1. VSEPR Theory:-

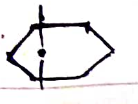
Valency shell electron pair Repulsion theory

This Theory was proposed by Gillespe and Nyhlon, to explain the shapes of molecules and Bond angles.

According to this theory the geometry of a molecule depends upon the no.of bond pairs and lone pairs on central atom. which arrange themselves in such a way that there is minimum repulsion between them. So, the molecule has minimum energy and maximum stability. Gillispie has proposed following rules to explain shapes of molecules and ions.

Rule 1:-

The shape of the molecule is determined by repulsions between the election pairs present in the Valence shell.

No.of e pairs	Shape of molecule	Bond angle
2	Linear —	180°
3	Trigonal planar △	120°
4	Tetrahedron 	109°.28'
5	Trigonal bipyramidal 	120° & 90°
6	octahedron 	90°
7	Pentagonal bipyramidal 	72° & 90°

Rule 2:-

The presence of lone pairs on the central atom causes slight distortion of the bond angles from the regular shape.

Since Lone pair occupies more space than Bond pair it exerts more repulsions on adjacent electron pair than a Bond pair.

The order of Repulsion is.

(Lone pair - Lone pair) > (Lone pair - Bond pair) > (Bondpair - Bondpair)

Due to repulsions between Lonepairs and adjacent electron pairs the bond angles will be reduced.

Eg:-	No. of Bond pairs	No. of Lonepairs	Bond angle
CH_3	4	0	109°.28'
NH_3	3	1	107°.48'
H_2O	2	2	104'.27'

Rule 3:-

The magnitude of Repulsion between Bond pairs depends on the electronegativity difference between central atom and other atom.

Eg:- Both NH_3 and NF_3 have tetrahedran shape with one corner occupied by a Lone pair.

NH_3 – 3 Bond pairs – 1 Lone pair – 107°. 48'

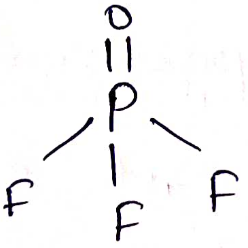
NF_3 – 3 Bond pairs – 1 Lonepair – 102°. 30'

Since Flourine is more electronegative it attracts the Bonding electron pair towards it than in NH_3. Hence the repulsions between Lonepair on Nitrogen and Bond pair decreases and gives a F-N-F bond angle of 102°. 30' compared with bond angle 107°. 48' in NH_3.

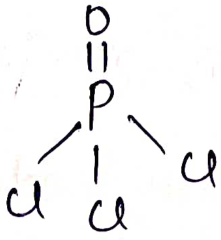
Rule 4:-

Double bond causes more repulsion than single-bonds and triple bonds cause more repulsion than double bonds.

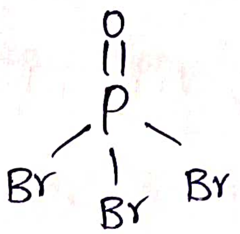
Eg:-



102°.5'



108°.5'



105°

→ Tetrahedral geometry.

Rule 5:-

Repulsions between pairs in filled shell is greater than in incomplete shell.

Eg:- H_2O and H_2S
(104°.27') (92°.2')

Rule 6:-

Iso Electronic species have Same structure. i.e the species with Same no. of valence electrons have Same structure.

Eg:-

BH_4, CH_4 and $\overset{+}{N}H_4$ – Tetrahedral shape

CO_3^{-2}, NO_3^- and SO_3 – planar triangle

CO_2, N_3^- and NO_2^+ – Linear.

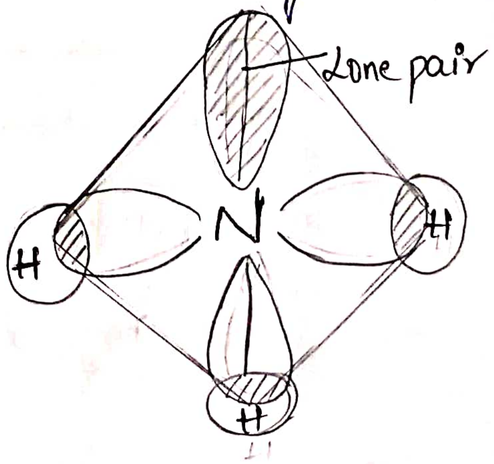
Some examples using VSEPR Theory:-

1. Structure of NH_3 molecule:-

→ In Ammonia, the central atom is Nitrogen.

→ Valence shell electronic configuration is $2s^2 2p^3$.

→ Out of these 5 valence electrons, 3 electrons are used to form bonds to 3 H-atoms and remaining 2 electrons constitute a lone pair.



N atom 2s [↑↓] 2p [↑|↑|↑]

NH_3 [↑↓] [↑x|↑x|↑x]

Lonepair H H H

→ Hence valence shell contains 8 electrons (4 electron pairs) i.e 3 Bond pairs and 1 Lone pair.

→ Since NH_3 molecule contains 4 electron pairs. The shape would be tetrahedran with 3 corners Occupied by 3 H-atoms and 4th corner is occupied by a Lonepair.

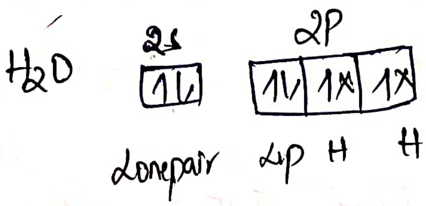
→ The presence of Lone pair causes slight distortion from 109°.28' to 107°.48'.

2. Shape of H_2O molecule :-

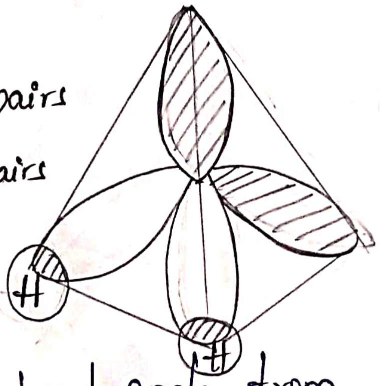
→ Valence shell electronic configuration of oxygen atom is $2s^2 2p^4$

→ Out of these 6 Valence electrons forms bonds with two H-atoms. The remaining 4 electrons Constitutes 2 Lonepairs (total = 8 electrons).

→ Thus in H_2O molecule it has 4 electron pairs, So, the shape would be tetrahedran with two positions Occupied by 2 Lonepairs.



2 Lonepairs
2 Bondpairs



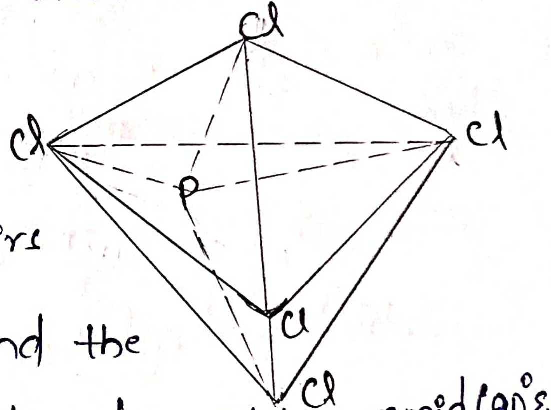
→ The two Lonepairs distort the bond angle from 109°.28' to 104°.27'.

3. Shape of PCl_5:-

→ The valence shell electronic configuration of central atom 'p' in PCl_5 is $3s^2 3p^3$.

→ These 5 valence electrons forms bonds with 5 chlorine atoms.

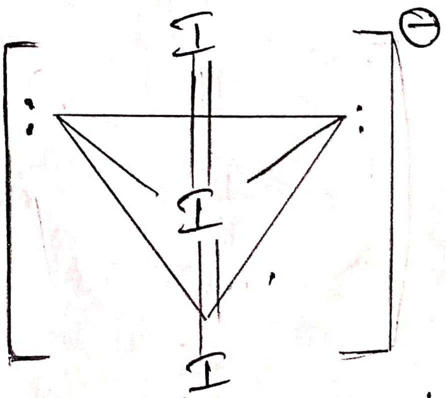
→ Hence, the valence shell of 'p' atom in PCl_5 contains 5 electron pairs ($10 e^-s$) so, the structure would be trigonal bipyramid.



→ Since there are no Lone pairs the structure is not disorted and the bond angles remains Same as for trigonal bipyramid (90° & 120°)

4. Tri iodide ion (I_3^-):-

→ If Iodine is dissolved in aq. KI, tri iodide ion I_3^- is formed.



→ The central atom in I_3^- is I.

∴ Valence shell electronic configuration of 'I' is $5s^2 5p^5$.

→ One of the outer electrons is used to form a bond with another Iodine, resulting in the formation of I_2

→ Thus, the valence shell of 'I' atom has 8 electrons.

→ One of the 'I' atom in I_2 molecule accepts a lonepair from an I^- ion. Thus forming I_3^- ion.

$$I_2 + I \longrightarrow [I - I \longleftarrow I]$$

→ Now, the valence shell of central 'I' atom possess 10 electrons (7 + 1+2) i.e 5 electron pairs.

→ Thus the shape would be "Trigonal bipyramid" with two Bondpairs and 3 lonepairs.

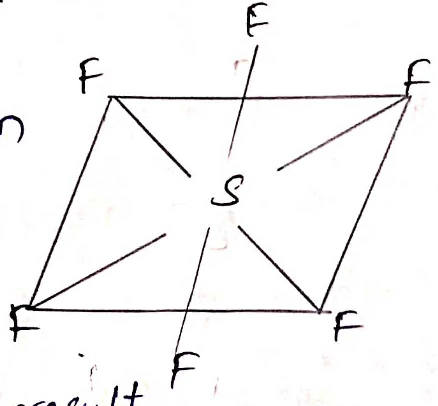
→ In order to minimize the repulsion forces, the 3 lonepairs occupies equitorial positions and Iodine atoms are located at the centre and in two apical-positions. Hence the ion is linear with a Bond angle of 180°.

5. Sulphur hexafluoride (SF_6):-

→ In SF_6, central atom is 'S'.

→ Valence shell electronic configuration of 'S' – $3s^2 3p^4$.

→ The 6 valence electrons are used to



with 6 'F' atoms as a result

→ Thus the structure is octahedral.

→ Since there are no Lonepairs, the structure is Completely regular with Bond angle of 90°.

2. Formation of Walsh diagram.

Walsh diagram :-

→ The stereo chemical aspects of bonds can't be explained by molecular orbital method.

→ Several workers have tried to modify the simple LCAO method to predict the geometries. The ~~basis for~~ the methods consists of Walsh diagrams.

Linear Combination of Atomic Orbitals

→ It is used to change in Energies between molecular orbitals of reference geometry and de-formed structure of Low symmetry.

→ BeH_2 is a tri-atomic species in which the molecular orbitals are formed from the combination of 1s orbitals of two Hydrogen atoms & 2s and one of the 2p orbitals of Beriyllium.

→ The remaining 2p orbitals of Beriyllium can't enter into bonding and remain as non-bonding molecular orbitals.

→ Before the linear combination of two 1s orbitals of Hydrogen (H & H') combine to give group orbitals. The group orbitals can be represented as $\varphi_H \pm \varphi_{H'}$.

→ The Linear Combination of 1s orbital has two possibilities $\psi_H + \psi_{H'}$ and $\psi_H - \psi_{H'}$.

→ The First and Second group orbital appropriate energy to overlap with 2s, 2p orbitals of Beriyllium.

First group → 2s
Second group → 2p

The Anti-Bonding molecular orbitals are formed by opposite combination of group orbitals and the orbitals of Beriyllium.

The molecular orbitals can be Represented as:-

$$\psi_g = a\psi_{2s} + b(\psi_H + \psi_{H'}) = \sigma_g \text{ --- ①}$$

$$\psi_u = c\psi_{2p} + d(\psi_H - \psi_{H'}) = \sigma_u \text{ --- ②}$$

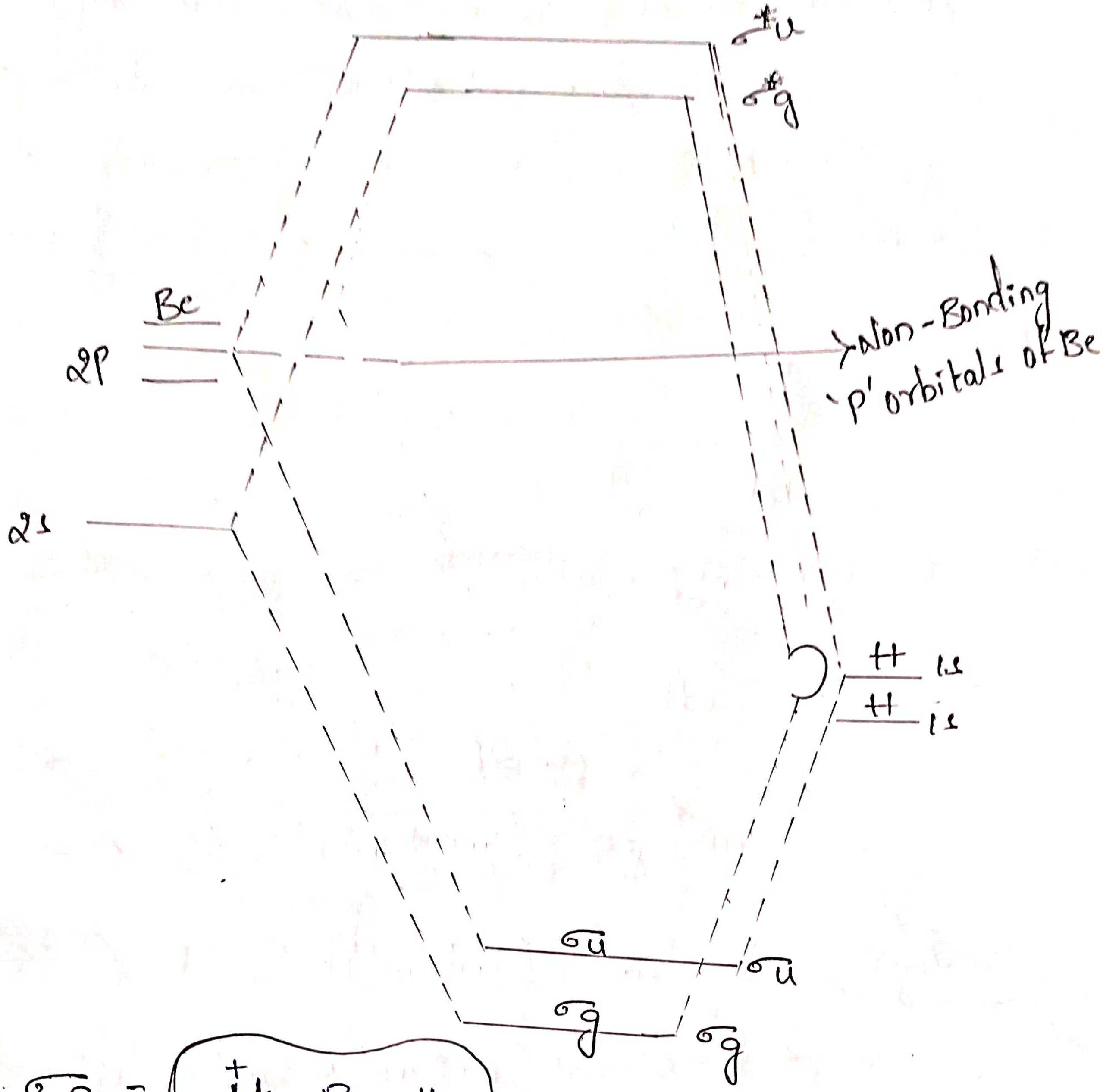
$$\psi_g^* = b\psi_{2s} - a(\psi_H + \psi_{H'}) = \sigma_g^* \text{ --- ③}$$

$$\psi_u^* = d\psi_{2p} - c(\psi_H - \psi_{H'}) = \sigma_u^* \text{ --- ④}$$

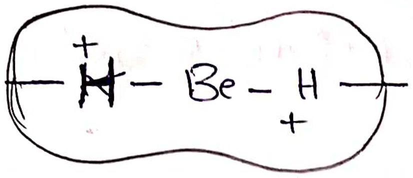
The M.O.E.L diagram for BeH_2 molecule:-

→ BeH_2 is a tri-atomic & Molecular orbital.

→ It is formed by the Combination of 1s of two Hydrogen atoms and 2s and one of the 2p orbitals of "Be". The remaining 2p orbitals are can't enter bonding remain as non-bonding Molecular orbitals.

