However, the contribution due to TIP in total magnetic susceptibility is quite small. It can be shown that second order Zeeman

∝

effect arises due to the mixing of ground state from higher excited states. For example, Ne (II) which has A_2g ground, state in octahedral system has χ_M (II order) = $8N \beta^2 / 10 Dq$

This explain why diamagnetic CO (III) Complex, $KMnO_4$, $K_2Cr_2O_7$ shows some magnetic moment..

However, the contribution of II order Zeeman effect towards magnetic susceptibility (TIP) is comparatively quite small in comparison to first order Zeeman effect. Thus the magnetic susceptibility of a system can be generally

$$\chi_M = \frac{N \beta^2 \mu^2}{3 KT} + N \propto$$

Where $\frac{N \beta^2 \mu^2}{3 KT}$ is contribution from I order Zeeman effect (i.e. temperature dependent paramagnetism) and

$N \propto$ is contribution from II order Zeeman effect (i. e., TIP).

4 (OR) :- Give expression for (i) μ_S (ii) $\mu_S + L(a)$ (iii) μ_J and explain terms of expressions. Paramagnetic property of substance depends upon (1) Spin motion and (2) Orbital motion of electron.

(i) μ_S :- The magnetic moment due to spin motion is given by the expression -

$$\mu_S = g \sqrt{S(S+1)} \text{ BM} \text{ ————— ①}$$

Where 'S' is the resultant spin angular momentum which is equal to the sum of the spin momentum of unpaired electrons, 'g' is called gyromagnetic ratio. In this case the value of 'g' is equal to '2'. Thus –

$$\mu_S = 2 \sqrt{S(S+1)} = \sqrt{4 S(S+1)} \text{ BM} \text{ ————— ②}$$

$$\mu_S = \sqrt{4 n/2 (n/2 + 1)} = \sqrt{n (n+2)} \text{ BM} \text{ ————— ③}$$

$$2 \mu_S + L = \sqrt{4S (S+1) + L (L+1)}$$

The magnetic moment is given by the equation either 2 or 3 is called spin only magnetic moments.

(ii) $\mu_S + L$:- For some transition metals ion the orbital contribution is also important and the magnetic moment of such substances is given by the expression are small i.e., the case of transition metal ion of first transition series-

$$\mu_S + L = \sqrt{4S (S+1) + L (L+1)}$$

Where S = sum of spin quantum number of the unpaired electrons L is the algebra sum of the magnetic quantum numbers of all the electrons.

(iii) μ_J :- It is seen that H – values often exceed μ_S but are seldom (rarely) as high as $\mu_S + L$, this is due to the quenching of orbital angular momentum. This is caused by electric field of other atoms, ions and molecules surrounding the metal ions. In the compounds such legend restrict the orbital contribution is lost. It is found that when the orbital contribution is present the magnetic moment is temperature dependant and if the orbital contribution is quenched (i.e. lost) the magnetic moment is independent of temperature.

The magnetic moment calculated by the following equation gives more accurate results and valid in the ease where multiplied separation are large i.e. the lanthanides and actinides. $\mu = g \sqrt{J(J+1)}$ where g = gyromagnetic ratio and is defined by the following equation :-

$$g = \frac{1 + J(J+1) + S(S+1) - L(L+1)}{2 J (J + 1)}$$

J = internal or inner quantum number. J value is obtained by L – S coupling and symbolically represented as, -

$$(S_1 + S_2 + S_3 + \dots) + (L_1 + L_2 + L_3 + \dots) \\ = S + L = J, \text{ Or,} \\ J = |L + S| \text{ to } |L - S|$$

-----X-----

4 (OR)

Q4 (b) Explain what do you understand from quenching of orbital angular momentum ?

Ans. :- In majority of cases, it has been observed (found) that magnetic moment of transition metal complexes does not coincide with its calculated value, according to the expression –

$$\mu_s + L = \sqrt{4s(S+1) + L(L+1)}$$

Where L and S are total orbital and spin momentum quantum number. In general, $\sqrt{4S(S+1)}$ is the contribution of spin motion and $\sqrt{L(L+1)}$ is the contribution of orbital motion towards magnetic moment. Now spin motion contribute in full in all cases but orbital motion in few contributes partially and in some case it does not contribute at all. It can be revealed by the following observed and calculated data.

Ions with Configuration	μ_J	$\mu_s + L$	μ_s only	μ exp(BM)
Ti ⁺³ - 3d ¹	1.55	3.01	1.73	1.7 – 1.8
V ⁺³ - 3d ²	1.63	4.49	2.83	2.8 – 3.1
Cr ⁺³ - 3d ³	1.70	5.21	3.87	3.7 – 3.9
Mn ⁺³ → 3d ⁴	0.00	5.50	4.90	4.8 – 4.9
Fe ⁺³ → 3d ⁵	5.92	5.92	5.92	5.7 – 6.0
Co ⁺³ → 3d ⁶	6.71	5.50	4.90	5.0 - 5.6
Co ⁺² → 3d ⁷	6.63	5.21	3.81	4.3 – 5.2
Ni ⁺² → 3d ⁸	5.59	4.49	2.83	2.9 – 3.9
Cu ⁺² → 3d ⁹	3.55	3.01	1.73	1.9 – 2.1

Cause :- In the complex, the motion of the electrons is very much restricted so that effectively the orbital moment is largely quenched.

The unpaired electrons in the first transition series metal ion are located in 3d orbital. These electron can generate orbital moment the condition should be such that they can go round the nucleus via these orbitals. For these three conditions must be met.

- The orbital should be degenerate.
- The orbital should be transformable.
- The orbital must not contain electrons of similar spin.

By application of crystal field the moment of electrons is restricted due to the on set of an energy barrier. The d_{2²} orbital is not equivalent to remaining orbital even if all given degenerate orbital would have been degenerate. Thus in any case the full contribution of orbital motion towards magnetic moment is not possible. It can be further derive that with A and E ground state, there is no orbital contribution but in crystal field state, orbital contribution takes place.

Magnetic moment of compounds of d-block element is best explained by –

$$\mu_{eff} = \mu_s \left(1 - \frac{k\lambda}{10Dq} \right)$$

μ_{eff} = It is the difference from μ_s value due to spin orbit coupling.

μ_s = Spin only mag. moment.

λ = Spin orbit coupling constant.

λ = -ve for more than half – filled configuration

λ = +ve for less than half filled configuration

K = It is constant which is

4 for A ground state and

2 for E ground state

10Dq = CFSP (Crystal field splitting parameter) for higher value of 10 Dq.

μ_{eff} is less than μ_s only and vice – versa.

Example :- Cr III is d³ system which is less than half – filled. Thus λ is + ve. From the above formula, μ_{eff} is less than μ_s . Ion Co⁺⁺ which is d⁷ system, λ is –ve so μ_{eff} is greater than μ_s .

Thus the magnetic moment of octahedral complex of Cr III is less than μ_s and that for Co⁺² is greater than μ_s value.

Explain Fajan's rule with reference to solubility of L₁I in non-polar solvents.

If the two ions A^+ and B^- are brought together to their equilibrium distance, the type of bond between them depends on the effect of one ion on the other. The positive ion attracts the electrons on the negative ion and repels the nucleus, thus distorting or polarizing the negative ion. If the polarization is quite small, then an ionic bond results. If the degree of polarization is quite small, then an ionic bond results. If the degree of polarization is large electrons are drawn from the negative ion to the positive ion and appreciable covalent bond results.

The extent of ion-distortion depends on both the power of an ion to distort the other i. e. its polarizing power and the susceptibility of an ion to distortion i.e. its polarizability. The polarization is related with covalent character as greater the polarization greater is the covalent character. Fajan has correlated the polarizability of an anion and polarizing power of cation. According to him, polarizing power of a cation depends upon the following three facts :-

- (1) Size of Cation :- Smaller the size greater is the polarizing power and vice – versa. So Li^+ has a greater polarizing power than cs^+ .
- (2) Charge of cation :- Greater the charge of cation greater will be polarizing power and vice-versa. Thus Al^{+3} has greater polarizing power than Mg^{+2} .
- (3) The electronic configuration of cation :- It is observed that Si^+ has a greater polarizing power than alkali metal cations because of the fact that it has d^{10} electronic configuration.

The polarizability of an anion depends upon its size i.e., greater the radius of an anion greater will be polarizability. The polarizability of I^- ion is greater than that of F^- ion. In alkali metal halides Li^+ has the greatest polarizing power on account of its small size while I^- ion has a largest polarizability due to its large size. Therefore, LiI has maximum covalent character among alkali metal halides . This explains that LiI is soluble in water but soluble in non-polar solvents.

4(e):- Difference between dipole moment and bond moment.

ANS:- Bond moment is defined as the product of the charge and distance between them in a polar bond. For example – in a HCl molecule, the charge q and the bond length 't',

$$\therefore \text{Bond moment} = q \times t$$

The resultant sum of bond moments are called dipole moment. For example in HCl molecule since there is only one bond, the bond moment and dipole moment is seen, in case of water molecule if the bond moment of OH bond is P then the dipole moment of water is given by the expression.

$$\sqrt{2p^2 + 2p^2 \cos \square}$$

Where \square = angle between two OH front. Thus the dipole moment and bond moment differs.

Example :- In CO_2 molecule $C-O$ bond has bond moment but the dipole moment for molecule is zero.

Magnetic moment of $[Fe(H_2O)_5NO]SO_4$ is 3.9 B.M.

In the complex $[Fe(H_2O)_5NO]^{++}$ ion, NO is in the form of NO^+ acts as ligand and so Fe is in +1 oxidation state Iron is +1 oxidation state is a d^7 system as shown below :-



There are three unpaired electron the magnetic moment.

$$\mu = \sqrt{n(n+1)} = \sqrt{3 \times 4} = \sqrt{12} = 3.7$$

Rest is the orbital contribution which is also expected in $T_2g^5 e_g^2$ system. Therefore the magnetic moment is 3.9.

Magnetic moment for $[COCl_4]^{2-}$, $[COBr_4]^{2-}$ and $[COI_4]^{2-}$ is 4.19 BM, 4.6 BM and 4.77 BM respectively.

In all the three complex, CO is in +3 oxidation state which is a d^7 system. Thus magnetic moment will be

$$\mu_s = \sqrt{n(n+1)} = \sqrt{3 \times 4} = \sqrt{12} = 3.7 \text{ B.M.}$$

Now, due to spin orbit coupling magnetic moment increases for more than half filled electronic system, the expression is –

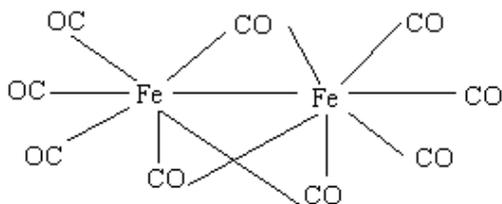
$$\mu_s = (1 - \frac{K\lambda}{10Dq}) \quad \text{where } \lambda = -ve,$$

We know that the strength of ligand Cl^- , Br^- , I^- varies as $Cl^- > Br^- > I^-$. Since we know for Cl^- , $10Dq$ is comparatively large $\frac{K\lambda}{10Dq}$ is small and thus μ_{eff} is comparatively smaller than Br^- and I^- ,

And increases to Br^- than I^- . That is why the magnetic moment for $[\text{CoCl}_4]^{-2}$, $[\text{CoBr}_4]^{-2}$, $[\text{CoI}_4]^{-2}$ is 4.19 BM, 4.69 BM and 4.77 BM respectively.

(c) Diamagnetic nature of $\text{Fe}_2[\text{CO}]_9$

ANS:- In $\text{Fe}_2(\text{CO})_9$, there are 6 terminal CO groups, three on each Fe atom and three bridging CO groups and one Fe – Fe bond also. It can be shown below –



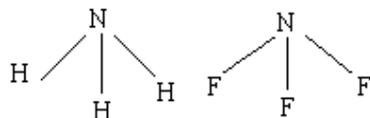
The effective number of Fe at

$$\begin{aligned} &26 \text{ (atomic number of Fe)} \\ &+6 \text{ (Contribution from terminal Co – groups)} \\ &+3 \text{ (Contribution from bridging Co groups)} \\ &+1 \text{ (Contribution from Fe – Fe bond)} \\ &= 36 \end{aligned}$$

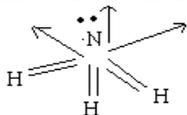
Thus, there is no unpaired electron and the compound is diamagnetic.

Difference in dipole moment of NH_3 and NF_3

The structures of NH_3 and NF_3 are as follows :-

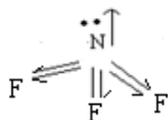


The bond moments and their directions are shown as below :-



In NH_3 molecule the direction of resultant bond moments, and the directions of moment of lone pair also moves in up ward direction. This leads to a high dipole moment.

In NF_3 molecule, the direction of resultant bond moments and the direction of moment due to lone pair oppose each other as shown below :-

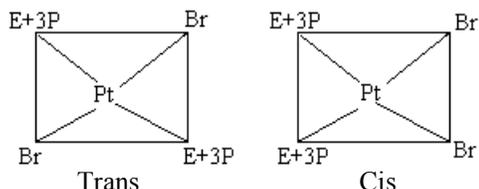


Thus the dipole moment decreases and hence resultant dipole moment becomes smaller.

(*)

Dipole moments value for the isomers of $[\text{Pt Br}_2(\text{E}+3\text{P})_2]$ differ.

The complex $[\text{Pt Br}_2(\text{E}+3\text{P})_2]$ is a square planar complex of pt (II). Pt has the following two geometrical isomers :-

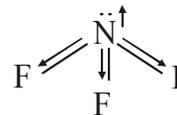


In Cis isomer the resultant of two Pt – Br bonds and two Pt – $\text{E}+3\text{P}$ bond are in opposite directions but not equal therefore the resultant will not be zero while in case of trans isomer resultant of one Pt Br and one Pt $\text{E}+3\text{P}$ will be equal and opposite to another the same bonds. Thus the resultant will be zero. Therefore, the dipole moment value for the two isomers will be different.

Lone pair electron influences bond moments :-

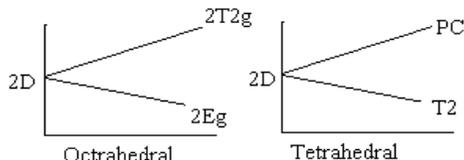
ANS:- Lone pair electron influences dipole moments. Dipole moment is the resultant of bond moments if we consider the example of NF₃ which is pyramidal, we find that the resultant of three NF₃ bond moment will be substantial but the observed bond moment of NF₃ is quite small (appears 0.2 Debye). The value indicates that the Lone pair also exhibit some moment which is opposite in directions and thus cancels the resultant bond moments.

In this way, the lone pair electrons influences the dipole moments.



Magnetic moment of octahedral and tetrahedral complexes of Cu(II) differ.

Cu(II) is a d⁹ system which has 2D as ground term. Its splitting in octahedral and tetrahedral crystal field are shown below :-



We know that the magnetic moment due to spin motion is given by $\sqrt{4s(S+1)}$ BM which comes equal to 1.732 BM in this case orbit motion gives rise to magnetic moment $\sqrt{l(l+1)}$ BM which is fully quenched in the case where the ground term is A or E i. e., in octahedral complex in the above case the orbital contribution is fully quenched. A small increase in magnetic moment data is however observed due to spin orbit coupling and magnetic moment is found to be approximately 1.88 BM.

In tetrahedral complex, since the ground term is T, there is partial contribution from orbital motion also. Thus the magnetic moment increases substantially from its spin only value and found to be approx. 2.3 to 2.4 B.M. Thus the magnetic moment of Cu(II) in Octahedral & Tetrahedral differs.

Magnetic moment of Cr(III) octahedral complex is less than μ_s value, but of Co(II) is greater than μ_s value.

The magnetic moment of d- block elements are best explained by $\mu_{eff} = \mu_s \left(1 - \frac{\lambda}{10Dq} \right)$. The difference

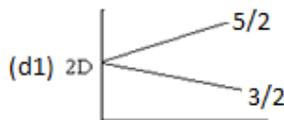
from μ_s value is due to spin orbit coupling where μ_s is spin only magnetic moment, λ = spin – orbit coupling constant, $10Dq = C F S P$.

We also knew that for less than half filled electronic configuration λ is positive but more than half filled electronic configuration λ is negative.

Cr (III) is a d³ system which is less than half filled thus λ is positive and from the above formula μ_{eff} is less than μ_s . In Co(II) which is a d⁷ system, λ is negative and so μ_{eff} will be greater than μ_s . Thus magnetic moment of Cr(III) octahedral complex is less than μ_s value but of Co(II) is greater than μ_s value.

Conditions under which $\mu_s, \mu_s + L, \mu J$ are valid ?

We knew that total orbital angular momentum and spin angular momentum is represented by a term. For example, 2D indicates total orbital angular momentum (L=2) and total spin angular momentum (S=1/2). These two vectors interacts under the influence of spin - orbit coupling to give J, which is from |L+s| to |L-s|. For example, 2D splits as -



The difference between two energy levels is equal to $5/2 \lambda$ where λ = spin orbit coupling constant. Now following two cases may arise -

Case (I) :- Kinetic energy of a system is greater than λ : In this case, the two micro states represented by J=3/2 and J=5/2 will be well populated and the system will be distributed, according to Maxwell Boltzmann lies rebution law between the two energy states. Here a particular J will not be very relevant and thus L and S both are used up to calculate the total angular momentum. Thus is the case where spin- orbit coupling is weaker and is frequently occurs in I transition series. The magnetic moment is calculated by the formula, -

$$\sqrt{L(L+1)4s(s+1)}$$

This is called μ_{s+L} value i. e.,

$$\sqrt{\mu_{s+L} = L(L+1) 4s(s+1)}$$

However, due to crystal field splitting it is quite clear that the degeneracy of d- orbital is up lifted and therefore

$$g = \frac{\sqrt{J(J+1)}}{2J(J+1)}; \text{ where } g \text{ is gyromagnetic ratio, and}$$

$$g = \frac{1 + S(S+1)L(L+1) + J(J+1)}{2J(J+1)}$$

This is called μ_J .

Therefore, orbital angular momentum of electron in d-orbital is not contributed in full towards the magnetic moment i.e. the orbital angular momentum is quenched as such the above formula (1) never holds good.

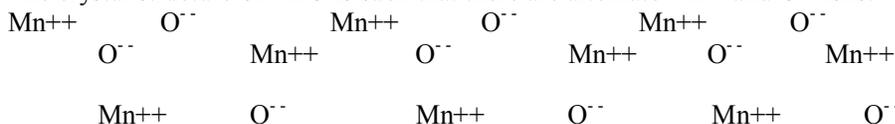
If it is fully quenched (it occurs in case of A and E ground state), the magnetic moment may be calculated by ignoring the orbital contribution ($L = 0$) = $\sqrt{4S(S+1)}$. This is called μ_s value. For the ions where the ground term is T, a little contribution of orbital motion is taken into account.

CASE (2) :- When λ is greater than the KE of the system it frequently occurs in lanthanides . Here the ground state is well populated so J is a good and relevant quantum member in place of L and S.

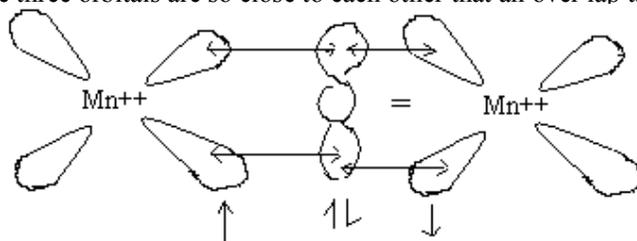
Thus μ is calculated according to formula.

MnO and $(\text{Cu}(\text{CH}_3\text{Coo})_2 \cdot \text{H}_2\text{O})_2$ are diamagnetic at room temperature but become paramagnetic when temperature is increased.

The crystal structure of MnO is such that there are alternate Mn^{++} and O^{--} ions.



There occurs a phenomenon super exchange between two neighbouring Mn^{++} ion through O^{--} ion. It is called linear super exchange because the three atoms are collinear. It may be explained as follows; Both Mn^{2+} ions have d – orbital having unpaired electron and O^{2-} ion with p-orbital having paired electrons. All the three orbitals are so close to each other that an over lap takes place as shown below :-



This overlapping forces the electron of one Mn^{2+} ion to align anti parallel to the electron of another Mn^{2+} ion due to which the magnetic moment cancels each other. This occurs at a low temperature when the KE is not sufficient enough to randomize the electronic spin. Under this condition magnetic moment fall from it's expected μ_s value. Thus MnO is anti ferromagnetic at low temperature but when it is heated above Neil's temperature due to it's KE randomization takes place and the system becomes ferromagnetic.

TRANSITION METAL CO-ORDINATION CHEMISTRY PART-II

Difference between step wise and overall stability constant of complexes. Relationship between them.

Principles of a method used for the determination of stability constant.

Stability constant :- When a complex is formed by a series of reactions –



The equilibrium constant of each step K_1, K_2, K_3 is given by the equation :-

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$

Where K_1, K_2, K_3 are known as step wise stability constants, if the formation of ML_n is given by



The overall equilibrium constant will be defined as –

$$K_{max} = \frac{[ML_n]}{[M][L]^n}$$

$$[M]$$

$$B_n = \frac{[ML_n]}{[M][L]^n}$$

$$[M][L]^n$$

Where B_n is called over all stability constant-

Relation between step wise stability and over all stability constant :-

For the above series of reactions $K_1, K_2, K_3, \dots, K_n$

$$= \frac{[ML][ML_2][ML_3] \dots [ML_n]}{[M][L][ML][L][ML_2][L] \dots [ML_{n-1}]}$$

$$= \frac{[ML_n]}{[M][L]^n} = B_n$$

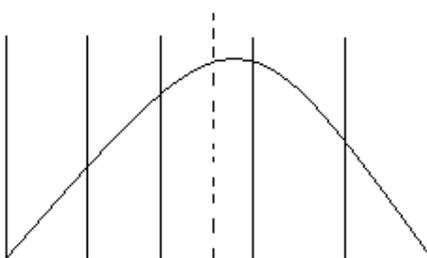
$$\text{Thus } B_n = K_1 \cdot K_2 \cdot \dots \cdot K_n$$

$$\text{i.e. } B_1 = K_1, B_2 = K_1 K_2, B_3 = K_1 K_2 K_3 \text{ and so on}$$

DETERMINATION OF STABILITY CONSTANT

If the complex forms only step the determination is very simple. We determine the total ion concentration and total ligand concentration and the two is mixed. If concentration of a metal or free ligand at any time can be measured, the stability constant can be evaluated directly when a series of reactions occurs for n - stability constant $n+2$ independent concentration measured are required. To avoid this **complexity** we use the following method.

A series of solutions with different concentration (mole fraction) of metal ion and ligand are prepared. The optical density of each solution is measured and plotted against the concentration of metal ion or ligand. A typical plot is shown below :



0.0	0.2	0.4	0.6	0.8	1.0 [M]
1.0	0.8	0.6	0.4	0.2	0.0 [L]

Fig

The job plot obtained when only one complex specified (species) ML_2 is formed between $[M]$ and $[L]$ indicates the maximum optical density point and it can be proved that –

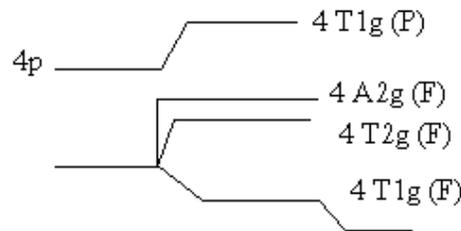
$$\alpha_{max} = \frac{[M]_{max}}{[M]_{max} + [L]_{max}}$$

Here, α_{max} is the maximum co-ordination number. Now from the value of α_{max} , β can be calculated as follows :-
 From the composition of any mixture of average number of ligand molecule complexed with each metal atom is known. α_{max} is related to the composition of mixture of the mixture of complex ion by the equilibrium

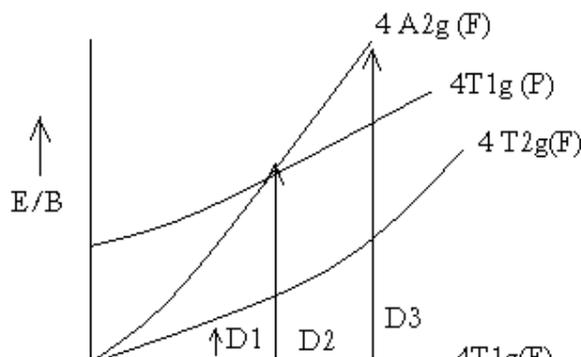
When the complex series are ML , ML_2 , ML_N and C is the total concentration of metal ion complex and **uncomplexed** in the solution.

Now $C = [M] + [ML] + [ML_2] + [ML_N]$
 and $[ML] = \beta [M][L]$
 So,

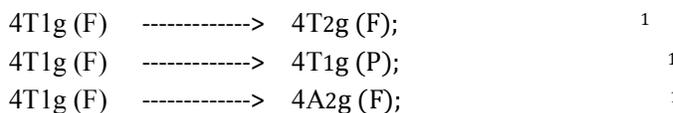
If a series of reactions with varying $[L]$ is prepared and concentration of L is measured in each then value of β : $\beta = 1, 2, \dots, N$ must be chosen so that the above equality holds absorption. This may be done e.g. by plotting α against concentration of L and determine the β s by the curve fitting procedure.
 CO^{+2}_{aq} :- This ion is $[Ce(H_2O)_6]^{+2}$. It is $d7$ system. The Orgel diagram is as follows



Following are the three transitions are expected in this case :-

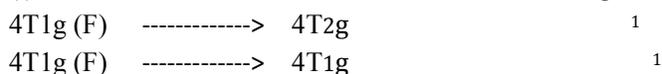


The transitions are
 159



In the spectra of above complex two peaks at 8000 cm^{-1} and $21,600 \text{ cm}^{-1}$ are observed. It is quite obvious that one peak among the above three transitions is missing. It is a reasonable guess that $4T1g(F) \longrightarrow 4A2g(F)$ will be missing because,

(i) It involves two electron transition. Therefore two peaks are assigned as -



The ratio :

$$\frac{4T1g(F) \longrightarrow 4T1g(P) \quad 21,600}{4T1g(F) \longrightarrow 4T2g(F) \quad 8,000} = \frac{1}{1} = 2.70$$

From the Tanabe – Sugano diagram it can be calculated that the ratio 2.70 comes at $\Delta/B = 0.96$ (I)

At this value of Δ/B (I) the transition $4T1g(F) \longrightarrow 4T2g(F)$ is observed at $E/B = 8.2$. The energy of spectrum is 8000 cm^{-1}

$$B = \frac{8000}{8.2}$$

$$B = 980 \text{ cm}^{-1}$$

Thus putting the value of B in equation (I) we can calculate Δ value

$$\Delta/B = 0.96$$

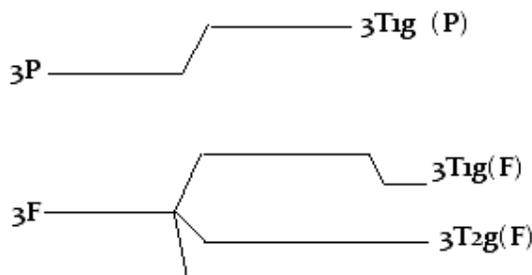
$$\Delta = 9,300 \text{ cm}^{-1}$$

CFSE : CFSE is the energy difference between bary centre and the ground state which is $6 Dq$ for d^7 system

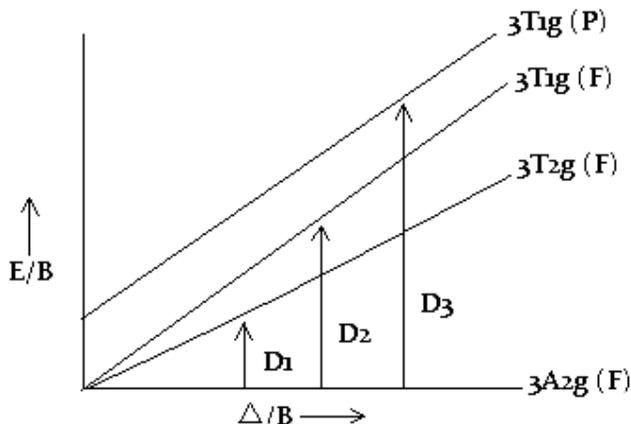
$$CFSE = 9,300 \times \frac{6}{10}$$

$$CFSE = 5580 \text{ cm}^{-1}$$

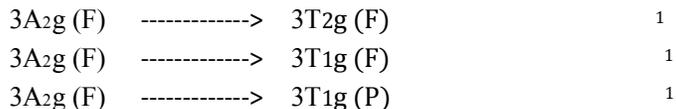
$Ni^{+2} \text{ aq}$: The ion is $[Ni(H_2O)_6]^{+2}$ is d^8 system. The Orgel diagram is as follows :-



Following are the transitions expected in this case :-

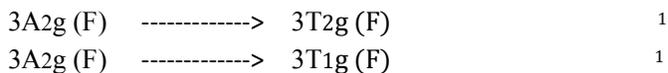


Following are the three transitions expected in this case :-



In the spectra of above complex two peaks at 8700 cm^{-1} and $14,500\text{ cm}^{-1}$ are observed. It is quite obvious that one peak among the above three is missing. It is a reasonable guess that $3A_{2g}(F) \text{-----}>3T_{1g}(P)$ will be missing because,

(i) This transition is high energy transition which is out of range of d – d transition. Therefore two peaks are assigned as -



First transition i.e. $3A_{2g}(F) \text{-----}> 3T_{2g}(F)$ occurs at $10 Dq$ so -

$$\boxed{10 Dq = 8,700 \quad 1}$$

The ratio :

$$\frac{3A_{2g}(F) \text{-----}> 3T_{1g} \quad 1}{3A_{2g}(F) \text{-----}> 3T_{1g} \quad 1} = \frac{1}{1} = 1.74$$

From the Tanabe – Sugano diagram it can be calculated that the ratio 1.74 comes at

$$\Delta/B = 0.98$$

Putting the value of Δ we can calculate the value of B as

$$\begin{array}{lcl}
 \Delta/B & = & 0.98 \\
 B & = & \frac{8700}{0.98}
 \end{array}$$

$$\therefore B = \boxed{905 \quad 1}$$

CFSE :- CFSE is the energy difference between barri center and the ground state which is $12 - Dq$

$$\begin{aligned}
 \text{CFSE} &= 8700 \times \frac{12}{10} \\
 &= 10,440 \quad 1
 \end{aligned}$$

$$\therefore \boxed{\text{CFSE} = 10,440 \quad 1}$$

Pb(CH₃)₄ is stable but Tl(CH₃)₄ is instable.

Pb⁺⁴ is soft acid, Tl⁺⁴ is hard acid and CH₃⁻ is soft base.

A hard and well prefer to combine with a hard base and a soft and well prefer to combine with soft base and thus more stable product will be obtained.

Hence Pb(CH₃)₄ is (soft - acid + soft base) is a stable complex and Tl(CH₃)₄ (hard acid + soft base) is instable.

The order of stability as predicted by crystal field theory and shown in figure is the same of Irving - Williams order of stability for complexes of these metal except Cu²⁺ due to distorted octahedral structure assume maximum CFSE.

The experimental values shown by dots are crossed for CFSE for each ion, the correction is done by subtracting the calculated CFSE values from experimental values we get a smooth curve which has corrected values (shown by crosses) since it indicates the expected regular increase in values. The ions i.e., Ca²⁺ (d⁰), Mn²⁺ (d⁵) and Zn²⁺ (d¹⁰) which do not have CFSE have experimental values on the smooth curve.

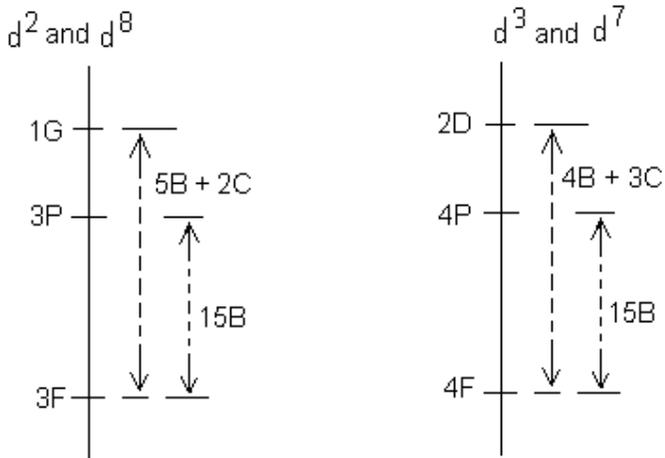
Adjusted crystal field model is ligand field model.

The term ligand field theory has often been used to designate the particular form of crystal field theory. According to crystal field theory the metal ion and the surrounding ligand atoms interact with one another in a purely electrostatic way and do not mix their orbitals or share electrons. It is not strictly true. Then the question is why we use crystal field theory still? To understand this, adjusted crystal field theory is provided with certain modification as a formalism to make prediction and calculation.

- (1) The degree of orbital overlap is not too great and the amount of overlap is small enough to be manageable in such a way.
- (2) The most straight forward modification of crystal field theory that make allowance for orbital overlap involved using all parameters of inter-electronic interactions. The three interaction parameters are the spin orbit, coupling constant and the inter-electronic parameter i.e. Slater integral F_n and Racah parameters B and C.

For example, in case of d² or d⁸ system the difference between 3F and 3P is 15 B and difference between 3F and 1D is (5B + 2C).

In case of d³ or d⁷ system, the difference between 4F and 4P is 15 B and difference between 4F and 2P is (4B + 3C) as shown below :-



- (3) In general $C \sim 4B$
- (4) Spin orbit coupling is important in determining the magnetic properties of transition metal complex.
- (5) The ξ value for the complexes taken as 70% to 85% of the free ion value but from electronic spectral data, it is found that crystal field theory and experiment can be brought agreement when parameters for the complexed ion are reduced by about the same factor from their free ion value in general.

$$B^1/B \sim C^1/C \sim 0.7 - 0.8$$

- (6) The ratio of $B^1/B = \beta$ series is also known as Nephelauxetic series for metal and ligand. Thus in order to calculate an energy level diagram and magnetic behaviour in ligand field theory in the same manner as in crystal field theory except that instead of assuming the free ion values for ϵ , B and C .

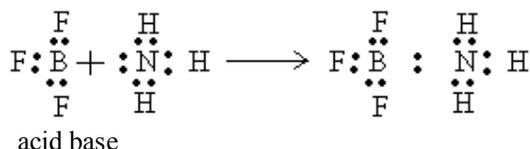
HSAB concept.

HSAB (Hard – soft Acid Base Concept)

Lewis definition :-

A base is any species that is capable of donating a pair of electrons to the formation of a covalent bond and an acid is any species that is capable of accepting a pair of electrons to form a covalent bond.

Ex. :-



Actually complex is interaction of acids and bases.

$\text{HF} < \text{HCl}$ (on the basis of radius)

$\text{H}_2\text{O}^2 < \text{H}_2\text{O}^1$ (on the basis of oxidation state)

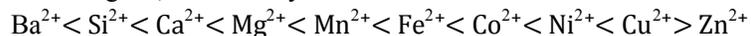
Greater the oxidation state, greater is the attraction of H^+ , so greater is bond, hence the liberation of H^+ ion is not easy.