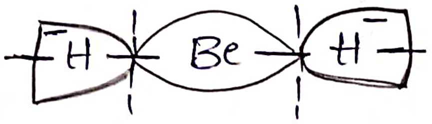


1. σ_g =

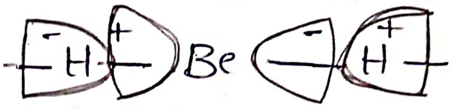


2. σ_u =

3. σ_g^* =

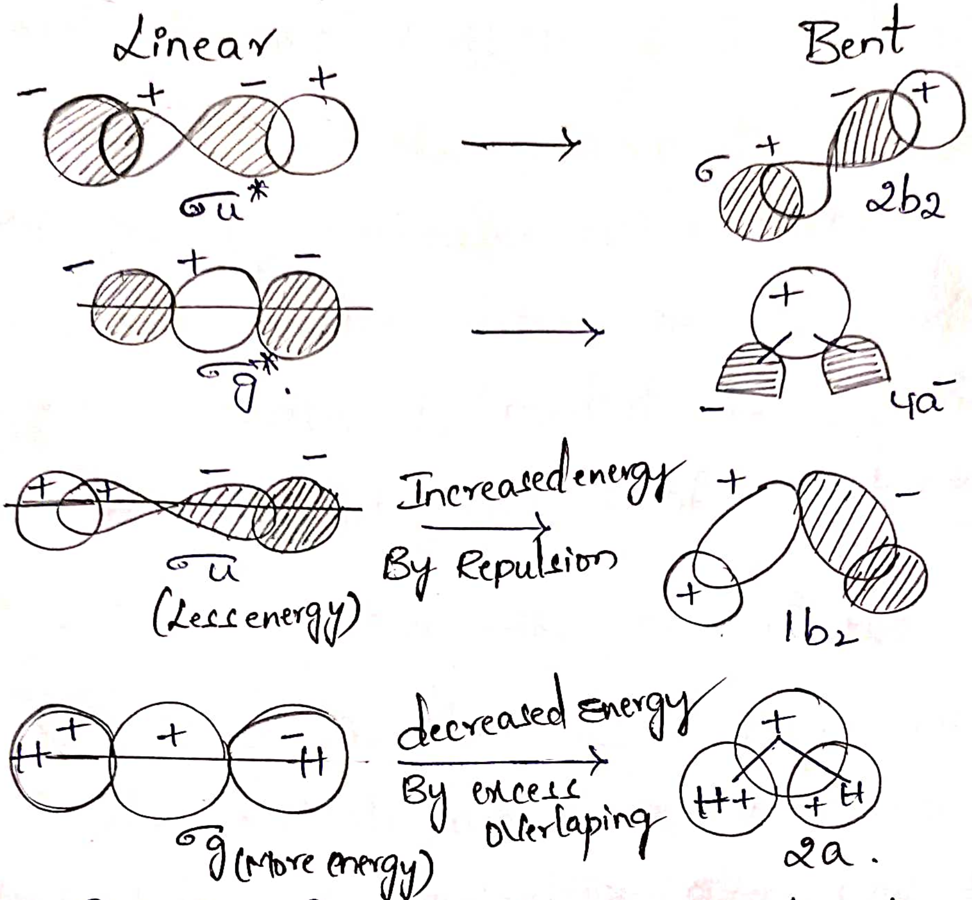


4. σ_u^* =



→ BeH_2 molecule is linear, Now, let us consider BeH_2 is a bent molecule and predict the energies of Bonding and Non-bonding & Anti-bonding molecular orbitals.

→ Open and shaded areas represents the sign (positive & Negative) of wave functions.



→ Consider first the σ_g orbitals, it is contracted from atomic wave function, that are every where are positive.

∴ Bonding there is an increase in overlap. The energy of σ_g repelled 2a, lowest Some what.

→ Secondary consider σ_u orbital, the energy of σ_u repelled $1b_2$ and extent of overlap decrease on Bending.

→ The increase in energy of $1b_2$ when compared to σ_u is more than the decrease in energy of 2a, when compared to σ_g as the destabilisation Energy is

-more than stabilisation energy in case of bent molecule of BeH_2, the molecule remains linear.

Walsh diagram of H_2O:-

→ The stereo Chemical aspects of bond can't be explained by molecular orbital method.

→ Several workers have tried to modify the Simple L.C.A.O method to predict the geometries, the basis for these methods consists of walsh diagrams.

→ Let us consider the case of H_2O.

H_2O is a tri-atomic species in which the molecular orbitals are formed from the combination of 1s orbitals of two Hydrogen atoms and 2s & one of the 2p orbitals of O_2.

→ The remaining 2p orbitals of O_2 can't enter in to bonding and remain as non-bonding molecular orbitals.

→ Before undergoing linear combination of two ~~is~~ orbitals of Hydrogen (H & H') combine to give group orbitals, the group orbitals can be represented as $\psi_H \pm \psi_{H'}$.

→ The linear combination of 1s orbitals has two possibilities i.e $\psi_H + \psi_{H'}$ & $\psi_H - \psi_{H'}$

→ The First group orbitals has appropriate energy to overlap with 2s orbitals of O_2.

→ The Second group has appropriate energy to overlap with the 2p orbitals of O_2.

→ The Anti-bonding molecular orbitals are formed by the combination of group orbitals & the orbitals of O_2.

The molecular orbitals can be represented as:-

$$\psi_g = a\psi_{2s} + b(\psi_H + \psi_{H'}) = \sigma_g \quad ①$$

$$\psi_u = c\psi_{2p} + d(\psi_H - \psi_{H'}) = \sigma_u \quad ②$$

$$\psi_g^* = b\psi_{2s} - a(\psi_H + \psi_{H'}) = \sigma_g^* \quad ③$$

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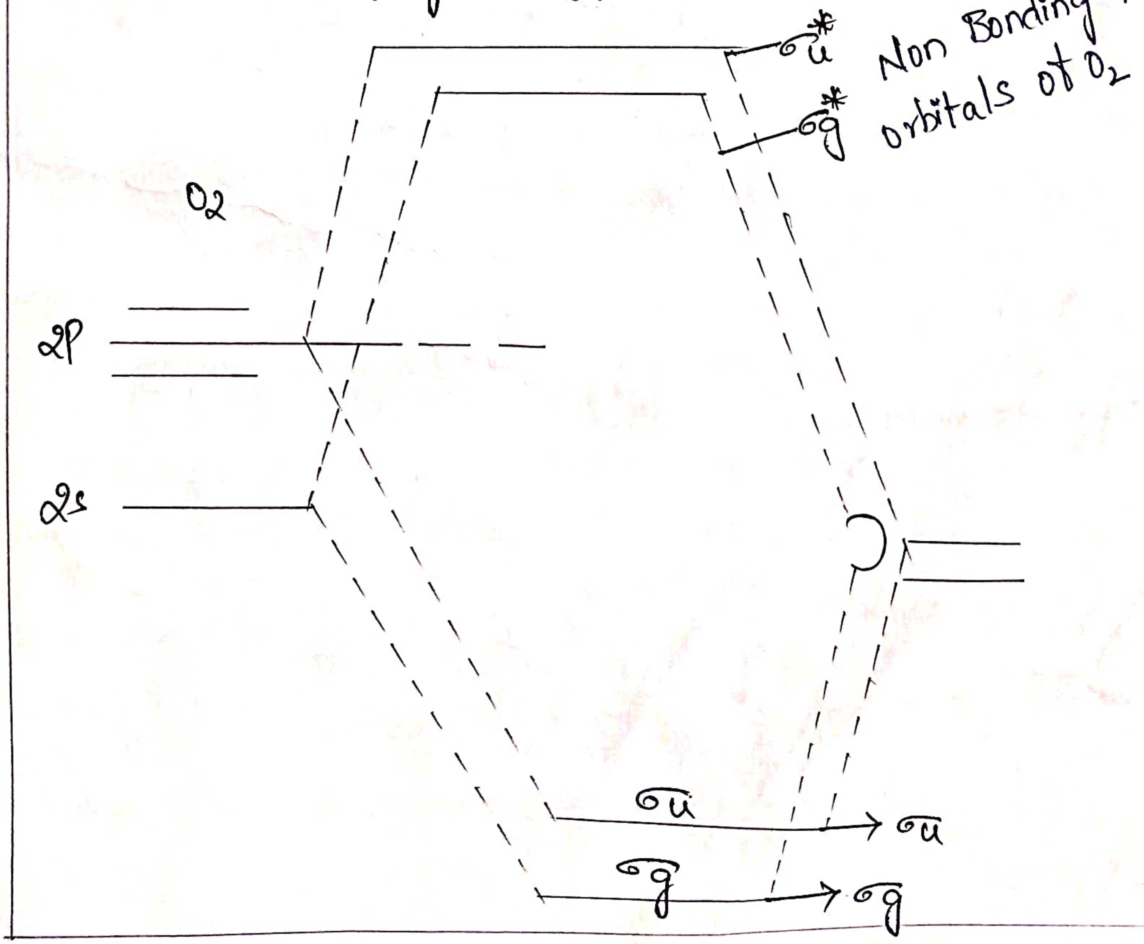
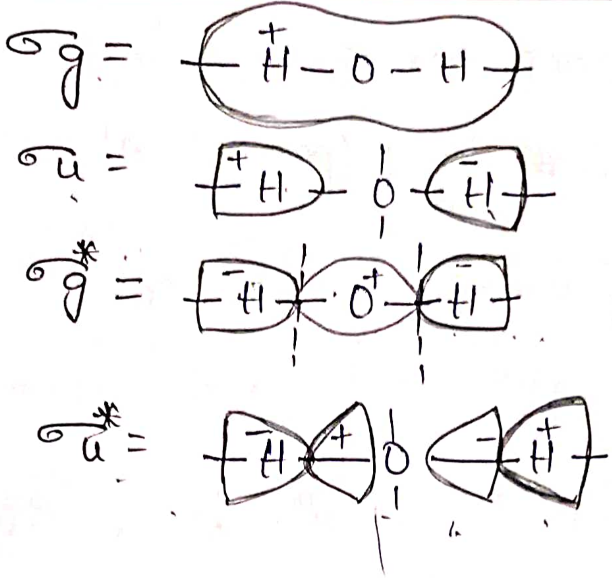
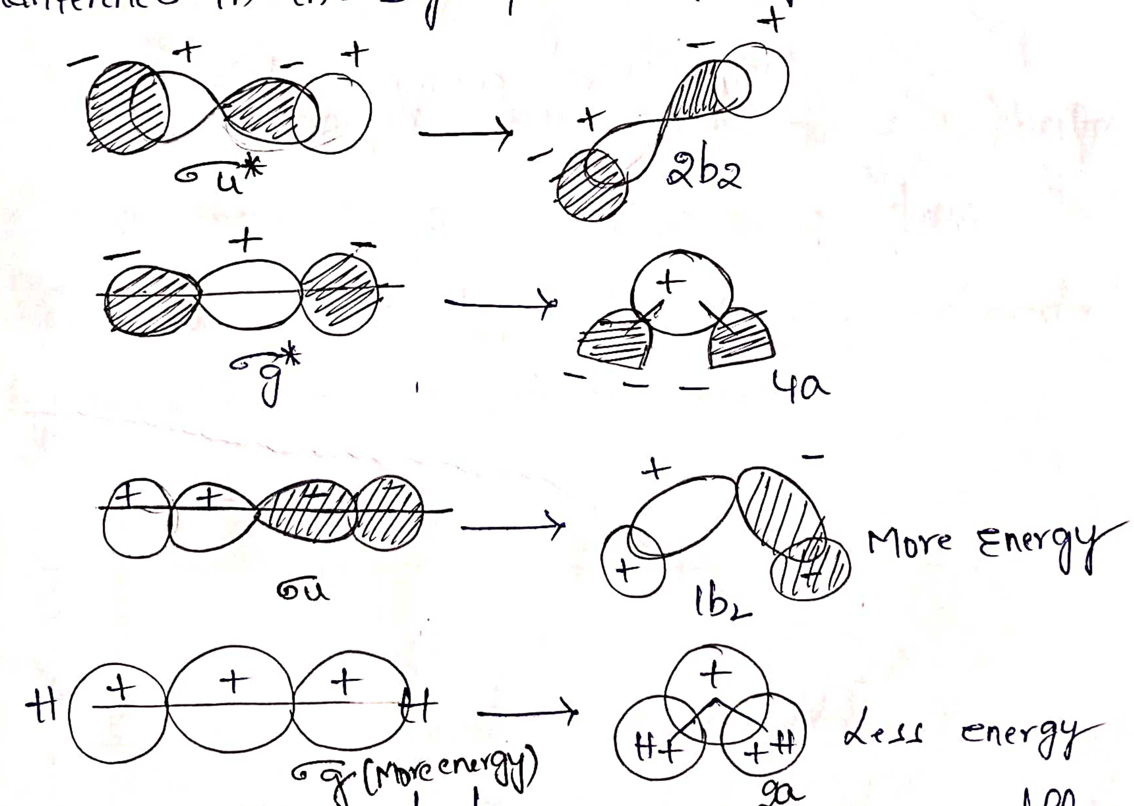
The M.O.E.L diagram for H_2O molecule:-





Actually H_2O molecule is Linear, Now Let us Consider H_2O is a bent molecule and predict the energies of Bonding, Non-bonding and Anti-bonding molecular orbitals. open and shaded areas represents the differences in the sign (positive & Negative) of wave functions



Destabilisation energy is the energy difference between $1b_2$ (more energy) & σ_u (less energy)

Stabilisation energy is Energy difference in between 2a, (less energy) & σ_g (mole energy)

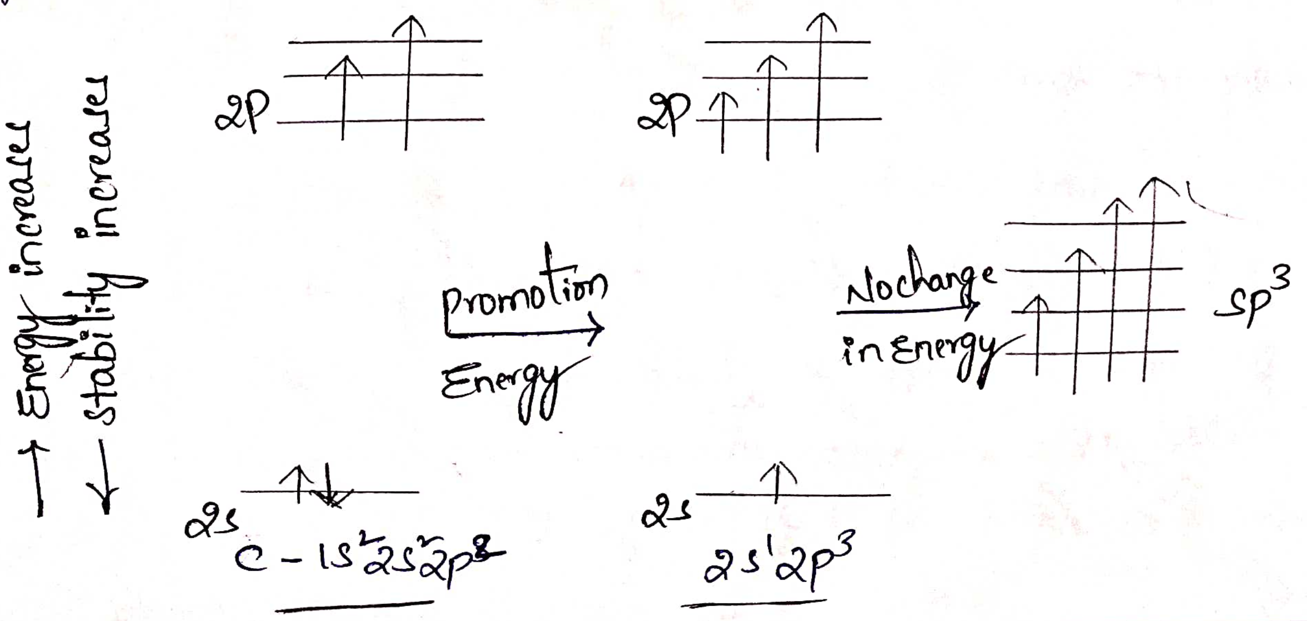
For H_2O molecule, destabilisation energy is less than the stabilisation energy.

∴ H_2O is present in Bent molecular form.

3. Bent's Rule & Energetics of Hybridisation.

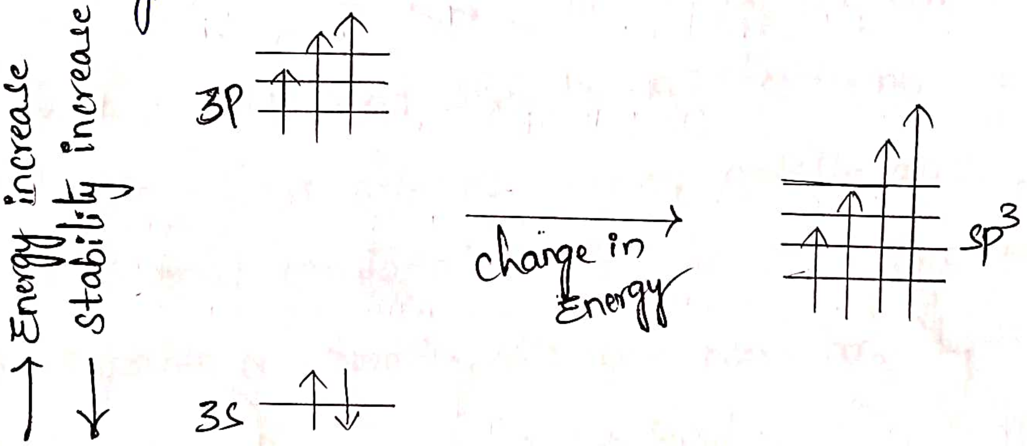
When a set of hybrid orbitals is constructed by a linear combination of atomic orbitals, The energy of the resulting hybrid is a weighted average of energies of participating atomic orbitals.

For example, when carbon forms 4 covalent bonds. although there is a promotion Energy from $1s^2 2s^2 2p^2 \longrightarrow 1s^2 2s^1 2p^3$. This is the independent of hybridisation to the valence state.



In phosphorous atom there is little initial promotion energy. The ground state is trivalent. as is the valence state. Any hybridisation will cost energy as a filled 3s orbital is raised in energy and half-filled 3p orbitals are lowered in energy.

This energy of hybridisation is of order of magnitude of bond energies and can be important in determining the structure of molecules.



Another factor which affects the most stable arrangement of the atom in a molecule is variation of bond Energy with hybridisation. The directed loby of s-p hybrid orbitals overlap more effectively than the undirected orbitals. The two lobed p-orbitals on the diffuse d-orbitals. The increased overlap results in stronger bonds. The molecule is thus forced to choose between higher promotion energies and better overlap for an s-rich hybrid (or) lower promotion energies and poorer overlap for an s-poor hybrid.

The effect of difference in hybrid bond strengths are shown by bond lengths in MX_n molecules with both Equitorial and axial substituents.

	r_{eq} (Pm)	r_{ax} (Pm)
PF_5	153.4	157.7
PCl_5	202	214.

An sp^3d hybrid orbital is a combination of $P_zd_{z^2}$ hybrids and SP_xP_y hybrids. the former make two linear hybrid orbitals bonding axially and later form trigonal equitorial bonds. The sp^2 hybrid orbitals are capable of forming stronger bonds and ~~by~~ they are shorter than the weaker axial bonds.

Bent's Rule:-

~~The~~It states that " More electronegative substituents prefer hybrid orbitals having less 's' character and more electro positive substituents prefer hybrid orbitals having more 's' character.

Eg:- i. When the electro negativities of substituents on the phosphorous atom differ as in mixed chlorofluorides PCl_xF_{5-x} and the alkyl phosphorous flourides B_xPF_{5-x}

It is experimentally obserlled that more Electronegative substituent occupies axial position and less electronegative Substituent occupies Equitorial position.

2. Fluromethanes:

In CH_2F_2 the F-C-F bond angle is less than $109\frac{1}{2}$ indicating less than 25% 's' character but H-C-H bond angle is larger and has more 's' character.

Bent's rule predicts that highly electronegative Substituents will attract 'p' character and reduce, bond angles is Compatible with the reduction in angular volume of the bonding pair when held tightly by an electro negative Substituent.

The mechanism operating behind, Bent's rule is not completely clear. One factor favouring increased 'p' character in electronegative Substituents is decreased bond angles of 'p' orbitals and decreased steric requirements of Electronegative Substituents. There may be an optimum "strategy" of bonding for a molecule, in which 's' character is concentrated in those bonds in which the electronegativity difference is small and Covalent bonding to important.

Bent's rule is useful tool in inorganic & organic chemistry. For example, it is used to supplement the VSEPR interpretation of structures of various non-metal flourides.

Molecular orbitals in tri atomic molecules & Ions:-

Eg:- 1. BeH_2

BeH_2 is a linear molecule and it is the first example of tri-atomic molecule. The molecular orbitals of this molecule are formed from 1s orbitals of Hydrogen atoms (labelled H & H') and 2s and one of the 2p orbitals of Beriyllium atom. The remaining two 2p orbitals of Beriyllium cannot enter into bonding because they are perpendicular to molecular axis and have zero net overlap with the hydrogen orbitals.

Four atomic orbitals involved in bonding and forms 4 molecular orbitals. Bonding M.O's are formed by linear combination of atomic orbitals. In order to form M.O's, the atomic orbitals of two H-atoms converted into group orbitals and then combine with symmetries of atomic orbitals of beriyllium.

Let H_1 be the 1s orbital on 1st Hydrogen atom.

and

H' be the 1s orbital on 2nd Hydrogen atom.

Hence (H+H') and (H−H') are two group orbitals.

The atomic orbitals of "Be" are 2s, $2P_x, 2P_y, 2P_z$.

from $D_{\infty h}$ character table, their symmetries are

G.O's

$2s - \sigma_g$

$2P_x - \pi_{ux}$ (N.B) $\qquad (H+H') - \sigma_g$

$2P_y - \sigma_u$ $\qquad (H-H') - \sigma_u$

$2P_z - \pi_{uz}$ (N.B)

Hence the atomic orbitals of 'Be' overlaps with G.O's of Hydrogen with matching symmetry and forms M.O's as follows

$2s + (H+H') \longrightarrow \sigma_g = 2\sigma_g$

$2s - (H+H') \longrightarrow \sigma_g^* = 3\sigma_g$

$2P_y + (H-H') \longrightarrow \sigma_u = 1\sigma_u$

$2P_y - (H-H') \longrightarrow \sigma_u^* = 2\sigma_u$

Since there is no matching symmetry for π_{ux} and π_{uz}. So, they remains as Non-Bonding.

The energy order of these M.O's are

$2\sigma_g < 1\sigma_u < 1\pi_{ux} < 1\pi_{uz} < 3\sigma_g < 2\sigma_u$

Be : $2s^1 2p^1$ $\qquad$ H $- 1s^1$

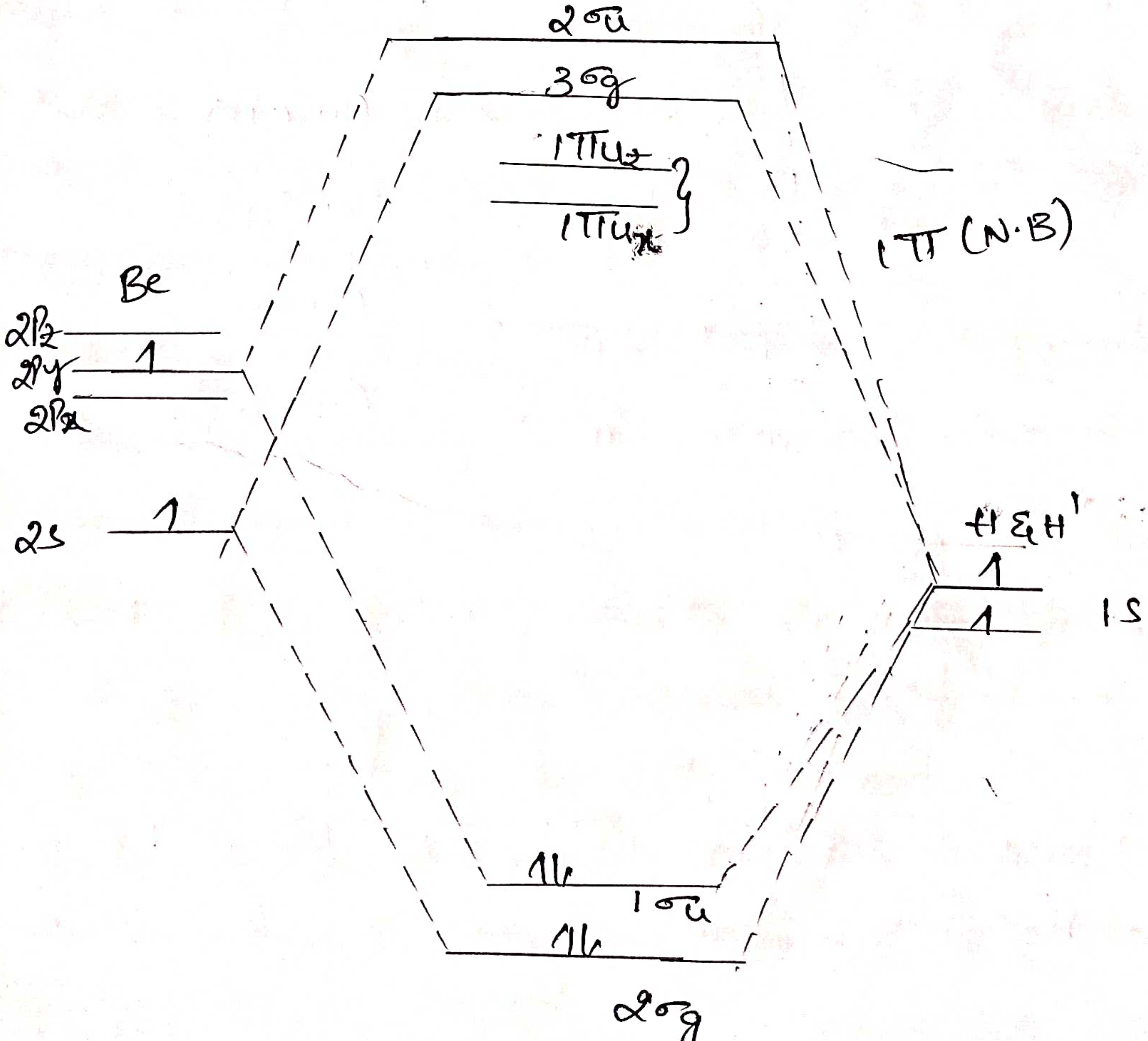
Total $= 2+2 = 4e_s^-$

The M.O Electronic Configuration is

$2\sigma_g^2 < 1\sigma_u^2 < 1\pi_{ux} < 1\pi_{uz} < 3\sigma_g < 2\sigma_u$

It can be observed that the lowest energy orbital $1\sigma_g$ is not shown in the diagram. It is formed from 1S orbital on 'Be' atom. which interacts very little with Hydrogen orbitals, because of large energy difference between them. Hence it remains as Non-Bonding.

M.O Energy level diagram for BeH_2 molecule is as follows.



4. Molecular orbital Theory:-

M.O Theory was put forward by Hund & Mulliken According to this theory a stable molecular system is formed with the nuclei at equilibrium distance.

Basic principles of M.O Theory:-

→ When nuclei of two atoms come close together, their atomic orbitals interacts resulting in the formation of molecular orbital. The atomic orbitals completely lose their identity after the formation of molecular orbitals

→ Each molecular orbital may be described by a wave-function ψ known as molecular orbital wave function.

→ Each molecular orbital wave function 'ψ' is associated with a set of quantum numbers which determine the energy and shape of M.O.

→ Each 'ψ' is associated with definite energy value and the total energy of the molecule is sum of energies of occupied M.O's.

→ ψ is such that ψ^2 represents the probability density (or) electron change density (probability of finding e^- in M.O)

→ Electrons in M.O's are filled according to Aufbau, Hunds and pauli's exclusive principles.

→ Electrons in the M.O's are influenced by all the nuclei present in the molecule.

The wave function describing a M.O may be obtained by one of the two procedures.

1. Linear combination of atomic orbitals (L.C.A.O)
2. United atom method.

Rules for linear Combination of Atomic orbitals :-

→ If two different types of atoms are overlaping, the energies of their atomic orbitals must be Same.

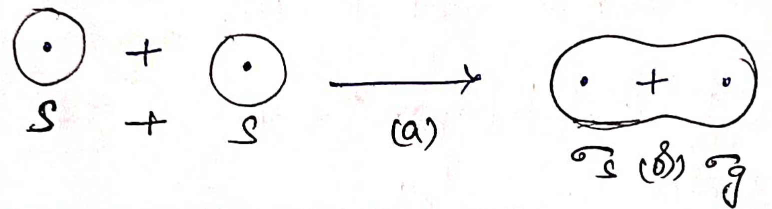
→ The atomic orbitals must overlap as much as possible. This implies that the atoms must be close enough for effective overlap.

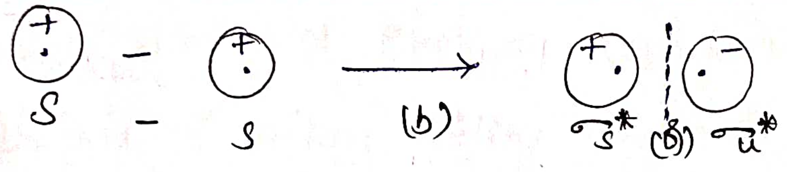
→ In order to produce bonding and antibonding M.O's either the Symmetry of two atomic orbitals must remain unchanged when rotated about internuclear line (or) both atomic orbitals must change symmetry in an identical manner.

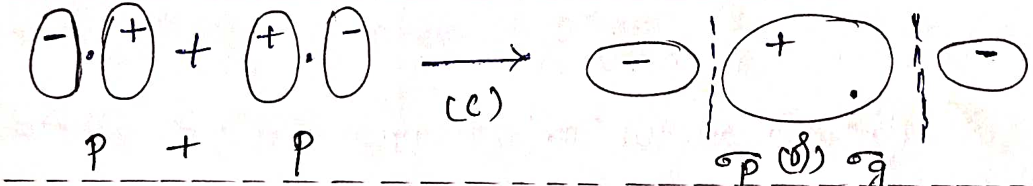
Symmetry of M.O's :-

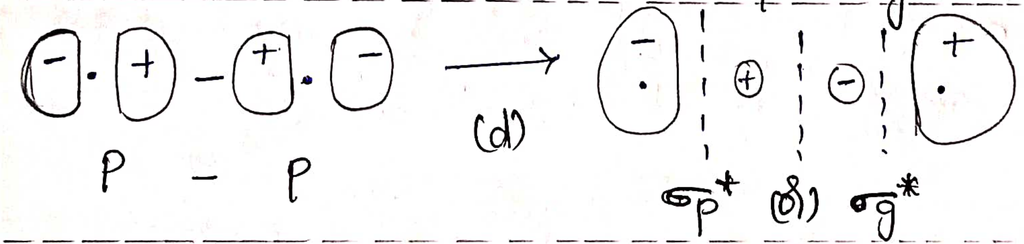
Some of the possible Combinations of atomic orbitals are Shown in following fig. Those orbitals which are cylindrically Symmetrical about the inter nuclear axis are called σ-orbitals. Analogous to an S-orbital the atomic orbital of highest symmetry. If the internuclear axis lies in a nodal plane, ~~a~~ π- bond results. In δ-bonds the internuclear axis lies in two mutually perpendicular nodal planes.

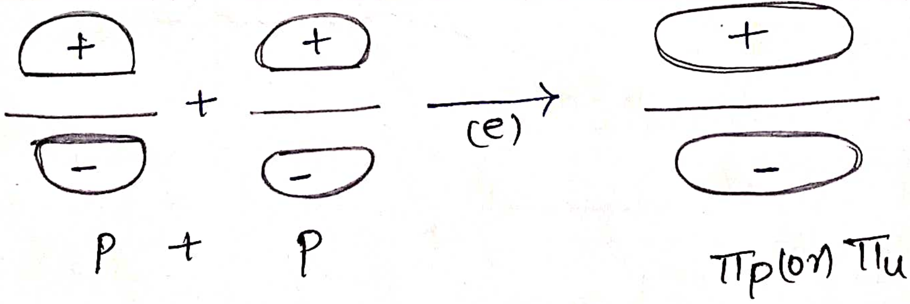
All antibonding orbitals possess an additional nodal plane perpendicular to the ~~M.O's~~ internuclear axis and lying between the nuclei. In addition, the M.O's may (or) may not have a centre of symmetry. In this regard π^*_{p-p} orbitals are ungerade and π_{p-p} orbitals are gerade.

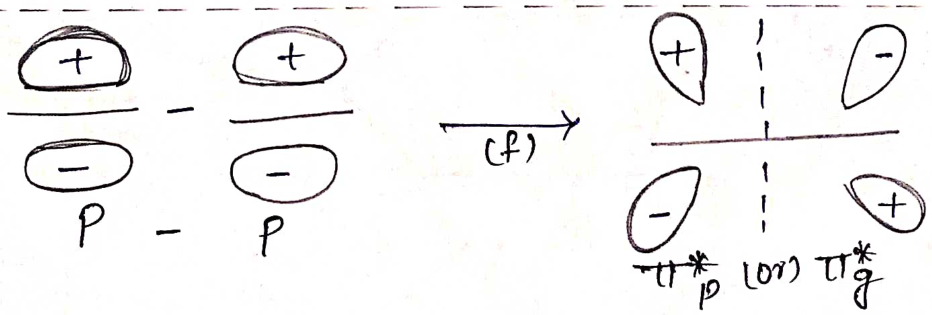












Symmetry of molecular orbitals formed from atomic orbital illustrating σ (a-d) and π (c, f) orbitals and bonding (a, c, e) and antibonding (b, d, f) orbitals.