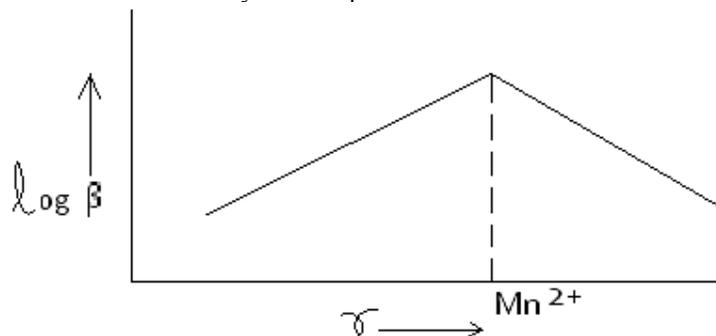
Because oxidation state of N in HNO_3 is greater than HNO_2 and effective charge is less ($-\frac{1}{3}$) than HNO_2 ($-\frac{1}{2}$). The strength of acid and base depends on its conjugate base and acid also.

Conjugate base of strong acid is Weak base. Conjugate base of Weak acid is strong base. Conjugate acid of strong base is Weak acid. Conjugate acid of Weak base is strong acid.

With a particular ligand, the stability of divalent metal cation was found to be



The radius is decreased in above series so stability is going to increase from Mn^{2+} to Zn^{2+} the stability is due to radius as well as CFSE, so we can have a diagram. The above series is known as Irving-Williams series or Natural series of stability of examples :-



HSAB POSTULATES:

- (1) Class (a) metal ions are hard acids
 Class (b) metal ions are soft acids
 Class (a) ligands are hard bases
 Class (b) ligands are soft bases
- (2) The boundary of classification is not rigid Boarder line acids and bases are also exist.
 eg. Soft Cr^{2+} Boarder line Cr^{3+} Hard Cr^{6+}
- (3) Hard acid interacts with hard bases. Soft acid interacts with soft bases.
 Boarder line acid interact with both hard and soft base.
 Boarder line bases interact with both hard and soft acids.
- (4) Hard – hard interaction is stable and is electrostatic in nature.



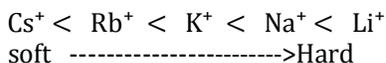
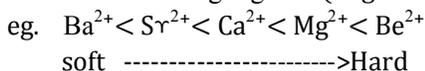
Soft – soft interactions is stable and covalent in nature :



- (5) Hard – Soft interaction is unstable for example - $\text{Ti}(\text{CH}_3)_4$ is unstable.
- (6) Electro negativity is the criteria for saying the hard and soft complexes-

Electro negativity () = ———

If the substance having high (high IP and high E_a) are hard and low are soft.



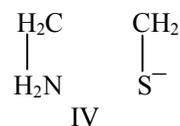
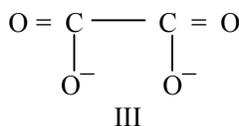
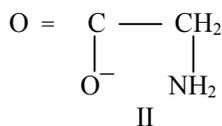
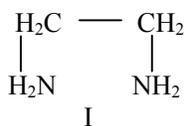
Hardness of $\text{N} < \text{O} < \text{F}$

$\text{N} > \text{P} > \text{As}$

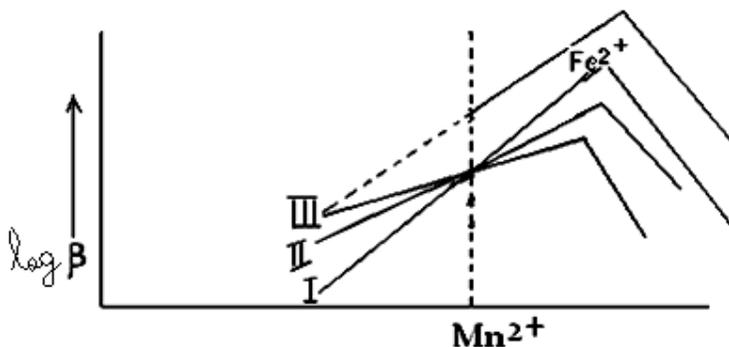
$\text{O} > \text{S} > \text{Se}$

- (7) In addition to π - bonding is also responsible for hardness and softness.
- (8) Electron withdrawing and releasing group is also responsible for hardness and softness.

Examples :-



We can plot a diagram with combination of above ligands with metal ion.



The diagram is known as Irving – Williams diagram and the effect is Irving-Williams effect.

By the Irving – Williams diagram we can classified the metal ion in two classes.

- I. Class (a) and Class (b) Metal Ions
- II. Class (a) and Class (b) Ligands

I Class (a) Metal Ions :

- (i) Alkali metal e.g. Li^+ , Na^+ etc.
- (ii) Alkali earth metal ion eg. Be^{2+} , Be^+ etc.
- (iii) Lower transition metal cations in higher oxidation state eg. Ti^{4+} , V^{5+} , V^{4+} , Cr^{6+} , Mn^{4+}

Class (b) Metal Ions :

- (i) Higher transition metal cations in any oxidation states eg. Pt^{4+} , Ir^{6+} , etc.
- (ii) Lower transition metal cations in low oxidation states eg. Ag^+ , Au^+ , Au^{3+} , Pt^{2+} , Pt^{4+} , Ti^{2+} , V^{2+} , Cr^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} etc.

II Class (a) Ligands :

Ligands which contain N, O, F are placed in class (a) ligand. Eg. NH_3 , RNH_2 , R_2NH , R_3N , H_2O , R_2O , ROH , β^- etc.

Criteria of classification : Those ligand contain non-metal of high electro negativity.

Class (b) Ligands : Ligands which contain P, S, $\text{B}\gamma$, I are places in class (b) ligands, eg. PR_3 , $\text{P}\phi_3$, RsH , R_2S , $\text{B}\gamma^-$, I^- .

Irving – Williams effect.

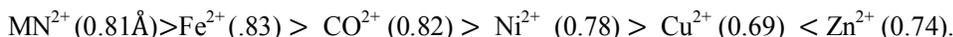
There are several factors which affects the stability of complexes such as –

- (a) Charge and size of metal
- (b) Charge and size of ligand
- (c) Chilate effect
- (d) Electro negativity of the central atom
- (e) Crystal field or Irving – Williams effect

The stabilities of high spin complexes of the ion between Ca^{2+} and Zn^{2+} with a given ligand vary in the order :



This order is known as Irving – Williams order or natural order of stability is consistent with charge to radius ratio concept, since the radii of these ions are in the order –



The high spin complexes of these ions are generally octahedral with exception of those of Cu^{2+} which form tetragonally distorted octahedral complexes.

The relative stability of high spin octahedral $[\text{M}^{\text{II}}\text{L}_6]^{2+}$ complexes of the first row transition elements can be shown by the following graphs :-

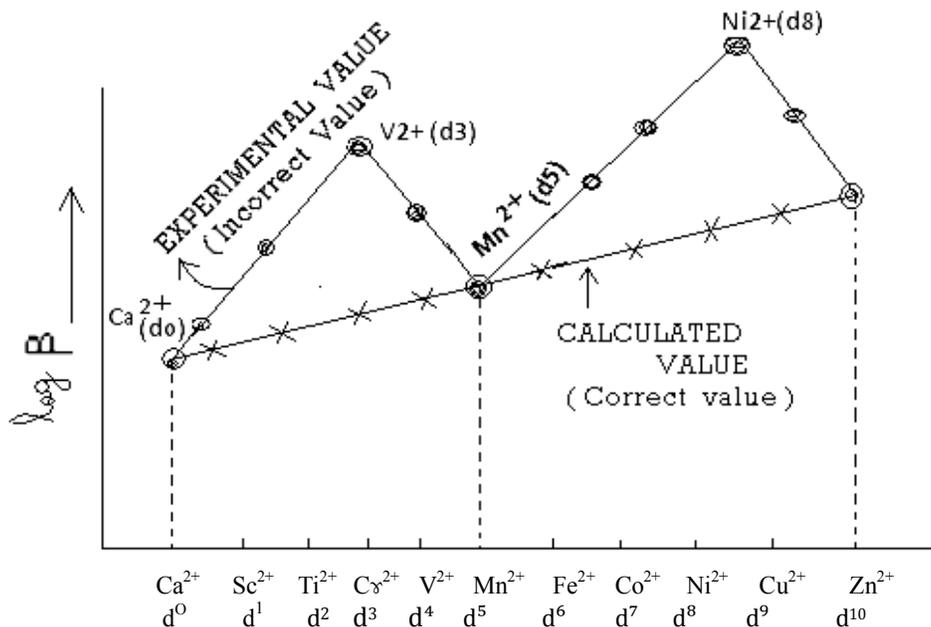
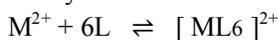


Fig.: The logarithms of stability constants for a series of $[M^{II}L_6]^{2+}$ complexes as predicted by crystal field theory –



$$B = \frac{[ML_6^{2+}]}{[M^{2+}][L]^6}$$

It is clear from the above figure that the octahedral complexes of V^{2+} (d^3 ions) and Ni^{2+} (d^8 ion) ions are the most stable with respect to their neighbours. This is because of the fact that the high spin (weak ligand) octahedral complexes of these ions have the greatest crystal field stabilization energy value.

d^1	$= 0.4 \Delta_0$	$0d^2$	$= 0.8 \Delta_0$
$d^3 (V^{2+})$	$= 1.2 \Delta_0$	$0d^4$	$= 0.6 \Delta_0$
d^5	$= 0.0$	d^6	$= 0.4 \Delta_0$
d^7	$= 0.8 \Delta_0$	$d^8 (Ni^{2+})$	$= 1.2 \Delta_0$
d^9	$= 0.6 \Delta_0$	d^{10}	$= 0.0$

eg. $B(CH_3)_3$ – Soft - CH_3 group is electron releasing.

SF_3 – Hard – F ion is electron withdrawing group.

From the Pauling – Pearson Paradox the stability can be explained i.e. greater the electro negativity difference greater will be the stability of compound.



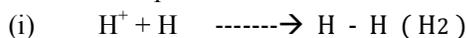
$$\Delta = F - Li \quad \Delta = I - Cs \quad \Delta = Li - I = 205 - 2.0 = 0.5$$

$$= 4 - 2 = 2 \quad = 2.5 - 1.8 = 0.7 \quad \Delta = F - Cs = 4 - 1.8 = 2.5$$

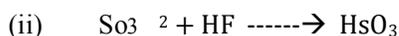
From value data LiF and LiF is the most stable but LiI is also stable. Such interactions give contradictory results.

So, we can say that inherent properties of acid and base dominate not hard – soft concept.

For Example :



Hard Soft



This reaction is also occur due to inherent properties of acid and bases.

d – d transition

The compounds of transition metals are coloured. The colour arises due to d- d- transition which is not shown by non-transition metal compounds. If non-transition metal compounds are coloured the colour is due to structure defect or charge transfer.

Transition metal cations having $d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$ configuration i.e. $Ti^{+3} V^{+3}, Cr^{+3}, Cr^{+2}, Co^{+2} Co^{+1}, Fe^{+2}, Ni^{+2}, Cu^{+2}$ show colour due to d- d transition.

Condition for color of compounds : ----->

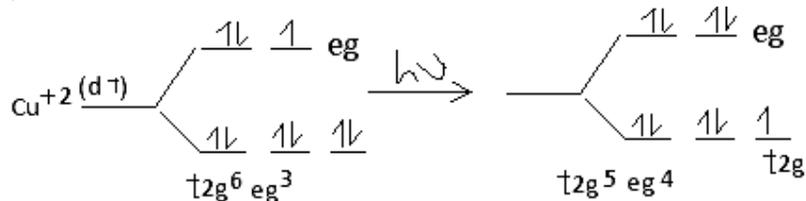
When visible light falls on a compound same light is absorbed and remaining light appears coloured. Thus colour of compound is complementary colour light is energy and so when a substance absorbs light. Electron present in it is excited and moves from lower energy level of compound to its higher energy level. Thus when a substance shows colour, absorption of light and transition of electron must occur.

Colour due to d- d- transition :----->

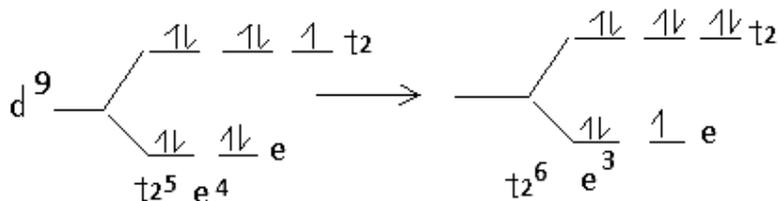
Compound as $CrCl_3, 6H_2O, CrCl_2, 6H_2O, CoCl_2 \cdot 6H_2O, NiCl_2 \cdot 6H_2O, CuSO_4 \cdot 5H_2O, FeCl_2 \cdot 6H_2O,$ etc. show colour due to d- d- transition colour is not so deep.

[The energy of d- orbitals of free ion is same] but in presence of ligands such as H_2O, NH_3, CN etc. the d- orbitals split, due to the splitting of d- orbitals depends on structure i.e. octahedral tetrahedral and square planer arrangement of ligands.

For example when light falls on a compound having octahedral structure eg. $CuSO_4 \cdot aq \rightleftharpoons [Cu(H_2O)_6]^{+2} SO_4^{-2}$, a portion of light is absorbed electron in the lower t_{2g} level get excited and goes to the upper level eg. Thus absorption of light and transition of electrons occurs and $CuSO_4 \cdot aq$ is blue. The transition can shown as :-



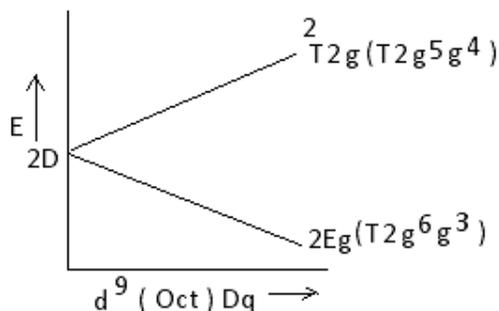
In case of tetrahedral compound as for example $(CuCl_4)^{-2} \cdot 2H^+$ the transition can be shown as



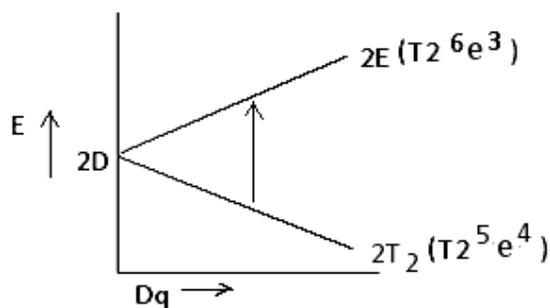
The transition shown in terms of $t_{2g} \text{ eg}$ or t_{2c} is not fully correct. Actually the transition occurs between terms i.e. $Cu^{2+}, d^9 \rightarrow \boxed{\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow}$

Term = 2 D

2 D split in octahedral field as :-

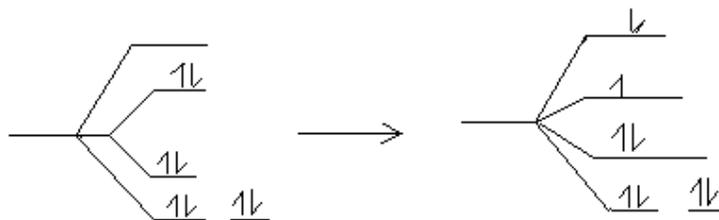


In case of tetrahedral term 2D splits as follows:-

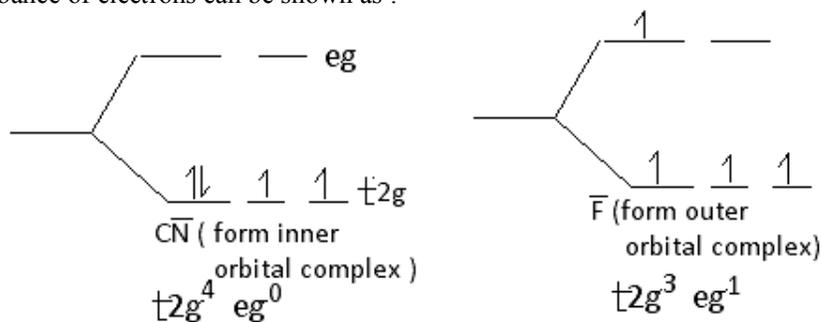


Colour is due to $2E \leftarrow 2T_2$ transition.

In case of square planer, as for example $[\text{Ni}(\text{CN})_4]^{2-}$ the disturbance of electrons and transition can be shown as -

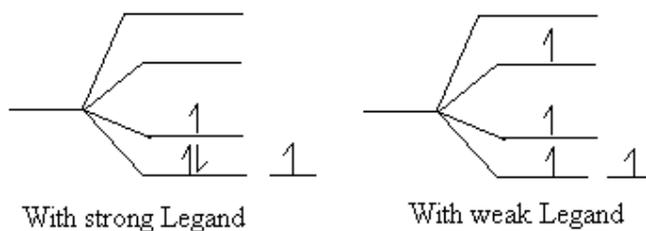


In octahedral field d^4 d^5 d^6 d^7 may have two type of arrangement depending upon the nature of ligand with F^- and CN^- disturbance of electrons can be shown as :-

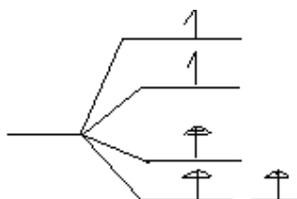
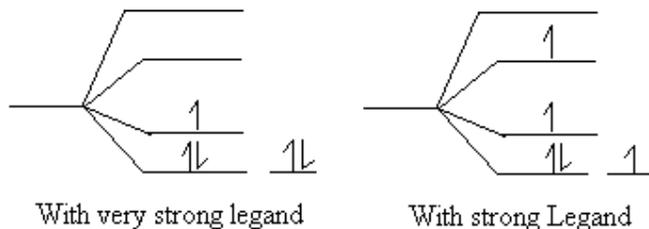


Similarly in square planer have different configuration with strong and weak ligend and d^9 have only one configuration.

Eg. d^4 ----->



d^5 ----->



Configuration are colourless as d-d transition does not occur

Charge transfer spectra :

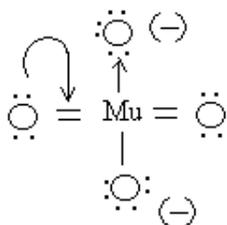
Charge transfer spectra involve a **redistribution** of electron density within a molecule so they are called 'redox spectra'. The existence of charge transfer bonds is connected with the electron donating and accepting properties of the ligand groups and the metal ions. Metal ions are classified according to their oxidizing power and ligand groups according to their "reducing power". For example the series for hex halo complexes are as



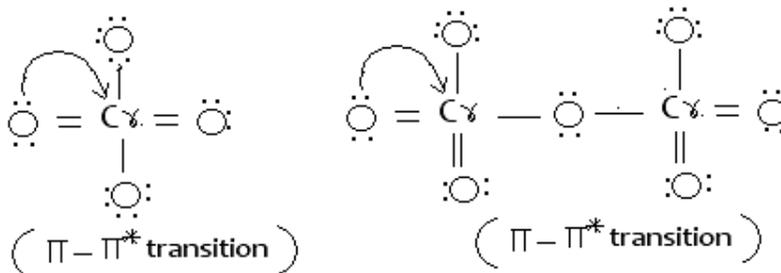
Rules :-

- (1) The greater the **Oxidising** power of the metal ion and the reducing power of the ligand group the lower the energy at which the charge transfer band appear. The charge transfer bands are the transition between molecular, orbitals of the complex ion.
- (2) The term which is result of inter electronic repulsion of molecular orbital is rarely involved in the charge transfer bands.
- (3) There are two broad classes :- ligand to metal ($L \rightarrow M$) and metal to ligand ($M \rightarrow L$). Charge transfer process of higher energy than d - d transition thus they be at the extreme blue red end of the visible spectrum or in ultraviolet region.
- (4) Nearly all absorbed charge transfer transitions are fully allowed i.e. they are $g \leftrightarrow u$ transition with $\Delta S = 0$ and hence the charge transfer band are strong.
- (5) Extension coefficient is $10^3 - 10^4$ or more.
- (6) Many forbidden C.T. transitions which give rise to weak bands, there are seldom observed because they are covered up by the strong C.T. bands.

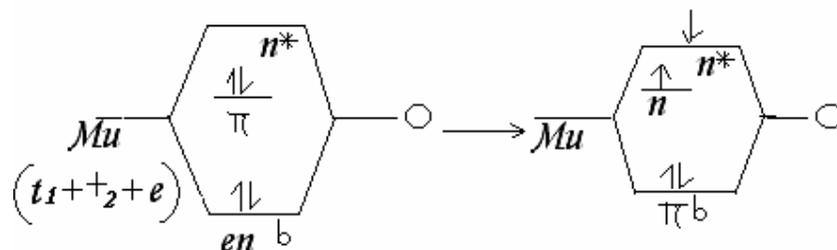
In case of covalent compounds charge transfer occurs, when there is multiple band. For example KMnO_4 can be shown as $\text{K}^+, \text{MnO}_4^-$ charge transfer occurs in MnO_4^- structure of MnO_4^- has $\text{Mn} = \ddot{\text{O}}:$



$\ddot{\text{O}}:\text{Mn} =$, there is $\sigma, \sigma^*, \pi, \pi^*$ and non-bonding orbitals when visible light falls on MnO_4^- , non-bonding electron on O absorbs. So we get light and get excited transition of electrons from π to π^* occurs which gives violet colour to MnO_4^- i.e. KMnO_4 . Similarly colour to $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_2\text{O}_7$ is due to $\pi - \pi^*$



In $Mn = \overset{\cdot\cdot}{O} \left[Mn = Mn, (\sigma) \right]$, The energy levels can be shown as -



L → M Transition in o complexes :

L → M Transition in hexa halo complexes can be shown as -

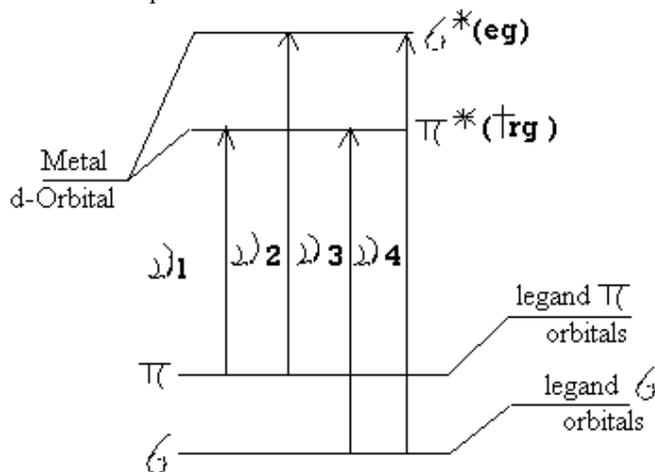


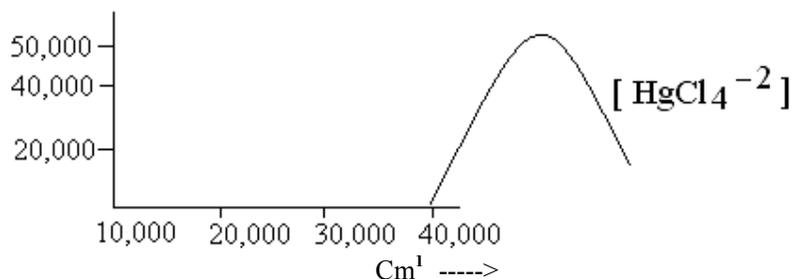
Fig.:- Partial M.O diagram for an $o ML_6$ complexes showing the four main classes of L → M C-T transfer. There are four types of transitions are occur.

- (1) Transition of the U_1 type is of lowest energy not shown by d^6 complexes like $Ir \beta \gamma 6^3$ and $Fe (CN)_6$. This transition is shown by $RuCl_6^{3-}$, $RuCl_6^{2-}$
- (2) Transition of U_2 type give the lowest energy C.T bond in trg^6 complexes (eg $pt x 6^2$ type)
- (3) Transition of the U_3 are broad and weak and are not observed.
- (4) U_4 set transitions is observed in a few case. In many cases they be beyond the range of observation.

L → M Transitions in Tetrahedral complexes:

For tetrahalo complexes eg. $Ni X_4^{2-}$, $Co X_4^{2-}$ and $Mu X_4^{2-}$ species strong L → M CT spectra is observed which is similar to $M X_4^{6+}$ complexes. Examples of L → M CT transitions.

- $HgCl_4^{2-}$ have absorption at 43.700
- $HgBr_4^{2-}$ have absorption at 40.000
- HgI_4^{2-} have absorption at 31.000

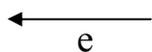


Some other examples of C.T. spectra :-

(a) Brown **rang**in nitrate test due to $L \rightarrow M^{+n} [Fe^{II} NO (H_2O)_5] SO_4$

(b) $[Fe(CN)_6]^{2-}$ is coloured because π^* on CN is empty so $M^{+n} \rightarrow L$ transition occurs
 $III \rightarrow II^+$
 $Fe \leftarrow C \equiv N$

(c) When $FeCl_3$ is treated with $K_4[Fe(CN)_6]$ blue colour is formed due to $L \rightarrow L$ transition



(d) $[(NH_4)_2 S_2]$ is yellow due to charge transfer from S^{2-} to S in S_2^{2-}

(e) In case of metal carbonyls eg $C \rightarrow (CO)_6 MO (CO)_6$ have intense colour due to transition from the bonding (metal) to anti bonding (ligand) components of the metal ligand π bonding interaction.

Usefulness :- Relative hardness of a base can be measured. Reaction enthalpy between hard and soft acid can be predicted.

Mc Daniel diagram and its usefulness :- Pearson had defined and classified acids and bases according to their hardness and softness. Very recently Drago in 1972-73 attempted to quantify the idea. According to HSAB concept a hard acid prefers to combine with a hard base and a soft acid combines with soft base. In a reaction



The enthalpy change of this reaction may be taken as tendency of any base to combine with A_n (hard acid) or A_s (soft acid).

Mc Daniel and Ce-Workers in 1975 chosen hard acid as H^+ and soft acid as CH_3^+ and for different bases heat of reaction were measured and thus affinities of the base towards the both acids were developed and plotted in figure (graph) as shown below :-

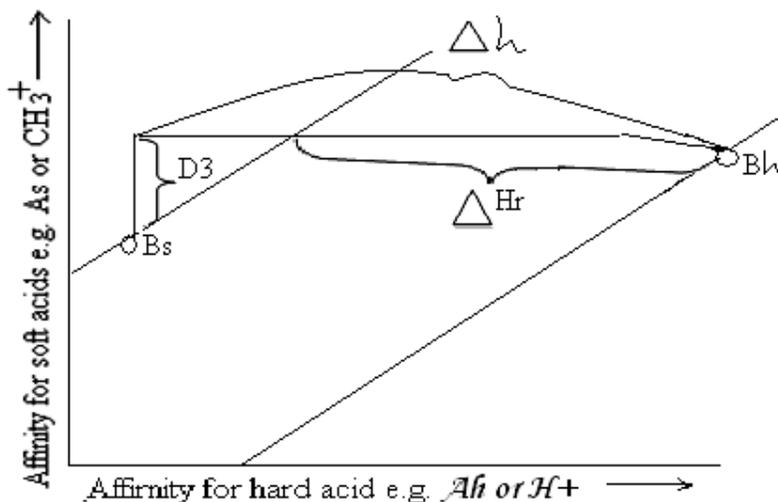
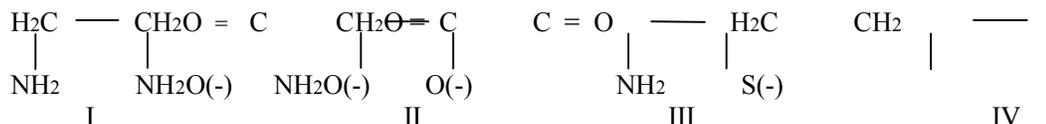


Fig. – Mc Daniel diagram illustrating HSAB parameters

The lines of unit slope can be drawn. The heat of reaction can directly be measured by the distance between these lines in either or - direction further more if two bases were to fall on the same as shown in figure

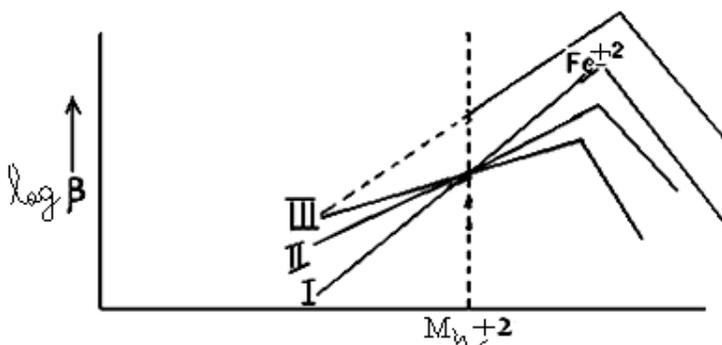
they would be equally soft. If the line for a given base lies above that for another, the first base is softer and the second is harder. Finally since strength is related to the magnitude of acid base interactions the further a given base lies from the origin the harder it is.

Example :-



We can plot a diagram with combination of above ligands with metal ion.

The diagram is known as IRWING WILLIAMS diagram and the effect is known as Irwing William effect.



By the Irwing Williams diagram we can classified the metal ion in two classes :-

1. Class (a) and Class (b) metal ions
2. Class (a) and Class (b) ligends.

I Class (a) Metal Ions :

- (i) Alkali metal Cations e.g. Li^+ , Na^+ etc.
- (ii) Alkaline earth metal ion eg. Be^{2+} , Be^+ etc.
- (iii) Lower transition metal cations in higher oxidation state eg. Ti^{+4} , V^{+5} , V^{+4} , Cr^{+6} , Mn^{+4}
- (iv) Class (b) Metal Ions :
- (v) Higher transition metal cations in any O.S. eg. Pt^{+4} , Ir^{+6} , etc.
- (vi) Lower transition metal cations in low oxidation states eg. Ag^+ , Au^+ , Au^{+3} , Pt^{+2} , Pt^{+4} , Ti^{+2} , V^{+2} , Cr^{+2} , Cr^{+3} , Mn^{+2} , Cu^{+2} etc.
- (vii) II Class (a) Ligands :
- (viii) Ligands which contain N, O, F are placed in class (a) ligand. eg. NH_3 , RNH_2 , R_2NH , R_3N , H_2O , R_2O , ROH , .
- (ix) Criteria of classification : Those ligend contain non-metal of high electro negativity.

Class (b) Ligands : Ligends which contain P, S, B, I are placed in class (b) ligends, eg. PR_3 , $\text{P}\phi_3$, RS_2H , R_2S , $\text{B}\phi_3$, I .

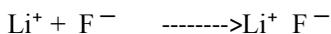
Criteria of classification :-

Those ligand contain lower electro negativity value are placed in class (b) type. Hence we can say that – Class (a) metal ion and class (a) ligend form stable complexes eg. Ti^{+4} can form stable complexes with N, O, I Similarly class (b) metal ion and class (b) ligends can form stable complexes eg. Ag^+ can form stable complexes with R_2S , R_2O etc.

To explain stability of complexes Pearson classified Metal ion and ligend as Hard Soft metal ions and ligend.

Postulates :-

- (1) Class (a) metal ions are hard acids
 Class (b) metal ions are soft acids
 Class (a) ligands are hard bases
 Class (b) ligands are soft bases
- (2) The boundary of classification is not rigid boarder line acids and bases are also
 eg. $\text{Cr}^{+2}\text{Cr}^{+3}\text{Cr}^{+6}$
 Soft boarder Hard\
- (3) Hard acid interacts with hard bases. Soft acid interacts with soft bases.
 Boarder line acid interact with both hard and soft base.
 Boarder line bases interact with both hard and soft acids.
- (4) Hard – hard interaction is stable and is electrostatic in nature.



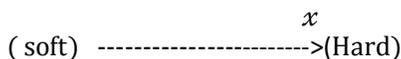
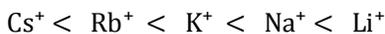
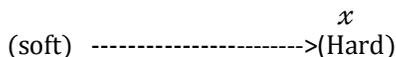
Soft – soft interactions is stable and is covalent in nature :



- (5) Hard – Soft interaction is unstable for example - $\text{Ti}(\text{CH}_3)_4$ is unstable.
- (6) Electro negativity is the criteria for saying the hard and soft complexes-

$$\text{Electro negativity } (x) = \frac{\text{IP} + \text{Ea}}{5.6}$$

If the substance having high x (high IP and high Ea) are hard and low x are soft.
 ex- $\text{Ba}^{+2} < \text{Sr}^{+2} < \text{Ca}^{+2} < \text{Mg}^{+2} < \text{Be}^{+2}$



Hardness of $\text{N} < \text{O} < \text{F}$



- (7) In addition to x, π bonding is also responsible for hardness & softness.
- (8) Electron with drawing & releasing group is also responsible for hardness and softness. Ex. :-
 $\text{B}(\text{CH}_3)_3$ Soft – CH_3 group is electron releasing
 BF_3 – Hard F^- ion is electron withdrawing group.
- (9) From the Pauling Pearson Paradox the stability can be explained i.e. Greater the electro negativity difference greater will be the stability of **compound**.

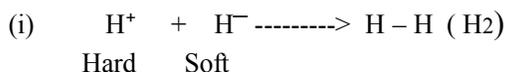


$$\begin{aligned} \Delta x &= x_{\text{F}} - x_{\text{Li}}, \Delta x = x_{\text{I}} - x_{\text{Cs}}, \Delta s = x_{\text{Li}} - x_{\text{I}}, \Delta x = x_{\text{F}} - x_{\text{Cs}} \\ &= 4 - 2 = 2 \qquad = 2.5 - 1.8 \qquad = 2.5 - 2.0 \\ &\qquad\qquad\qquad = 0.7 \qquad\qquad\qquad = 0.5 \qquad\qquad\qquad = 4 - 1.8 \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 2.2 \end{aligned}$$

From the x value data LiF and CsF is most stable but CsI is also stable such interactions gives contradictory result.

So we can say that Inherent properties of acid and base dominate not Hard Soft concept.

For example :-





This k^u is also occur due to inherent properties of acid and bases.

Lability and inertness of complexes.

Ans.:- The term labile and inert show the speed or rates at which the substitution of one ligand by other occurs these terms represent the Kinetics stability of complexes. There is no correlation between thermodynamic and kinetic stability term eg $[\text{Hg}(\text{CN})_4]^{2-}$ which is thermodynamically very stable (formation constant = 10^{42}) is labile. Since in solution it exchanges CN ligands with labeled cyanide ion $^{14}\text{CN}^-$ at a very fast rate.
 $[\text{Hg}(\text{CN})_4]^{2-} + 4 \text{ }^{14}\text{CN}^- \rightleftharpoons [\text{Hg}(^{14}\text{CN})_4]^{2-} + 4 \text{C}^-$

Similarly $[\text{Co}(\text{NH}_3)_6]^{3+}$ which is thermodynamically unstable is remain unchanged in acid solution. The lability of compound depends on the activation energy. Higher the value of activation energy lower will be the lability.

Labile and Inert octahedral complexes according to VBT :-

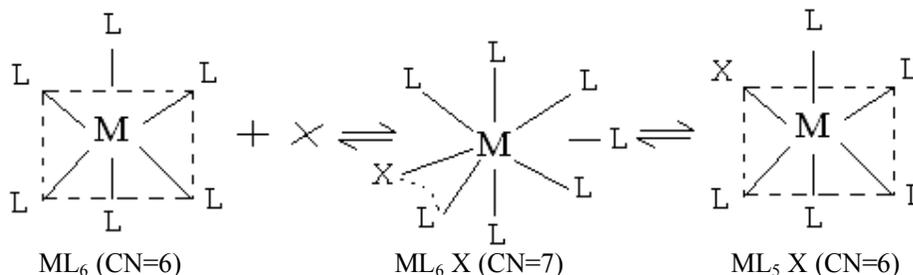
(i) Outer-orbital octahedral complexes :

Outer orbital octahedral complexes (sp^3d^2) hybridization are generally labile because bond of sp^3d^2 is weaker than d^2sp^3 bond. Ex. - $\text{Mn}^{2+}(3d^5)$, $\text{Fe}^{2+}(3d^6)$, Co^{2+} , $\text{Ni}^{2+}(3d^8)$ (Octa).

(ii) Inner orbital octahedral complexes :

The 6 electrons are paired up in t_{2g} set and empty e_g set are left.

(a) In the labile inner orbital octahedral complexes there is at least one d-orbital of t_{2g} set empty so that this empty d-orbital may be used to accept the electron pair from the incoming ligand in forming the transition state (unstable intermediate) with coordination no. 7. The formation of T s can b e shown as



(b) In the inert inner orbital oct. complexes every d-orbital of t_{2g} set contains at least one electron.

Labile and Inert oct complexes according to CFT :-

The octahedral complexes formed by the ions for which there is large loss in CFSE are least labile in such complexes are inert. On the other hand the loss in CFSE is little or no loss the complexes are labile.

Ex. - d^0d^1 and d^2 complexes are labile while d^3 , d^4 , d^5 and d^6 compound is inert order of inertness, $d^6 > d^3 > d^4 > d^5$

Loss in CFSE for SN_1 meeh, -4 O, -2.00 - 1.43 - 0.86

Loss in CFSE for SN_2 meeh-8.52 - 4.26 - 2.98 - 1.70

Hence the order of lability -

$d^6 < d^3 < d^4 < d^5$

Both high spin and low spin octahedral complexes of d^8 ion (eg Ni^{2+}) are inert because there is much loss in CFSE while a/c to VBT d^8 form outer orbital complex which are labile.

Both high spin and low spin oct. complexes of d^{10} ion are labile.

Factors affecting the lability and inertness of complex.

(1) Charge of the Central ion :-

With the increase of the charge of the central metal ion for the iso electronic complexes there is a decrease in lability eg. (a) The lability of complexes $[AlF_6]^{3-}$, $[SiF_6]^{2-}$, $[PF_6]^{-}$ and $[SF_6]^0$ is in the order

Lability order :- $[AlF_6]^{3-} > [SiF_6]^{2-} > [PF_6]^{-} > [SF_6]^0$

Cation charge :- $+3 < +4 < +5 < +6$

(c) The rate of water exchange represented by $[M(H_2O)_6]^{n+} + 6H_2O^* \rightleftharpoons [M(H_2O^*)_6]^{n+} + 6H_2O$ decrease with the increase of cationic charge in the series as rate of water

exchange - $[Na(H_2O)_6]^+ > [Mg(H_2O)_6]^{2+} > [Al(H_2O)_6]^{3+}$

Cationic charge - $+1 < +2 < +3$

(2) Radii of the Central ion :- The lability increases with the increase of ionic radius eg. Order of lability

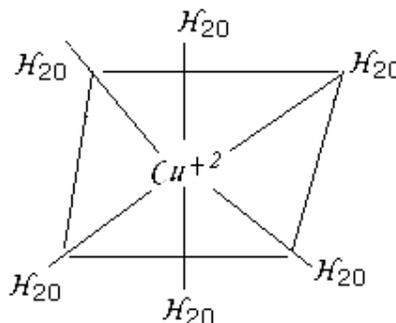
$[Mg(H_2O)_6]^{2+} < [Ca(H_2O)_6]^{2+} < [Sr(H_2O)_6]^{2+}$

Cationic size (Å) $0.65 < 0.99 < 1.130$

(3) Charge to radius ratio values :-

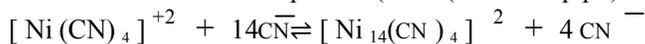
The complexes having the central metal ions with largest charge to radius ratio will react slowest.

Ex. - $[Ni(H_2O)_6]^{2+}$ - d^8 system has largest value of half life. So are inert $[Cu(H_2O)_6]^{2+}$ reacts most rapidly due to the below the square plane of the tetragonally distorted octahedral shape of $[Cu(H_2O)_6]^{2+}$ are water molecule lying in the square plane react slowly



(4) Geometry of the complex :-

The 4 - Co-ordinated complexes (both Td and Sq. pl) are more labile than 6 - Co-ordinated complexes



Draw molecular diagram for an octahedral complex having non-donor non-acceptor ligand.

In Molecular orbital theory the assumption of a point charge model was modified with the inclusion of covalent character symmetry adopted linear combination of ligand orbital give rise to ligand group orbitals and these ligand group orbitals combine with the metal orbitals of proper symmetry and thus bonding anti bonding and new bonding molecular orbitals are formed electrons are filled in these molecular orbitals and thus magnetic and spectral properties are explained. The metal electrons and charge transfer spectra can also be explained on the basis of molecular orbital theory. Although in explaining the properties we arrive to nearly same conclusion as it was in crystal field theory.

The theory can be developed in octahedral complexes where ligand contain only orbital of σ - symmetry containing lone pair. If these orbitals designated as σ_x , σ_{-x} , σ_y , σ_{-y} , σ_z , σ_{-z} .

The symmetry adopted linear combination of these orbitals mainly ligand group orbitals and appropriate symmetry labelling of metal orbitals for first transition series viz (one 4s, three 3p, five 5d) are as follows :-

Symmetry Class	Metal atomic orbitals	Composite of ligand σ - orbitals
A _{1g}	$\Phi 4s$	$\Sigma a = \sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}$

	$\phi_3 dx^2$	$\Sigma x^2 = \frac{1}{\sqrt{5}} (2\sigma_z - \sigma_x - \sigma_y - \sigma_{-x} - \sigma_{-y})$
Eg	$\phi_3 dx^2 - y^2$ $\phi_4 px$	$\Sigma x^2 - y^2 = \frac{1}{\sqrt{5}} (\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$ $\Sigma x = \frac{1}{\sqrt{2}} (\sigma_x - \sigma_{-x})$
T1u	$\phi_4 py$ $\phi_4 pz$	$\Sigma y = \frac{1}{\sqrt{2}} (\sigma_y - \sigma_{-y})$ $\Sigma z = \frac{1}{\sqrt{2}} (\sigma_z - \sigma_{-z})$
T2g	$\phi_3 dxy$ $\phi_3 dxz$ $\phi_3 dyz$	

Table :- Symmetry classification of orbitals for Regular octahedral complexes.

Non-degenerate triply degenerate and doubly degenerate bonding and anti bonding molecular. Orbitals will be produced by combination of orbitals of A_{1g} symmetry, T_{1u} symmetry and E_g symmetry respectively. T_{2g} orbital (Triply degenerate) remain non-bonding. The energy level diagram can be shown below :-

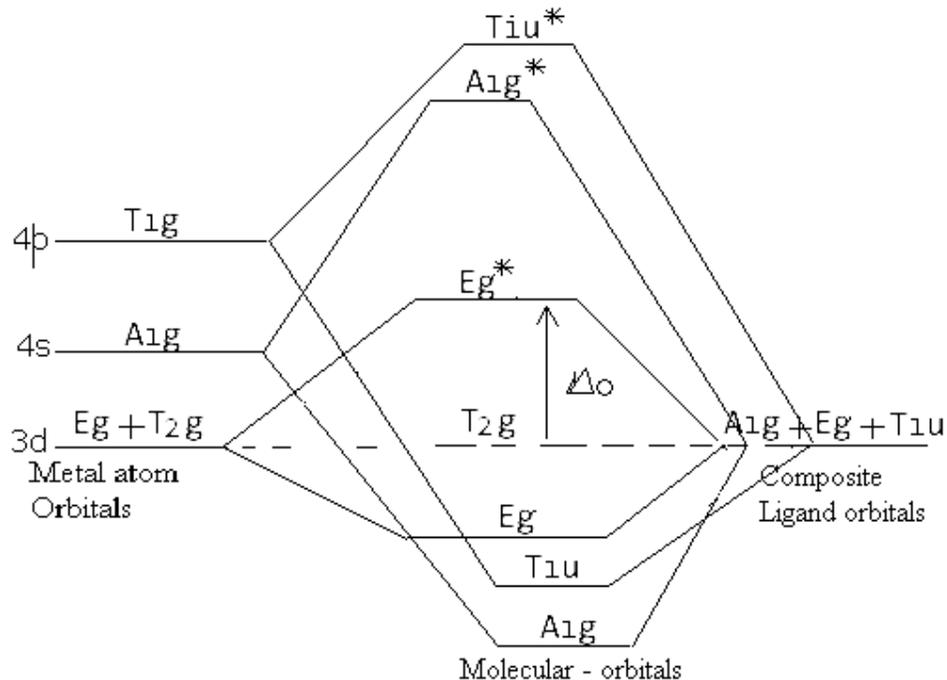


Fig.:- Energy level diagram for a regular octahedral complex.

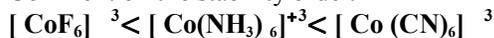
A molecular orbital nearer to ligend group orbital is having mainly ligend character and the orbital nearer to metal atom have mainly metal character.

Spectral and magnitude properties can be explained by filling electron in usual way.

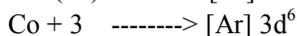
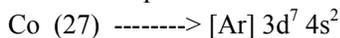
The electron in e_g , t_{2g} , e_g are mainly ligand electrons. Metal electrons distributed in t_{2g} and e_g^* orbitals just in a similar manner as it was in crystal field theory.

Lability and inertness of a complex can also be explained on the basis of above diagram.

Comment on the stability order.

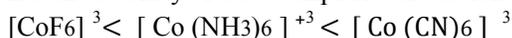


All the complexes of Co are octahedral in which Co is in +3 Oxidation state.

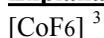


Hence it is a d^6 system.

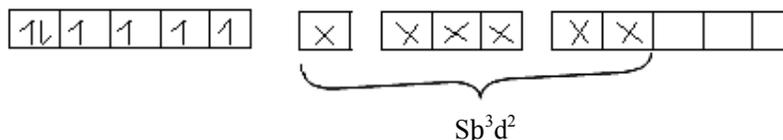
But the stability of Co - complexes are as follows :-



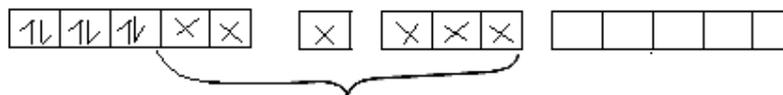
Explanation on the basis of VBT :-



Since F is a weak ligand so it can not force the 3d electron to pair up. Each F gives a pair of electron and are accommodated by six sp^3d^2 orbitals. sp^3d^2 hybridization gives octahedral structure.



This is high spin and outer orbital complex, hence labile and can take part in reaction. In case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{CN})_6]^{3-}$ Since both NH_3 and CN^- is strong ligands so pairing of electron occurs.

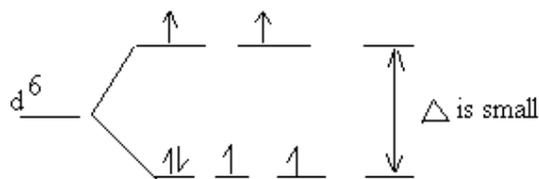


d^2sp^3 hybridization gives rise to octahedral structure both are low spin complex and inner orbital complex so their lability reduced as compared to $[\text{CoF}_6]^{3-}$ and they do not take part in reaction so rapidly.

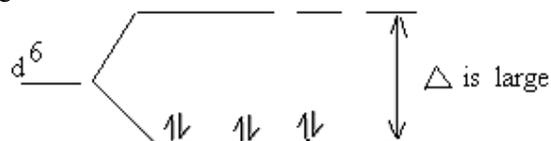
Explanation on the basis of CFT:-



Since F is weak ligand so CFSE is small. Therefore electrons in eg orbital are not forced to pair - up. The configuration remain same as shown below :

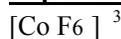


While in case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{CN})_6]^{3-}$ NH_3 and CN^- both are strong ligand so electrons in orbital are forced to pair up with t_{2g} electron. Hence configuration is like this :-

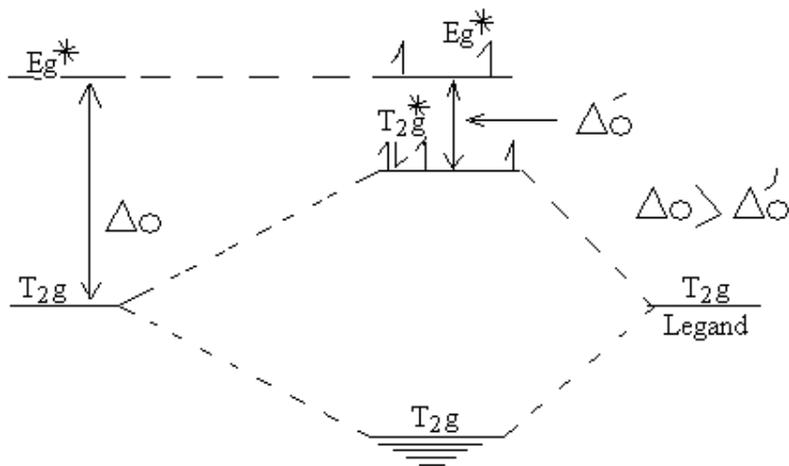


From CFT it can be said that complex having larger value of Δ , greater will be the stability. But above two theory do not give satisfactory reason of stability of above co-complexes, we can explain it by molecular orbital theory.

Explanation on the basis of MOT :-

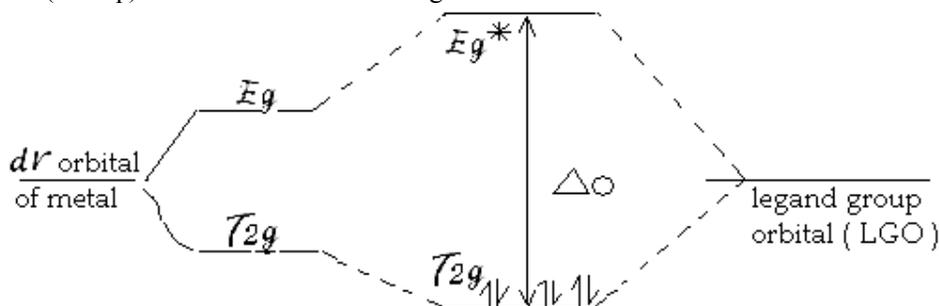


There occurs π - bonding in this complex. Here F^- acts as donor ligand. The $p\pi$ orbitals are filled and of lower energy than the metal T_{2g} orbital. In this case the latter orbitals are destabilized relative to E_g^* - orbital and hence the value of Δ_o is diminished.

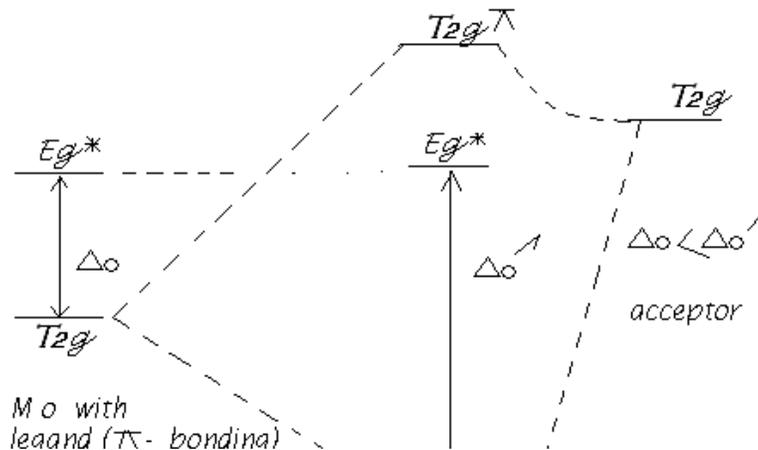


In case of $[Co(NH_3)_6]^{3+}$

This is the case of octahedral which containing only σ - bonding. Thus the energy between lower T_{2g} of metal and E_g^* is Δ_o ($10 Dq$). The molecular orbital diagram is shown below :-



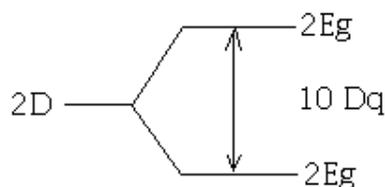
In case of $[Co(CN)_6]^{3-}$:- Here the ligand CN^- acts as acceptor ligand. So of higher energy than the metal ion T_{2g} orbital. The splitting of T_{2g} orbital into T_{2g}^b and T_{2g}^* MO on combining with the π - orbitals (of T_{2g} symmetry) take place as shown below. In this case the net result of π - interaction is that the metal T_{2g} orbital are stabilized relative to E_g^* molecular orbitals.



This from the MOT consideration it can be seen that the value of Δ_0^1 is less than Δ_0^1 (10 Dq) in case of $[\text{CoF}_6]^{3-}$ and in case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ the value of Δ_0^1 is equal to 10 Dq while in case of $[\text{Co}(\text{CN})_6]^{3-}$ the value of Δ_0^1 is greater than Δ_0^1 (10 Dq) and we know that greater the value of Δ_0^1 greater will be the stability hence the stability order is as follows :-

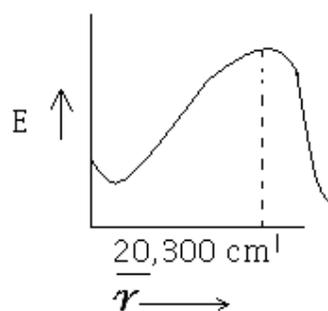


Comment on E-value... $[\text{CoF}_6]^{3-}$ shape of bond 10 Dq value and CFSE for T1^{0+3} aq and Cu^{+2} aq
 T1^{0+3} aq is d^1 system. The Diagram is as follows :-



Transition is $\text{T}2g \rightarrow 2Eg$

The peak obtained at $20,300 \text{ cm}^{-1}$ can be represented as -



i) The transition is Laporte forbidden because the ground state and excited state both have parity g \rightarrow g transitions are Laporte forbidden transitions. But it is spin allowed transition. Such transition has

(ii) This transition occurs at 10 Dq so $10 \text{ Dq} = 20,300 \text{ cm}^{-1}$

(iii) Shape of Bond :- Due to Jahn Teller distortion, two closely shaped peaks are expected :-

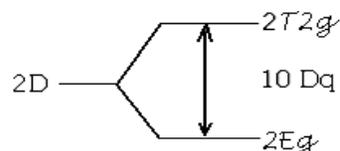
Due to merger of these two peaks a broad and peak observed.

(iv) CFSE : It is energy difference between centre and the ground state which in case of $[\text{T1}(\text{H}_2\text{O})]^{+3}$ is 4 Dq thus the value will be

$$20,300 \times \frac{4}{10} = 8,120 \text{ cm}^{-1}$$

$\text{CFSE} = 8120 \text{ cm}^{-1}$

Cu^{+2} is a d^9 system. The Orgel diagram is as follows :-



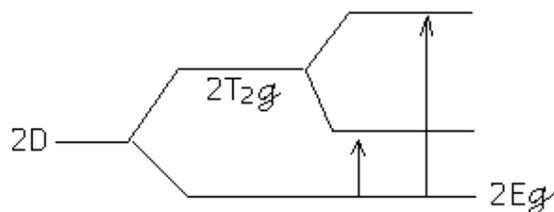
The transition is $2Eg \rightarrow 2T2g$ and the peak obtained at $12,00 \text{ cm}^{-1}$ is as shown below :-



- (i) - Value :- The transition is laporte forbidden because the ground state and excited state both have parity g \rightarrow g transition are laporte forbidden transition but it is spin allowed transition. Such transition has value $1 \sim 10$.
- (ii) Dq Value :- This transition occur at $10 Dq$ so

$$10 Dq = 12,000 \text{ cm}^{-1}$$

- (iii) Shape of bond :- Due to John-Teller distortion, two closely spaced peaks are expected.



But, due to merger of these two peaks a broad and asymmetry peak is observed.

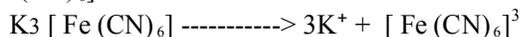
- (iv) CFSE : It is energy difference between barricentre and the ground state which in case of $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$ is $6 Dq$. Thus the value will be -

$$12,000 \times \frac{6}{10} = 72,00 \text{ cm}^{-1}$$

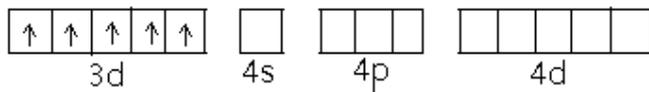
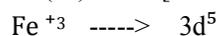
$$\text{CFSE} = 72,00 \text{ cm}^{-1}$$

Aqueous solution of $\text{K}_3 [\text{Fe}(\text{CN})_6]$ is poisonous but of $\text{K}_4 [\text{Fe}(\text{CN})_6]$ is not .

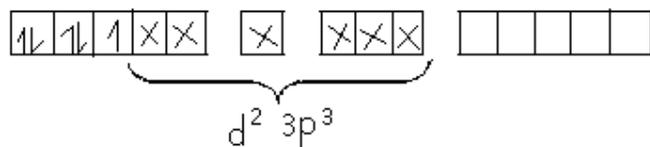
In case of $\text{K}_3 [\text{Fe}(\text{CN})_6] \rightarrow$



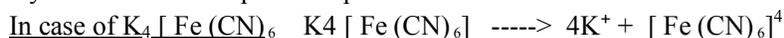
Here, Fe is in +3 oxidation state



Since CN is strong ligand so electrons present in orbitals are forced to pair up.



Hybridization is $d^2 sp^3$ so shape is octahedral.



In this compound Fe is in +2 oxidation state so it is d^6 system :-



$$3T_{1g}(F) \text{ -----} \rightarrow 3A_{2g}(F) = 3$$

In the spectra of above complex two peaks, one at 17,200 cm⁻¹ and the another at 25,000 cm⁻¹ are observed. It is quite obvious that one peak among the above there is missing. It is reasonable gases that 3T_{1g}(F) -----> 3A_{2g}(F) will be missing because –

- (i) it involves two electron transition.
- (ii) It is out of range because it occurs at 35,000 cm⁻¹ whereas nearer to charge transfer bond.

Therefore, two peaks are assigned as :-

$$3T_{1g}(F) \text{ -----} \rightarrow 3T_{2g}(F) = 17,200 \text{ cm}^{-1}$$

$$3T_{1g}(F) \text{ -----} \rightarrow 3T_{2g}(P) = 25,600 \text{ cm}^{-1}$$

The ratio :-

$$\frac{3T_{1g}(F) \text{ -----} \rightarrow 3T_{1g}(P) = 25,600}{3T_{1g}(F) \text{ -----} \rightarrow 3T_{2g}(F) = 17,200} = 1.49$$

From the Tanabe Sugano diagram it can be calculated that the ratio 1.49 comes at

—

At this value of Δ/B ; the transition 3T_{1g}(F) -----> 3T_{2g}(F) is observed. At E / B = 25.9 the energy in the spectrum is 17,200cm⁻¹

—

∴ B = _____ therefore,

$B = 664 \text{ cm}^{-1}$

Thus putting the value of B in equation (i) we have Δ value :-

$$\begin{aligned} \Delta &= 2.8 \times B \\ &= 2.8 \times 664 \\ &= 1859.2 \text{ cm}^{-1} \end{aligned}$$

$$\therefore \boxed{10Dq = 1859.2 \text{ cm}^{-1}}$$

Using the data obtained for 10 Dq and B we can calculate the transition 3T_{1g}(F) -----> 3A_{2g}(F). It will be found to occur at about 36,000 cm⁻¹ we get a peak at that point which indicate that the above calculation is correct.

Calculation of CFSE :

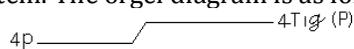
CFSE is the energy difference between barricentre and the ground state which is 6 Dq in this case :-

$$\begin{aligned} \text{CFSE} &= 1859.2 \times 6 \\ &= 11155.2 \text{ cm}^{-1} \end{aligned}$$

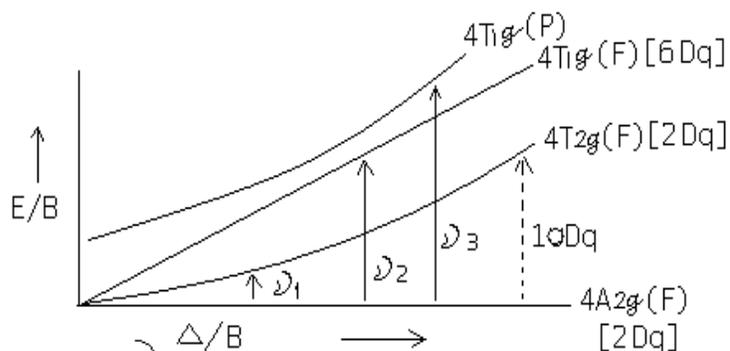
∴

$\text{CFSE} = 11155.2 \text{ cm}^{-1}$

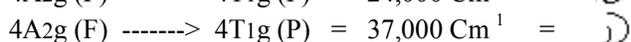
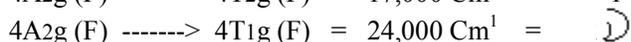
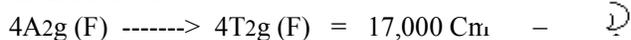
C_{Cr}⁺³ aq = C_{Cr}⁺³ aq the ion is [C_{Cr} (H₂O)₆]⁺³. It is d³ system. The Orgel diagram is as follows :-



Following are the transitions expected in this case :-



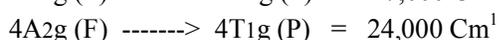
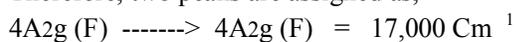
Transitions are :-



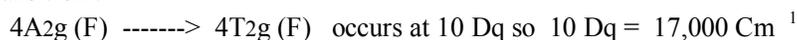
In the spectra of above complex, two peaks at $17,000 \text{ Cm}^{-1}$ and $24,000 \text{ Cm}^{-1}$ is observed. It is quite obvious that one peak among the above three, is missing. It is reasonable guess that $4A_{2g}(F) \rightarrow 4T_{1g}(P)$ will be missing because –

(i) This transition occurs at $37,000 \text{ Cm}^{-1}$ which is charge transfer (C.T.) region so it is out of range.

Therefore, two peaks are assigned as,



Rest Transition :



The ratio



$$= 1.58$$

From the Tanabe Sugano diagram it can be calculated that the ratio 1.58 comes at

$$\frac{17,000 \text{ Cm}^{-1}}{B} = 2.45$$

$$\Rightarrow \boxed{B = 6.95 \text{ Cm}^{-1}}$$

By using the data obtained for $10 Dq$ and B we can calculate the transition $4A_{2g}(F) \rightarrow 4T_{1g}(P)$. It will be found to occur at about $37,000 \text{ Cm}^{-1}$ we get a peak at that point which indicates that the above calculation is correct.

Calculation of CFSE :-

CFSE is the energy difference between barricentre and the ground state which is $12.Dq$

$$CFSE = 17,000 \times 12 / 10$$

∴

$$\boxed{CFSE = 20,400 \text{ Cm}^{-1}}$$

TRANSITION METAL CO-ORDINATION CHEMISTRY PART-III

GENERAL FEATURES OF ORGAL DIAGRAM

- (1) d^n & d^{10-n} has same ground state term (free ion term). It means d^1 and d^9 , d^2 and d^8 , d^3 and d^7 , d^4 and d^6 have same ground state term.
- (2) S and P free ion term do not split. D field ion term splits into T_2 and E crystal field term. field ion term F splits into T_1 , T_2 , and A_2 crystal field terms i.e.

Free ion terms	-----	C.F. terms
S & P terms	-----	do not split
D	-----	T_2 and E
F	-----	$T_1, T_2, \& A_2$
- (3) Free ion terms and crystal field terms have same multiplicity.
- (4) Octahedral symmetry give rise to gerade term. Tetrahedral symmetry has no centre of symmetry thus it gives neither gerade (g) nor ungerade (u) terms.
- (5) Tetrahedral and octahedral symmetry have reverse splitting.
- (6) d^n & d^{10-n} have reverse splitting patterns. It means d^1 and d^9 , d^2 and d^8 , d^3 and d^7 , d^4 and d^6 have reverse splitting pattern.
- (7) d^n & d^{n+5} have same splitting pattern. It means d^1 & d^6 , d^2 & d^7 , d^3 & d^8 , d^4 & d^9 have same splitting pattern.
- (8) Free ion form & transforms into A_1 and free ion term 'P' transforms into T_1 , crystal field terms,
- (9) Terms of the same symmetry are mixed together for e.g. $3T_{1g}$ (P) & $3T_{1g}$ (F) are mixed together. As a result of this energy of $3T_{1g}$ (P) is increased & that of $3T_{1g}$ (F) is decreased, only those transitions are allowed which is non parity change. It means for transition ground & excited state must have different parity.

We know that s, p, d, f have different parity i.e. s \rightarrow g, p \rightarrow u, d \rightarrow g, f \rightarrow u. then according to this rule s \rightarrow p, p \rightarrow d, d \rightarrow p are only allowed transitions.

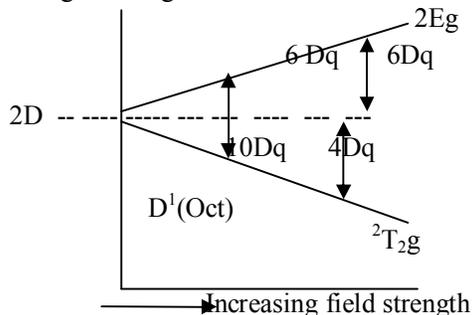
In tetrahedral d - d transition is not laporte forbidden because there is not any parity i.e. u and g terms. But in octahedral d - d transitions are laporte forbidden because it involves same parity i.e. g terms. This intensity of d - d transition in octahedral complexes are faint while intensity of d - d transition in tetrahedral complex are dense.

- (2) Symmetry selection rule :- A/c to this rule, those transition are only symmetrically allowed transition in which ground and excited states have same multiplicity. It means $\Delta S = 0$.

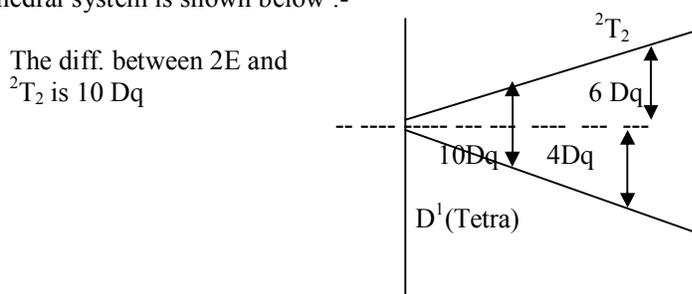
Where ΔS = diff. between the multiplicities of ground and excited states

CO-ORDINATION NUMBER (ORGAL DIAGRAM)

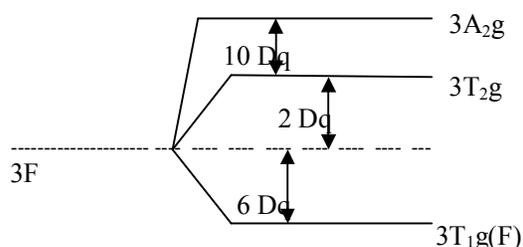
- (i) O.D. for d^1 system :- In the case of d^1 system the free ion term is 2D O the approach of octahedral crystal field it splits into ${}^2T_{2g}$ and $2E_g$ which are known as crystal field terms. The variation in the energy of crystal field terms with increasing field strength for d^1 system is shown below :-
The difference between $2E_g$ and ${}^2T_{2g}$ is $10 Dq$



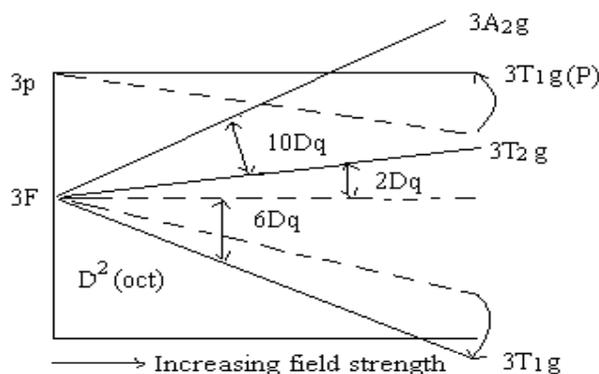
In this case, on the approach of tetrahedral crystal field $2D$ splits into $2E$ and 2T_2 known as crystal field terms. The variation in the energy of crystal field terms with increased field strength for d^1 tetrahedral system is shown below :-



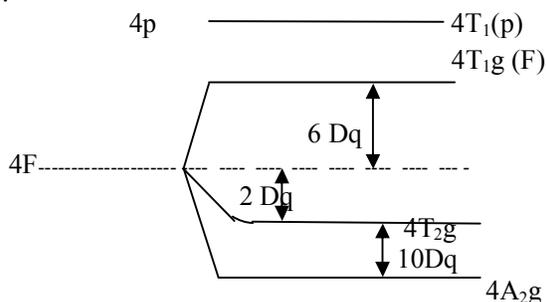
(2) Orgal diagram for d^2 :- In the case of d^2 system the free crystal ion term is $3F$ and $3p$. On the approach of octahedral crystal field, $3F$ splits into $3T_{1g}$, $3T_{2g}$, and $3A_{2g}$. $3p$ does not split but it is transformed into $3T_{1g}(p)$. It is shown below :-



Terms of same symmetry are mixed together. As a result of this the energy of $T_{1g}(p)$ is increased and energy of $T_{1g}(F)$ is decreased. The variation in the energy of crystal field terms with increasing field strength d^1 octahedral system



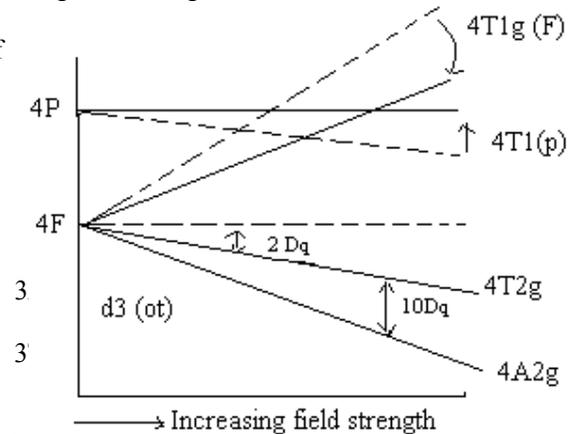
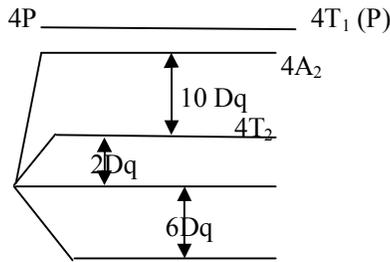
(3) Orgal diagram for d^3 :- in the case of d^3 system, the free ion term is $4F$ and $4P$. On the approach of octahedral crystal field, it splits into $4A_{2g}$, $4T_{1g}$ crystal field terms, $4P$ does not split but it is transformed into $4T_{1g}$. It is shown as :-



Terms of the same symmetry i.e. $4T_{1g}(F)$ & $4T_{1g}(P)$ are mixed together. As a result the energy of $4T_{1g}(P)$ is increased while that of $4T_{1g}(F)$ is decreased.