Molecular orbital Electronic configuration:-

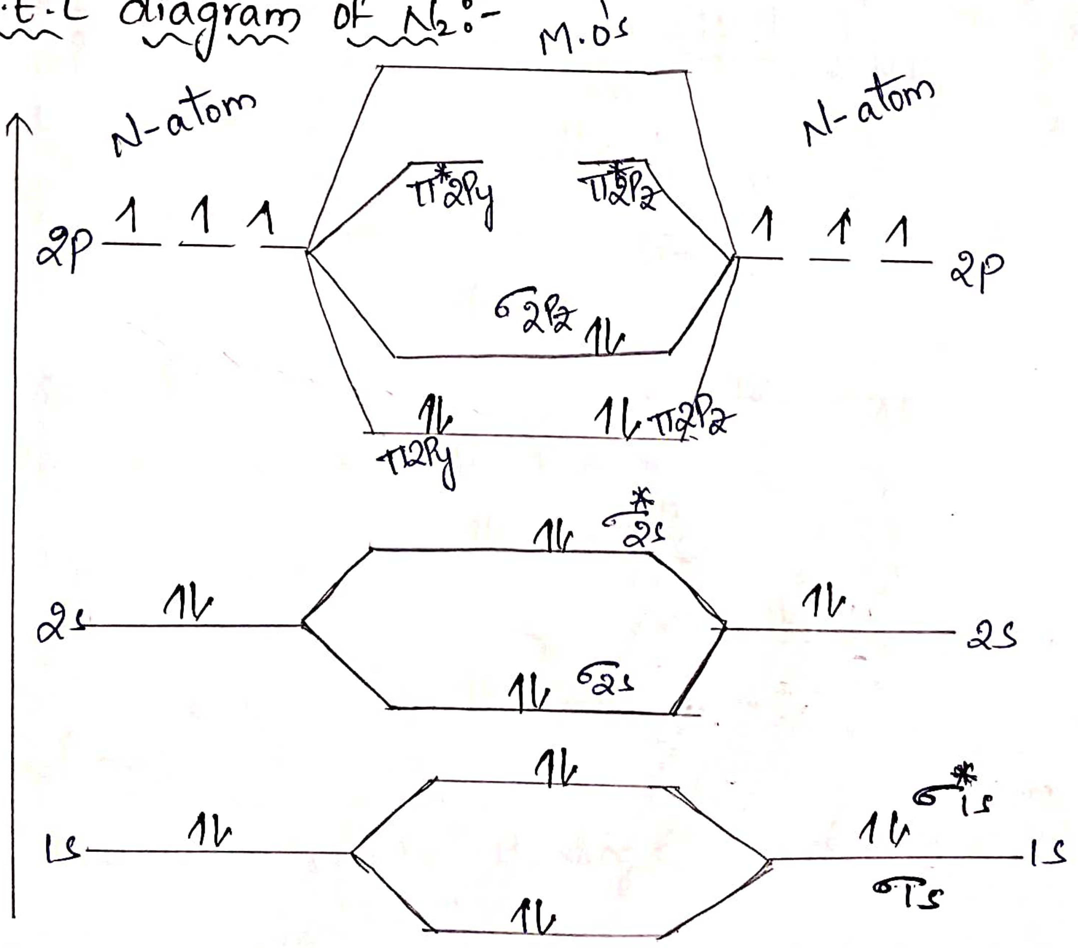
Order of electronic configuration of molecular orbitals of atoms with less atomic number than oxygen is.

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s}\ \pi_{2p_y} = \pi_{2p_y} < \sigma_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \pi^*_{2p_z}$

Order of Electronic configuration of Molecular-orbitals of atoms ~~as~~ like oxygen (O) atoms with more than atomic number of oxygen is

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$

M.O.E.L diagram of N_2:-



Bond order:-

Bond order = $\frac{1}{2}$ (number of Bonding e^- — number of Antibonding e^-)

$= \frac{10-4}{2}$

$= 6/2$

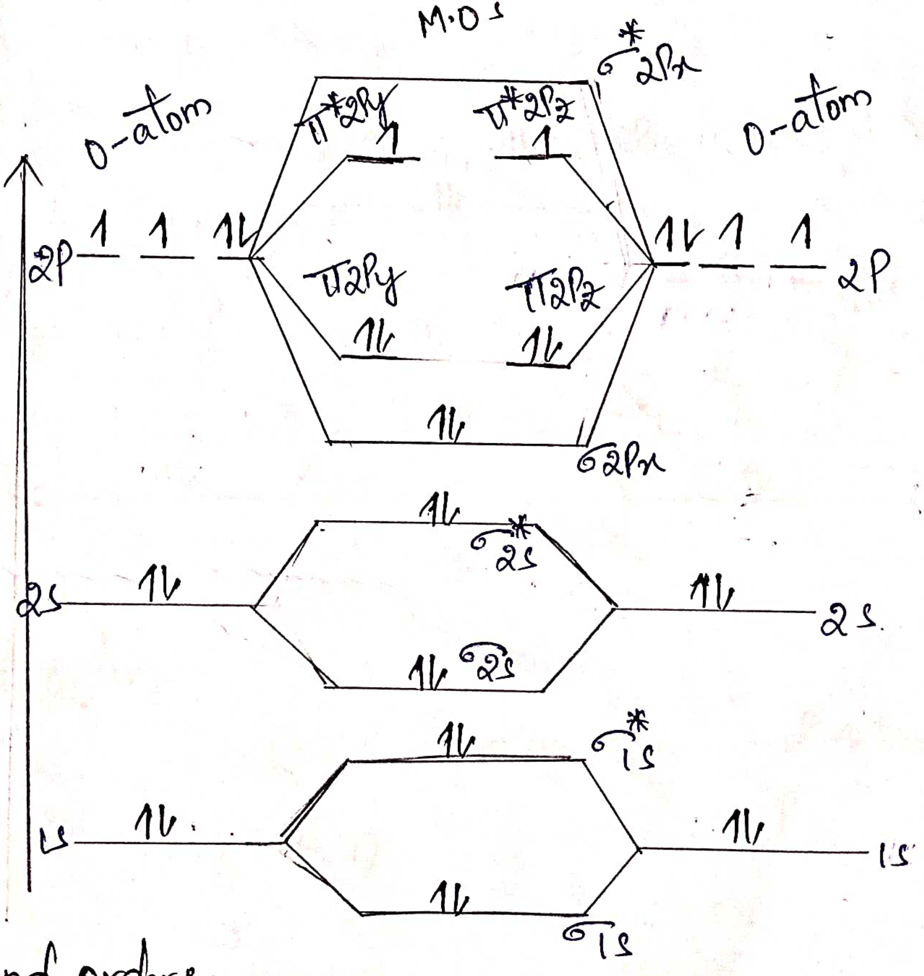
$= 3$

Bond order = 3

Means N=N

Magnetic property - Diamagnetic

M.O.E.L diagram of O_2:-



Bond order:-

Bond order = $\frac{1}{2}$ (No.of Bonding e^- - No.of A·B e^-)

$= \frac{1}{2}(10-6)$

Bond order = 2

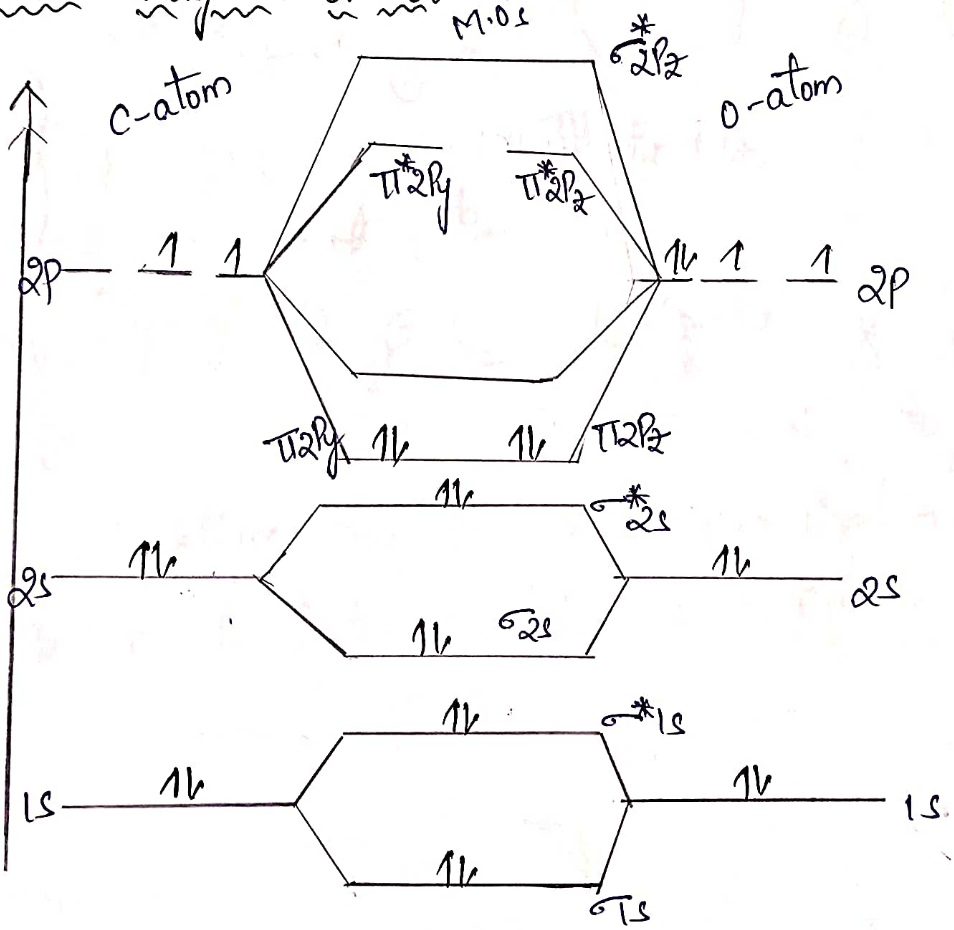
Means O=O

Magnetic property = paramagnetic.

M.O configuration of O_2 is

$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_x^2 \sigma 2P_y^2 \sigma 2P_z^2 \pi 2P_y \pi 2P_z \pi^* 2P_y^1 \pi^* 2P_z^1$

M.O.E.L diagram of CO:-



Bond order:-

$= \frac{1}{2}$(No.of Bonding e^-_s − No.of Antibonding e^-_s)

$= \frac{1}{2}(10-4)$

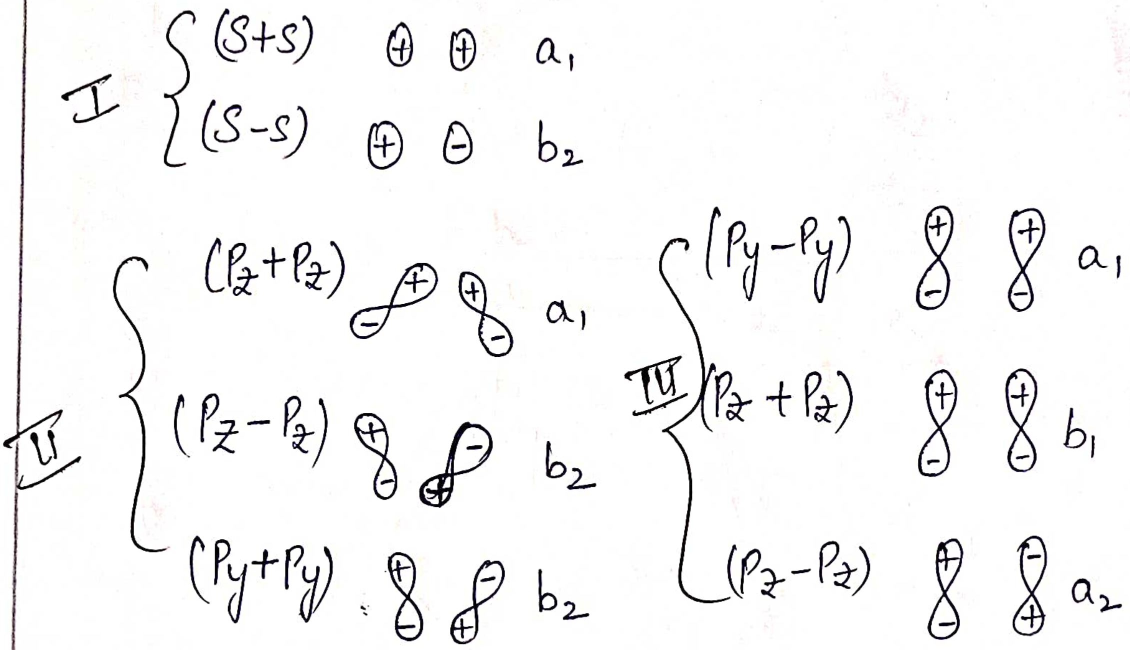
$= 3$

Magnetic property - Diamagnetic

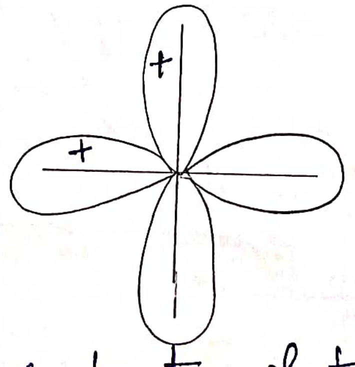
Bondorder "3" Means C≡O

M.O.E.L diagram of NO_2^- :-

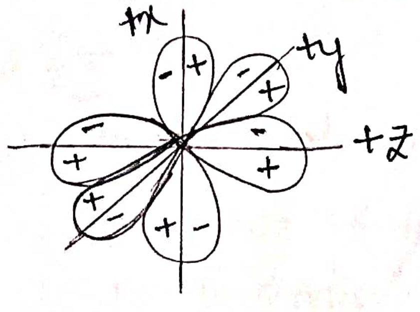
Group orbitals for the O_2 atom in NO_2^-, derived from the 2s and 2p atomic orbitals are given below.



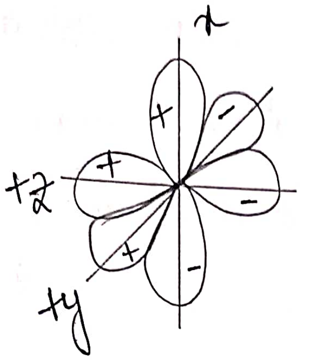
Where for s orbitals co-ordination of two O_2 atoms (I), atomic orbitals of N atom in NO_2^-.

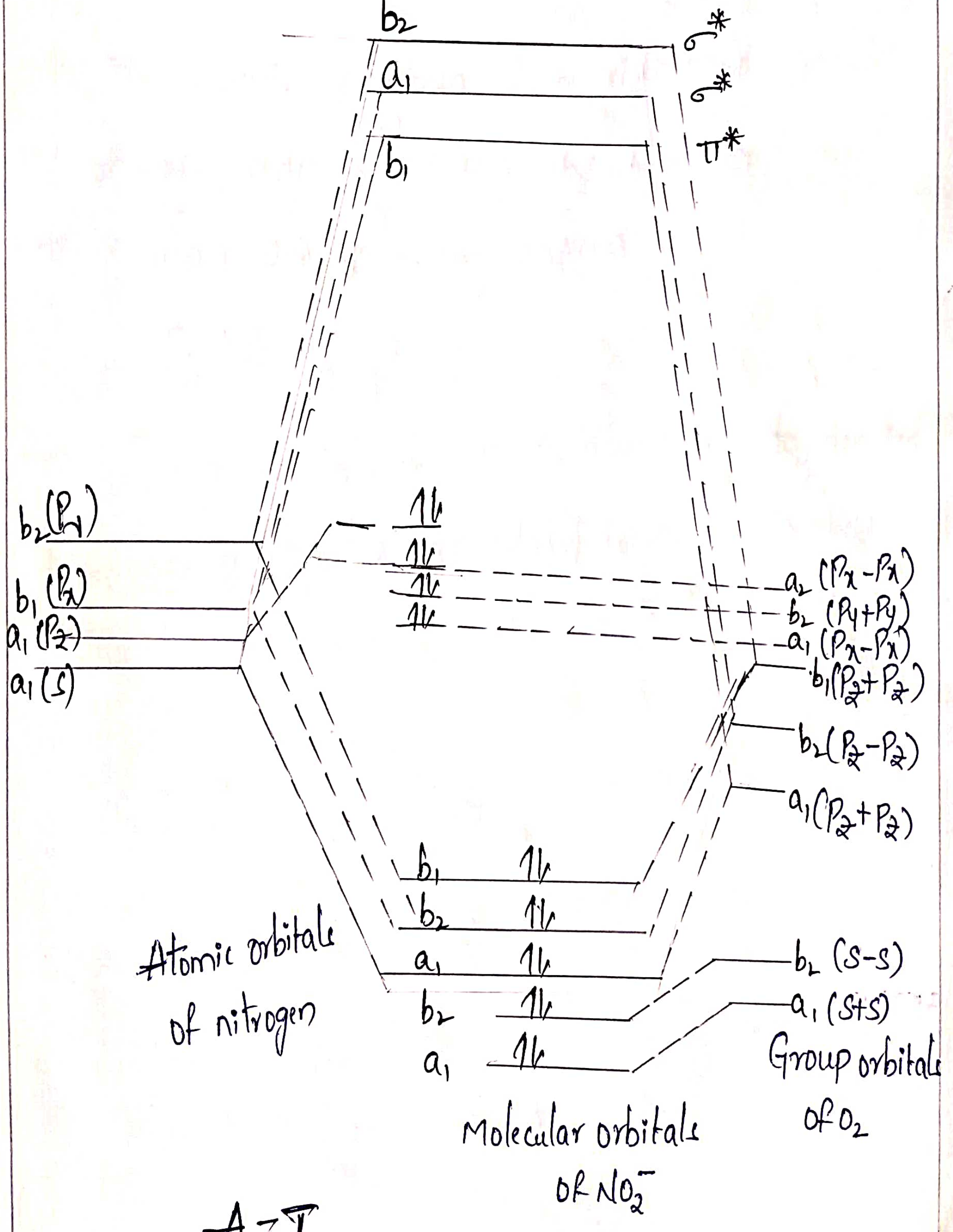


For II combination of two O-atoms, atomic orbitals of left hand side "O" in NO_2^- are



For (iii) combination of two O-atoms, atomic orbitals of Right hand side "O" in NO_2^- ~~atom~~ are:





A=I

The Px and Py atomic orbitals on Nitrogen:-

The plane of the anion is the yz plane and the x-axis is perpendicular to that plane.