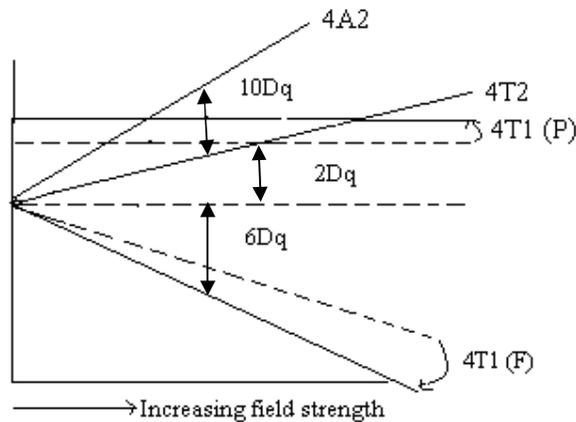
The variation in the energy of crystal field terms with increasing field strength is shown below :-

On the approach of tetrahedral crystal field the splitting of $4F$ is reversed to that of the octahedral i.e. it is $4T_1$, $4T_2$, $4A_2$, $4P$ transforms into $4T_1$. It is shown as :-



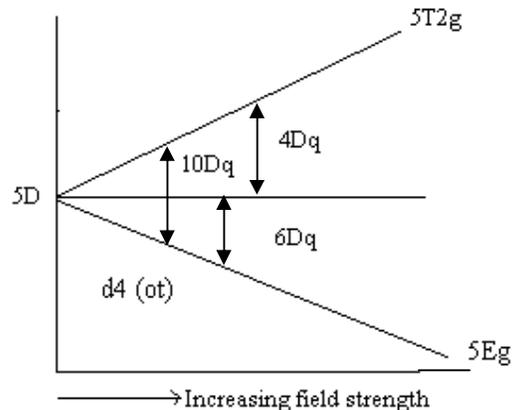
Terms of the same symmetry i.e. $4T_1(P)$ and $4T_1(F)$ are mixed together. As a result the energy of $4T_1(P)$ is increased and that of $4T_1(F)$ is decreased.

This variation in the energy of crystal field terms with increasing field strength is shown below



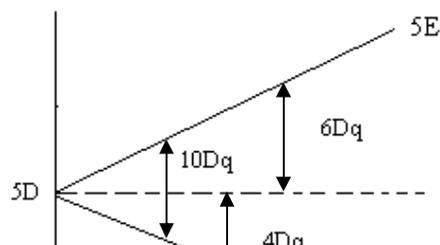
Orgal diagram for d^4 :- In this case the free ion term is $5D$. On the approach of octahedral crystal field it splits into $5E_g$ and $5T_{2g}$ crystal field terms. The variation in the energy of crystal field terms with increasing field strength is shown below :-

The diff. between $5T_{2g}$ and $5E_g$ is $10Dq$



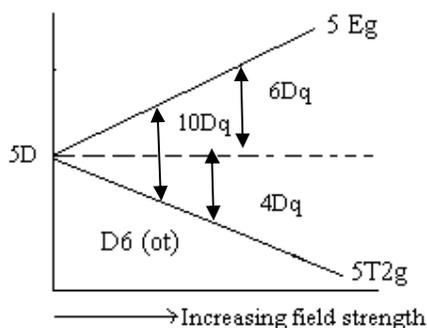
On the approach of tetrahedral crystal field $5D$ splits into $5T_2$ and $5E$ crystal field terms. The variation in the energy of crystal field term with increasing field strength is shown below :-

The diff. between $5E$ & $5T_2$ is $10Dq$

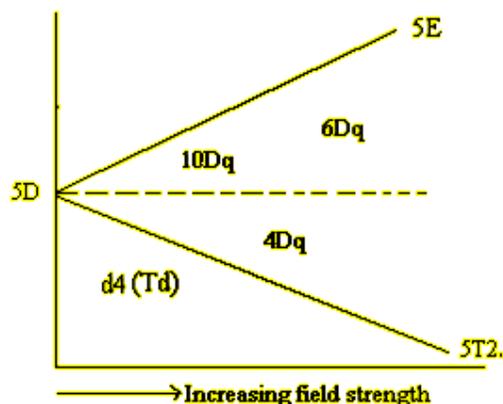


Orgal diagram for d6 :- In the case of d6 system the free ion term is 5D. On the approach of octahedral crystal field 5D splits into 5T_{2g} & 5E_g crystal field terms. The variation in the energy of crystal field term with increasing field strength is shown below :-

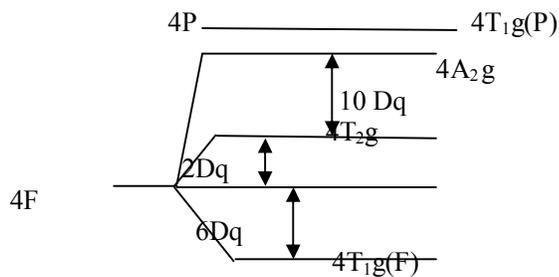
The difference between 5 E_g & 5 T_{2g} is 10 D_q



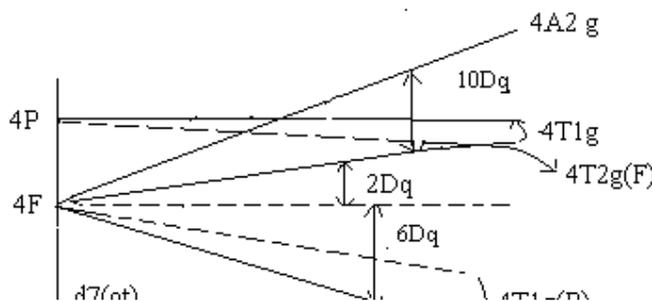
On the approach of tetrahedral crystal field 5D splits into 5E & 5T₂ crystal field terms. The variation in the energy of crystal field terms with increasing field strength is shown below :-



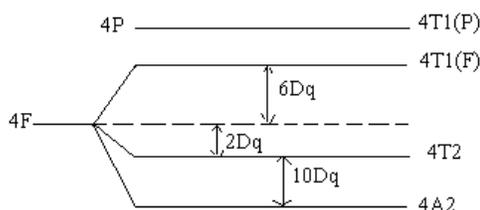
Orgal diagram for d⁷ :- In the case of d⁷ system the free ion term is 4F & 4P. On the approach of octahedral crystal field, 4F splits into 4T_{1g}, 4T_{2g}, and 4A_{2g}, 4P does not split but transform into 4T_{1g}. It is shown below :



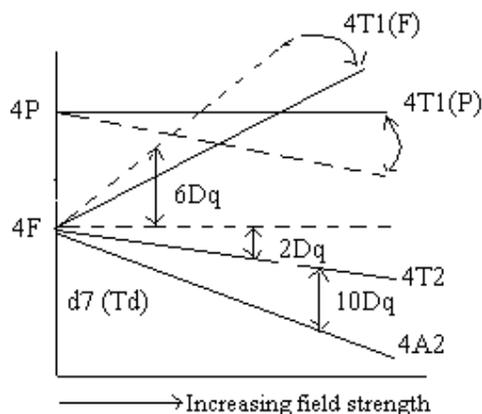
Terms of same symmetry i.e. 4T_{1g}(P) & 4T_{1g}(F) are mixed together. As a result of this, energy of 4T_{1g}(P) is increased and energy of 4T_{1g}(F) is decreases. The variation in the energy of crystal field terms with increasing field strength is shown below :-



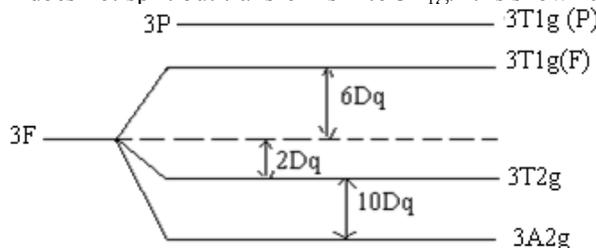
On the approach of tetrahedral crystal field 4F splits into $4A_2$, $4T_2$ and $4T_1$ crystal field terms. 4P does not split but transforms into $4T_1$. It is shown as :-



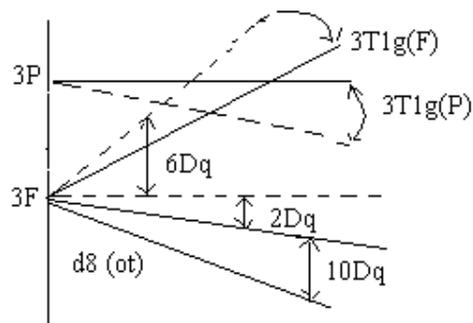
Terms of same symmetry are mixed together. As a result of this energy of $4T_1$ (F) is decreased while that of $4T_1$ (P) is increased. The variations in the energy of crystal field terms with increasing field strength is shown below-



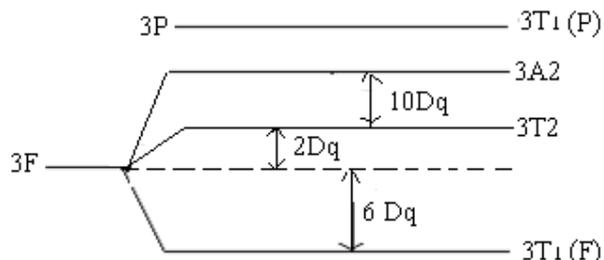
Orgal diagram for d^8 :-In the case of d^8 system, the free ion term is $3F$ & $3P$. On the approach of octahedral crystal field, $3F$ splits into $3A_{2g}$, $3T_{2g}$ and $3T_{1g}$, $3P$ does not split but transforms into $3T_{1g}$. It is shown as :-



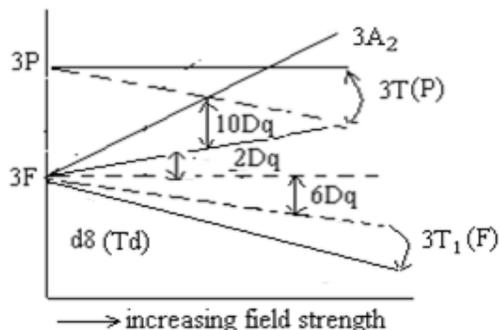
Terms of same symmetry i.e. $3T_{1g}$ (P) & $3T_{1g}$ (F) are mixed together. As a result energy of $3T_{1g}$ (P) is increased and energy of $3T_{1g}$ (F) is decreased. The variations in the energy of crystal field terms with increasing field strength is shown as :-



On the approach of tetrahedral crystal 3F splits into 3T₁, 3T₂ & 3A₂. 3P does not split but transforms into 3T₁. It is shown in Terms of the same symmetry i.e. 3T₁(P) and 3T₁(F) are mixed together :-

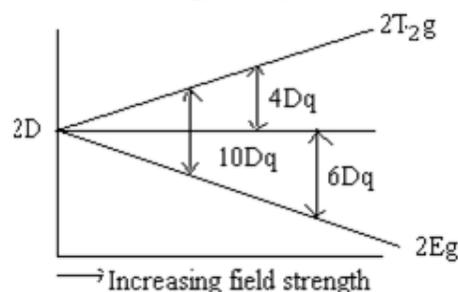


As a result of this energy of 3T₁(P) is increased and that of 3T₁(F) is decreased. The variations in the energy of crystal field terms with increasing field strength is shown as :-

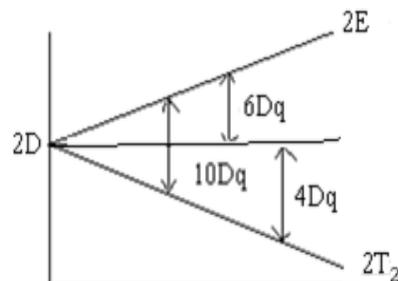


Orgal diagram for d⁹ :- In the case of d⁹ system, the free ion term is 2D on the approach of octahedral crystal field, 2D splits into 2Eg and ²T_{2g} crystal field terms. The variation in the energy of crystal field terms with increasing field strength is given below :-

The difference between 2Eg and 2T_{2g} is equal to 10Dq.



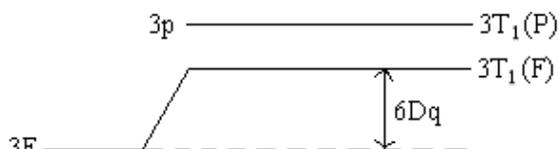
On the approach of tetrahedral crystal field 2D splits into ²T₂ and 2E crystal field terms. The variation in the energy of crystal field terms with increasing field strength is shown as -



Orgal diagram for d⁵ and d¹⁰ :-

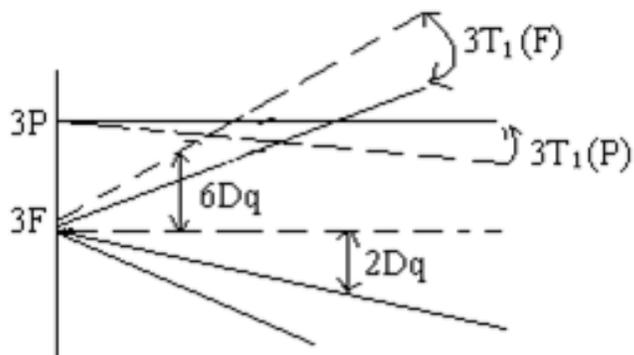
For d⁵ only one term 6 s is obtained which is transformed into 6A_{1g}. For d¹⁰ only one free ion term 1s is obtained, which transforms into A_g. Therefore orgal diagram for d⁵ and d¹⁰ is not possible.

❖ d²(Td) :- On the approach of tetrahedral crystal field 3F splits into 3A₂, 3T₂ and 3T₁, 3p does not split but transforms into 3T₁. It is shown as :-



The terms of same symmetry i.e. $3T_1(F)$ and $3T_1(P)$ are mixed together as a result of which energy of $3T_1(F)$ is decreased and that of $3T_1(P)$ is increased.

The variation in the energy of crystal field terms with increasing field strength as shown below :-



TRANSITION METAL CO-ORDINATION CHEMISTRY PART-IV

A complex ion is formed by the combination of more than two independent existing species. Example –

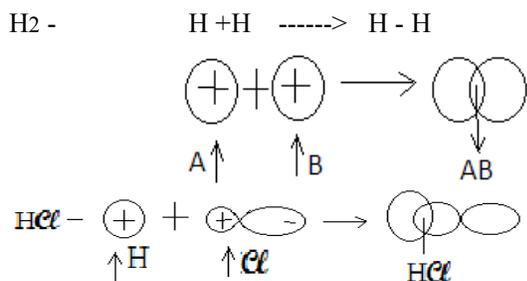


we have to study of theories:

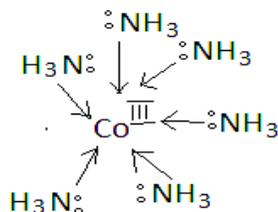
(i) VBT (ii) CFT (iii) MOT (iv) Ligand field model

Pauling who proposed Helical model of atom also gave Electro neutrality principle

VALENCE BOND THEORY OF COMPLEXES :-



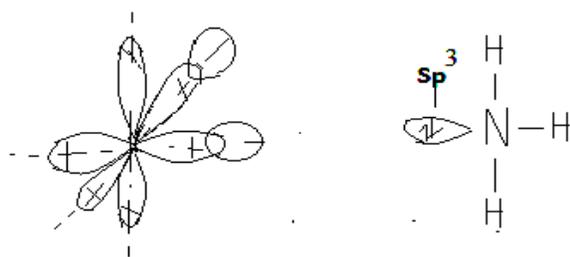
[Co (NH₃)₆]⁺³ 3 Cl⁻ (Octahedral)



Co-ordinate bonds are 6- bond & therefore the no. of 6- bonds in this complex =6

6 orbitals on Co(III)

d² sp³



d² sp³ Orbital

Valence bond is explained simply as

BOX DIAGRAM

[Co (NH₃)₆]³⁺

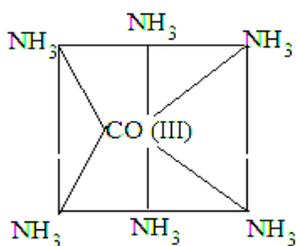
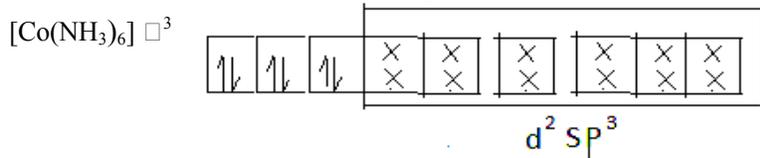
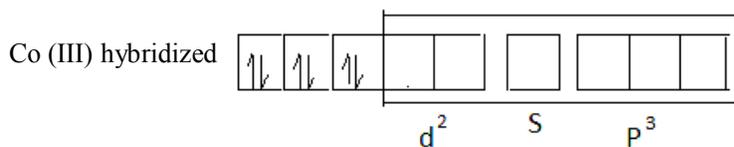
Co (27) -----> 3d⁷ 4s²

Co (III) -----> 3d⁶

191



Co (III) excited

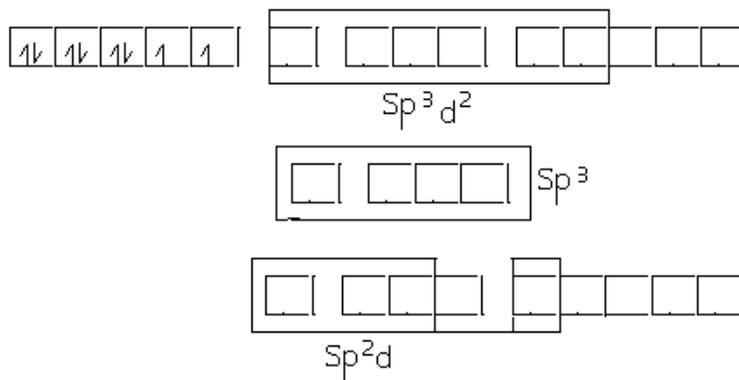


Structure :- Octahedral
Dia magnetic
Inner orbital complex

Inner orbital complex is more stable due to low energy level d- orbital.

DEFECTS OF VALENCE BOND MODEL :-

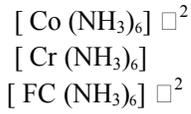
1. Fails to explain colour
2. Even though a system may have Ni(II) Oct. Same no. of unpaired electrons, they Ni(II) Tet. Differ slightly in magnetic moment Ni(II) Sq.pl.



3. $[\text{Co}(\text{CN})_6]^{3+}$
Inner orbital complex
Why CN^- forms inner orbital complex
Whereas F^- forms outer orbital complex.
Can not explain through VB – model.

$[\text{CoF}_6]^{3+}$
Outer orbital complex

- 4 $[\text{Co}(\text{NH}_3)_6]^{3+}$
 $[\text{Fe}(\text{CN})_6]^{3+}$
 $[\text{Cr}(\text{NH}_3)_6]^{3+}$ } Inert complex



When they put into water after some time they dissociate into their ions & so they are labile complexes.

Outer orbital complex :- labile .

Inner orbital complex : If empty

Orbital = Labile.

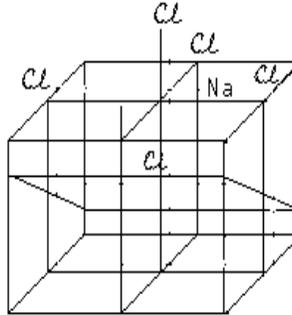
If no empty orbitals = Inert VB – model does not explain to what extent of a complex will be inert or labile.

CRYSTAL FIELD MODEL

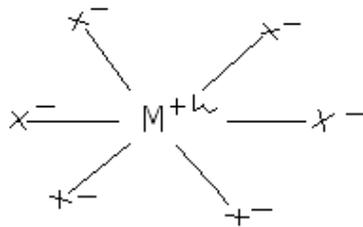
This model is purely electrostatic (or ionic)

$NaCl$ ionic compound

Operating force = ionic lattice.
FCC.



In complexes :-



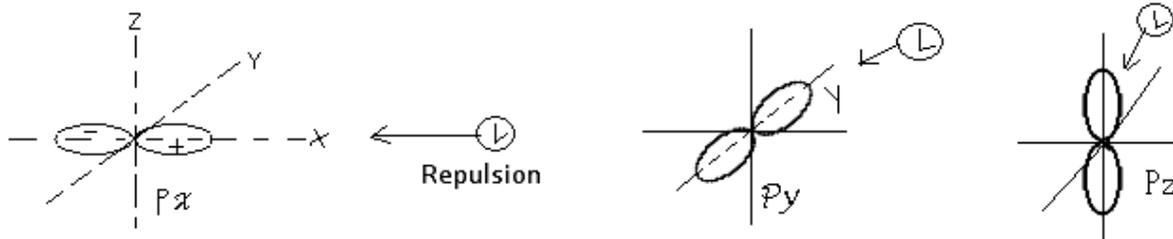
Metal ion is present in the ligand field M^{+n} s, p_x , p_y , p_z , d_{xy} , d_{xz} , d_{yz} , $d_{x^2 - y^2}$, d_{z^2} orbital. Electron charged cloud s-orbital does not split in crystal field of the ligand.

s – orbitals do not split in octahedral, tetrahedral & crystal field.

d – Orbitals split in the crystal field.

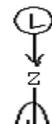
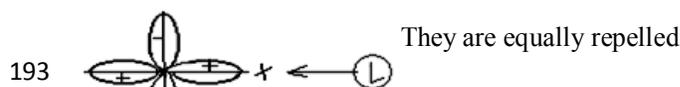
f – Orbitals split in the crystal field.

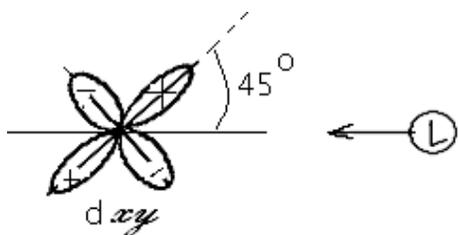
Splitting is due to repulsion between the metal ions orbital & the ligand orbital which are both (-) vely charged. S – orbital is mono degenerated hence it does not split in CF.



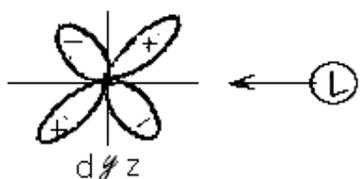
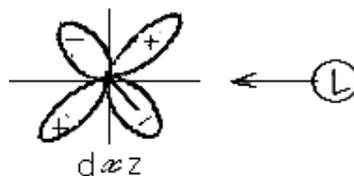
In x, y, z, r – orbitals are equally repelled hence the question of spitting does not arise

d – Orbitals :-

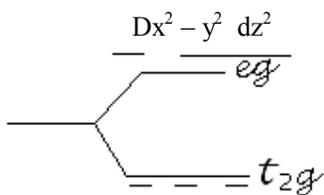




Less repulsion



$Dx^2 - y^2$ & dz^2 are more repelled than d_{xy} , d_{xz} & d_{yz} .



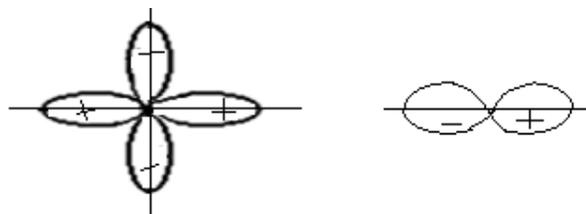
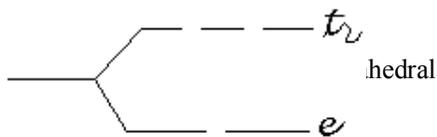
In Octrahedral

d_{xy} , d_{xz} , d_{yz}

In t_{2g} & e_g, 'g' is for centro - symmetry

t = Triply degenerate

e = double degenerate



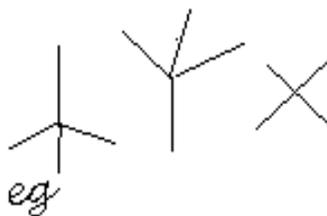
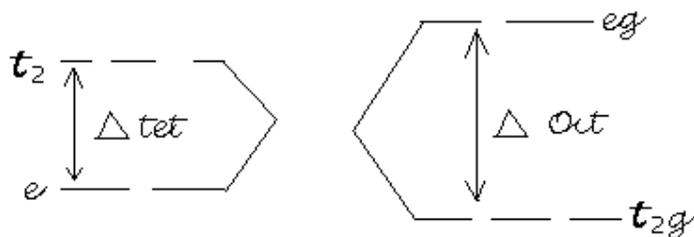
Centro - symmetry

(grade) g

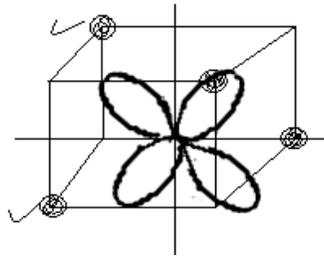
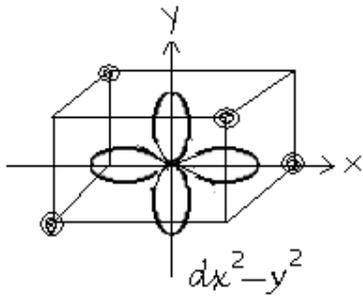
in centro symmetry

(u)

'g' terminology should not be exist in tetrahedral.



In case of oct, repulsion is more so $\Delta_{oct} > \Delta_{tet}$



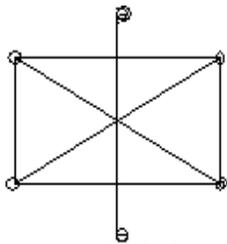
Only two of them are lying to the direction of lobes.

In case of oct, 4 are lying to the direction of lobes.

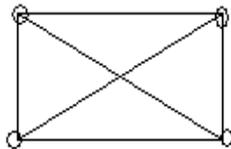
$\Delta_{oct} = 2 \Delta_{tet}$

$\Delta_{tet} = 4/9 \Delta_{oct}$

Or $\Delta_{tet} \approx 1/2 \Delta_{oct}$

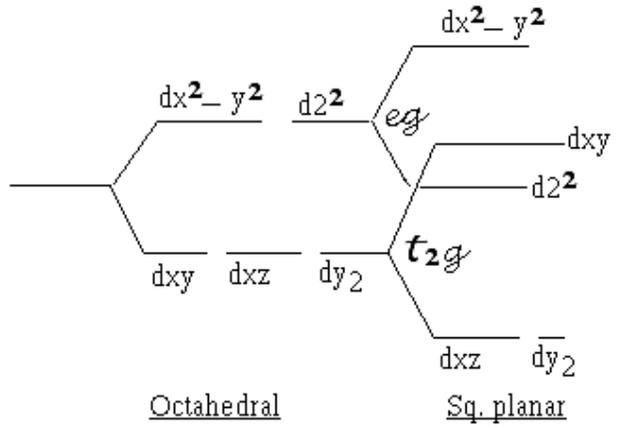


Octahedral

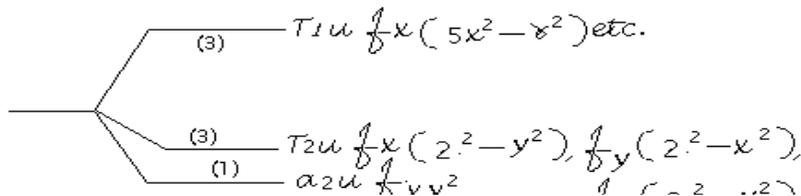
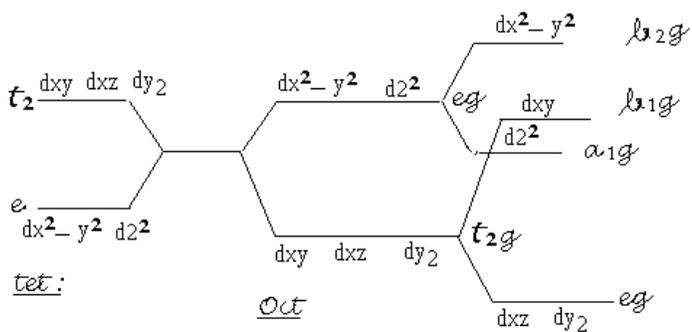
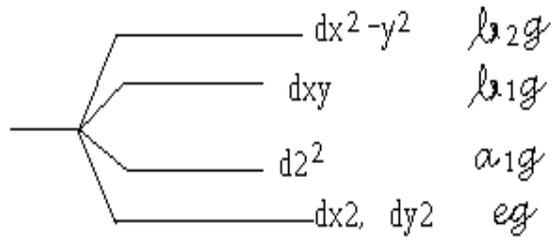
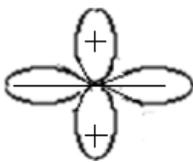


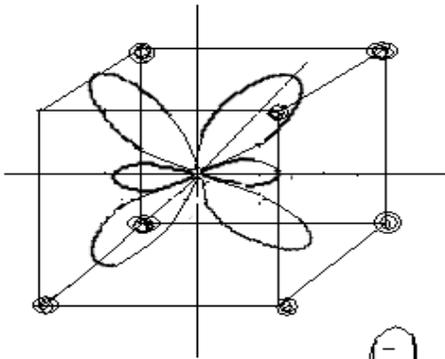
Sq. planar

(no ligand in Z-direction)



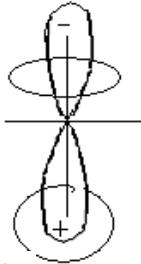
In the xy plane of dz^2 there is charge distribution hence $d2^2$ will be slightly more repelled than dxz, dy^2



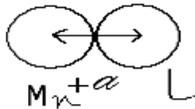
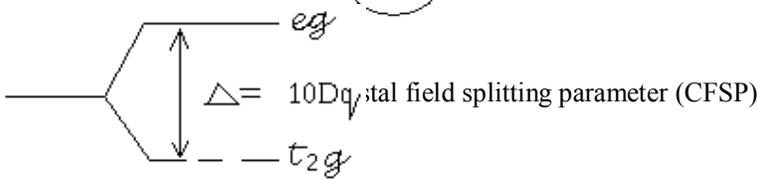
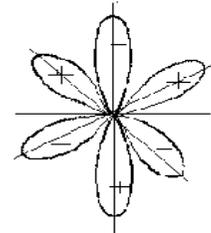


In f - orbitals :- The lobes are directed towards each corners of the cube.

$$\left. \begin{array}{l} f(x^2 - z^2) \\ f(z^2 - y^2) \\ fz(x^2 - y^2) \end{array} \right\} \rightarrow$$

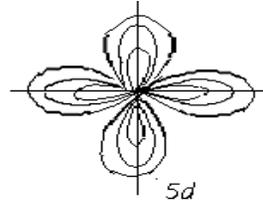
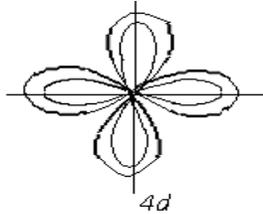
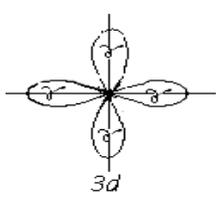


$$\left. \begin{array}{l} f(5x^2 - 3r^2) \\ fy(5x^2 - 3r^2) \\ fz(5x^2 - 3r^2) \end{array} \right\}$$



$$\Delta = 10 Dq = \frac{5}{3} \frac{Z e^4}{a^5} \text{ for (-) vely charged ligands.}$$

Dhere Z = Charge of the metal ion
 e = Charge of the ligand
 a = distance between the metal ion & ligand
 r = distance of extension of orbital in space



$$\mu = \text{Charge} \times \text{distance}$$

$$\Delta = 10 Dq = \frac{5}{6} \frac{Z \mu e^4}{a^6} \text{ for polar molecule ligand}$$

Factors controlling the magnitude of Δ :-

1. Oxidation state of metals ion, - greater is the oxidation state, greater will be Δ .
 Increase in oxidation state by one unit increases Δ 1.5 times, for example :-

$$\left. \begin{array}{l} M^{2+} = \Delta = 10,000 \text{ cm}^{-1} \\ M^{3+} = \Delta = 15,000 \text{ cm}^{-1} \end{array} \right\}$$

$M^{3+} = \Delta = 15,000 \text{ cm}^{-1}$ Provided L is same, geometry is same.
 $M^{4+} = \Delta = 22,500 \text{ cm}^{-1}$

2. Nature of transition metal series :-

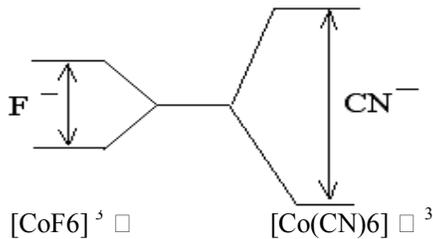
Δ 1st series $<$ Δ 2nd series $<$ Δ 3rd series

Because r_4 1st series $<$ r_4 2nd series $<$ r_4 3rd series

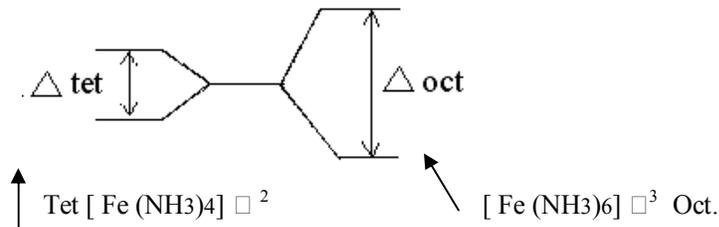
There is increase of 30% in Δ value, when one goes from first to second and then second to third series.

eg; $\left. \begin{array}{l} \text{Co}^{2+} \quad 10,000 \text{ cm}^{-1} \\ \text{Rh}^{2+} \quad 13,000 \text{ cm}^{-1} \\ \text{Ir}^{2+} \quad 16,000 \text{ cm}^{-1} \end{array} \right\}$ Provided L is same, geometry is same.

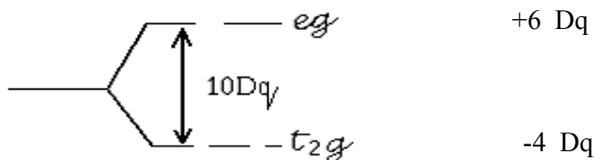
3. Nature of ligand :-



4. Geometry of the complex :-



$\Delta_{\text{tet}} \approx \frac{1}{2} \Delta_{\text{oct}}$



1. Splitting of orbitals in crystal field, follows centre of gravity rule.

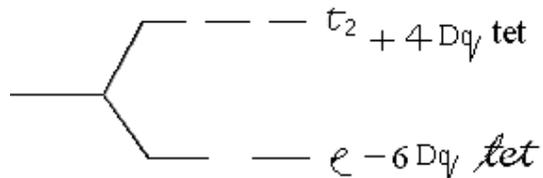
Applying Centre of gravity rule :-

$3x + 2 = 0$

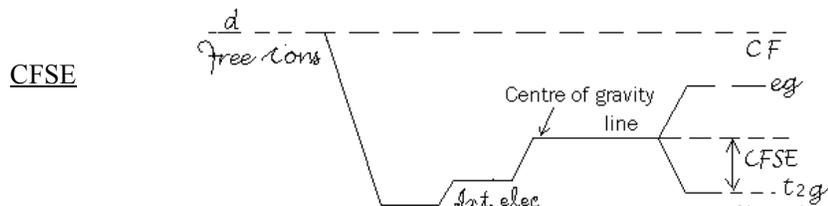
Because t_{2g} is triply degenerate

$2 \times [\quad] = 10 Dq$

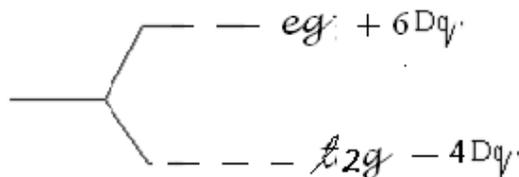
$\frac{\quad}{5} = -20 Dq$
 $= -4 Dq$



T_{2g} is triply degenerated 3



Both T_{2g} & e_g are stabilized in the CF. But T_{2g} is more stabilized than that of e_g . The energy difference between the Centre of gravity line and the lowest orbital in the CF is called CFSE.

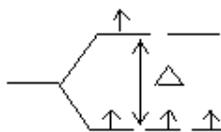


CFSE

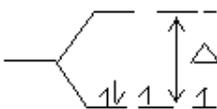
For d^1	- 4 Dq
d^2	- 8 Dq
d^3	- 12 Dq
{ d^4	- 6 Dq (WF) Spin free or low spin complex
{ d^4	- 16 Dq (SF) Spin paired or high spin complex.
{ d^5	- 0 (WF)
{ d^5	- 20 Dq (SF)
{ d^6	- 4 Dq (WF)
{ d^6	- 24 Dq (SF)
{ d^7	- 8 Dq (WF)
{ d^7	- 18 Dq (SF)
{ d^8	- 12 Dq (WF)
{ d^8	- 12 Dq (SF)
{ d^9	- 6 Dq (WF)
{ d^9	- 6 Dq (SF)
d^{10}	- 0 (WF SF)

Spin free & spin paired complex.

d^4 , d^5 , d^6 , d^7 they can form spin free & spin paired complexes in octahedral geometry depending upon the strength of the ligand.



If $\Delta < P$, it will be spin free

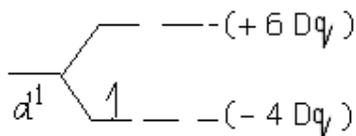


$\Delta > P$ Spin paired

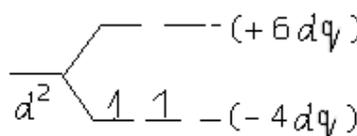
Where P = Pairing energy

Spin paired complexes are more stable than Spin free complexes.

Greater the magnitude of CFSE greater will be stability.

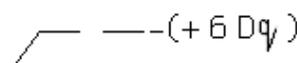
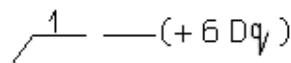


CFSE = - 4 Dq



CFSE = - 8 Dq

D^2 is more stable than d^1



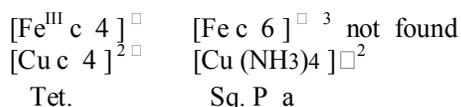


(Para magnetic)
CFSE = - 6 Dq Spin Free

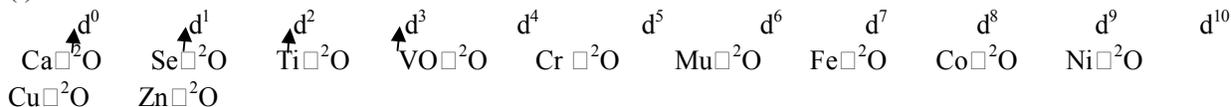
(More stable Para magnetic)
CFSE = - 16 Dq Spin paired

Effect of CFSE on Thermodynamic properties :-

- (i) Radius
- (ii) Hydration energy
- (iii) Lattice energy
- (iv) Distribution of cations in lattice
- (v) Geometry of complexes

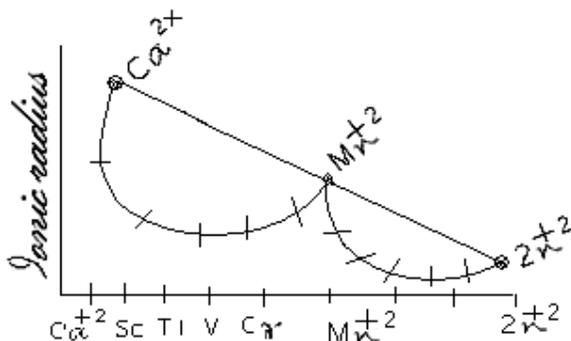


- (i) Effect of CFSE on radius :-



- (ii) They are in a particular series
- (iii) All are ionic compounds
- (iv) Ionic radius of the metal ion $M \square^2$ has been determined in MO by X-ray, d^0 d^5 d^{10} for $\text{Ca} \square^2$, $\text{Mu} \square^2$ $\text{Zn} \square^2$

theoretical & practical values of ionic radius are equal.



For others, $\text{O} \square^2$ is a weak ligand so spin free complex & octahedral geometry.

For d^0 d^5 d^{10} theoretical & experimental value are same.

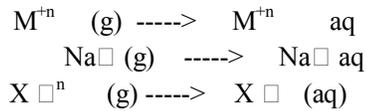
For d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9 variation occurs.

For d^0 d^5 d^{10} CFSE = 0

Therefore those systems which have CFSE – values they are differ in theoretical & experimental value of ionic radius.

CFSE decreases the ionic radius. Hence variation in radius is due to CFSE.

- (ii) Effect of CFSE on hydration energy :-



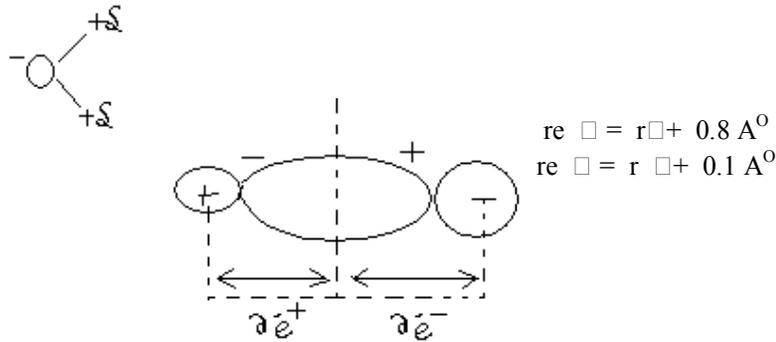
Energy released when one mole of gaseous ion is converted into aqua ion, this is called hydration energy.

$$\Delta H_{hy} = - \frac{Z^* e^2}{r_e} \text{ where,}$$

Z^* = eff nuclear charge of the ion
 e = Charge of the electron
 D = Dielectric cost for medium

For $H_2O = 80$

r_e = equilibrium distance between ion and water.



18 electron structure is more polarizing than 8 electron structure, due to this, 18 electron structure has more hydration energy, e.g.-



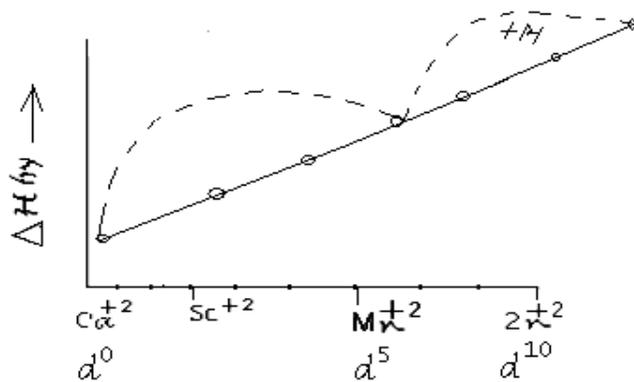
8 electron str. 18 electron str.

K^+ ion has lower hydration energy than K^+ ion i.e. cation < anion

- 1) Charge on the ion.
- 2) Radius of the ion.
- 3) Nature of cations
- 4) Nature of anions
- 5) CFSE ———

$$\Delta H_{hy} = - \frac{Z e^2}{r_e} \quad r_e^+ = r^+ + 0.8$$

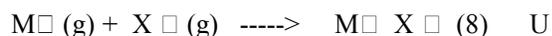
$$r_e^- = r^- + 0.1$$



ΔH_{hy} will be greater than expected due to CFSE

3. Effect of CFSE on lattice energy :-

The energy released in the formation of one mole of ionic solid from its gaseous ion.



$$U = \frac{-2z^+z^-AN}{r_0(1-1/n)}$$

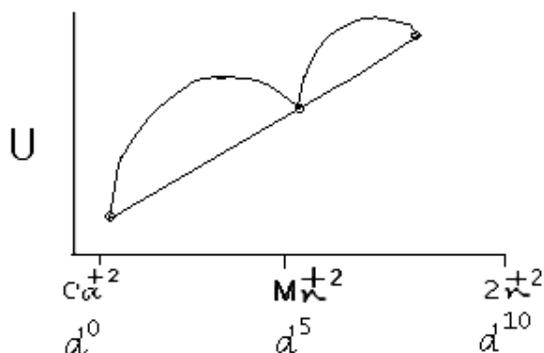
N = Avogadro's no

A = Madulung court

n = Court depending on inert gas configure of the ion

$r_0 = r^+ + r^-$ (Int nuclear distance,

- (i) Greater the charge greater will be U
- (ii) Greater the radius lower will be U
- (iii) 8 – electron structure compounds have lower U Value than 18 – electron structure.
- (iv) CFSE



So, the CFSE is going to affected thermodynamic properties like -

- (i) Ionic radius
- (ii) ΔH_{hy}
- (iii) U

TERMS IN CRYSTAL FIELD

Free ion M^{+n}

Ti +3 d^1

V +3 d^2

In the free ion,

Orb – ang. Momentum

Spin, ang, momentum

INTERACTIONS :- (i)

- (i) l
- (ii) S

Inter electronic interaction or repulsion in free ion.

For first series l , & interactions are weak, S Strong.

2nd Series l , & stronger

, weaker

For Lanthanides l - - very strong, , very weak

d^2 System :

	+2	+1	0	-1	-2
<i>me</i>	1	1			

$l - l = L$

L = Total orb. ang. Momentum
 = Orb. ang. Momentum for an electron

$$M_L = \sum m_l$$

$$= 2 + 1 = 3$$

L = 3 is symbol = F

=0	1	2	3	4	5
s	p	d	f	g	h

S	P	D	F	G	H
=0	1	2	3	4	5

S = Total spin ang. Mom.

Here for d² system, L = 3

∴ Spectroscopic symbol = F

$$M_S = \sum m_s$$

$$= \frac{1}{2} + \frac{1}{2} = 1 \therefore S = 1$$

Spin multiplicity = 2S + 1, 2 x 1 + 1 = 3

Spectroscopic term = 3F

	Term
d ¹	2D
d ²	3F
d ³	4F
d ⁵	6S
d ⁶	5D
d ⁷	4D
d ⁸	3F
d ⁹	2D

Free ion ground term

Orbital degeneracy = 2L + 1

Spin degeneracy = 2S + 1

Term degeneracy = (2L + 1) (2S + 1)

Q:- What is the degeneracy for 3F?

For 3F,

$$L = 3, S = 1$$

$$(2 \times 3 + 1)(2 \times 1 + 1) = 7 \times 3 = 21 \text{ Ans.}$$

Where L = Total angular momentum



$$J = |L + S| \text{ to } |L - S|$$

For 3F, L = 3, S = 1

$$J = |3 + 1| \text{ to } |3 - 1|$$

$$J = 4, 3, 2$$



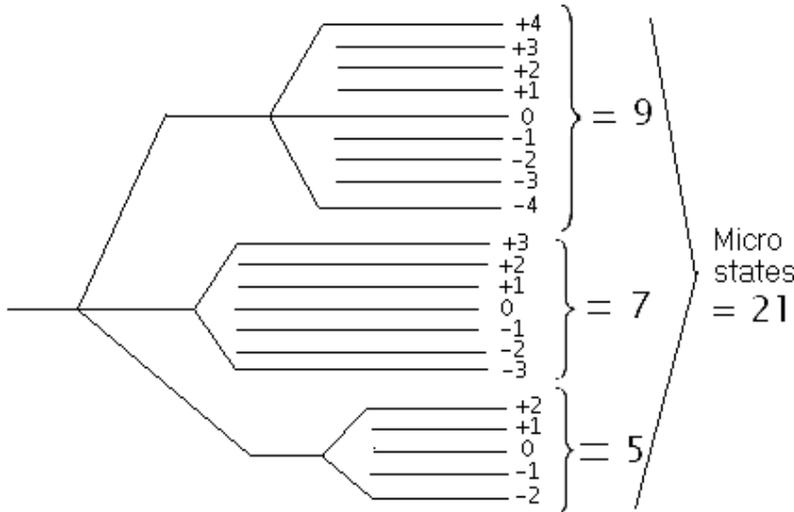
∴ State : S. M. Symbol J



Split without mag. field

While J – split in mag. field

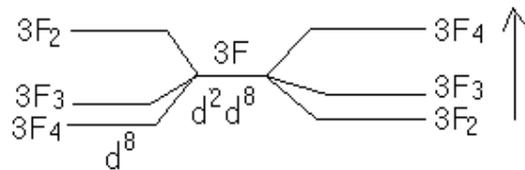
In mag. field J splits into $2J + 1$ parts i.e. degeneracy of $J = 2J + 1$



The splitting in J – value is known as Z E E M A N Effect.

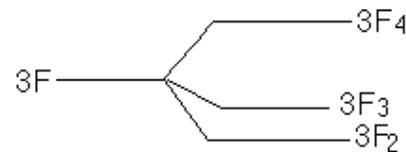
d2

d8 If we have less than half filled configuration minimum J lies lowest. For d^2 system. For more than half filled maximum J lies the lowest. For d^8 system.



Invert multiplet (more than half filled) Normal multiplet

If the J-values are in increasing order such splitting are known as Normal multiplets as in d^2 system.

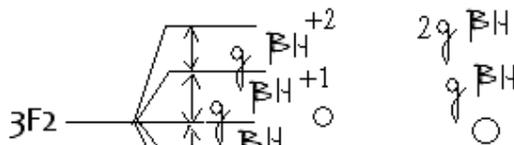


Russel – Saunder’s Coupling L – S coupling where λ is L – S coupling constant for d^n configuration.

ζ Zeta) – S coupling constant for an electron.

$$\lambda = \frac{\pm \zeta}{2S} \quad S = \text{Total spin,}$$

Energy of states is expressed in λ such as 1λ , 2λ , 3λ etc. or energy of multiplets is expressed in terms of λ .



In magnetic field Zeeman effect,

$$Jg \beta H$$

B = Bohr magneton, $\beta = \frac{eh}{4\pi me}$

H = Strength of mag. field

$$g = \frac{1 + 4S(S+1) - L(L+1) + J(J+1)}{2J+1}$$

Energy gap = $g \beta H$

Degeneracy of a configuration :-

deg = $\frac{L^2 n}{Lr 2n - r}$ Where n = no of orbital in confi. for p, n = 3, d, n = 5
 r = no of electrons in config.

for d^1 system, $\frac{L10}{L1 10 - 1}$

$$= \frac{L10}{L9} = \frac{10 L9}{L9} = 10$$

Thus degeneracy gives the total possible microstates.

For d^1 : G.T = $2_D = 10^{deg}$

$$(2L+1)(2S+1) = 5 \times 2 = 10$$

For d^1 only 2D term & no other excited term.

2_D G.T = 2D no other excited term

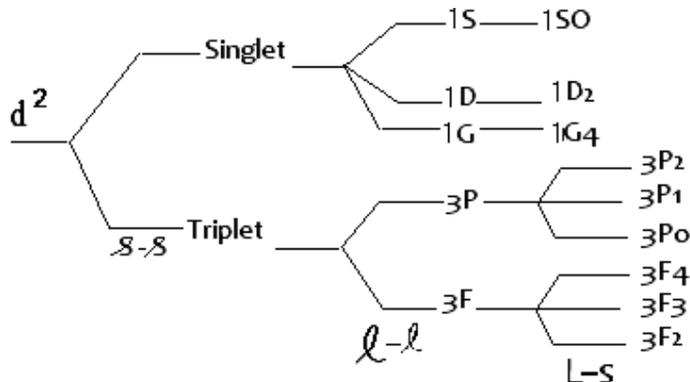
d^2 :- degeneracy $\frac{L10}{L2 L 10 - 2} = \frac{10 \times 9}{2 L 8} = \frac{L9}{L8} = 45$ micro states

$d^2 = 3F \rightarrow 21$ micro states.

For d^2 system, there are other free ion terms i.e. excited terms

For d^2 d^8 }	3 F
	3 P
	1 G
	1 D
	1 S

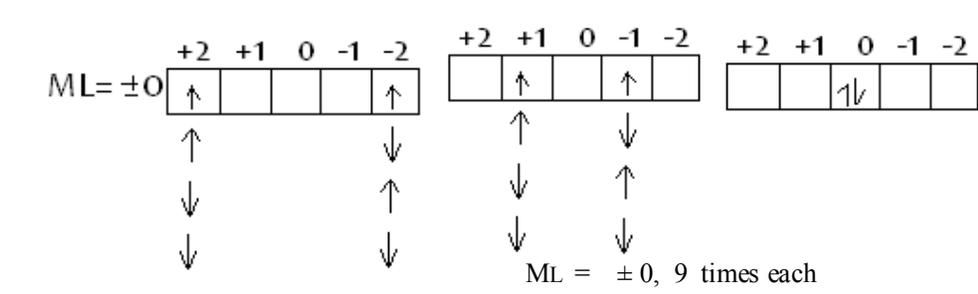
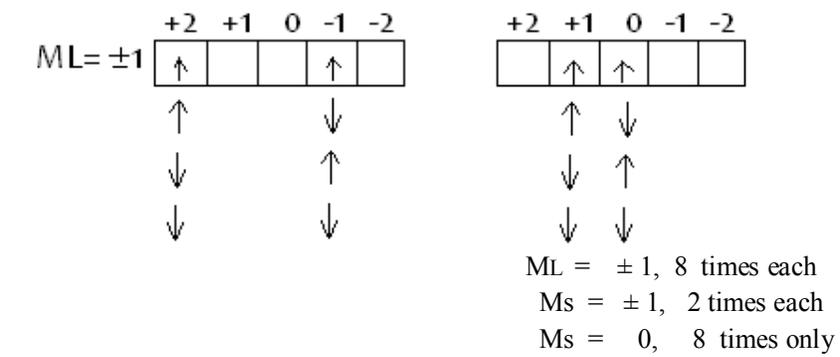
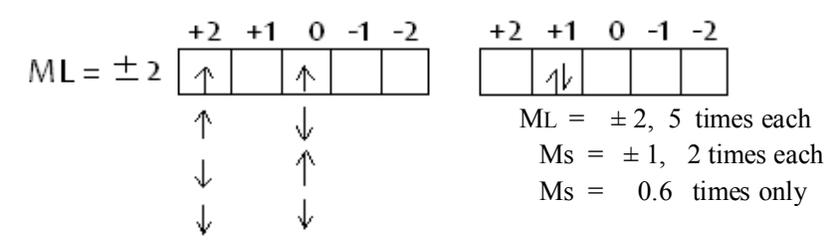
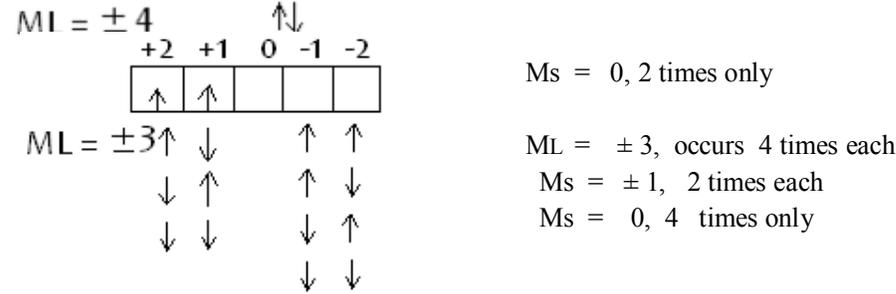
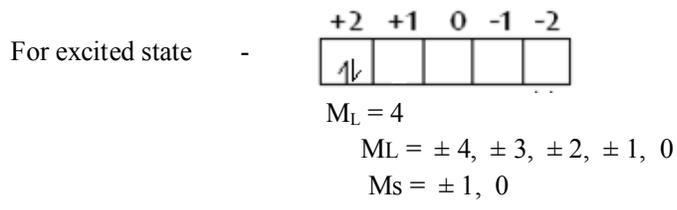
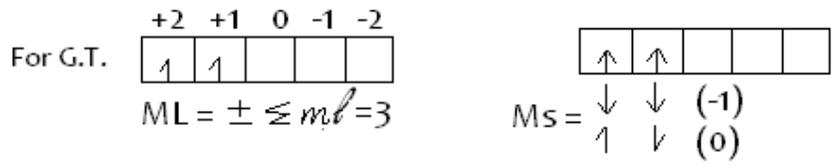
Q. :- Show the L-S coupling scheme for d^2 system



For P

$$\begin{array}{l} S = 1, \quad L = 1, \\ |L+S| \quad \text{to} \quad |L-S| \\ |1+1| \quad \text{to} \quad |1-1| \\ 2, \quad 1, \quad 0 \end{array}$$

$S=0, L=4, (L+S)=4$
 Q. :- Derive the free ion terms for d^2 system?



$M_s = \pm 1, 2 \text{ times each}$
 $M_s = 0, 5 \text{ times only}$

$M_L = \pm 4$	2	$M_s = \pm 1,$	20
± 3	8	$M_s = 0,$	<u>25</u>
± 2	10		45
± 1	16		
0	<u>9</u>		
	45		

With singlet, triplet will not be associated but with triplet, singlet will be associated.

Subtracting orbital multiplicity '9' from $M_s = 0$ values and spin multiplicity '1' from each M_L value $M_L = \pm 4, 1$ times each = $G = 9$ microstates.

$M_L = \pm 3, 3 \text{ times each}$

$M_L = \pm 2, 4 \text{ times each}$

$\pm 1, 7 \text{ times each}$

0, 8 times each

Subtracting orbital multiplicity 7 from each M_s values & spin multiplicity '3' from each M_L values :-

$M_L = \pm 2,$	1 times each	1G
$\pm 1,$	4 times each	3F
0,	5 times each	1D
		3P
		1S

Subtracting orbital multiplicity 5 from $M_s = 0$ (Singlet) values & spin multiplicity 1 from each M_L values.

$M_L = \pm 1, 3 \text{ times each}$

0, 4 times only

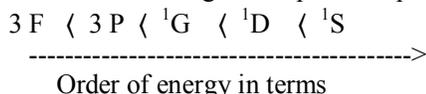
Subtracting orbital multiplicity 3 from M_L values.

$M_L = 0$ 1 time only subtracting orbital multiplicity 1.

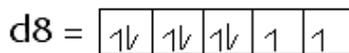
HUND'S RULE

(1) Terms having maximum spin multiplicity lies lowest.

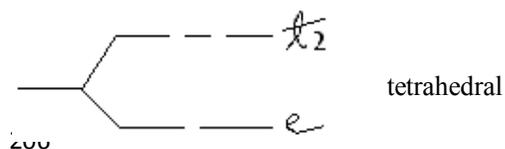
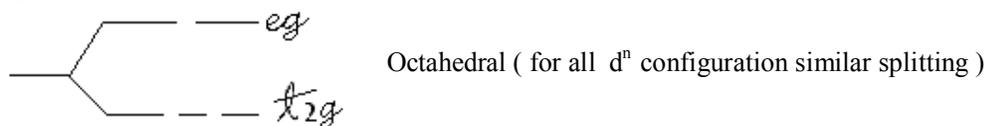
(2) If there are terms having same spin multiplicity than term with highest L - value lies lowest.



The rule is valid for free ions only.



$d^1,$	d^9	2D	$\equiv d^2$
d^2	d^8	3F, 3P	
d^3	d^7	4F, 4P	
d^4	d^6	5D	
d^5		6S	





Ground state configuration Excited state configuration

- S orbital does not split – (X) s term – XV oct (-) because it is mono degenerate.
- P – orbital ----- X, P term ----- XV tet (+)

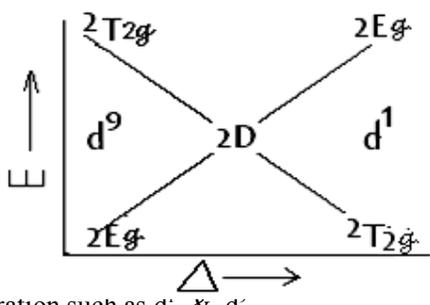
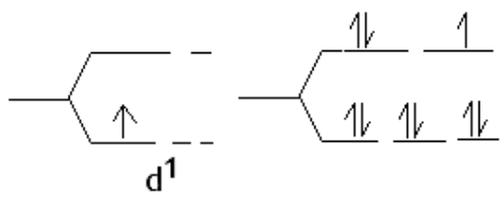
All the term px, py, pz are giving to be equally repelled hence p – orbital does not split. Except S & P terms, all other terms are going to split in CF, d – orbital split in CF (✓)

D term split in eF (✓)

Sum of the matrices is (-ve), hence D, terms split.

d – orbital splits because it is repelled in some cases higher than the other.

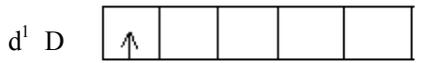
f orbital split in CF (✓) F term ✓ d¹, d⁹ 2D



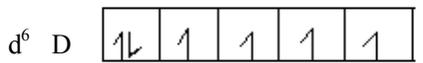
Terms split in invert way for identical terms configuration such as d¹ & d⁹.

HOLE FORMALISM

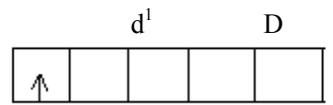
- Electron is negatively charged.
- Presence of an electron in an orbital is considered as Negative hole.
- Absence of electron is considered as positive hole.
- If two configurations have same no. of similar holes the terms split in a similar way.
- If two configuration have same no. of opposite holes the terms split invert to each other.
- As V oct is (-) & V tet is (+) the splitting of terms in oct. & tet. Is invert for a particular configuration.



One negative hole, Four (+) holes.



One (-) hole because all the rest 5 electrons are symmetrical. Four (+) holes.



One (-) hole



One (+) hole

Invert to each other

dⁿ & dⁿ⁺⁵

- | | | | |
|----------------|----------------|---|-------------------|
| d ¹ | d ⁶ | } | Similar splitting |
| d ² | d ⁷ | | |
| d ³ | d ⁸ | | |

Terms for dⁿ & dⁿ⁺⁵ configuration split in a similar fashion.

d^n & d^{10-n}

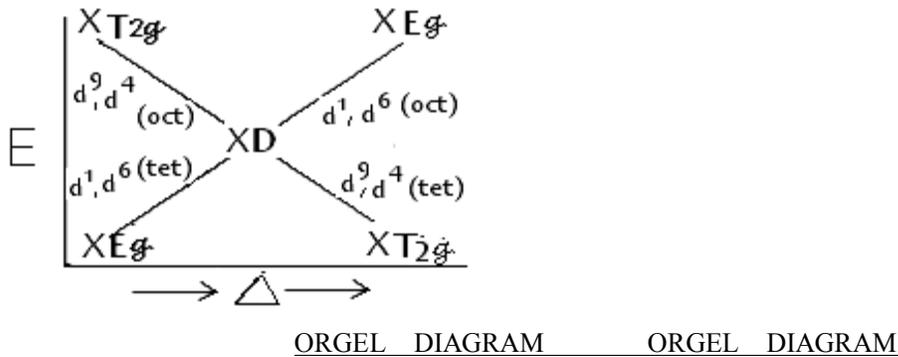
d^1 d^9
 d^2 d^8
 d^3 d^7

} Invert splitting

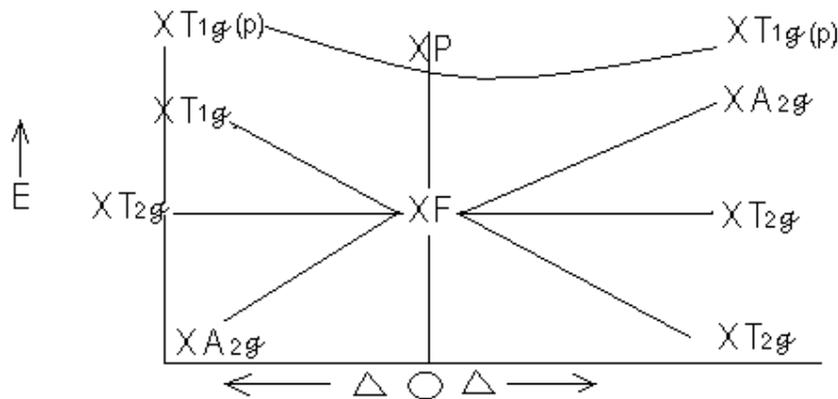
Terms for d^n & d^{10-n} configurations split invert to each other in a particular CF.

d^n & d^{10-n} -----> Invert splitting

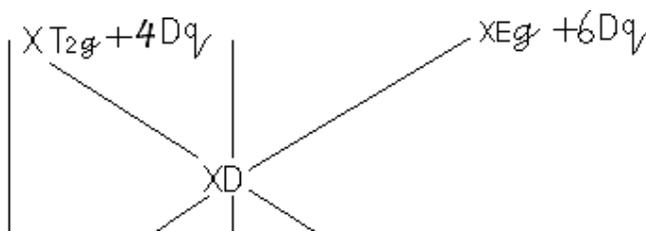
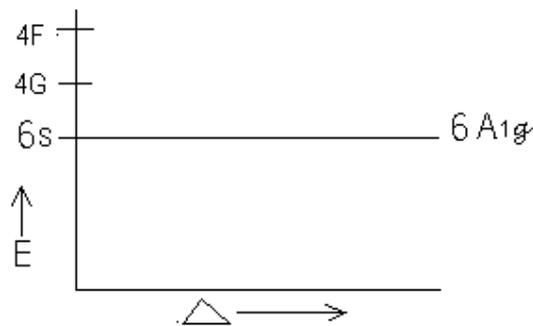
d^n & d^{n+5} -----> Similar splitting

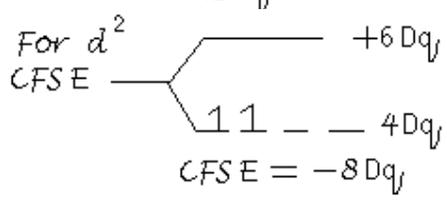
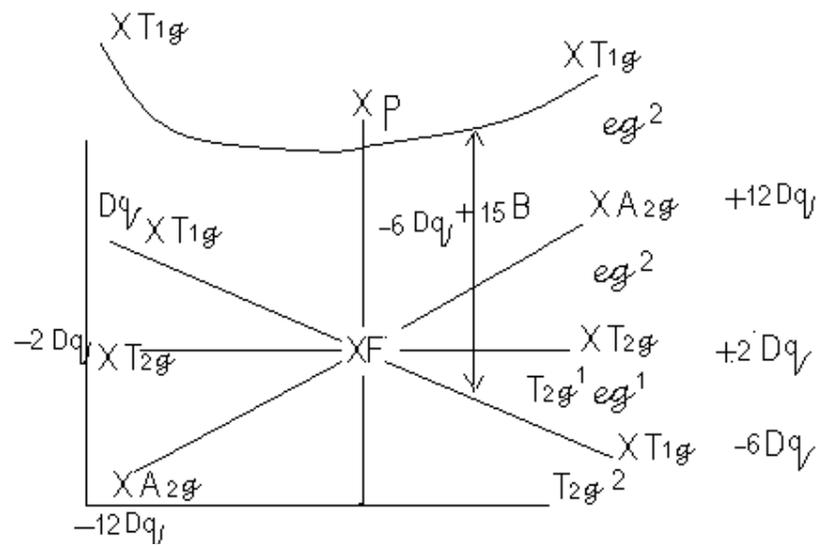
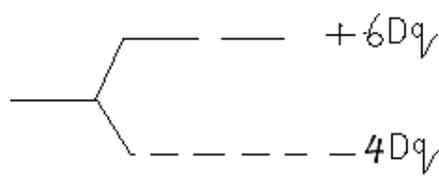


The plot of E vs Δ is known as Orgel diagram -



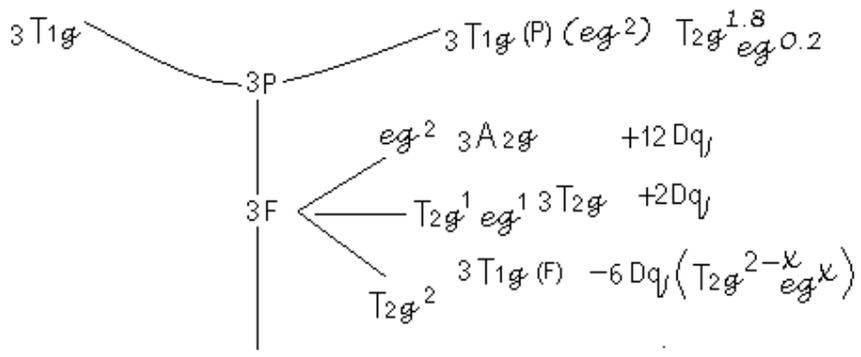
d^2, d^7 (Oct)
 d^3, d^8 (Tet)
 For d^5 , G. T. = 6s
 Orgel diagram for d^5 system :-





A/C to term - splitting = $-12Dq$

Energy associated with the ground term in the crystal field is known as CFSE :-



$$6 \times 3 + 2 \times 3 + 12 \times 1$$

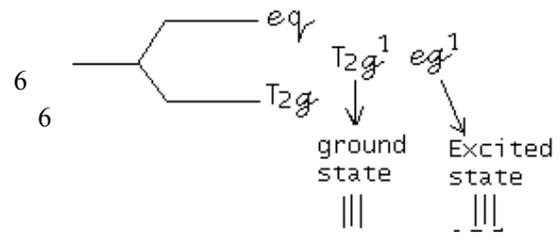
$$18 + 6 + 12 = 0$$

The discrepancy between orbital splitting and term - splitting in d^2 or d^7 is due to mixing of $3T_{1g}(F)$ and $3T_{1g}(P)$

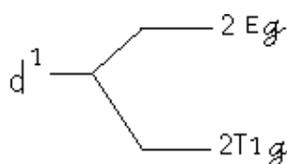
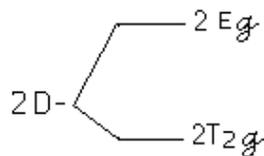
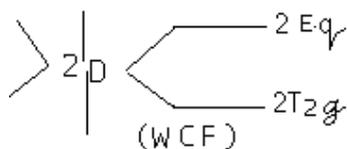
$$4(2 -) + 6$$

$$8 + 4 + 6$$

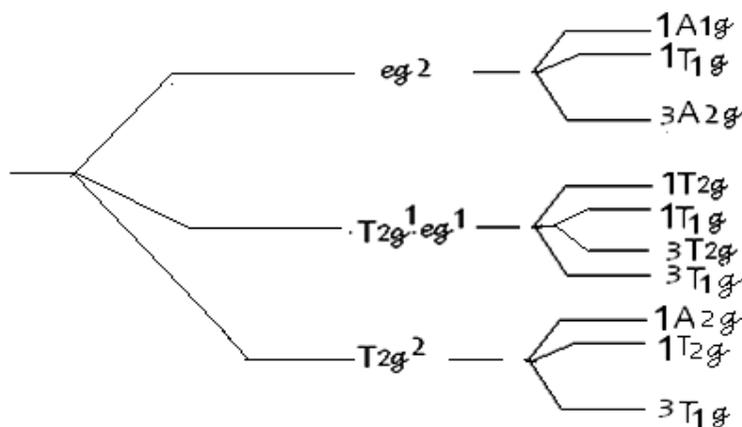
$$10 = 2, \quad = 0.2$$



d¹ (SCF)



d² (SCF) :-



CF

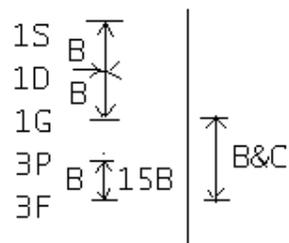
Ground term remain the same but the energy of excited term changes.