B=II

→ The atomic p-orbitals of the left-hand O_2 atom.
→ z-axis re-defined along the O-N bond axis.
→ x-axis perpendicular to the plane of the molecule.
→ y-axis perpendicular to the x and z.

C=III

→ The atomic p-orbital of the right hand O_2 atom.
→ z axis redefined along the N-O bond axis.
→ x and y are mutually perpendicular.

C = IV

→ Group orbitals for the O_2 atoms in NO_2^- derived from the 2s and 2p atomic orbitals.

5. Experimental evidence for dπ - Pπ bonding:-

Phosphorous - Oxygen bond in phosphoryl Compounds:-

In the case of dπ - Pπ bonding, we can interfere the presence of a σ bond. when two ~~b~~ atoms are at a distances shorter than the sum of their vanderwaals radii. The detection of π-bond depends on strengthening of a bond and stabilisation of charge distribution etc.

The example for existance of π- bonding is in phospine oxide. Tertiary phosphines are unstable relative to oxidation.

$$2R_3P + O_2 \longrightarrow 2R_3PO$$

This reaction takes place more readily that aliphatic phosphine must be protected from atmospheric oxygen.

Tri aryl phosphines are more stable but oxidised readily.

$$Ph_3P \xrightarrow[(or)\,KMnO_4]{HNO_3} Ph_3PO$$

In contrast, aliphatic amines do not have to be protected from atmosphere although they can be oxidised

$$R_3N + HOOH \longrightarrow (R_3NOH)^{+}OH^{-} \xrightarrow{-H_2O} R_3NO$$

Amine oxides are decomposed ~~b~~ on heating.

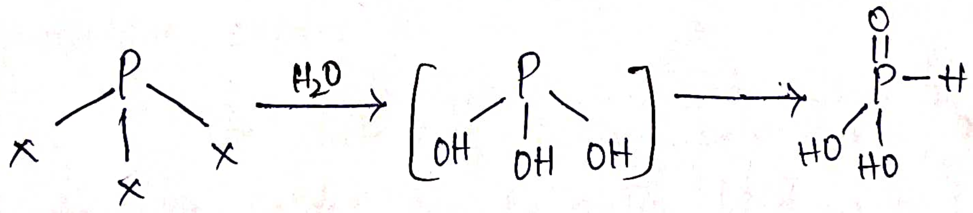
$$Et_3NO \xrightarrow{\Delta} Et_2NOH + CH_2=CH_2$$

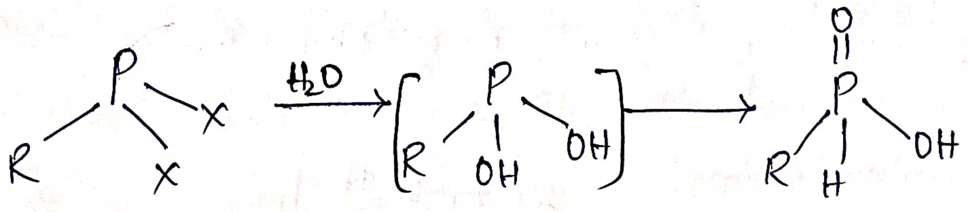
Teritiary phosphine oxides form more stable oragano phosphorous compounds

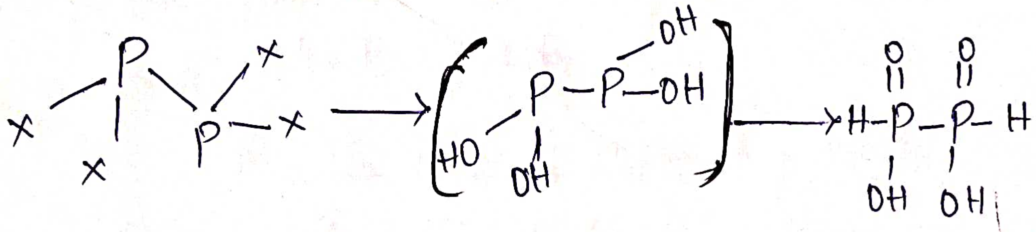
Those oxides with no β-hydrogen atom are particulaly Stable. Trimethyl phosphine oxide and triphenyl - phosphine oxide do not decompose below 700°C. They are not reduced even by heating with metallic sodium. The tendency of phosphorous to form P→O (or) P=O linkages is one of the driving forces of phosphorous chemistry and is used to predict the reactions and structures.

Eg:-

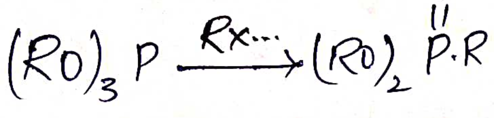
Lower phosphorous acids exists in four co-ordinate structure even though they are prepared by hydrolysis of 3 co-ordinate halides.





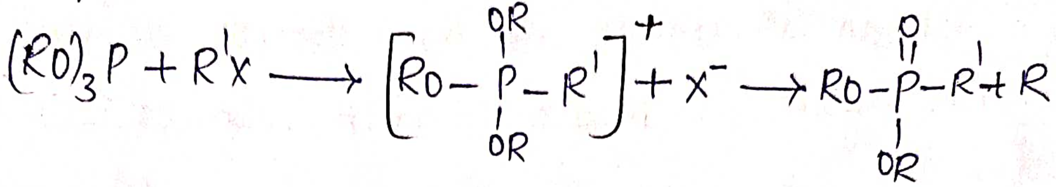


A typical reaction is rearrangement of trialkyl phosphite to a phosphonate.



$$(RO)_3P \xrightarrow{Rx\cdots} (RO)_2\overset{O}{\overset{\parallel}{P}}.R$$

In this equation, if Rx is replaced by Equimolar amounts of R'x the role of alkyl halide in the formation of alkoxy phosphonium salt is revealed.



$$(RO)_3P + R'X \longrightarrow \left[RO-\underset{OR}{\overset{OR}{P}}-R' \right]^+ + X^- \longrightarrow RO-\underset{OR}{\overset{O}{\overset{\parallel}{P}}}-R' + R$$

The final difference between amine oxides and phosphine oxides lies in the polarity of molecules. The dipole moment of trimethyl amine oxide is 16.7×10^{-30} cm and in triethyl phosphine oxide : is 14.6×10^{-30} cm. A Consequence of this polarity is tendency of amine oxides to form hydrates $R_3NO \cdot H_2O$, and their greater basicity relative to phosphine oxides.

The difference between behaviour of amine oxides and phosphine oxides can be rationalized in terms of possibility of back bonding in the latter. where as amine oxides are restricted to a single structure containing a dative N–O bond, $R_3N \rightarrow O$ and phosphine oxides having contributions from $d\pi - p\pi$ bonding between phosphorous and oxygen atoms.

$$\underset{\text{I}}{R_3P^+ \longrightarrow O^-} \longleftrightarrow \underset{\text{II}}{R_3P=O}$$

The double bond character introduced by latter strengthens the bond and gives stability of phosphorous–oxygen linkage. This extra stability cannot be attributed to ionic resonance energy. Because the dipole moment of nitrogen compound is greater than that of Phosphorous Compound

The comparision of bond energies also supports the above interpretation. The dissociation energies of P=O bonds in various compounds B lies in the range of 500- 600 KJ/mole and for N→O is about 200- 300 KJ/mole. Hence P=O bond is stronger than N→O bond.

In phosphine oxides, the stretching frequency provides an indication of the strength of the bond. The competition between electronegativity of substituent groups and the strength of P=O bond provides support for a π-bonding model but not for the alternative dative σ bond model. A σ bond might be expected to be destabilised ~~b~~ as electron density is removed from phosphorous requiring it to withdraw electrons from P→O bond weakening it. In contrast, if the oxygen can back bond to the phosphorous a d-pπ bond, the induced change on phosphorous can be diminished and P=O bond strengthened.

The two resonance forms of phosphorous yields are

$$\underset{I}{R_3\overset{+}{P}} - \overset{\ominus}{C}H_2 \longleftrightarrow \underset{\underline{II}}{R_3P=CH_2}$$

These two resonance forms contribute to the stability of phosphorous yields but not to ammonium yields, $R_3\overset{+}{N}-\bar{C}H_2$. This is due to difference in reactivity. Ammonium yields are generally quite, basic & quite reactive. Phosphorous yields are less basic to abstract a proton from water & not dissolving in water unless strong acids are present.

6. Symmetric and unsymmetric H-bonding.

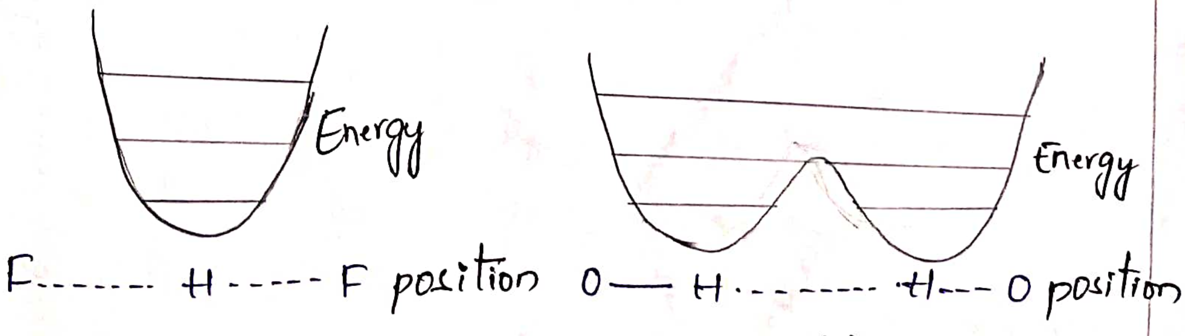
Symmetric H-bonding:-

Eg:- HF_2^- ion

In HF_2^- ion, flouride ions are relatively immobile with respect to lighter Hydrogen and the motion of the later can be considered to a first approximation as a vibration in a potential well with an average position midway between the flourides.

Unsymmetric H-bonding:-

Unsymmetric H-bonds posses two potential wells in which the Hydrogen can vibrate ocassionally and excited thermally to jump to other well. In this the Hydrogen will be in one potential well (or) another potential well by rapid methods such as diffraction.



(a) (b)

(a) Energy and position of H-atom in symmetric HF_2^- system.

(b) Energy and position of H-atom in unsymmetric O-H···O system.

In (a) the average position of H-atom is midway between the flouride ions.

In (b) the positional sketch on left represents the average position of H-atom in the left potential well and dotted sketch represents average position for other potential well.

In Symmetric H-bonding, the e^- density is equal on bothsides. In unsymmetric H-bonding more e^- density is concentrated in the shorter link.

*1. Crystal Field Theory [C.F.T].

Crystal Field Theory was first proposed by "Hans Bethe" in 1929. It was a model based on purely electrostatic interaction between the ligands and the metal ion.

The transition metal which forms the central atom in the complex, is regarded as a positive ion of charge equal to the oxidation state. This is surrounded by negative ligands (or) neutral molecules which have a lone pair of electrons.

If the ligand is neutral molecule such as NH_3, the negative end of the dipole in the molecule is directed towards the metal ion.

The important assumptions of C.F.T are:-

→ The ligands are treated as negative point charges (or) point dipoles, approching the positive central metal ion.

→ Electrostatic force of attraction exists between the ligand and metal ion.

→ The interaction between the electrons of central ion and those of ligands are entirely repulsive. Thus repulsive interactions are responsible for the splitting of d-orbitals.

→ The five d-orbitals which are degenerate in an isolated gaseous metal ion, splits into different energy levels under the influence of electrostatic field of ligand.

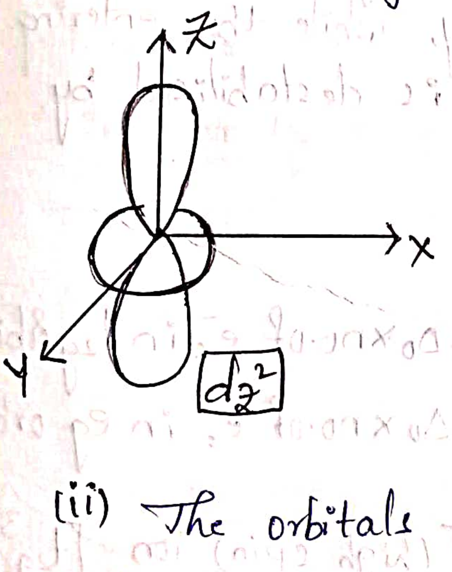
→ The splitting of d-orbitals varies with different geometries of the complex.

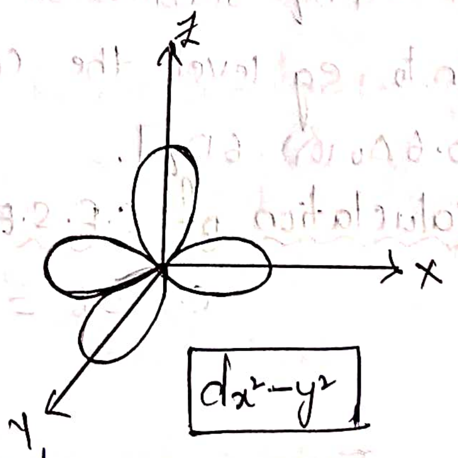
Spatial arrangement of Five d-orbitals:-

In order to understand clearly, the interactions that are responsible for crystal field effects in transition metal complexes, it is necessary to have a knowledge on geometrical relationships (shapes) of the five d-orbitals.

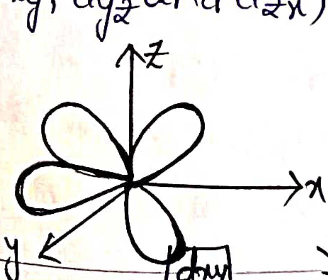
On the basis of the orientation of the lobes of the five d-orbitals with respect to co-ordinates, they are divided into two groups.

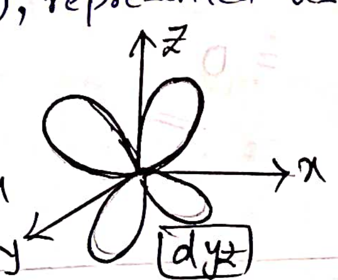
(i) The orbitals which have their lobes along the axes are called as "axial orbitals" (d_{z^2} and $d_{x^2-y^2}$), represented as "e_g" set

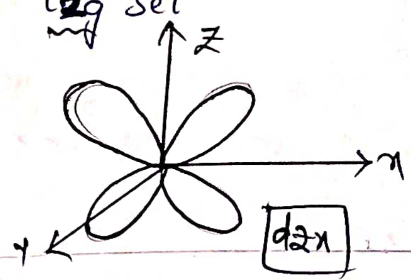




(ii) The orbitals which have their lobes in between the axis are called as "non-axial orbitals" (d_{xy}, d_{yz} and d_{zx}), represented as "t_{2g}" set







Tetragonal disortion of Octahedral complexes:-

If all the six ligands are situated at equal distances from the central metal ion, then the complex is said to be regular octahedron.

When the distances ~~fr~~ of ligands from the central metal ion are unequal, the structure is said to be irregular (or) distored octahedral complexes.

Distorted octahedral complexes may be of three types.

(i) Diagonally distorted octahedral complexes:-

These are obtained when the distortion of a regular octahedron takes place along a "two-fold axis".

(ii) Trigonally distorted octahedral complexes:-

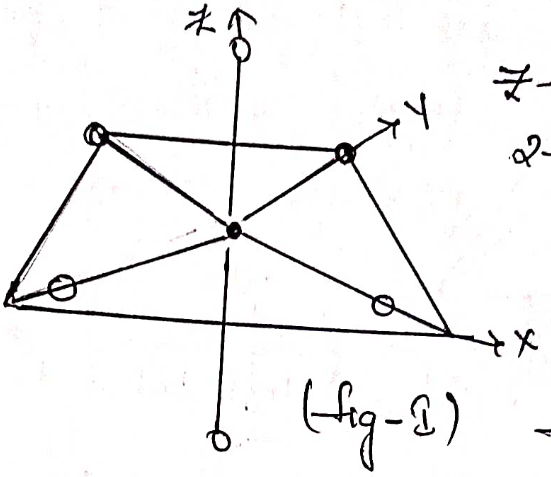
Here the distortion takes place along a "three-fold axis".