	WCF	SCF
d ¹	G. T. remains the same (✓)	√(G.T.)
d ²	✓	✓
d ³		

For half filled t_{2g}³ A_{2g}
 t_{2g}⁶ A_{1g}
 $\frac{1}{1k} \frac{1}{1k} e$ For e² A₂
 $\frac{1}{1k} \frac{1}{1k} e$ For e⁴ A₁

B & C

Racah parameters :-



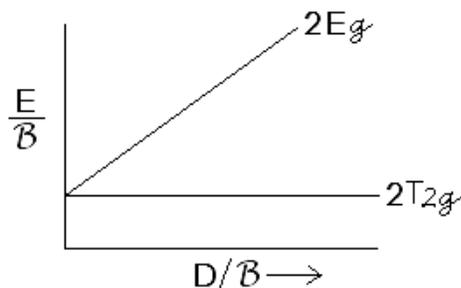
Energy gap between terms of same spin multiplicity is expressed in terms of B .
 Energy gap between terms of different spin multiplicity depends both by B & C .

$$B = 10,00 \text{ cm}^{-1}$$

Orgel diagram is most valid for d^1 & d^9 system. For $d^2, d^3, d^4, d^6, d^7, d^8$, it is not going to be so useful.

d^1 & d^9 :- No inter electronic repulsion. For the system, when there is inter electronic repulsion Orgel diagram is not so applicable.

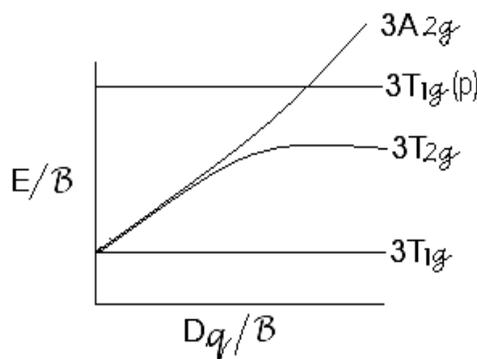
TANABE – SUGANO DIAGRAM



T. S. Diagram

At fixed C/B

Tanabe – Sugano diagram is valid for d^2 to d^8 system.



(At fixed C/B)

	<u>WCF</u>	<u>SCF</u>
d^1	2 T_{2g}	2 T_{2g}
d^2	3 T_{1g} (G.T.)	3 T_{1g} (G.T.)
d^3	4 A_{2g} „	4 A_{2g} „
d^4	} 5 E_g	3 T_{1g}
d^5		6 A_{1g}
d^6		5 T_{2g}
d^7		4 T_{1g}
d^8		3 A_{2g}
d^9	2 E_g	2 E_g

For d^4 ($T_{2g}^4 \equiv T_{2g}^2$) \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow

For d^5 \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow
 d^5 d^1

For d^6 , T_{2g}^6 completely filled $^1A_{1g}$

For d^7 $T_{2g}^6 e_g^1$

$$A_{1g}, E_g, A_{1g} = 1$$

$$= 2 E_g, \quad E_g = 2$$

MAGNETIC PROPERTIES

In a magnetic field, paramagnetic substance is going to be attracted.

(i) Electronic spin :- Paramagnetic arises due to spin – angular momentum.

(ii)

$$s = \sqrt{4s(S+1)} \quad \text{for transition elements}$$

$$1 = \text{---}$$

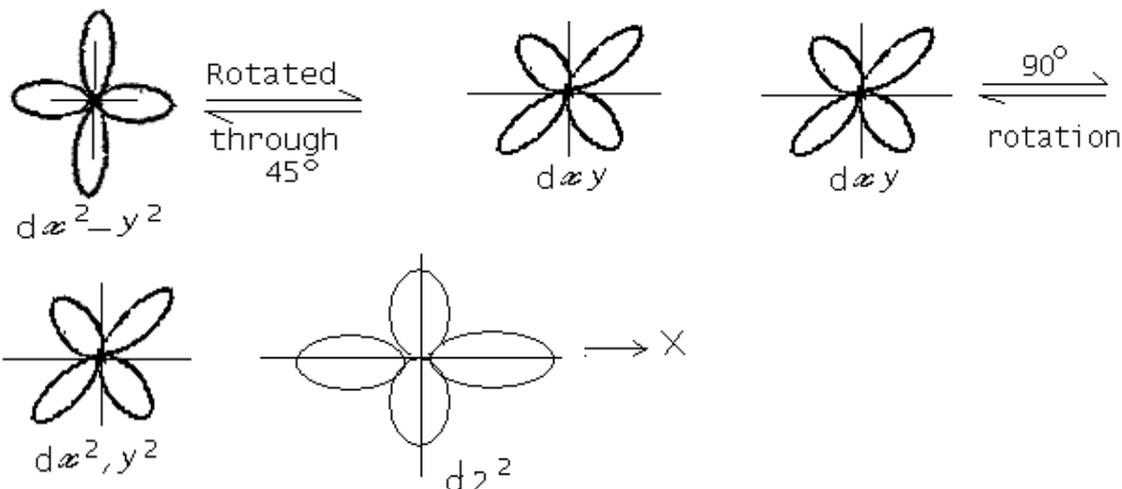
ML

$$ML + S = \sqrt{4s(S+1) + L(L+1)} \quad \text{valid for transition metal}$$

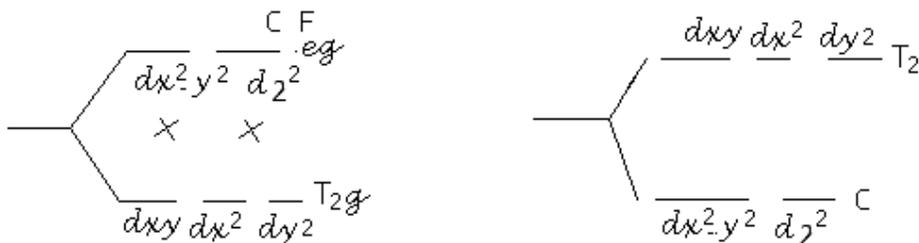
$$J = g \sqrt{J(J+1)} = \quad s \quad \text{valid for Lanthanides}$$

$$\frac{L(L+1) + J(J+1)}{2J+1}$$

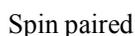
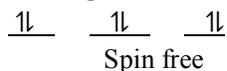
Experimental value is slightly greater than s value. It may be due to orbital configuration. Reduction or Quenching of orbital angular momentum.



1/5 of orbital angular momentum is going to be reduced or quenched even in the free ion.



In the CF, further 1/5 of orbital angular momentum is going to be reduced. 1/3 orbital contribution is expected in CF complex. If the lower one is going to be evenly occupied there will be no orbital contribution. i.e.



d ¹	T _{2g} ¹ (there will be orbital contribution)	√
	expt) 2T _{2g}	
	<u>Spin Free</u>	<u>Spin Paired</u>
d ²	T _{2g} ² √ 3 T _{1g}	
d ³	T _{2g} ³ X evenly occupied	
	4 A _{2g} , expt = s	
d ⁴	T _{2g} ³ eg ¹ X 5 Eg	T _{2g} ⁴ ≡ T _{2g} ² √ 3 T _{1g}
d ⁵	T _{2g} ³ eg ² X 6 A _{1g}	T _{2g} ⁵ ≡ T _{2g} ¹ √ 2 T _{2g}
d ⁶	T _{2g} ⁴ eg ² √ 5 T _{2g}	T _{2g} ⁶ X ¹ A _{1g}
d ⁷	T _{2g} ⁵ eg ² √ 4 T _{1g}	T _{2g} ⁶ eg ¹ X ≡ 2 Eg
d ⁸	T _{2g} ⁶ eg ² X 3 A _{2g}	X 3 A _{2g}
d ⁹	T _{2g} ⁶ eg ³ X 2 Eg	X 2 Eg

If the ground term is T, - there will be orbital - contribution

$$s = \sqrt{n(n+2)} = \sqrt{4s(S+1)}$$

$$s = \sqrt{4s(S+1) + L(L+1)}$$

No orbital contribution yet the experimental $s > s$. The reason may be L - S coupling . The effect of L - S coupling actually called in directed orbital contribution.

A₂ } Even (in directed orbital contribution)
 E } No direct orbital contribution

For A₂ & E terms there are in directed orbital contribution

$$eff = s \left(\frac{K}{10 Dq} \right)$$

Value of K	E	A ₂	A ₁
	2	4	0

For less than half filled contribution -----> ⊕

$$eff \{ Ms$$

For more than half filled configuration ----> ⊖ eff } Ms. Due to L - S coupling the cept value may be less or more than value.

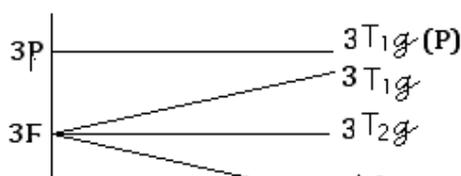
$\underbrace{L \ S \ \rightarrow \ J}_{\text{Coupling}}$

is a parameter for L - S coupling for a system. ζ parameter for L - S coupling for an individual electron.

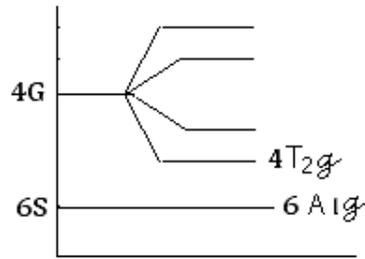
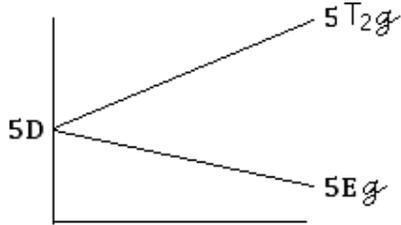
$$(\text{Zeta}) \zeta = \pm \frac{\hbar^2}{2m} S = \text{Total Spin}$$

e.g. $300 = \frac{\hbar^2}{2 \times 1} = 600 \text{ cm}^{-1}$

- d¹ → 2 T_{2g} --- Direct orbital contribution :-
- d² → 3 T_{1g}
- d³ → 4 A_{2g}
- d⁴ → 5 Eg



$$d^5 \rightarrow 6 A_{1g}$$



$$d^6 \rightarrow 5 T_{2g} \text{ --- Direct orbital configuration}$$

$$d^7 \rightarrow 4 T_{1g}$$

$$d^8 \rightarrow 3 A_{2g}$$

$$d^9 \rightarrow 2 E_g$$

In strong crystal field in d^4, d^5, d^6, d^7

$$T_{2g}^4 \equiv T_{2g}^2 \equiv 3T_{2g} + \boxed{{}^1T_{2g} + {}^1E_g + {}^1A_{1g}}$$

$$T_{2g}^5 \equiv T_{2g}^1 \equiv 2T_{2g}$$

$$T_{2g}^6 \equiv 1 A_{1g}$$

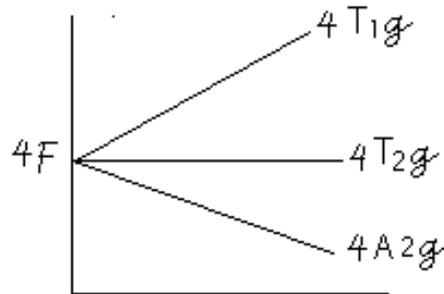
Q:- eff for $C\square\square 3$ complexes is lower than s .

$$C\square(24) \rightarrow d^6$$

$$C\square\square 3 \rightarrow d^3$$

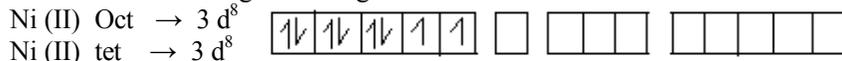
Free ion term = $4F$

$$\begin{aligned} \text{eff} &= s \left(\frac{K}{10 Dq} \right) \\ &= s \left(\frac{K}{10 Dq} \right) \end{aligned}$$



Since $>$ is $-ve$ hence the whole system become positive therefore, eff is going to be less than one due to $L - S$ coupling. So $C\square\square 3$ complex is lower than s .

Q:- Which one will have greater mag. moment.



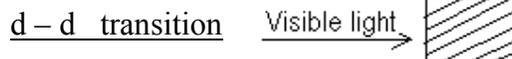
$Ni(II) \text{ Oct} \rightarrow \text{Gr. Term} \rightarrow 3 A_{2g}$ $\text{eff} > s$ in direct orbital contribution.

$Ni(II) \text{ tet} \rightarrow \text{Gr. Term} \rightarrow 3 T_{1g}$ $\text{eff} \gg$ direct orbital contribution.

$\text{tet} > \text{Oct}$

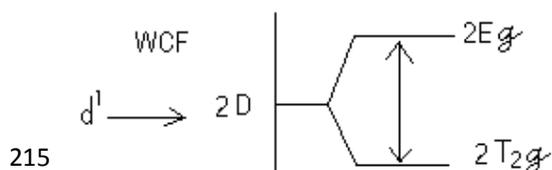
$$\text{eff} = s \left(\frac{K}{10 Dq} \right)$$

VIBGYOR



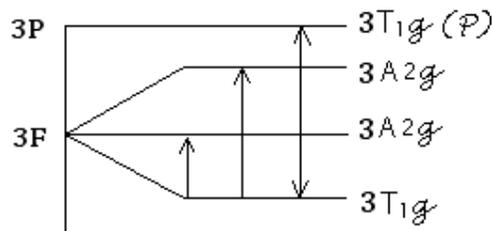
To be colour :

- (1) Presence of light is must, complementary colour.
- (2) Transition of electron occurs from lower energy level to higher energy level.



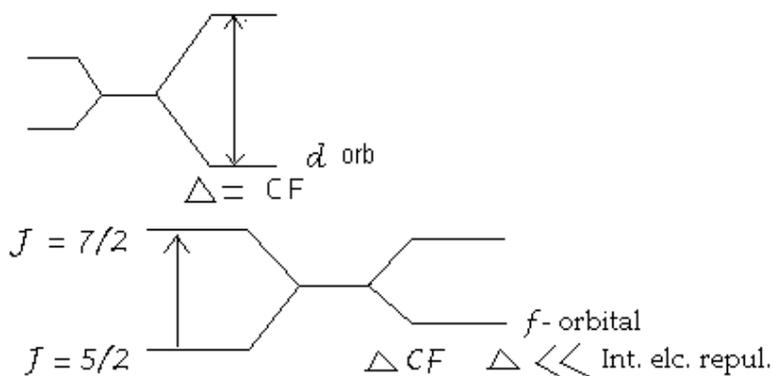
After absorption of light, Configuration $t_{2g}^1 e_g^1$

[Ti (H₂O)₆]³⁺ Oct & spin free transitions occurs within the level of d – orbitals are called d – d – transition. The electronic transitions occur from the term to the next higher state in the C F.

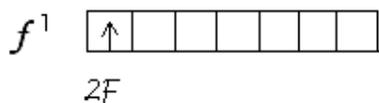


In d- d- transition, transitions occur within the terms due to crystal field effect.

In f – f transition, it occurs within the terms due to inter electronic repulsion f – f transition or J – J transition.



Inter electronic repulsion



$$L = 3, \quad S = 1/2$$

$$J = L + S \quad \text{to} \quad L - S$$

$$2s + 1 = 2 \times \frac{1}{2} + 1 = 2 \quad \begin{matrix} = 3 + 1/2 & \text{to} & 3 - 1/2 \\ = 7/2 & \text{to} & 5/2 \end{matrix}$$

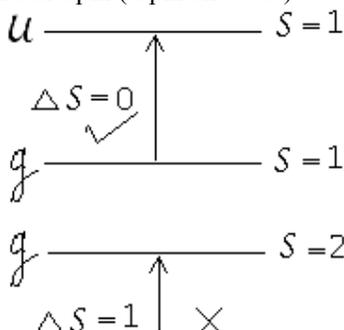
$$\frac{\frac{2}{2} + \frac{1}{1}}{\frac{2+2}{2}} = \frac{4}{2} = 2$$

SELECTION RULES FOR ELECTRONIC TRANSITION :-

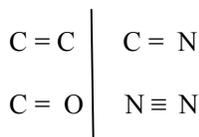
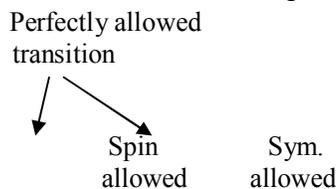
(1) $\Delta S = 0$, symmetry allowed, S = Total Spin (Spin allowed)

Symmetry allowed transition are

g → u
u → g



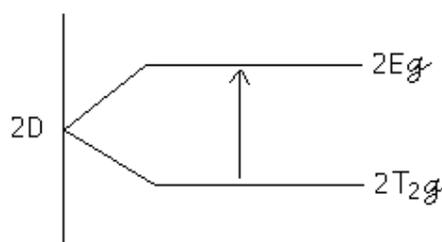
Such transitions are called perfectly allowed transition. Such transitions occur in case of charge transfer.
 Charge transfer →



In multiple bond system

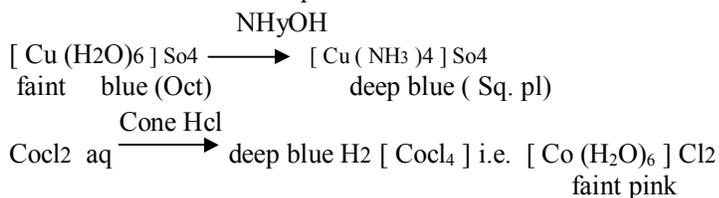
(eta) $\epsilon \approx 10,000$, colour is very deep

- (ii) Spin allowed but symmetry forbidden i.e. $\Delta s = 0$
 d-d transition is spin allowed but symmetry forbidden.
 $\Delta s = 2 - 2 = 0$
 $g \rightarrow g$



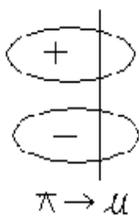
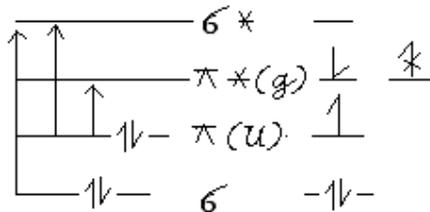
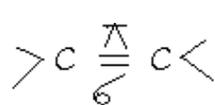
$\epsilon = 10$, Colour is faint

This transition is called Laporte forbidden transition.

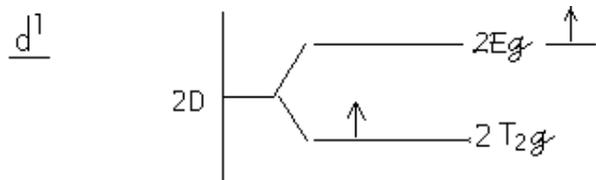
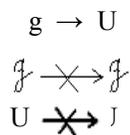


SELECTION RULE

- | | | |
|---------------------|---|--|
| (i) $\Delta s = 0$ | $g \rightarrow u$ | ϵ |
| spin allowed | sym. Allowed, | 10,000 charge transfer |
| (ii) $\Delta s = 0$ | $g \rightarrow g$ | |
| spin allowed | sym. forbidden,
(Laporte forbidden) | 10 d-d transition |
| (iii) spin allowed | symm. forbidden, | 100 d-d in tet. but with d-p mixing |
| (iv) spin allowed | symm. forbidden, | 1000 d-d in transition but with intensity stealing |
| (v) spin allowed | symm. forbidden, | 0.1 (very very faint) |

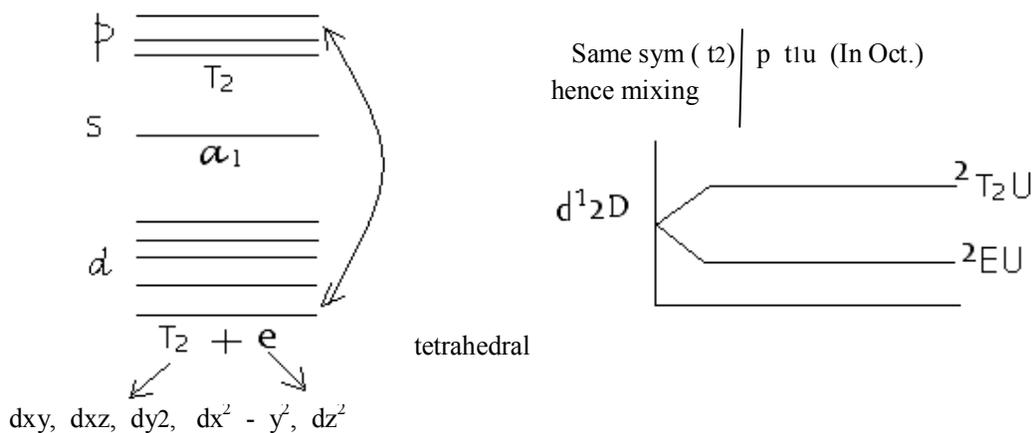


$U \rightarrow g$



d - d transition is spin allowed, symm. forbidden transition.

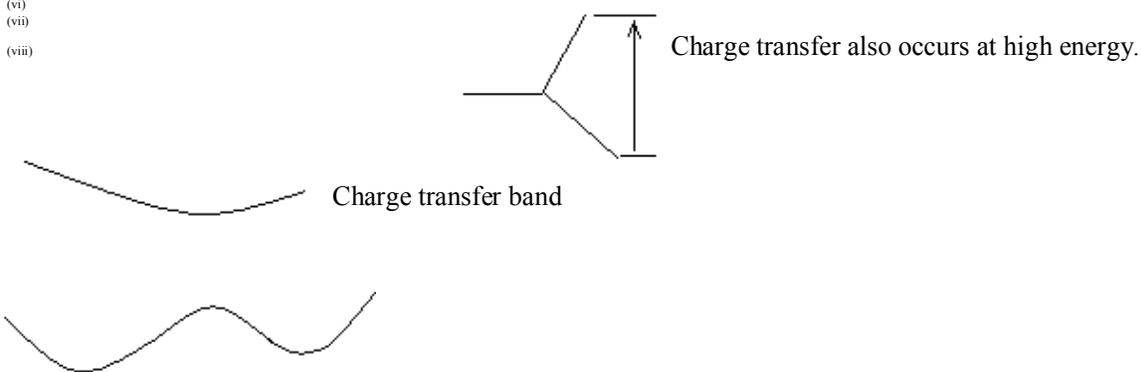
d - p mixing due to this mixing, colour of tetrahedral complexes are more deep.



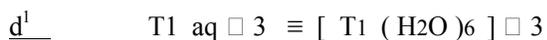
$2E_g$, $2T_{2g}$, is no longer pure some p - character also exists so transition will be more allowed, hence E value greater - colour intense.

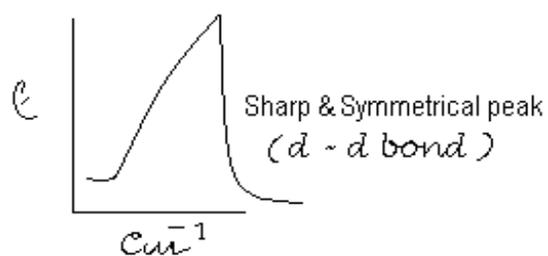
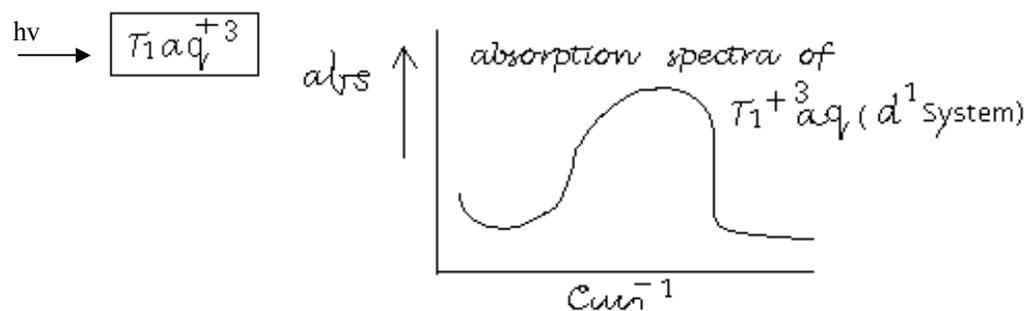
Intensity Stealing :-

- (i) CFSE (Δ) is larger, transition will occur at high energy.
- (ii) At high energy, charge transfer band also occurs.
- (iii)
- (iv)
- (v)
- (vi)
- (vii)
- (viii)



- (ix) Due to vibration, vibronic coupling (interaction) occurs.
- (x) Intensity of d - d band increases due to this vibronic coupling.





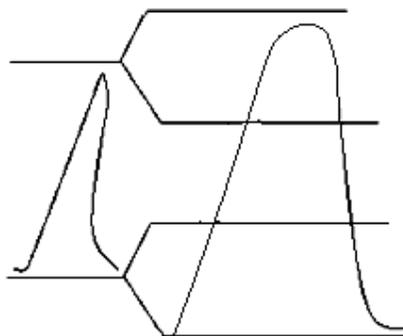
Theoretically

d - d bands are broad & unsymmetrical experimentally.

Q:- Why d - d bands are broad & unsymmetrical ?

- Ans.:- (i) Vibronic coupling
(ii) Distortion in structure
(iii) L - S coupling effect.

Selection Rule is valid for free ion. In complexes, metal ion is not free metal ion vibration & ligand. Vibration intervals, due to this the terms are impure, hence d - d transition occurs.

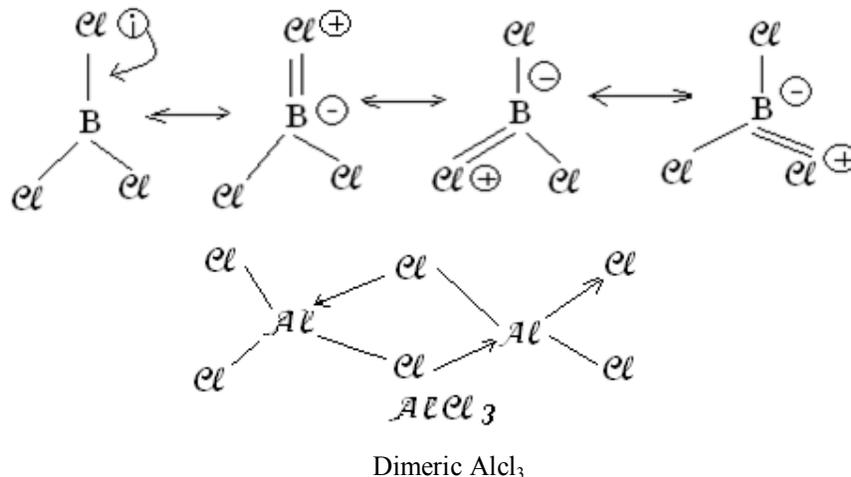


INORGANIC

Q.N. - 8

8(c) :- Bcl_3 does not dimerise but $AlCl_3$ dimerises.

ANS. :- Bcl_3 are stabilized by resonance and exist as monomers whereas $AlCl_3$ is stabilized by dimerization in which Cl atom forms co-ordinate bond.

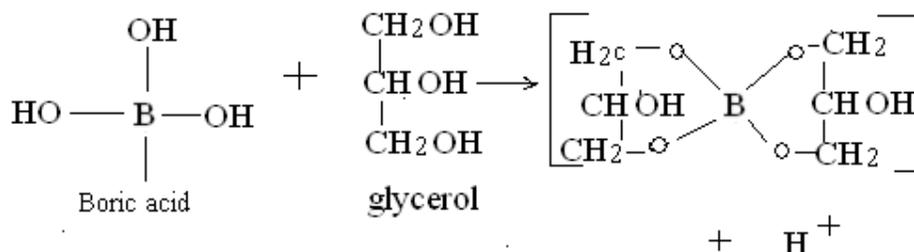


Further $p\pi - p\pi$ overlap becomes ineffective in $AlCl_3$ due to the larger size of Cl - atom.

Some important Questions to be solved.

Qn. :- Boric Acid behaves as strong acid in presence of glycerol.

ANS. :- Due to the complex formation boric acid behaves as a strong acid in presence of glycerol.



Qn. :- Though C-Cl bond energy is weaker than Si - Cl bond energy yet $SiCl_4$ is not hydrolyzed but $SiCl_2$ is hydrolyzed.

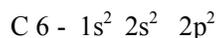
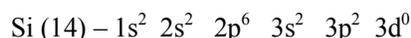
ANS. :- The reaction of ion and water is called hydrolysis. Hydrolysis is favored if ion has (i) charge - high (ii) radius - Small and (iii) d-orbital - empty.

From the question ----- $SiCl_4$ $SiCl_2$

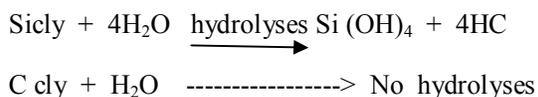
Charge on central atom --- +4 +4

Radius \longleftrightarrow Almost identical

D - orbital Total empty no d - orbital



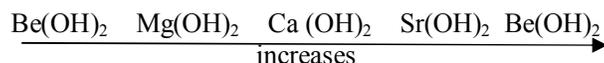
Thus C – atom cannot expand its valiancy hence tetra halide of carbon of is resistant to hydrolyses and because of the availability of the empty 3d – orbital in Si – atom, the lone pairs of electrons of attacking water molecules can be accommodated and thus SiCl₄ is readily hydrolyzed.



Tl⁺ is more stable than Tl⁺³. Tl is the heaviest member of group IIIA having valence state electronic configuration ns²np¹. Due to inert pair effect it shows (N – 2 = 3 – 2 = 1) i. e. +1 state in stead of +N i.e. +3, where N = group number. Therefore Tl⁺¹ is more stable than Tl⁺³.

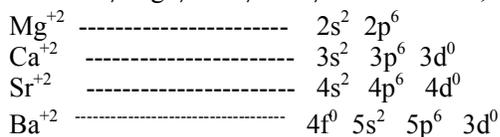
Order of basic strength of alkaline earth metal hydroxides

Metallic character increases from Be to Ba so force character of MO increases from BeO to BaO⁴ Due to increase in size from Be⁺² to Ba⁺², M⁺²-OH attraction decreases from Be(OH)₂ to Ba(OH)₂ and so dissociation of M(OH)₂ ⇌ M⁺²+2OH⁻ increases and basic character also increases therefore the basic strength of alkaline earth metal hydroxides is -



Qn. Order of M P for alkaline earth metals.

ANS. :- In solid state alkaline earth metals ex..... as M⁺², 2C in lattice. Radius of M⁺² decreases from Be⁺² to Ba⁺² and hence electro-static attraction decreases from Be to Ba. On this basis it is expected that p should have the order Be > Mg > Ca > Sr > Ba. However, the order is Be > Mg < Ca > Sr < Ba .



It is reported that due to participation of d-orbital in Ca and f – orbital in Ba, bond strength increases in M⁺², 2C due to d – d – and f – f overlap and in p of Ca and Ba show deviation. Due to greater extension of 4d in Sr relative to 3d, d – d overlap is not so effective.

Qn. Stability of N – 2 oxidation state for p block metals.

ANS. :- P block metals show variable oxidation states of +1 and +3. For lighter elements +3 state is more stable than +1 state but for the heavier element +1 state is more stable than +3 state.

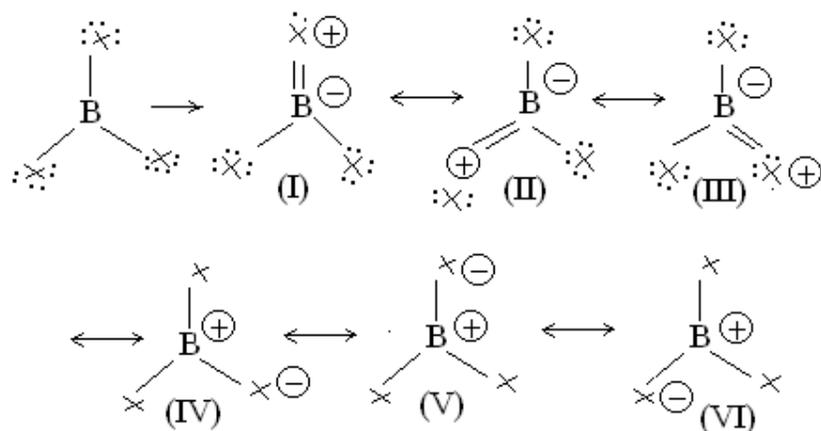
+3 state arises due to involvement of all the electrons in ns² np¹ and is termed as N – state. +1 state arises due to involvement of only np¹ and non participation of ns² electron and is termed N-2 states. The N-2 state thus arises due to inert pair effect.

The stability of +3 state is because ΔHs for M(s) -----> M(r) is very high and this is not compensated by the energy released in the formation of three bonds which are predominantly covalent.

Qn.

Order of acidic strength of Bx₃ (X = F, Cl, Br, I)

ANS. :- All boron halides are typical electron deficient compounds as they have only octal of electrons round B-atom in stead of octal of electron. Hence they are bonafide lanes acids. Since the lane pair of electrons of halogen is engaged in $p\pi - p\pi$ overlap therefore, B – atom acquires negative charge. But with the increase in size the strength of IT bonding decreases and thus amount of negative charge on B – atom decreases. Due to which electron accepting power increases and hence the acid strength increases.



Q : Order of acidic strength of oxy acids of Cl.

ANS. :- Chloride forms four oxy acids :-

$HCl^{+1}O$	-----	Hypochlorous acid
$HCl^{+3}O_2$	-----	Chlorous acid
$HCl^{+5}O_3$	-----	Chloric acid
$HCl^{+7}O_4$	-----	Perchlionic acid

With the increase in the value of oxidation number of the central halogen atom i. e. Cl , in oxy acids of chlorine, the acid strength increases because more and more electrons are going to be accepted by the central atom of the acid. Therefore, the relative strength of oxy acids of chlorine following the trend.

Q Effective nuclear charge for K(19) and Cu (29)

ANS. :- Potassium :

$$K_{19} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

$$\therefore \text{Screening constant } S = 10 + 8 \times 0.85 + 0$$

$$= 10 + 6.80$$

$$= 16.80$$

$$\therefore \text{Effective nuclear charge } Z^* = Z - S$$

$$Z^*_k = 19 - 16.80$$

$$= 2.20 \text{ Units}$$

Copper :

$$Cu_{29} :- 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

$$\text{Or } [18] 3d^{10} 4s^1$$

$$\therefore \text{Screening constant } S = 18 + 10 \times 0.85 + 0$$

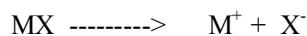
$$= 18 + 8.5$$

$$= 26.5$$

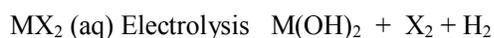
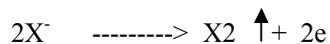
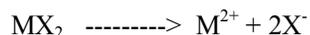
∴ Effective nuclear charge (Z*)
 $Z^*_{Cu} = Z - S$
 $= 29 - 26.5$
 $= 2.5 \text{ Units}$

Q : Alkali and alkaline earth metals are not isolated by the electrolysis of aqueous salt solution.

ANS. :- The aqueous solutions of alkali and alkaline earths upon electrolysis give metal hydroxides M(OH) or M(OH)₂ instead of pure metal, M. Hence alkali or alkaline earth metals are not obtained by the electrolyses of their aqueous solutions. :



And,

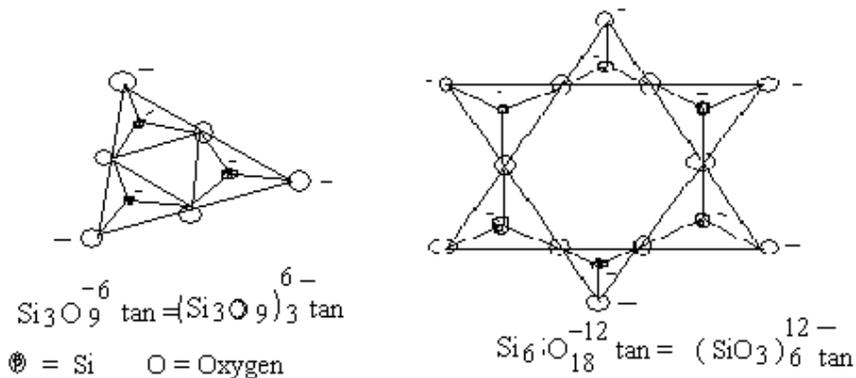


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Qn. Silicate form chain and ring structures.