(iii) Tetragonally distorted octahedral complexes:-

These are also called as Tetragonal complexes, which are obtained when the distortion of a regular octahedron takes place along a "four-fold axis".

The tetragonal complexes are obtained by any of the following two ways.

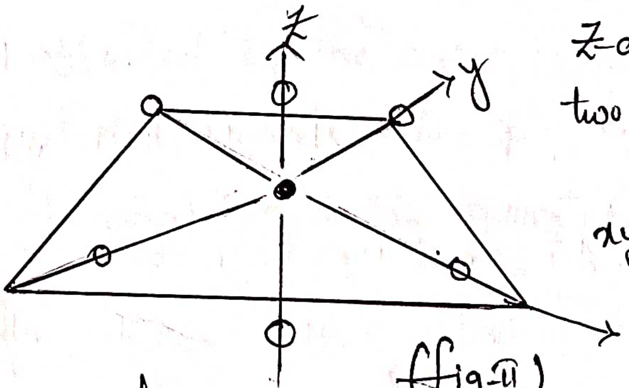
a) If the two trans ligands lying on the z-axis in an octahedron are moved away from the central metal cation. So, that their distance from the metal cation is slightly greater than it is for the other four ligands lying in the XY-plane, we get a tetragonal structure with two long bonds along the z-axis and four short bonds in xy-plane.



Z-axis having 2- long bonds & xy- plane having four short bonds.

(fig-I)

b) If the two trans ligands at the z-axis are brought near the central metal cation. So, that their distance from the metal cation is smaller than it is the other four ligands in x-y plane, we get a tetragonal structure with two short bonds along the z-axis and four long bonds in xy-plane.



Z-axis having two short bonds & xy-plane having four long bonds.

(fig-II)

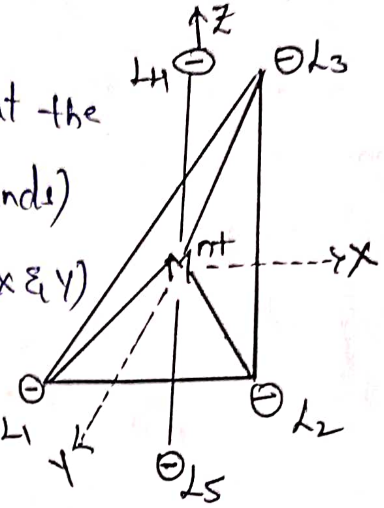
Crystal field effects:-

Splitting of d-orbitals in trigonal bipyramidal geometry:-

If the co-ordination no. of metal is 5, the geometry commonly equal by the metal ion is trigonal-bipyramidal.

The metal ion occupy the centre of the trigonal bipyramid and the ligands occupying the

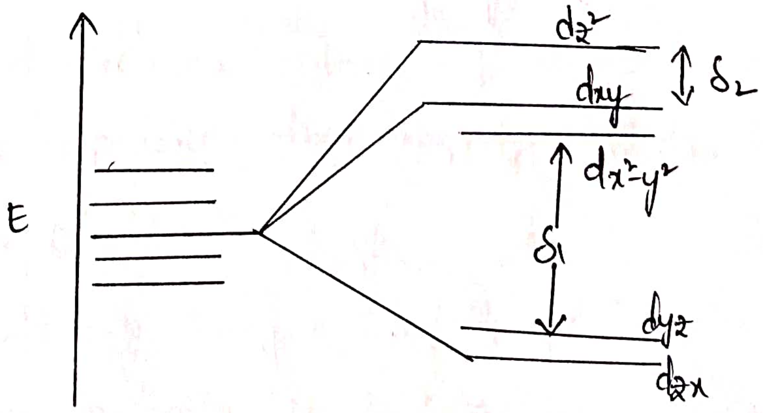
5 corner of Trigonal bipyramid is shown as follows.



From the fig, it is clear that the 3 ligands L_1, L_2, L_3 (Equitorial ligands) are present in between the axis (x & y) and the ligands L_4, L_5 ~~falph~~ (axial ligands) are present along z-axis.

Since the lobes of the d_{z^2} orbital lies directly in the path, the approaching ligands (L_4 & L_5). The electrons in these orbital experiences more repulsions than the other d-orbitals.

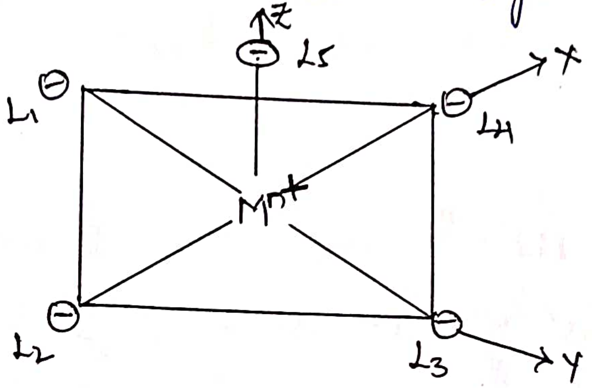
All the lobes of d_{xz} and d_{yz} orbitals lies between the axis. Hence these orbitals experiences relatively less repulsions. An electron in d_{xy} (or) $d_{x^2-y^2}$ orbital is not effected by the axial ligands but strongly repelled by equitorial ligands. The splitting pattern of d-orbitals in trigonal bipyramidal geometry is as shown in fig.



In general δ_2 is $2/3 > \delta_1$

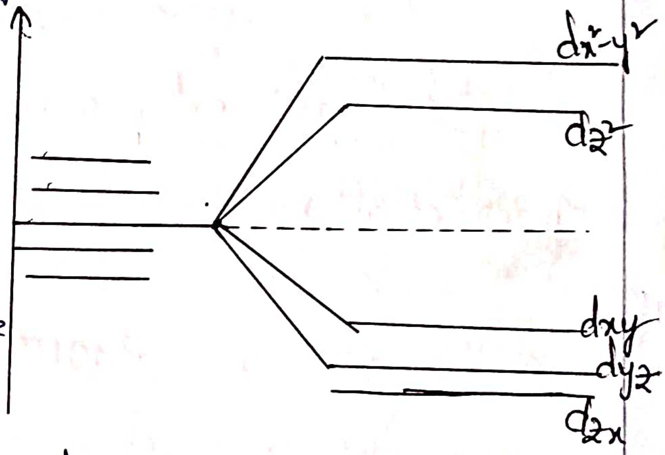
Splitting of d-orbitals in Square pyramidal geometry:-

—The metal ion occupies the centre of Square pyramid at the 5 ligands occupies the 5 corners of Square pyramid as shown in fig.



The splitting pattern of d-orbitals in Square pyramidal geometry is as shown in fig.

Since the lobes of $d_{x^2-y^2}$ orbital lies directly in the path of approaching ligands (L_1, L_2, L_3 & L_4) the electrons present in this orbital experiences more repulsions than the other d-orbitals.



Since the lobes of d_{xy}, d_{yz} are in between the axis, the electrons in this orbital experiences relatively less repulsions than the d_{z^2} and d_{zx} orbitals.

Applications of CFT:-

→ This theory Can be used to predict the most favourable geometry of a complex.

→ It accounts for the fact that Certain four Co-ordinated Complexes are Square planar where as others are tetrahedral.

→ It also explains the fact that certain ligands form outer orbital octahedral complexes where as others form inner orbital octahedral complexes. They in turn correspond to high-spin and low spin complexes.

→ The greatest achievement of this theory is its sucess in interpreting the magnetic properties taking into consideration the orbital contributions also.

→ The colours of transition metal complexes can be readily interpreted using this theory.

→. Spectral properties of many transition metal complexes can be easily explained by this theory.

*2. JAHN TELLER DISTORTION.

In order to explain why certain octahedral complexes undergoes distortion to get distorted octahedral geometry, a Theorem was put forward by John-Teller is known as John-Teller theorem.

Statement:-

Any non-linear molecular system in a degenerate electronic state will be unstable, and will undergo some sort of distortion to lower its symmetry and remove the degeneracy.

Symmetrical and Unsymmetrical (asymmetrical) t_{2g} and e_g orbitals :-

The t_{2g} and e_g orbitals which are empty, half filled and completely filled are said to be symmetrical orbitals and the orbitals other than those are called as unsymmetrical orbitals.

i.e

$$t_{2g}\begin{cases} t_{2g}^0,\ t_{2g}^3,\ t_{2g}^6 \cdots\cdots\rightarrow \text{symmetrical} \\ t_{2g}^1,\ t_{2g}^2,\ t_{2g}^4,\ t_{2g}^5 \text{---}\rightarrow \text{unsymmetrical} \end{cases}$$

$$e_g\begin{cases} e_g^0,\ e_g^4 \cdots\cdots\rightarrow \text{Symmetrical} \\ e_g^1,\ e_g^3 \text{----}\rightarrow \text{Unsymmetrical} \end{cases}$$

e_g^2 → Symmetrical in High spin Complexes $[(d_{x^2-y^2})^1 (d_{z^2})^1]$

e_g^2 → Unsymmetrical in Low spin complexes $[(d_{x^2-y^2})^0 (d_{z^2})^2]$

Conditions for distortion:-

1) If the electrons in the d-orbitals are symmetrically arranged, they will repel all six Ligands equally. Thus there is no distortion [regular octahedral geometry].

2) If the electrons in the d-orbitals are unsymmetrically arranged, they will repel some ligands more than other ligands, hence the distortion occurs.

Conditions for various types of distortion can be summarised as

t_{2g} (sym) + e_g (sym) $\longrightarrow$ No distortion

t_{2g} (unsym) $\longrightarrow$ slight distortion

e_g (unsym) $\longrightarrow$ } $\longrightarrow$ strong distortion

$e_g^2 [(d_{x^2-y^2})^0 (d_{z^2})^2]$ in L_3-complexes $\longrightarrow$ }

Cause of distortion:-

Consider the distortion produced by the presence of e_g orbitals in a complex of Cu^{+2} ion (d^9 system).

The configuration of this ion is $t_{2g}^6 e_g^3$ in both the fields. Thus these are two possible configurations.

(I) $\longrightarrow$ $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})^1$

(II) $\longrightarrow$ $t_{2g}^6 (d_{z^2})^1 (d_{x^2-y^2})^2$.

From the above two configurations, it is clear that the t_{2g} orbitals are symmetric (since completely filled) and e_g orbitals are asymmetric, strong distortion, which is due to the repulsion of ligands by the electrons occupying e_g orbitals.

In configuration I, the d_{z^2} orbital is completely filled (doubly occupied) and $d_{x^2-y^2}$ is singly occupied.

Thus the ligands along the z-axis will experiences more repulsions than the other four ligands in xy-plane.

Hence

i) The ligands along the z-axis tend to move away from Cu^{2+} nucleus and

ii) The ligands in xy-plane tend to move closer, (due to higher effective nuclear charge) to Cu^{+2} nucleus, resulting in elongation of octahedron. This is called tetragonal elongation (or) z-out distortion with two long bonds and four short bonds (as shown in fig. I)

In the configuration II, the $d_{x^2-y^2}$ orbital is doubly occupied and d_{z^2} orbital is singly occupied. Thus the ligands in xy-plane are repelled and moved away from the central metal ion, resulting in elongation of bonds in xy-plane and the ligands along z-axis moves closer to the nucleus of Cu^{+2} ion.

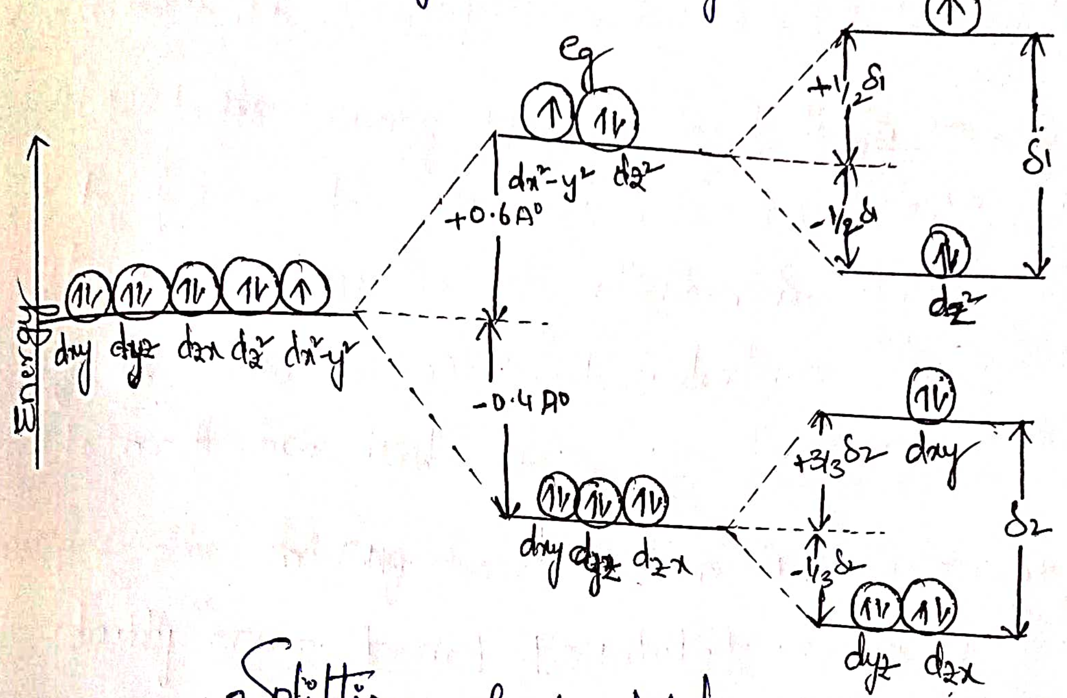
~~Hence~~ Hence there will be two short bonds and four long bonds. This is called tetragonal compression (or) z-in distortion (as shown in fig. ⓘⓘ)

In order to minimize the repulsions with the ligands, the d_{z^2} must be doubly occupied and $d_{x^2-y^2}$ is singles. Hence the two ligands approaching along the z-axis are only subjected to greater repulsions than the four ligands in xy-plane, resulting in distorted octahedral structure [Tetragonal elongation].

Thus the configuration I is highly stable with less energy than the configuration II.

Hence the configuration I is considered.

i.e $t_{2g}^6 (d_{z^2})^2 (d_{x^2-y^2})$



Splitting of d-orbitals of Cu^{+2} ion (d^9 system) in octahedral complexes caused by John-Teller ~~abo~~ effect (according to configuration I).

In the above diagram δ_1 and δ_2 represent the splitting of eg^3 and t_{2g}^6 levels respectively and

$\Delta_0 >>>> \delta_1 > \delta_2$.

For t_{2g} electrons there is no net energy change, because the four electrons in d_{yz} and d_{zx} are stabilized by $4 \times (-1/3\,\delta_2) = -4/3\,\delta_2$ and the two electrons in d_{xy} are destabilised by $2 \times (2/3\,\delta_2) = 4/3\,\delta_2$. Thus.

Net energy for t_{2g} electrons = energy loss + energy gain

$= 4/3\,\delta_2 - 4/3\,\delta_2$

$= 0.$

In the splitting of eg levels, the two electrons are stabilised by $2(-1/2\,\delta) = -\delta_1$ and the one electrons is destabilised by $1 \times (1/2\,\delta_1) = 1/2\,\delta_1$.

Net energy gain for eg electrons = Energy gain + Loss...

$= 1/2\,\delta_1 - \delta_1$

$= -\delta_1/2$

Hence the net energy change is $\delta_1/2$ which provides the driving force of distortion. This energy is called "John-Teller Stabilisation energy."

Consequences of John-Teller distortion:-

→ John-Teller distortion effects the reactivity of complexes.

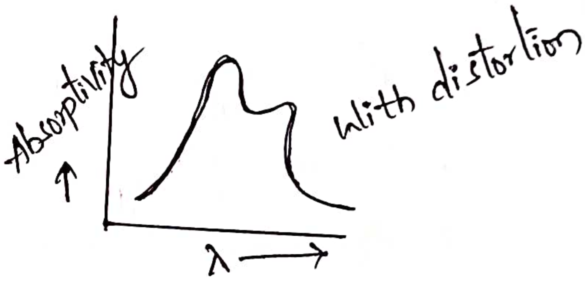
Eg:- $[Cu(H_2O)_6]^{2+}$ exchanges two of its H_2O molecules which are present along the elongated, z-axis more rapidly than the four H_2O molecules in xy-plane.

→ If the no. of chelate rings in a complex increases the stability of the complex will decrease.

Eg:- $[Cu(en)_3]^{2+}$ contains 3-chelate rings is less stable and $[Cu(en)_2(H_2O_2)]^{+2}$ contains only 2-chelate rings is more stable.

This is due to distortion along the z-axis and also due to the strain in the chelate rings.

→ The absorption spectra of complexes with distortion shows a gaussian curve with shoulder, where as the absorption spectra of complexes, with no distortion shows only a gaussian curve.



Limitations of C.F.T:-

→ According to C.F.T the nature of and is purely ionic (electrostatic), which is quite un realistic. It failed to explain covalent nature of M–L bond.