ANS. :- Simple silicates has SiO₄⁻² tetrahedral Si – O bond energy is high (106 K cal), Si has the property of forming complex silicates like chain and ring structures by forming – Si – O – Si – O – linkage. The complex silicates are formed by sharing of O of SiO₄⁻² - tetrahedral.

When two oxygen atoms of SiO₄ tetrahedral is shared (i) cycle or ring silicates and (ii) chain silicates are obtained.

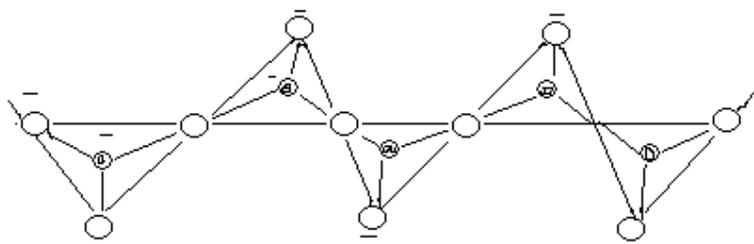


(Cycle silicates)

Examples (i) Ca₃ (Si₃O₉) [Wollastonite]

(ii) $\text{Be}_2\text{Al}(\text{Si}_6\text{O}_{18})$ [Beryl]

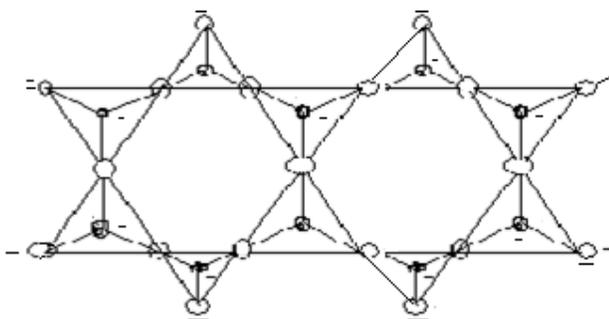
Chain Silicates :



$(\text{SiO}_3)_n 2n^-$ Chain

Example :- $\text{Li}_2\text{Al}(\text{SiO}_3)_n$ [Spodumenu]

Double chains are formed when two SiO_3 units are joined together the formula forms out to be $(\text{Si}_4\text{O}_{11})_n^{-6n}$



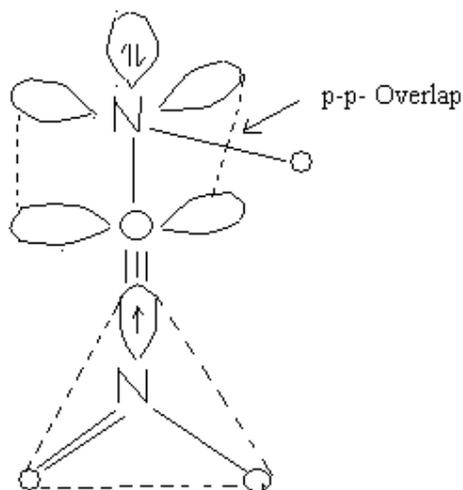
In this chain some tetrahedral share two O and some share three O- atoms –

Example :- $\text{Ca}_2\text{Mg}_5\text{Si}_4\text{O}_{11}(\text{OH})_2$ [Tremolite or Amphibole]

Qn. N_2O , NO , NO_2 exist but the corresponding p – compounds do not exist.

ANS. :- Size of N is small relative to size of p. Hence due to small size and lack of d – orbital in its outer most configuration N shows properties different from p.

Due to small size N, p- p overlap in N_2O , NO & NO_2 is possible and these compounds exist. But in case of p, due to its large size p – p overlap is not effective. Hence the corresponding compounds of p do not exist.

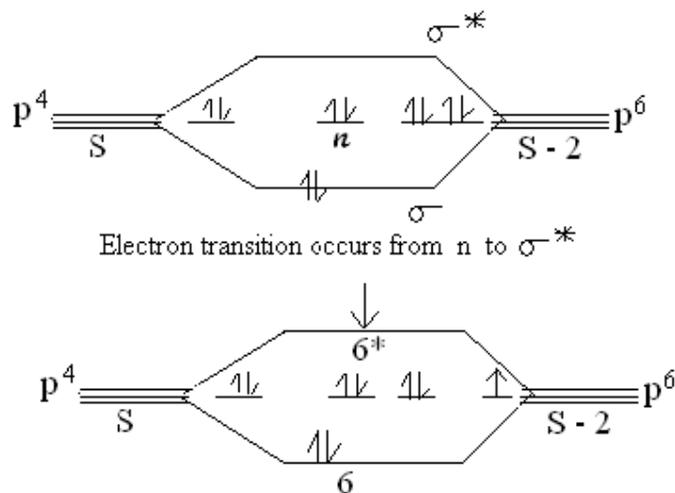


Qn. Oxy acid of S in +6 oxidation state is H₂SO₄ but of Te is H₆TeO₆.

ANS.:- The maximum covalence of S is 6 and of Te is 8. Due to maximum covalence 8 for Te, the oxyacid of Te in +6 state is H₆TeO₆.

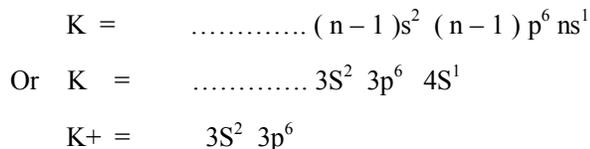
Qn.- (NH₄)₂S₂ is yellow:

ANS.:- (NH₄)₂S₂ is yellow due to charge transfer from S⁻² – S in S₂²⁻. Charge transfer occurs from non-bonding (n) to σ* (anti bonding) orbital.

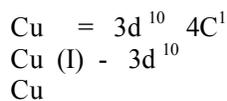


Qn. Fixed oxidation state of K variable oxidation states for Cu.

ANS. :- In case of K fixed oxidation state of +1 is found, the +1 oxidation state is formed by electron loss as I. PI is low.



Due to stable (n-1)s² (n-1)p⁶, I. p II is very high and so +2 oxidation state is not possible. In case of Cu, due to participation of (n-1)d¹⁰ electron, it has variable oxidation states i.e.



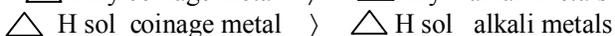
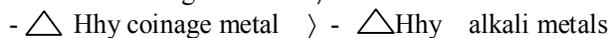
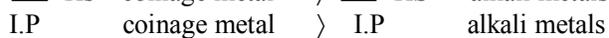
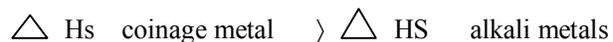
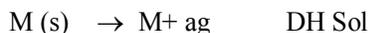
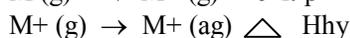
(II)

-

3d

K is a base metal but Ag is noble metal.

ANS. :- Oxidation potential of coinage metal is less positive than alkali metals. The less positive oxidation potential is due to high sublimation energy and high I. p. of the coinage metals. Thus coinage metals are poor reducing agent relative to alkali metals.



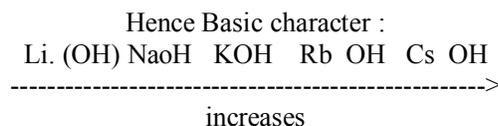
Alkali metals for example K, due to low I. P. and low ΔH_s sublimation have high value of E^0 and easily react with H_2O to form HOH base i. e. KOH base one recalled base metals. Coinage metals for example Ag due to high I. P. and high ΔH_s sublimation E^0 and does not react with water to form base. Hence Ag is noble metal.

Q. Explain :-

(a) Order of basic strength for MOH ($M = \text{alkali metals}$)

Ans. :- The metallic character increases from Li to Cs and so basic character of Metal hydroxides increases from Li to Cs.

In MOH , radius of M^+ increases from Li^+ to Cs^+ and hence attraction between M^+ and OH^- decreases from Li^+ to Cs^+ consequently dissociation of MOH to $M^+ + OH^-$ increases and basic strength increases.



As a matter of fact MOH are strong bases and are 100% ionized.



-----X:-----

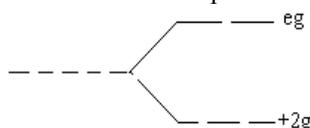
TRANSITION METAL CO-ORDINATION CHEMISTRY PART-V

Compare valence bond, crystal field and molecular orbital models with properties of complexes.

Three general theories have been used as bonding models to explain the various properties of complexes.

(1) Valence Bond Theory: - It is given by L Pauling and it closely related to the hybridization and geometry of complex ions. From the valence bond point of view the formation of a complex is a reaction between Lewis base (L) and Lewis acid (N and M term) with the formation of a co-ordinate covalent bond between metal and the ligand. Depending upon the strength of ligand rearrangement of electronic configuration of free M^+ ion is postulated and vacant orbital of M ion hybridizes to produce hybrid orbital. These hybrid orbital are used up for bonding e. g., $d^2s p^3$ hybridization gives octahedral shape, $sp^3 d^2$ also octahedral, sp^3 gives rise to tetrahedral and dsp^2 gives square planar shape for the complex ion.

(2) Crystal Field Theory: - It was developed by Bethe and Vanvlock. Crystal field theory assumes that the only interaction between M and L is an electrostatic one as a result of which the fine metal d orbital split into different sets e.g., in octahedral crystal field d – orbital splits as follows :-



The occupancy of electron depending upon the strength of crystal field and the pairing energy enables to explain the spectral and magnetic properties of complexes. It also explains the liability and other variations in data such as lattice energy, hydration energy.

Electrons prefer t_2g orbital because $10Dq$ is greater than pairing energy. Thus it is a diamagnetic complex. Spectral properties can be explained by the use of T-S diagram, where A_1g is the grand state. The complex is expected to be inert due to large CFSE.

(3) The molecular orbital energy level diagram can qualitatively be shown as:-

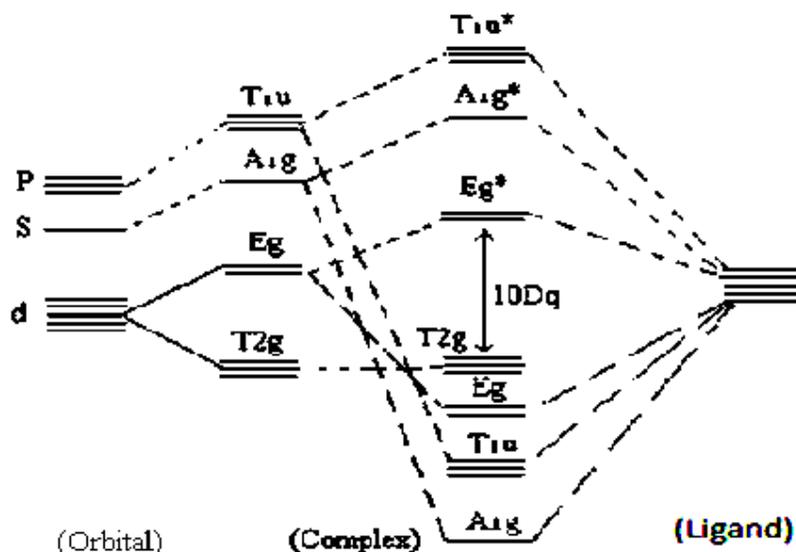
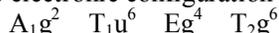


Fig. :- Molecular orbital diagram for an octahedral complex showing relation between MOT, CFT and VBT.

It is certain that the overlap of 4s and 4p orbital with the ligands is considerably better than that of 3d - orbital. As a result A_{1g} and T_{1g} molecular orbital are the lowest in energy and the corresponding A_{1g}^* and T_{1g}^* anti bonding orbital the highest in energy. The E_g and E_g^* orbital arising from the 3d- orbital are non bonding (in a 6, only system) and not displaced.

Electrons may now be added to the molecular orbital of the complex in order of increasing energy. In complex such as $[\text{Co}(\text{NH}_3)_6]^{+3}$, there will be a total of 18 electrons, 12 from lone pairs on the N- atom and 6 from the $3d^6$ configuration of Co^{+3} ion. The electronic configuration will then be -



The complex is dia magnetic because the electrons pair in the T_{2g} level rather than enter the higher energy E_g^* level. If this energy tiff is small as in $[\text{CoF}_6]^{-3}$, the electrons will be distributed $T_{2g}^4 E_g^{*2}$.

Thus both molecular orbital theory and crystal field theory accounts for the magnetic and spectral properties of octahedral complex ions by supposing the existence of two sets of orbital separated by an energy gap, $10Dq$. If this energy is greater than the pairing energy, low spin complexes will be formed, but if the energy necessary to pair the electrons as greater than $10Dq$, higher spin complex will result.

Comparison of MOT, CFT and VBT

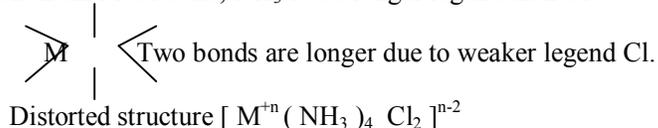
Both MOT and CFT account for the spectral and magnetic properties of octahedral complex ions by supposing the existence of two sets of orbital separated by an energy gap, $10Dq$, of the energy necessary to pair the electrons is greater than this, high spin complexes will form; otherwise low spin complexes form likewise, the visible spectra of complexes are attributed -- eg^* , The qualitative results of CFT and MOT are quite similar although the fundamental assumption purely electrostatic perturbations versus orbital mixing seem considerably different. One might say that CFT gives the right answer for wrong reasons, it is said that CFT is "too good to be true", i. e. it is easy to understand and apply, but it's physical reality is poor - a point charge model does not represent a complex. On the other hand, MOT is "too true to be good", i.e. it correspond so closely to reality that the simplicity of CFT is largely lost. This points to the crux of the difficulty of the MOT; computational problems. The estimation of the appropriate overlap integrals in the absence of accurate wave functions presents many difficulties. For many purposes a qualitative molecular orbital approach is adequate and we may use it without too much concern for the computational problems.

The differences in basic assumption of both CFT and MOT describe complexes in terms of interactions between the metal orbital and the ligands are the greater this interaction, the greater will be $10Dq$. Since the six ligands always will donate 12 electrons to fill the A_{1g} , T_{1u} and E_g orbital, the d- electrons will occupy the T_{2g} and E_g^* lands, subject to the influence of the size of $10Dq$ and so the distribution of electrons is identical to that predicted by simple CFT. The magnitude of $10Dq$ now results from the strength of legend metal bond rather than from electrostatic effects.

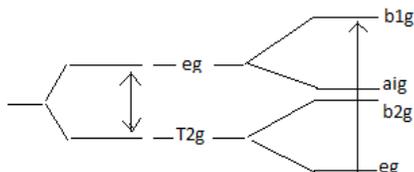
For strongly bonding ligands the A_{1g} , T_{1g} and E_g levels will be lowered mere and hence the anti bonding orbital E_g^* , T_{1u}^* and A_{1g}^* are correspondingly raised. As the ligands are moved away from the metal the overlap of orbital decreases, the bonding is weakened and the orbital move closer to their bary centre. In the extreme, with the ligands removed completely, we obtain the degenerate d-orbital as in CFT.

The UBT in it's usual form concentrates on the formation of a d^2sp^3 hybrid from the metal orbital. The A_{1g} , T_{1u} and E_g molecular orbital are served from the single $4s$, three $4p$ and two of the five $3d$ orbital of the metal. As is commonly the case with simple valence bond descriptions, the excited states are ignored.

M- NH_3 bond is different from M-Cl bond, NH_3 is a stronger legend than Cl.



Distortion in structure is due to in equivalence of ligands. Distorted octahedral structure means Tetragonal structure.



Splitting is asymmetrical because doubly degenerate eg splits into single b_{2g}

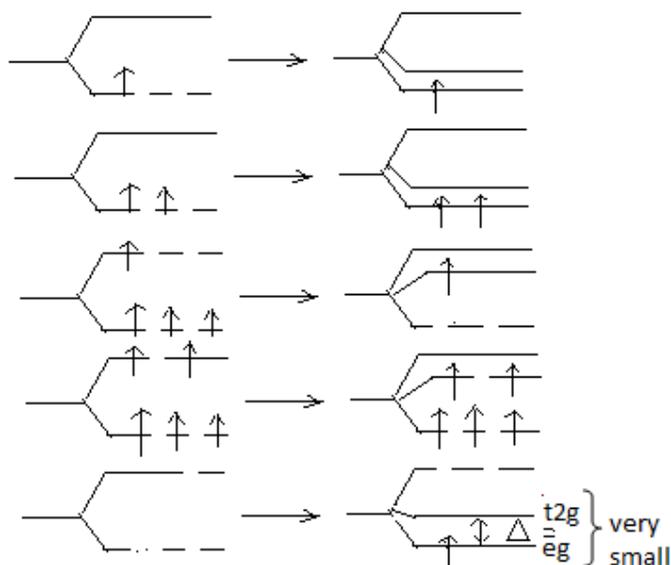
JOHN TELLER DISTORTION

Even if, ligands are all equivalent, we get distorted structure.

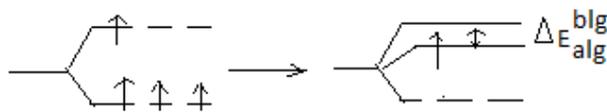
JOHN TELLER THEOREM

Orbitally degenerate system distorts itself to remove the degeneracy.

If degenerate orbital are unevenly occupied degeneracy is lost.

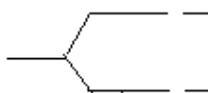


distortion due to t_{2g} is very very small and it is not detectable. This means no distortion occurs due to t_{2g} .



The energy gap between a_{1g} & b_{1g} is appreciable, so distortion occurs only due to eg set of orbital.

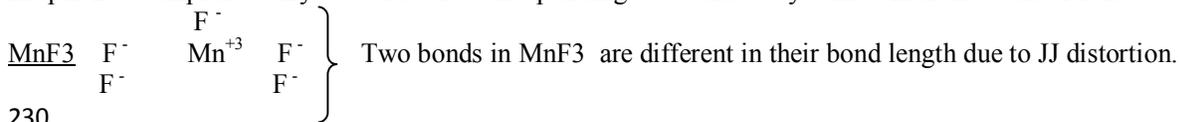
OCTRAHEDRAL SPIN FREE

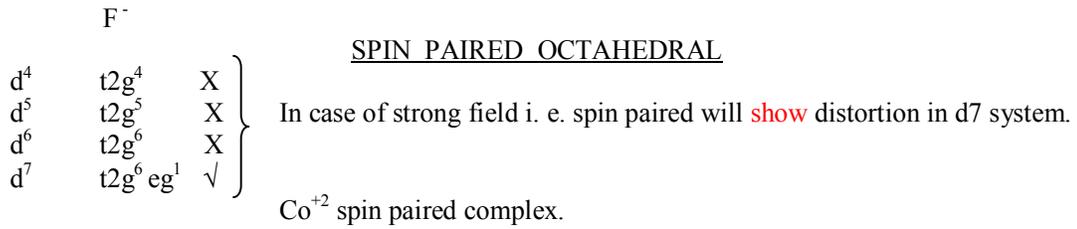


DISTORTION

d^1	t_{2g}^1	X	d^6	$t_{2g}^4 eg^2$	X
d^2	t_{2g}^2	X	d^7	$t_{2g}^5 eg^2$	X
d^3	t_{2g}^3	X	d^8	$t_{2g}^6 eg^2$	X
d^4	$t_{2g}^3 eg^1$	✓	d^9	$t_{2g}^6 eg^3$	✓
d^5	$t_{2g}^3 eg^2$	X			

In spin free complexes only two structure corresponding to d_4 and d_9 systems which show distortion.



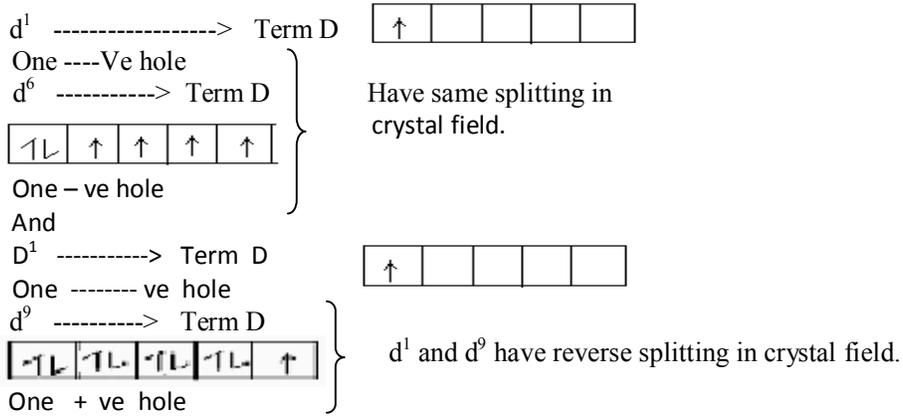


Hole – formation :-

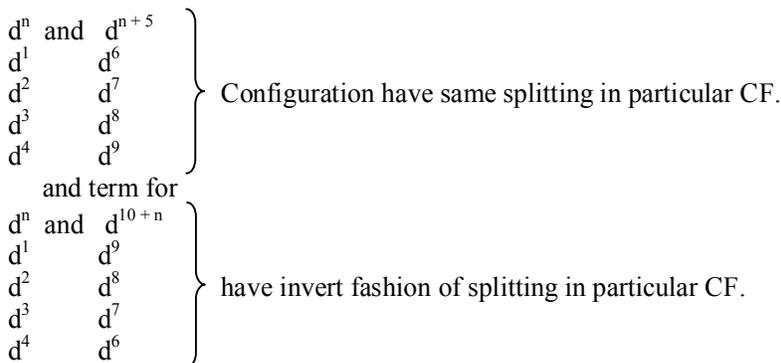
The splitting of term (Russel Saunder's Term) is governed by hole formalism.

In it

- (i) Electron is considered as negative charge.
- (ii) Presence of an electron is considered as negative hole.
- (iii) Absence of electron is considered as positive hole.
- (iv) If two configurations have same number of similar holes, the terms split in a similar way.
- (v) If two configuration have same number of opposite holes the terms splits invert to each other.
- (vi) As V_{oct} (potential energy of octahedral) is negative and V_{tet} is positive, the splitting of terms in oct and tet is invert for a particular configuration.
Hole formalism is also known as equivalency, e. g. –



So, we can generalized it i. e., Term for

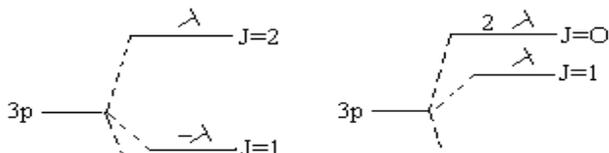


Similarly p^n and p^{6-n} configurations and f^n and f^{14-n} have same set of Russel Saunder's Term.

Now, let us take the example of d^2 and d^8 system. There is reversal of J – values.

The J values for $d^2 = 0, 1, 2$

While for $d^8, J = 2, 1, 0$

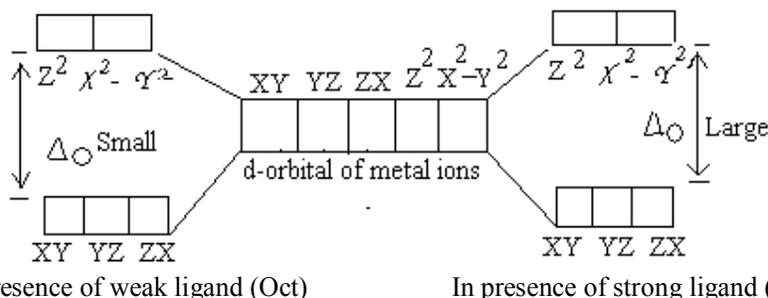


The spacing in between the different J values.

Spectra-chemical series (in respect of L F T).

Stronger ligands are those which exert a strong field on the central metal ion and hence have higher splitting power while the weak ligands are those which have weak field on the central metal and relatively lower splitting power.

For example, strong ligand like CN^- give larger value of Δ and weak ligand like F^- yield a smaller value of Δ



The common ligands are arranged in the order of their increasing splitting power to cause d- orbitals splitting, the series is called spectra-chemical series.

- $I^- < Br^- < Cl^- < SCN^- < N_3^- < (C_2H_5O)_2 p_5 < F^-$
- $< (NH_2)_2 CO < OH^- < C_2O_4^{2-} < H_2O < NCS^- < H^-$
- $< CN^- < NH_2^- < CO_2 < NH_3 < C_5H_5N < en < SO_3^{2-}$
- $< NH_2OH < NO_2^- < phen < H^- < CH_3^- < CN^- < Co$

A similar series can be prepared with respect to metal ions using same ligand in same C.N. It may be given as :-

- $Mn^{+2} < Ni^{+2} < Co^{+2} < Fe^{+2} < V^{+2} < Fe^{+3} < Cr^{+3} < V^{+3}$
- $< Co^{+3} < Mn^{+3} < Rh^{+3} < Pd^{+4} < Ir^{+3} < Pt^{+3}$

But the series does not remain intact on changing the ligand or co-ordination number.

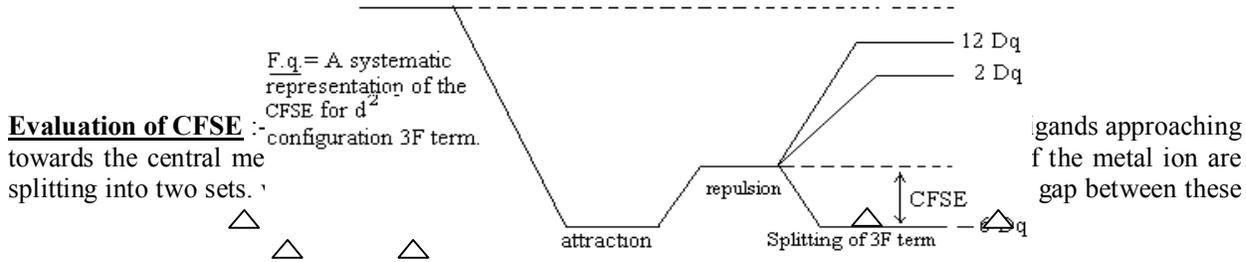
- Uses :-** (i) It can be used to decide the weak field or strong field nature of ligand in V. B. T.
- (ii) Comparative Δ values can be correlated with the magnetic properties and spectral properties of complex in C. F. T.

LIMITATIONS :-

- (i) This series is prepared using metal ion in usual oxidation state. If metal ion is taken in unusual oxidation number, the metal, ligand interaction may be different and hence, the relative order of Δ may be reversed.
- (ii) For some metals, even in usual oxidation number the inversion in order has been observed.
- (iii) If a ligand does not form desired complex in same oxidation number, theoretical calculations are used to get Δ value.

Crystal field stabilization energy.

The difference between the lowest energy level of a term split by a crystal field and the centre of gravity of the term in the crystal field is known as the crystal field stabilization energy as shown in diagram (d^2 case).



two sets is equal to 0 (or $10 Dq$). The energy of t_{2g} set is lowered by $2/5 \Delta_o$ ($= 0.4 \Delta_o$) or $4 Dq$ while that of eg set is raised by $3/5 \Delta_o$ ($= 0.6 \Delta_o$) or $6 Dq$ relative to the energy of hypothetical degenerate d-orbitals.

Thus each electron occupying t_{2g} orbitals decreases the energy of d-orbitals by $-0.4 \Delta_o$ ($= -4 Dq$) while that going into eg orbitals increases its energy by $+0.6 \Delta_o$ ($= +6 Dq$).

Now, let us consider a d^{p+q} ion with p - electrons in t_{2g} and q electrons in eg orbitals. So, we can write,

$$\left. \begin{array}{l} \text{Gain in energy due to } q \text{ electrons} \\ \text{in eg - orbitals (in terms of } \Delta_o \text{)} \end{array} \right\} = +0.6 \Delta_o \times q$$

$$\& \text{ lose in energy due to } p \text{ - electrons in } t_{2g} \text{ orbitals (in terms of } \Delta_o \text{)} \left. \right\} = 0.4 \Delta_o \times p$$

Thus,

$$\text{Net change in energy for } d^{p+q} \text{ ion (in terms of } \Delta_o \text{)} = [-0.4 p + 0.6 q] \Delta_o$$

$$\text{Since, } \Delta_o = 10 Dq$$

Thus,

$$\text{Change in energy (in terms of } Dq \text{)}$$

$$= [-0.4 p + 0.6 q] \times 10 Dq$$

$$= [-4 p + 6 q] Dq$$

This change in energy is called crystal field stabilization energy. Since it stabilizes d - orbitals by lowering energy which results from their splitting into t_{2g} and eg orbitals.

Thus, we can say that CFSE for d^0 (Low spin and high spin) d^5 (high spin) and d^{10} (low spin and high spin) is always zero.

- (1) If p = pairing energy which is the energy required to pair two electrons against electron - electron repulsion in the same orbital and m = No. of paired electrons,

Then,

$$\text{CFSE for } d^{p+q} \text{ ion} = [-0.4 p + 0.6 q] + m.p$$

(ii) d^3 System :- (LS & HS) = $[-0.4 \times 3 + 0.6 \times 0] \Delta_o + 0 \times p$
 $= -1.2 \Delta_o = 12 Dq$

(iii) d^4 System :- For LS complex - $d^4 = t_{2g}^3 e_g^1$ & $m = 1$
 Then CFSE = $[-0.4 \times 4 + 0.6 \times 0] \Delta_o + 1 \times p$
 $= -1.6 \Delta_o + P = 16 Dq + p$

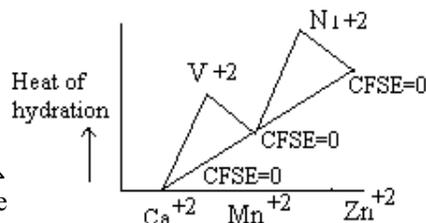
For HS Complex, $d^4 = t_{2g}^3 e_g^1$ and $m = 0$, then

$$\text{CFSE} = [-0.4 \times 3 + 0.6 \times 1] \Delta_o + 0 \times p$$

$$= -0.6 \Delta_o = -6 Dq$$

USES OF CFSE :-

- (i) In determining the structure of compounds.
- (ii) Stabilization of oxidation states, eg., $[\text{Co} (\text{H}_2\text{O})_6]^{+2}$ is more stable than $[\text{Co} (\text{H}_2\text{O})_6]^{+3}$. This is because of the fact that Co^{+2} (d^7) has much higher value of CFSE in weak octahedral complex ($\text{CFSE} = 0.8 \Delta_o$) than Co^{+3} (d^6) in the same configuration ($\text{CFSE} = 0.4 \Delta_o$)
- (iii) Stereo Chemistry of complex :- CFSE values also predict why Cu^{+2} ion forms square planar complexes rather than tetrahedral or octahedral complex in both the field, Because Cu^{+2} ion (d^9) has a much higher CFSE value in a square planar configuration ($\text{CFSE} = 1.22 \Delta_o$) than in octahedral ($\text{CFSE} = 0.6 \Delta_o$) or tetrahedral configuration ($\text{CFSE} = 0.18 \Delta_o$).
- (iv) Heats of hydration of divalent ions of first row transition elements eg; the hex hydrated ions $[\text{M} (\text{H}_2\text{O})_6]^{+2}$ are high spin octahedral complexes and for HS complex, CFSE is minimum (zero for d^0 (Ca^{+2}), d^5 (Mn^{+2}) and d^{10} (Zn^{+2}) ions and maximum ($= 1.2 \Delta_o$) for V^{+2} , d^3 and d^8 (Ni^{+2}) ions as shown below :



Crystal field splitting parameters (Δ_o)

The magnitude of Δ_o for a complex depends on the nature of the central metal ion and the nature of the ligands.

The ligand properties such as size, charge, permanent dipole moment, μ_0 and polarizability $\propto \Delta_o$

influences this strength. Since,

$$\mu_i = E \alpha \quad \text{where } E = \text{polarizing field and total dipole moment.}$$

$\mu = \mu_o + \mu_i$, μ_i = induced dipole moment. The σ -bonding strength and π -bonding strength of ligands also affect Δ_o , but these factors are not for CFT but for MOT. Δ_o is usually treated as a semi empirical parameters and hence obtained from experimental data, generally from spectra, from magnetic and thermodynamic data. For example, in case of d^1 system (Oct) –

$$CFSE = -4 Dq, \Delta_o = 20,400 \text{ cm}^{-1} \text{ \& } Dq = 2040 \text{ cm}^{-1}$$

$$CFSE = 4 \times 2040 = -8160 \text{ cm}^{-1}$$

On the basis of experimental data a general conclusion were drawn concerning the magnitude of Δ_o . These Δ_o are most valid for high spin complexes and especially those of metal ions in their normal oxidation states.

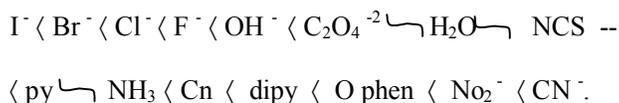
(1) Δ_o Increases about 30% to 50% from 3d to 4d and by about the same amount again from 4d to 5d complexes.

of $[\text{Co}(\text{NH}_3)_6]^{+3}$	$\Delta_o = 23,000$
$[\text{Rh}(\text{NH}_3)_6]^{+3}$	$\Delta_o = 34,000$
$[\text{Ir}(\text{NH}_3)_6]^{+3}$	$\Delta_o = 41,000$

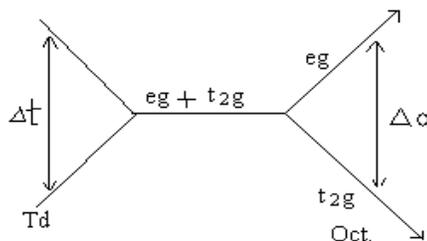
(2) Δ_o is about 40% to 80% larger for complexes of trivalent than for divalent cations. e-g, hydrated cations in the 3d series falls in the range 7,500 to 12,500 cm^{-1} . For divalent cations and for trivalent cations that of 13,500 to 21,000 cm^{-1} .

(3) Δ_o varies between 8000 and 14000 cm^{-1} . For most divalent 3d complexes.

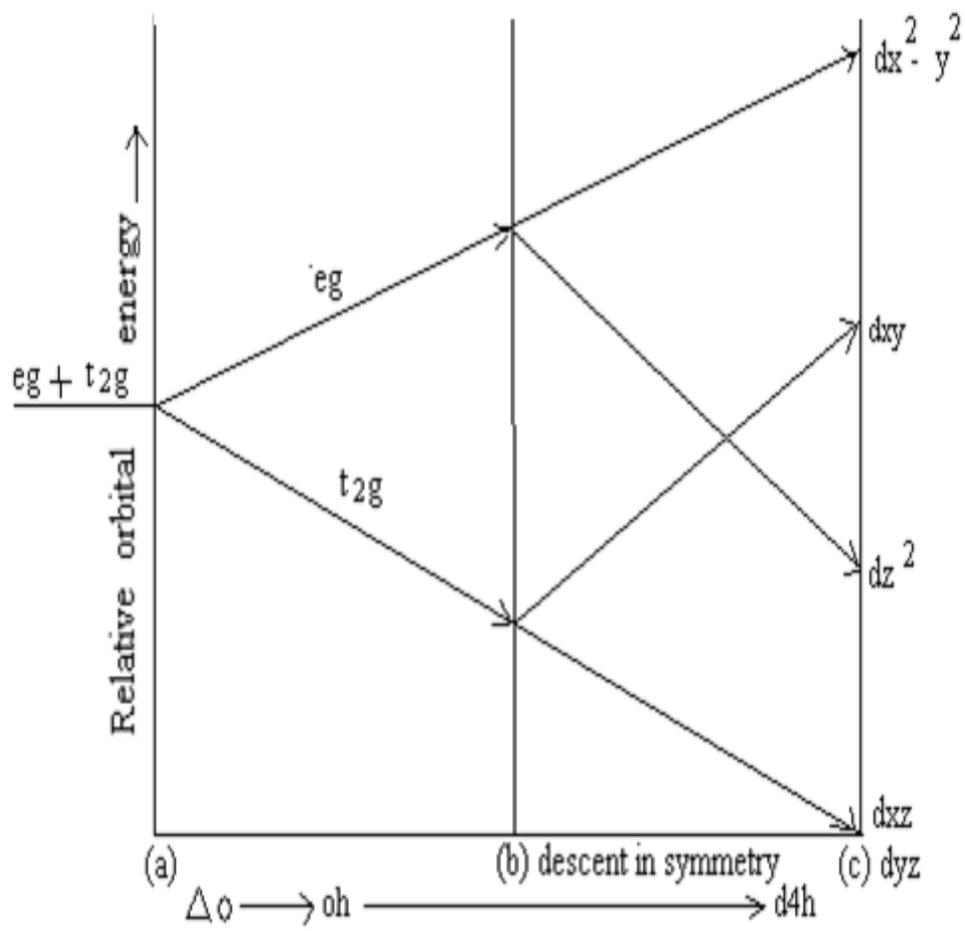
(4) The common ligands may be arranged in a regular order known as spectro-chemical series on increasing value of Δ_o .