→ C.F.T considers only the metal ion d-orbitals & does not talks about ,P_x, P_y, P_z and ligand π-orbitals. So, all properties dependent upon ligand, orbitals are not explained.

→ C.F.T failed to explain about the relative strengths of Ligands.

for eg:- It gives no explanation why OH^- has smaller splitting power than H_2O.

→ C.F.T is unable to consider the possibility of the existence of π- bonding in complexes despite of its frequent existance in complexes of metals in low (or) high oxidation states.

→ C.F.T failed to explain the back donation of electrons from M to Ligand in complexes containing CO and CN as ligands.

Dynamic John- Teller Effect:-

In Some complexes no distortion can be detected in the room temperature, but additional evidence shows that the John- teller effect operates.

Eg:- $[Cu(H_2O)_6]^{2+}$

$Cu^{+2} \longrightarrow d^9$ system $\longrightarrow t_{2g}^6 eg^3$

Since eg^3 is unsymmetrical, we expect a strong distortion. But it does not show distortion at room temperature. when it is cooled to 20K it shows tetragonal distortion. This is called dynamic John- -Teller effect.

"The distortions in which the bond length differences are not measurable is called dynamic John Teller distortion.

[At room temperature the rapid interconversions among the distorted structures takes place very rapidly. The time needed for the rapid interconversions of distorted structures is so less compared with the measurement of interconversions by physical methods. Hence we can't observe the distortion at room temperature].

Unit-III

3. Experimental evidence for π- bonding in complexes:-

π- bonding is important in determining patterns of ligand substitution reactions. It is also central to understanding reactivity and stability in organo metallic complexes. we have to examine the evalution of π- bonding in metal carbonyl complexes and their derivatives.

The stability of metal carbonyl complexes depends upon the ability of carbon monoxide to accept metal election density into its π*. Although carbon monoxide is a weak base towards Hydrogen ion (or) BH_3, it has a significant affinity for election rich metals.

For example, it reacts with metallic Nickel at modest temperatures to form gaseous $Ni(CO)_4$. In which metal-metal bonds in Nickel, must be broken for a complex to form, are quite strong. Carbon monoxide acts as a σ donar ($OC \rightarrow M$) and a π- acceptor ($OC \leftarrow M$) to yield a strong bond.

$$M + C \equiv O \longrightarrow M^- - C \equiv O^+ \longleftrightarrow M = C = O$$

Chrystallagraphy:-

The M–CO bonding model described above suggests that the greater extent of π- bonding, more than the C–O bond will be lengthened and M–C bond shortened.

Metal- Carbon bond length in carbonyl complexes provides a better measure of double bond character because these lengths are more sensitive to changes in bond order.

If the covalent radii of an 'sp' carbon atom and of metal atom to which it is bound are known summation of too should give the length expected for metal-carbonyl single bond, the one with no π-bonding, then this value will be compared with measured bond length to determine the extent of π-bonding present.

Metal - carbonyl π-bonding is found in phosphine and phosphite derivatives of hexa carbonyl -chromium. Substitution R_3P for CO in $Cr(CO)_6$ creates a complex, in which one Co group lies trans to phosphorous ligand. The two trans ligands will complex for same π-orbital but carbon monoxide is a better π acid (π-acceptor) than the phosphine (Fig ②). As a result $Cr-Co_{eq}$ bond (184.4 pm) should be shorter relative to $Cr-Co_{eq}$ (188.0 pm) and Cr-Co (191.58 pm) in $Cr(CO)_6$.

In general, π-accepting ability of phosphine increases as electronegativities of its substitutents increases. Thus the π acidity of $P(OPh)_3$ to be greater than that of PPh_3.

It is found that Cr-P bond length in phosphite complex (230.9 pm) is shorter than in the phosphine complex (242.2 pm). The carbonyl ligand trans to the phosphorous ligand would be expected to receive more π electron density in phosphine complex than in phosphite complex. which leads to shorter metal-carbon bond for phosphine derivative (184.4 pm) as compared to that of phosphite complex (186.1 pm)

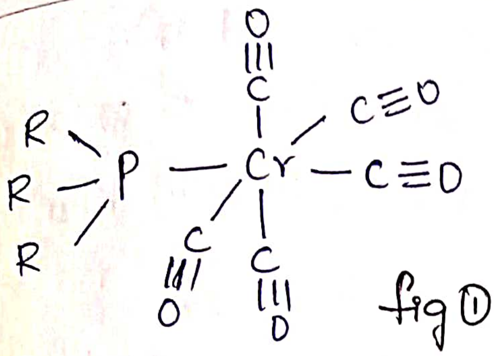


fig ①

Structure of phosphine & phosphite derivatives of hexa carbonyl chromium.

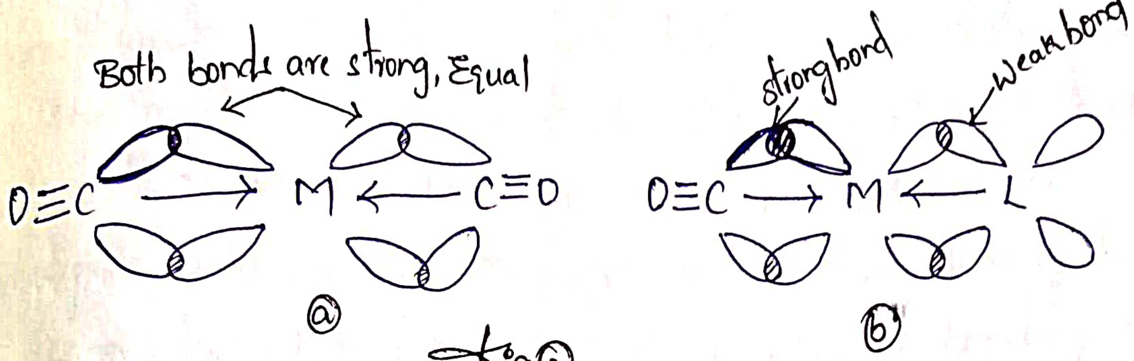


fig ②

Good overlap of two 'CO' π* orbitals with metal d-orbital.

Superior overlap of 'CO' π* orbital with metal d-orbital of compared to poorer overlap b/w ligand 'd' & metal 'd' orbital.

Infrared spectroscopy:-

The most widely used method for analysing metal carbonyl complexes is IR spectroscopy. The frequency of IR absorption associated with a C-O stretching vibration is a measure of resistance of the bond to displacement of its atom. Hence the stretching frequency provides a qualitative measure of bond strength; with stronger bonds in general gives rise to IR absorptions at higher frequencies.

IR absorptions of Some Metal Carbonyl Complexes.

Compound	frequency (cm⁻¹)
$[Mn(CO)_6]^+$	2090
$[Cr(CO)_6]$	2000
$[V(CO)_6]^-$	1860
$[Ti(CO)_6]^{2-}$	1748
$[Ni(CO)_4]$	2060
$[Co(CO)_4]^-$	1890
$[Fe(CO)_4]^{2-}$	1790

On the basis of absorption maxima, C-O bond strengths order is $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$ & $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$.

As M-C π bonding increases, the C-O bond becomes weaker, Greater the +ve change on the central atom, less the metal can donate e^- density into π* orbitals of CO ligands to weaken the C-O bond. In contrast in carbonylate anions metal has greater electron density to be dispersed, with the result that M-C π bonding is enhanced and C-O bond is diminished in strength.

Unit - III

1. Molecular Orbital Theory [M.O.T].

According to C.F.T, the nature of metal-Ligand bonding is purely ionic. i-e there exists an electrostatic force of attraction between the metal & Ligand. But there are Some complexes in which there is no electrostatic force of attraction, but behaves as an complexes. This is due to the existance of Some covalent character [Bonding] between metal and Ligand, which is supported from the experiments like ESR, NMR... etc. The covalent bonding in complexes can be explained by molecular orbital theory.

The main assumptions of M.O.T are:-

→ Molecular orbitals are formed by the overlapping of atomic orbitals (or by linear combination of Atomic orbitals) of central metal ion with the atomic orbitals of Ligands with similar energies.

→ The overlaping is possible whenever the Conditions of energy and symmetry permits.

→ The M.O's thus formed may be of Bonding, Anti bonding (or) Non-bonding character.

→ The no. of molecular orbitals formed is always equal to the no. of atomic orbitals taking part in the overlaping process.

→ M.O.T considers in account of all the outer orbitals in addition to the d-orbitals.

M.O Theory to octahedral Complexes:-

The formation of M.O's in a complex involves both σ and π overlaps of orbitals of metal and Ligand.

Sigma bonding in octahedral complexes:-

The overlap of metal orbitals and ligand orbitals along the bond axis leads to a σ-bonding,

The application of M.O theory to octahedral complexes involves the following steps:

→ Classification of metal orbitals into σ-symmetry.

→ formation of LGO's,

→ Formation of Molecular orbitals,

→ Molecular orbital energy level diagram.

→ Classification of metal orbitals into σ-Symmetry:-

In an octahedral complex, the metal ion is surrounded by six ligands placed along the +x, -x, +y, -y, +z and -z axis.

If we take 3d series metal ion, the valence orbitals of the metal are 4s, $4p_x$, $4p_y$, $4p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$, a total of a valance atomic orbitals. From Oh character table, these are classified as

4s : A_{1g} (or) a_{1g}

$4p_x$, $4p_y$, $4p_z$: T_{1u} (or) t_{1u}

$3d_{z^2}$, $3d_{x^2-y^2}$: E_g (or) e_g

$3d_{xy}$, $3d_{yz}$, $3d_{zx}$: T_{2g} (or) t_{2g}

Out of . . . .

only those metal orbitals, which have their lobes directed along the coordinate axes are favourable for σ - overlap

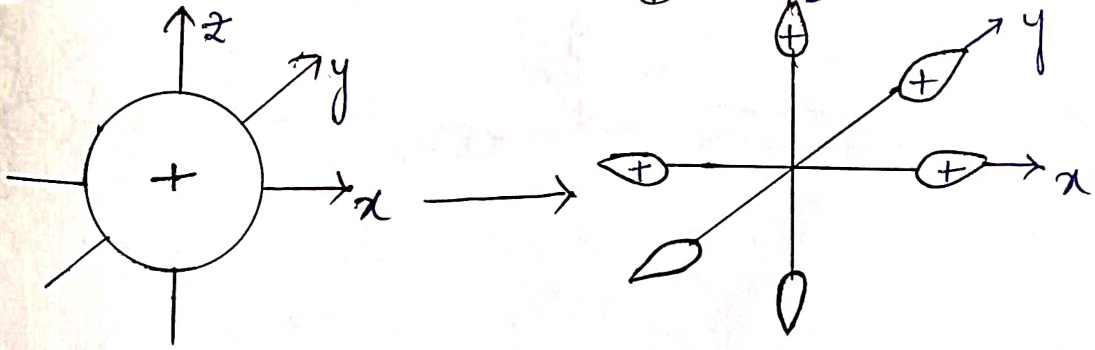
[Because the ligands are present along the co-ordinate axes].

— Hence a_{1g} (4s), t_{1u} ($4P_x, 4P_y, 4P_z$) and e_g ($d_{z^2}, d_{x^2-y^2}$) are capable of forming σ - bonds and t_{2g} (d_{xy}, d_{yz}, d_{zx}) remains as non-bonding. Since T_{2g} orbitals lies in between the axes.

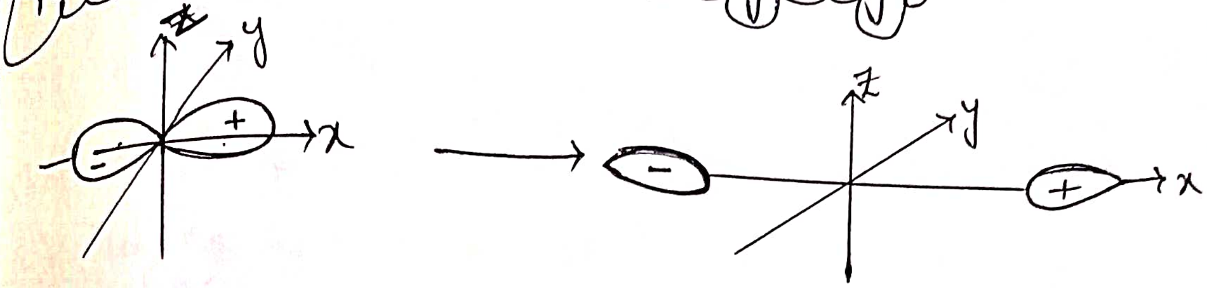
→ Formation of LGO's:-

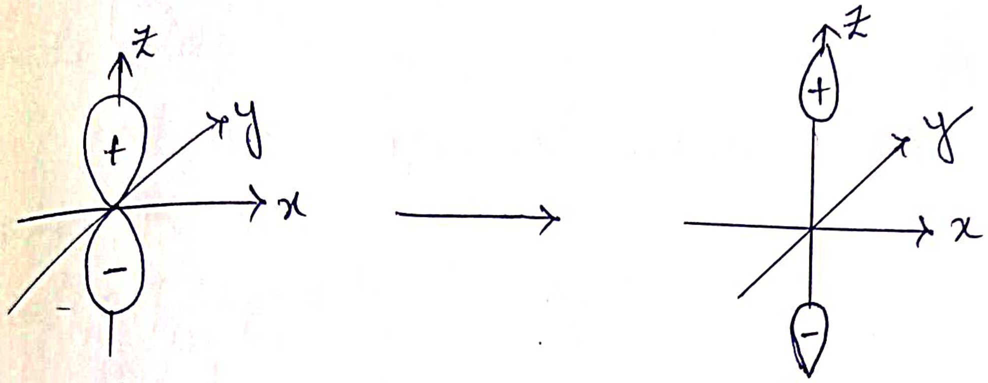
Before overlaping of ligand orbitals with metal atomic orbitals, the six ligand orbitals combine together linearly to form six group σ - orbitals, called as σ - L.G.O's, these orbitals possesses same symmetry as that of metal orbitals which are capable of forming ~~σ orbit~~ σ - bonds.

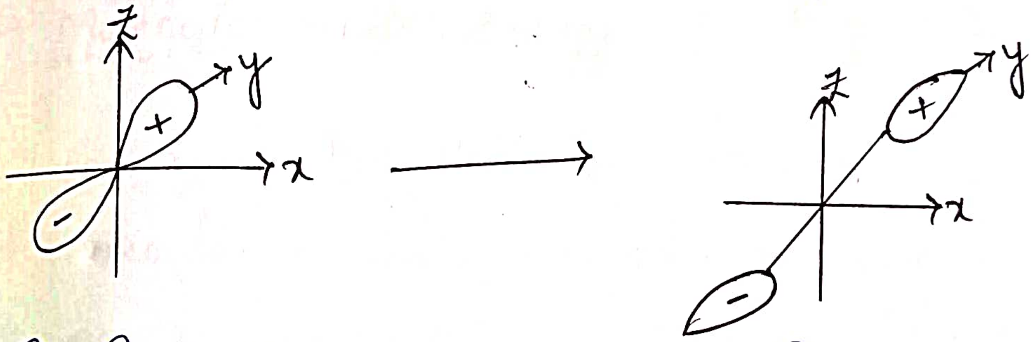
Formation of L.G.O with a_{1g} Symmetry:=



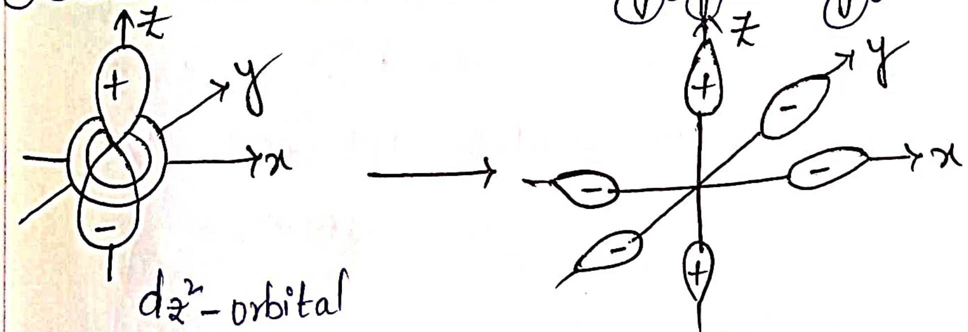
Formation of L.G.O with the Symmetry:-

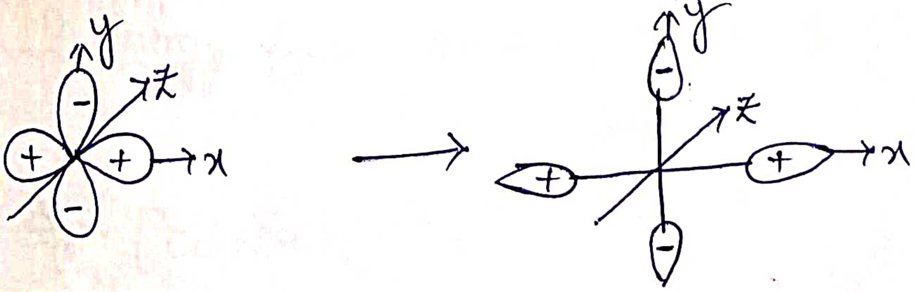






Formation of L.G.O with Eg symmetry:-





→ Formation of Molecular orbitals:-

The six atomic orbitals of the Central ~~ato~~ metal ion [$4s, 4P_x, 4P_y, 4P_z, 3d_{z^2}, 3d_{z^2-y^2}$ with a_{1g}, t_{1u}, e_g, symmetries respectively overlap with six L.G.O's along the bond axes, forming six sigma bonding M.O's and six sigma antibonding molecular orbitals. [only those orbitals of metal and ligand which has identical symmetry can overlap].