(5) The crystal field splitting parameter for tetrahedral complex Δ_t has values which are about 40% to 50% of Δ_o . This value is very close to the theoretical value which from pure electrostatic CFT is $\Delta_t = -4/9 \Delta_o$.



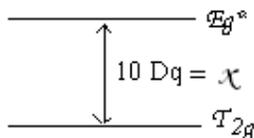
(6) For certain complexes in which Δ_o values is very close to the actual value of Δ_o for the metal atom in the complex, the change in temperature effects on its magnetic properties. As shown in figure, between b and c the further splitting up of the d-orbitals becomes increasingly tetrahedrally distorted that is two trans ligands are moved away and the remaining four equatorial ligand moved closer to the central atom.



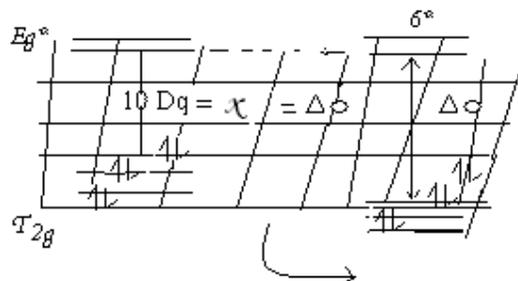
F^- is weak but CN^- is strong ligand.

Both the ligands have π orbitals. π orbital of F^- is filled while the π symmetry orbital of CN^- is empty.

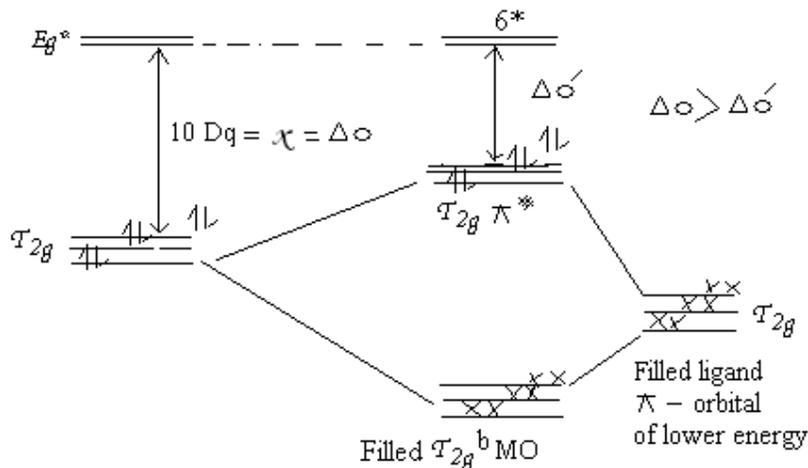
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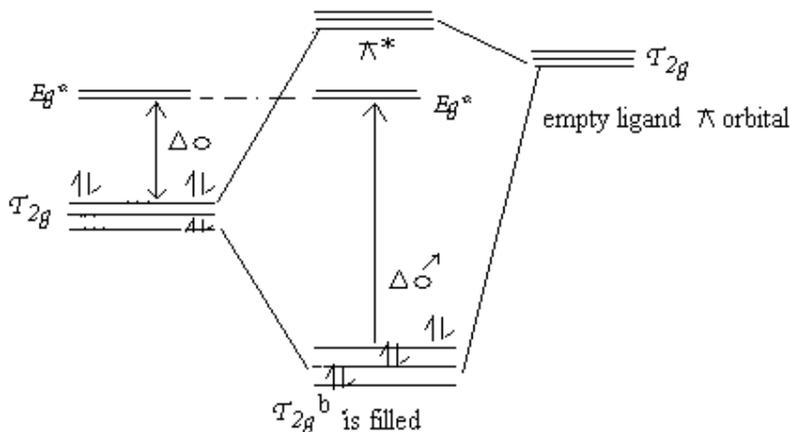
Now, if F^- is taken as ligand the MO diagram will be modified as :



GO TO THE NEXT TURN



Metal electrons now distributed which is less than the $10 Dq$ value (i. e. x) or Δ_o . Thus F^- is a weak ligand (donor ligand). If CN^- is taken as ligand the M.O. diagram will be modified as :-



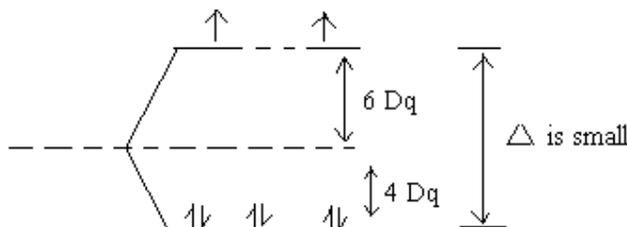
In this case, the net result of π interaction is that the t_{2g} orbitals are stabilized relative to the e_g^* MOs i. e. the metal t_{2g} electron will go into the t_{2g}^b MOs which are of lower energy than that t_{2g}^+ MO and thus value of $10 Dq$ (i. e. Δ_o) or Δ_o increased to Δ_o' . Δ_o is a strong ligand. (acceptor ligand).

CFSE for Co^{+2} spin free octahedral and of Co^{+2} spin paired octahedral differs.

In both spin – free and spin paired octahedral complex Co is in +2 oxidation state.

In spin free complex Co^{+2} is surrounded by weak ligand while in spin paired complex, Co^{+2} is surrounded by six strong ligands [CFSE () is large which is greater than pairing energy] so, electron in orbitals are forced to pair up in t_{2g} orbital.

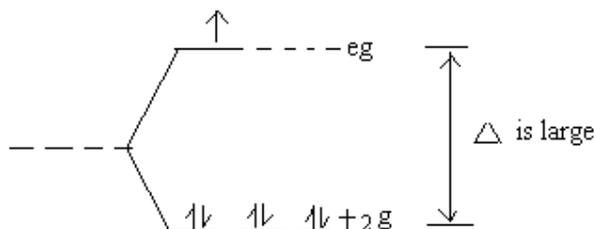
Since Co^{+2} is d^7 system, the configuration in oh weak field is like this



Configuration :- $t_{2g}^5 e_g^2$

$$\begin{aligned} \text{CFSE} &= (-4) \times 5 + (+6) \times 2 \\ &= -20 + 12 = -8 Dq \end{aligned}$$

In case of strong field, the configuration becomes like this $t_{2g}^6 e_g^1$ and degeneration orbital split as follows :



$$\text{CFSE} = (-4) \times 6 + (+6) \times 1 + P$$

Where P = Pairing energy

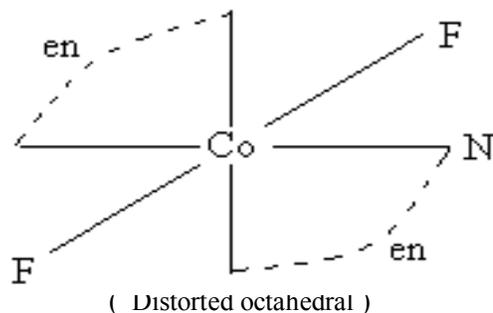
$$= -24 + 6$$

$$= -18 Dq + P$$

As we know that higher the magnitude of CFSE, greater is the stability. Hence Co^{+2} spin – paired octahedral complex is more stable than spin free octahedral complex.

$[Co(CN)_2F_2]^+$ is distorted octahedral.

$[Co(CN)_2F_2]^+$ is mixed ligand complex. It is a complex of Co^{+3} ion with $(CN)_2$ and two fluorine as ligand. Ethylene diamine (en) is bidentate ligand bonded through two nitrogen atoms. Thus there are four Co– N bonds and two Co– F bonds. Since F^- is a weaker ligand than ethylene diamine, so Co– N bond is shorter CO– F is larger, thus the octahedron is not perfect octahedron but it is distorted octahedron as shown below :-



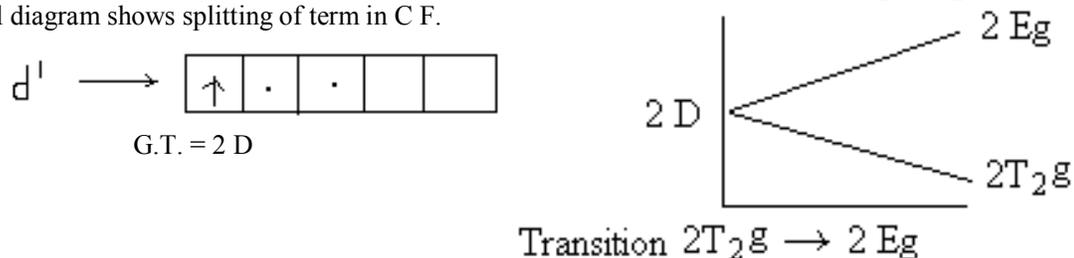
Lone pair of F & N repel each other leads to elongation of Co – F bond.

Orgel diagram :-

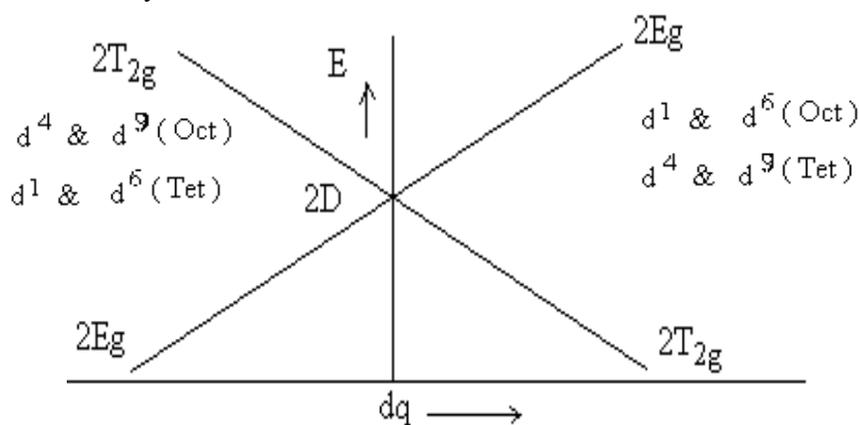
By making the assumption that the value of $15 B$ is same in the complexes ion as well as free ion. Orgel is able to use that weak field splitting of the energy terms and to show the variation of energy of each terms with increases Δ_{crd} .

Orgel diagram is most valid for d^1 and d^9 because there is no inter electronic repulsion. In other configuration there is other excited state terms and have inter electronic repulsion due to this the Orgel diagram is not valid in those cases.

USES :- From Orgel diagram, we can predict the electronic transition of metal ion. Orgel diagram for d^1 system – Orgel diagram shows splitting of term in C.F.



Other configuration which are related to d^1 configuration (i. e. system) are d^9 , d^4 and d^6 . A combined diagram can be drawn for all the four systems in both tetrahedral and octahedral fields. -

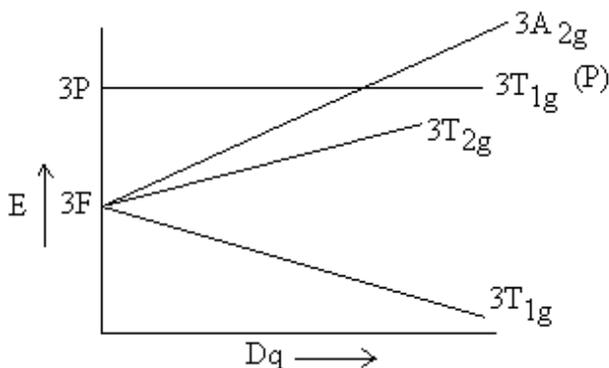


Only one transition is possible either $2T_{2g} \rightarrow 2E_g$ or $2E_g \rightarrow 2T_{2g}$

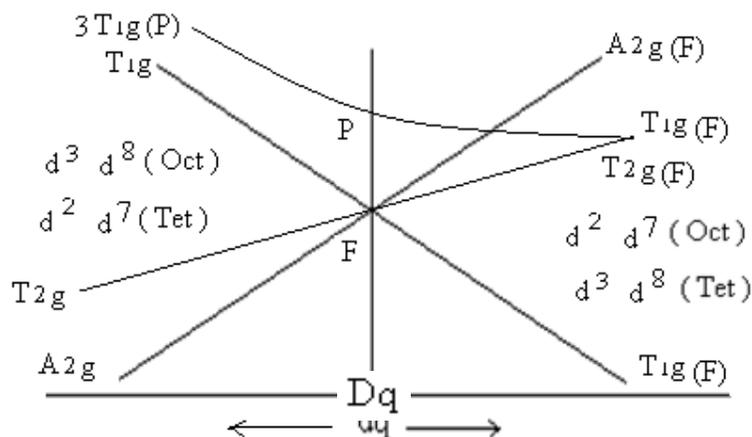
[Note :- The suffix 'g' is omitted in case of Tet]

Orgel diagram for d^2 :- It has ground term $3F$ and next excited state $3P$. Following three important features must be taken in account :-

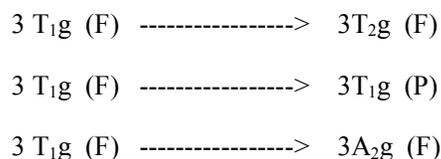
- (1) States with identical designation never cross.
- (2) The crystal field states have the same spin multiplicity as the free ion state from which they originate.
- (3) When there are only one states then depends primarily on the crystal field strength whereas when there are two or more states of identical designation show a curvature because they interact one another as well as crystal field.



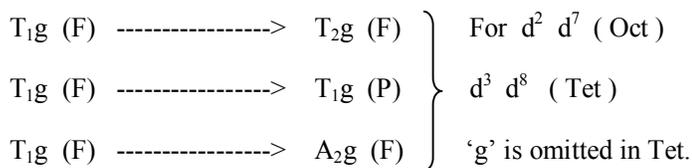
Other systems which are related to d^2 system are d^3 , d^7 & d^8 , A combined diagram can be shown as for all the four systems – both Oct and Tet case.



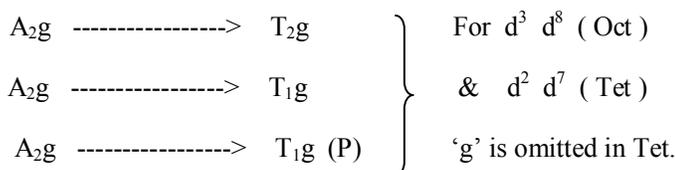
Here, three transitions are possible for d^2 (Oct), i. e.



Or, in general –



And,

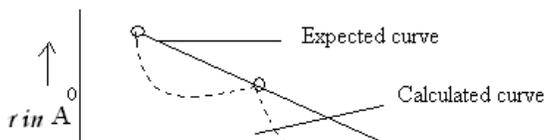


Effect of CFSE on thermodynamic properties.

Variation of ionic radius :-

A/c to normal periodic trend ionic radius should decrease smoothly from Ca^{+2} to Zn^{+2} due to increased effective nuclear charge resulting from poor shielding power of d- electrons. But when actual radius is plotted against corresponding metal ion three maxima are observed at Ca^{+2} , Mn^{+2} and Zn^{+2} . Incidentally only these three ions have ionic radius constant with expected value this is due to CFSE. These three ions are d^0 , d^5 and d^{10} respectively and have symmetrical field. Hence there is no attraction in their ionic radius.

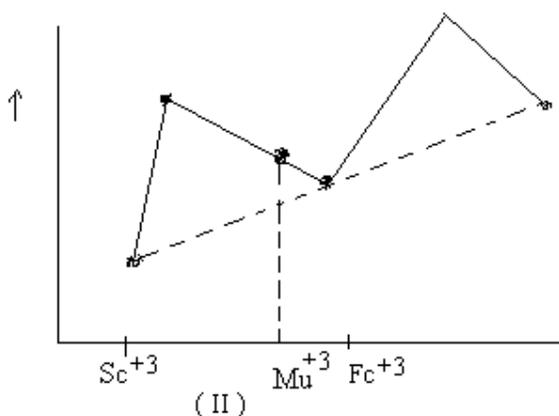
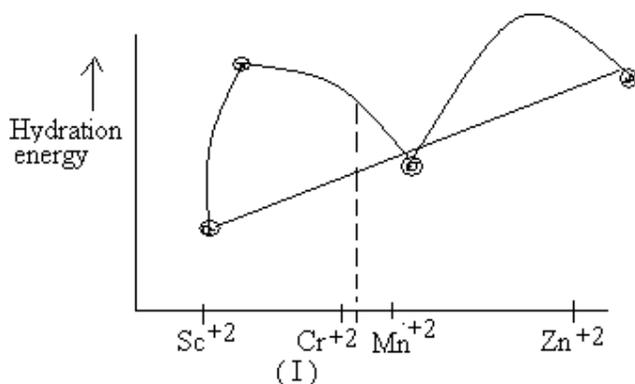
From Sc^{+2} (d^1) to V^{+2} (d^3) CFSE increases, so ionic radius decreases Cr^{+2} (d^4) has smaller value of CFSE than d^3 system so ionic radius is larger. Thus we obtain a more or less semi circular curve in the first half and same pattern is repeated in the second half. M^{+3} ion also show similar trend.



- (2)
(3)
(4)

δ^-

Variation of hydration energy :-



The graph (I) shows variation of hydration energy of M^{+2} ion. Hydration energy is given by ,

$$\Delta H_f = \frac{-Z e^2}{r e} \left(1 - \frac{1}{D}\right)$$

Z = effective nuclear charge

C = electronic charge

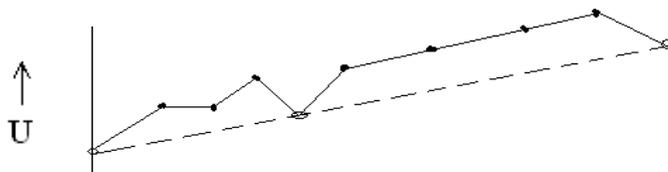
D = Dielectric constant

$r e$ = equilibrium distance between the centre of gravity of dipole molecule and value of the ion.

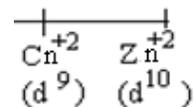
- (a) Ca^{+2} (d^0) Mn^{+2} (d^5) & Zn^{+2} (d^{10}) show minima in curve because they have zero CFSE value.
 (b) Cr^{+2} (i. e. d^4) has lower ΔH_f because it's $r e$ is large.
 (c) Similarly for M^{+3} ions minima are observed at Sc^{+3} (d^0 system) and Fe^{+3} (d^5 system) as they have no CFSE.
 (d) Mn^{+3} has lower CFSE have large $r e$ because of unsymmetrical distribution of electrons in t_{2g} and e_g orbital.

Hence actual plot is like a semicircle in the first half and same pattern is repeated in the second half.

- (5) Variation of lattice energy :-



Kcal/
moles



Lattice energy is given by following relation :-

$$U = \frac{Z^{+2} Z^{-} AN}{r_0} (1 - 1/r)$$

$Z^{+2} Z^{-}$ = effective charge for cation & anion

A = Madelung's constant

N = Avogadro's number

r_0 = inter nuclear distance

(a) As r_0 decreases lattice energy increases in this case also for M^{+2} ions these are minima at Ca^{+2} (d^0), Mn^{+2} (d^5) and Zn^{+2} (d^{10}).

(b) CFSE increases from Sc^{+2} to V^{+2} consequently r_0 decreases and lattice energy value increases. For Cr^{+2} CFSE value decreases and hence r_0 increases and U decreases.

Similarly for M^{+3} ion, same pattern of diagram comes for lattice energy versus number of d-electron.

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Factor influencing Δ in complexes.

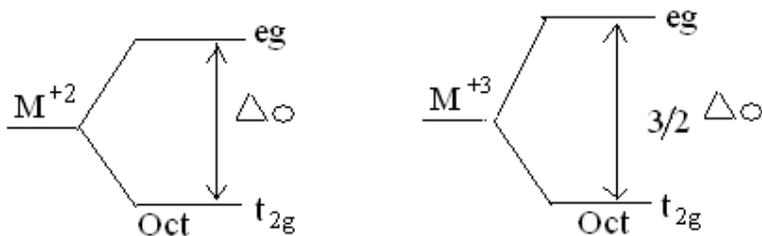
The extent of crystal field splitting or magnitude of Δ has been found to be influenced by the following factor :-

(1) Nature of metal ion :-

The charge on the cation and the size of the metal ion have been found to influence the magnitude of Δ greatly.

(a) Charge on the cation :- Complexes formed by cations with higher oxidation state have higher Δ value than that of lower oxidation state complexes. This is due to high polarizability power of these cations, e.g.; $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$ has Δ_o value = $17,400 \text{ cm}^{-1}$ while $[\text{V}(\text{H}_2\text{O})_6]^{+2}$ has Δ_o value = $12,600 \text{ cm}^{-1}$.

In general, increase in oxidation number by one, the Δ_o value becomes 3/2 to its previous Δ_o value.



In case of complexes having the cations with different number of d-electrons but the same charge, the magnitude of Δ_o decreases with the increase in the number of d-electrons, e.g., Δ_o for $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ is $9,300 \text{ cm}^{-1}$ while that of $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ (d^8) is $8,500 \text{ cm}^{-1}$ (oxidation state Δ_o)

(b) The size of cation :- The magnitude of Δ_o becomes considerably larger in the second ($4d^4$) and third ($5d^4$) transition series because of the increase in the size of cation. It has been found that Δ_o values are more in $4d^4$ complexes as compared to $3d^6$ complex. Similarly Δ_o value increases by the same amount from $4d^4$ to $5d^4$ complexes.

For example :- $(\text{NH}_3)_6]^{+3}$

$$3d^6 \Delta_o \text{ for } [\text{Co} (\text{NH}_3)_6]^{+3} = 23,000 \text{ cm}^{-1}$$

$$4d^6 \Delta_o \text{ for } [\text{Rh} (\text{NH}_3)_6]^{+3} = 34,000 \text{ cm}^{-1}$$

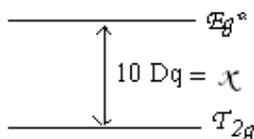
$$5d^6 \Delta_o \text{ for } [\text{Ir} (\text{NH}_3)_6]^{+3} = 41,000 \text{ cm}^{-1}$$

(2) Nature of ligand :- The properties of the ligand that influence the magnitude of Δ_o are its size, charge, dipole amount,

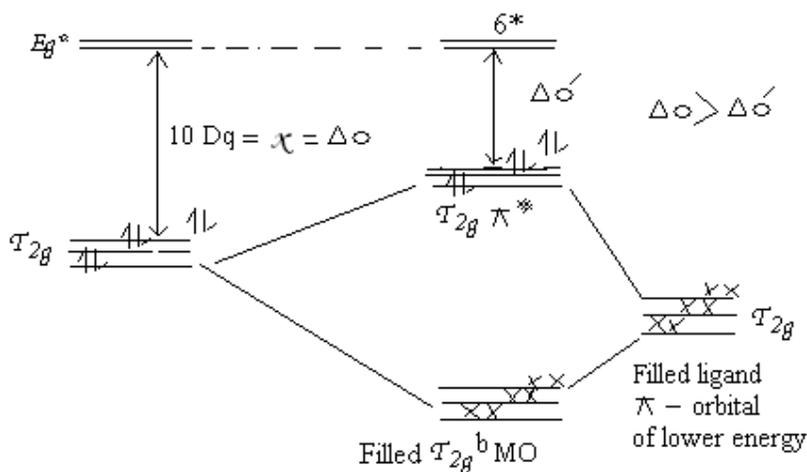
F^- is weak but CN^- is strong ligand.

Both the ligands have MO's of π - symmetry with the difference that the π - orbital of F^- is filled while the π - symmetry orbital of CN^- is empty.

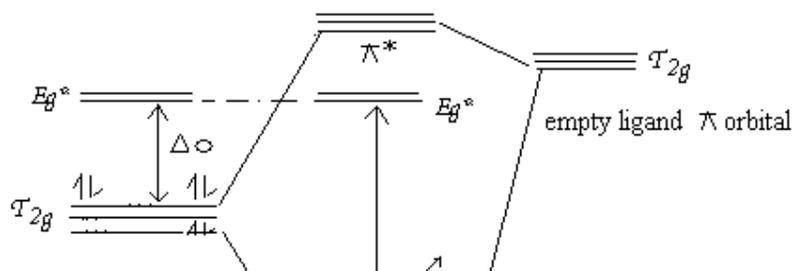
We know that according to MO diagram of ML_6 where L is 6 - bonding electron only metal electron distributes into T_{2g} and E_g^* MO as shown below and the difference in energy level is termed as $10 Dq$.



Now, if F^- is taken as ligand the MO diagram will be modified as :



Metal electrons now distributed which is less than the $10 Dq$ value (i. e. x) or Δ_o . Thus F^- is a weak ligand (donor ligand). If CN^- is taken as ligand the M.O. diagram will be modified as :-



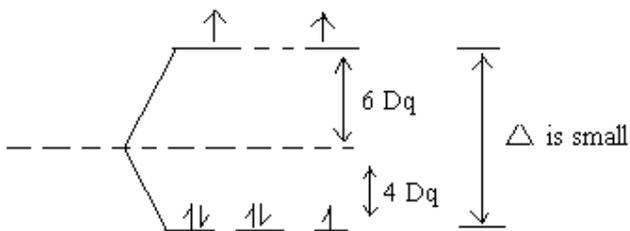
In this case, the net result of π interaction is that the t_{2g} orbitals are stabilized relative to the eg^* MOs i. e. the metal t_{2g} electron will go into the t_{2g}^b MOs which are of lower energy than that t_{2g}^+ MO and thus value of $10 Dq$ (i. e. χ) or Δ_o increased to Δ_o' . Thus CN^- is a strong ligand. (acceptor ligand).

CFSE for CO^{+2} spin free octahedral and of CO^{+2} spin paired octahedral differs.

In both spin – free and spin paired octahedral complex CO is in +2 oxidation state.

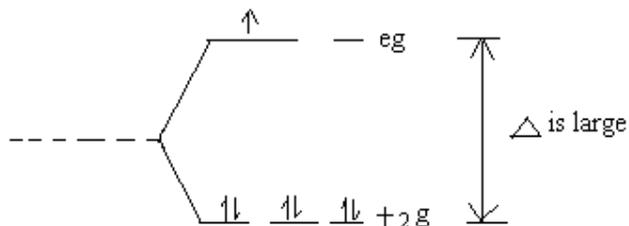
In spin free complex CO^{+2} is surrounded by weak ligand while in spin paired complex, CO^{+2} is surrounded by six strong ligands [CFSE (Δ) is large which is greater than pairing energy] so, electron in orbital are forced to pair up in t_{2g} orbital.

Since CO^{+2} is d^7 system, the configuration in oh weak field is like this



Configuration :- $t_{2g}^5 eg^2$
 $CFSE = (-4) \times 5 + (+6) \times 2$
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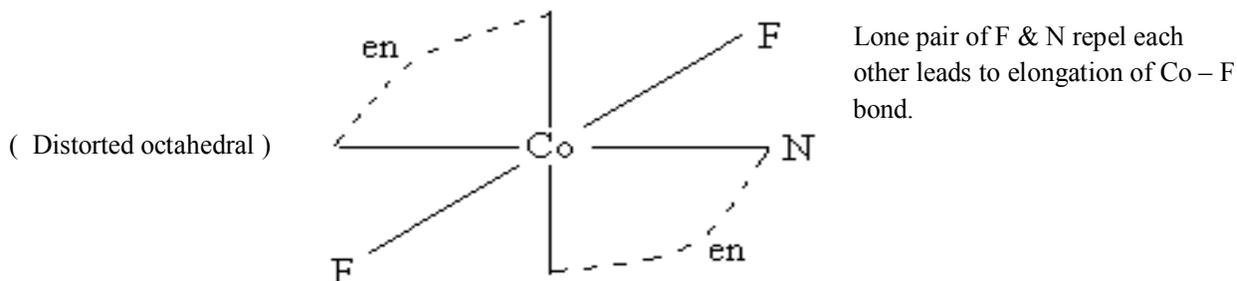


$CFSE = (-4) \times 6 + (+6) \times 1 + P$
 Where $P =$ Pairing energy
 $= -24 + 6$
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As we know that higher the magnitude of CFSE, greater is the stability. Hence Co^{+2} spin – paired octahedral complex is more stable than spin free octahedral complex.

[$CO(en)_2F_2$]⁺ is distorted octahedral.

[$CO(en)_2F_2$]⁺ is mixed ligand complex. It is a complex of CO^{+3} ion with $(en)_2$ and two fluorine as ligand. Ethylene diammine (en) is bidentate ligand bonded through two nitrogen atoms. Thus there are four Co – N bonds and two Co – F bonds. Since F^- is a weaker ligand than ethylene diammine, so Co – N bond is shorter Co – F is larger, thus the octahedron is not perfect octahedron but it is distorted octahedron as shown below :-

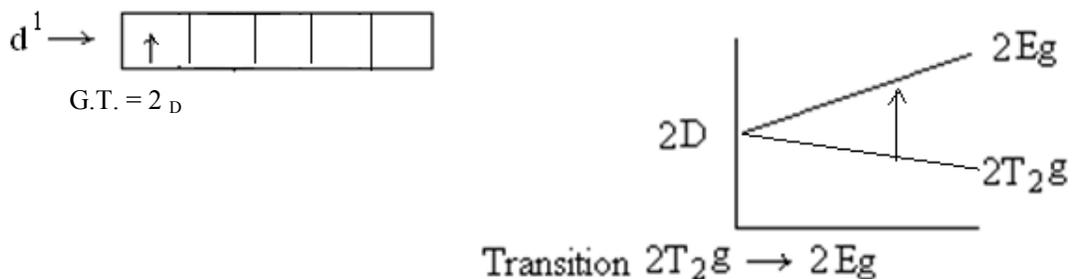


Orgel diagram :-

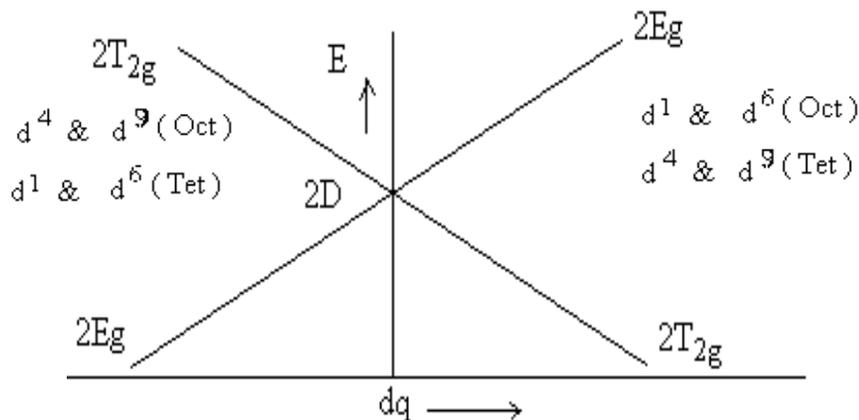
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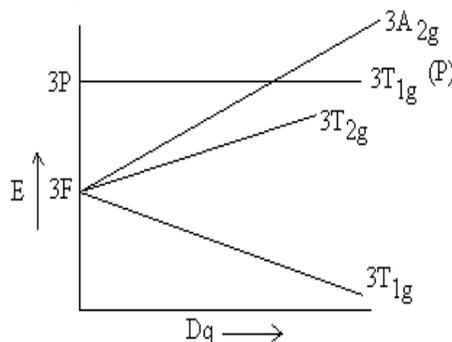
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[Note :- The suffix 'g' is omitted in case of Tet]

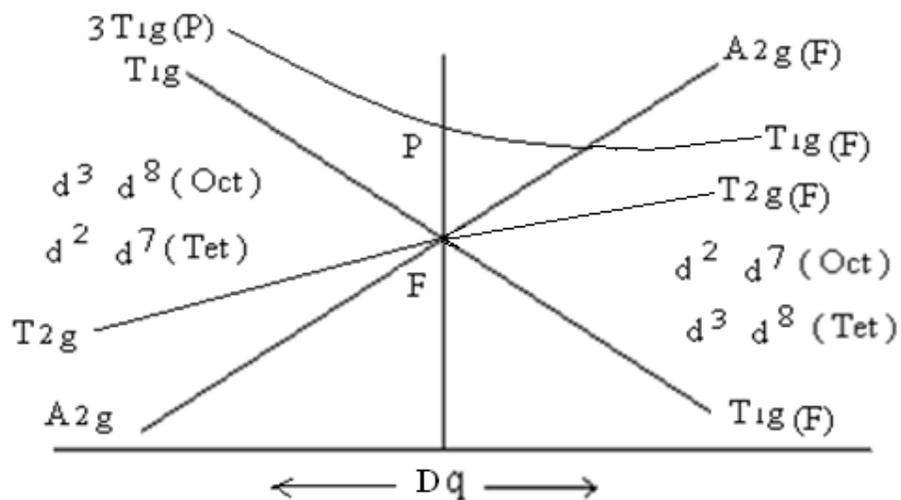
Orgel diagram for d^2 :-

It has ground term $3f$ and next excited state $3p$. Following three important features must be taken in account :-

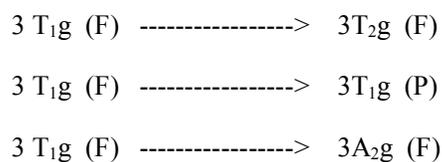
- (1) States with identical designation never cross.
- (2) The crystal field states have the same spin multiplicity as the free ion state from which they originate.
- (3) When there are only one states then depends primarily on the crystal field strength whereas when there are two or more states of identical designation show a curvature because they interact one another as well as crystal field.



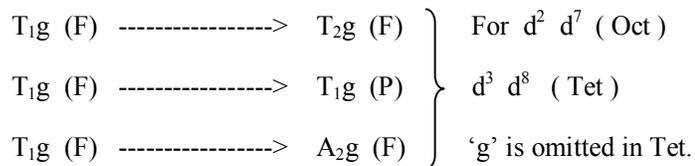
Other systems which are related to d^2 system are d^3 , d^7 and d^8 . A combined diagram can be shown as for all the four systems both oct and tet case.



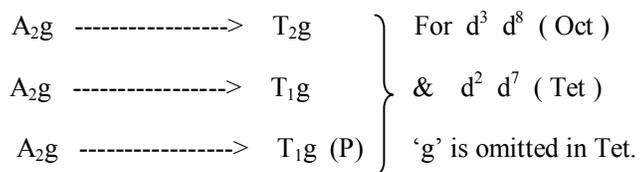
Here, three transitions are possible for d^2 (Oct), i. e.



Or, in general –



And,



THE END