→ Molecular orbital Energy level diagram:-

This diagram shows the logical ordering of molecular orbitals as per these energies, The diagram is constructed on the assumption that the energy order is

$$\sigma \text{ L.G.O's} < (n-1)d < ns < np$$

$$\text{i.e} \quad \sigma \text{ L.G.O's} < 3d < 4s < 4p$$

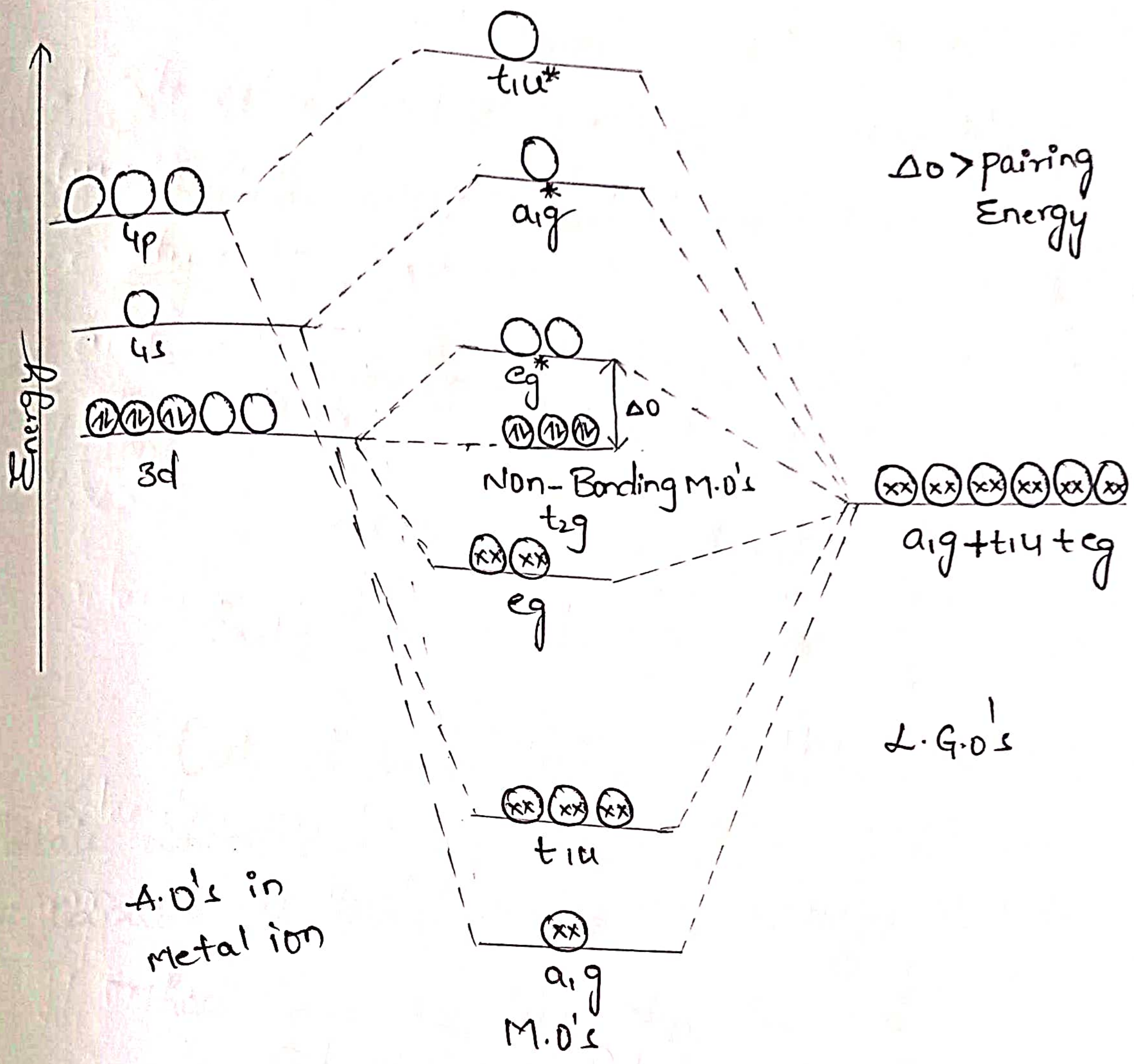
Eg:- $[Co(NH_3)_6]^{3+}$

M.O Energy level diagram for a complex with strong Ligand

Eg:- $[Co(NH_3)_6]^{3+}$

The stronger ligands like NH_3 splits, the 6 Bonding M.O's into 3 energy states via. A_{1g} as lower state, T_{1u} as Middle state with triply degenerate and E_g as higher state with double degenerate.

$Co^{+3} \longrightarrow (Ar)\,3d^6$



From the above diagram it is clear that the 12 electrons from $6NH_3$ ligands are occupied by a_{1g}, t_{1u} and e_g bonding M.O's and the valence electrons of Co^{+3} [d^6 system] occupies the t_{2g} non-bonding M.O.

The energy gap between t_{2g} and e_g^* M.O's is takes as Δ_o (or'). Since NH_3 is strong ligand

π- bonding in octahedral complexes:-

If the ligand is both σ as well as π donar, [F^-, Cl^-, Br^-, I^-, O^{2-}, OH^-, CO_3^{2-}] is capable of forming π-bonds with transition metal ions.

Eg:- $[CoF_6]^{3-}$

The Symmetries of the valence orbitals of ions are

s - a_{1g} d_{xy}, d_{yz}, d_{zx} - t_{2g}

p_x, p_y, p_z - t_{1u} $d_{x^2-y^2}, d_{z^2}$ - e_g.

Out of these 9 valence orbitals, only those orbitals which are perpendicular to the bond axes are capable of forming π- bonds with the L.G.O's.

Those are t_{2g} [d_{xy}, d_{yz}, d_{zx}] and t_{1u} [p_x, p_y, p_z]

The ligand group orbitals capable of π- interactions in an octahedral complex are t_{2g}, t_{1u}, t_{2u}, t_{1g}.

Since the metal orbital t_{1u} (p_x, p_y, p_z) has already participated in the σ bonding, it forms π-bonds in a very slight extent.

The t_{2g} orbital of metal ion interacts with the t_{2g} LGO and forms π - B.M.O and π anti B.M.O's.

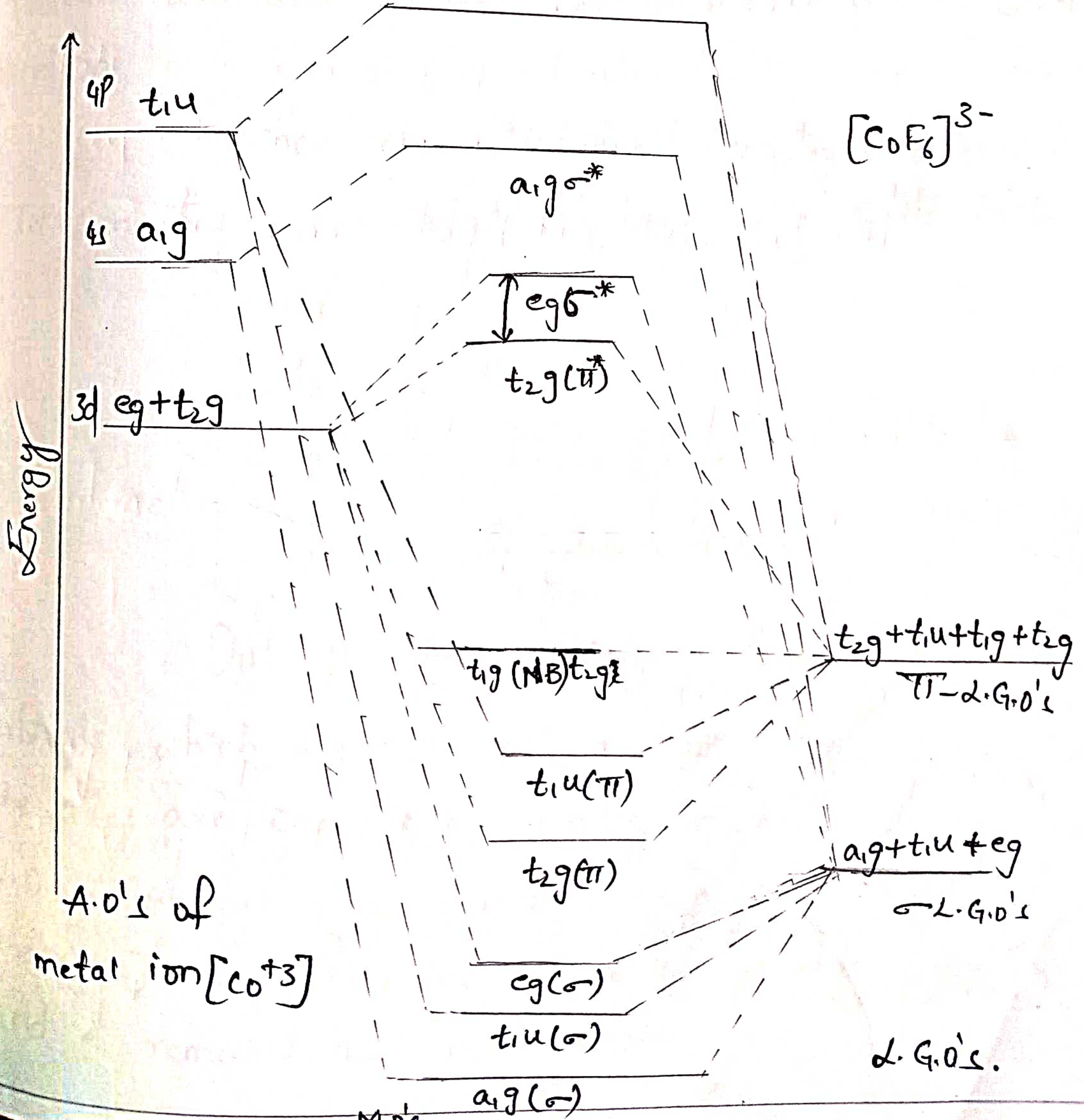
[As t_{2g} orbital of metal ion interacts with the t_{2g} LGO and forms π]

As there is no matching symmetry for the LGO's t_{2u} and t_{1g}, the remains as non-bonding.

The members of a_{1g}, t_{1u}, e_g ex of metal ion participates in σ-bonding with the σ-LGO's. [a_{1g}, t_{1u} and e_g].

The energy order of the M.O's are

σ LGO's < π LGO's < 3d < 4s < 4p.



Since flourine is more electronegative than Co^{+3} ion, the flourine s.p orbitals (L.G.O's) lie at a lower energy than the corresponding metal 3d orbitals and their electrons occupies t_{2g} π-M.O and the metal ion electrons ($3d^6$) occupies t_{2g}-π^*-M.O's.

The level of e_g^* is unefected by π-interaction

Δ_0 is reduced as a result of the π- bonding.

$[\Delta_0 < P.E]$

M.O diagram for Tetrahedral complexes:-

For a tetrahedral complex, the valence orbitals available on the central metal will be 3d, 4s and 4p.

Since the tetrahedral complexes belong to Td symmetry, the metal orbitals will splits into

a_1 : s

t_2 : p_x, p_y, p_z

e : d_{z^2} and $d_{x^2-y^2}$

t_2 : d_{xy}, d_{yz} and d_{zx}

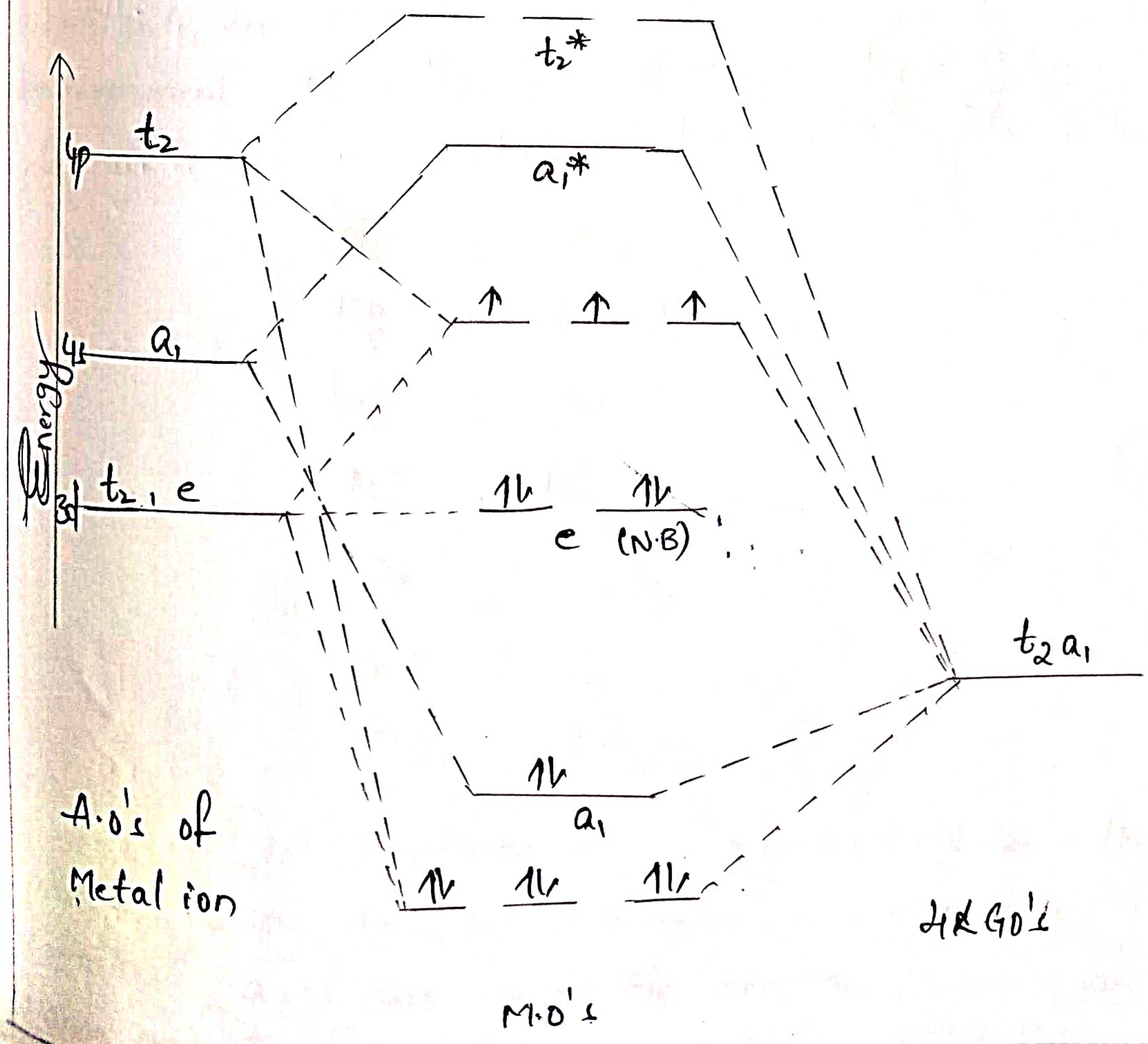
Out of these 9 valence orbitals, only those orbitals which have their lobes directed in between the axes are capable of forming σ-bonds with the L.G.O's [Because the ligands are present in between the axes]. Hence a_1 and t_2 are of bonding symmetry and e remains as non-bonding.

The four αGO's, which are capable of forming σ-bonds with the metal orbitals are having the symmetries a_1 and t_2.

The t_2 αGO's can interact with both sets of metal t_2 orbitals [p_x, p_y, p_z, d_{xy}, d_{yz} and d_{zx}] to give three sets of σ-M.O's. Out of these 3 σ M.O's, one is bonding M.O, one is slightly anti-bonding M.O and one is clearly Anti-bonding M.O.

The σ- M.O diagram for the tetrahedral complex is as follows.

Eg:- $[CoCl_4]^{2-}$



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[$\Delta_0 < P.E$]

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t_2 : P_x, P_y, P_z

e : d_{z^2} and $d_{x^2-y^2}$

t_2 : d_{xy}, d_{yz} and d_{zx}

Out of these 9 valence orbitals, only those orbitals which have their lobes directed in between the axes are capable of forming σ-bonds with the L.G.O's [Because the ligands are present in between the axes]. Hence a_1 and t_2 are of bonding symmetry and e remains as non-bonding.

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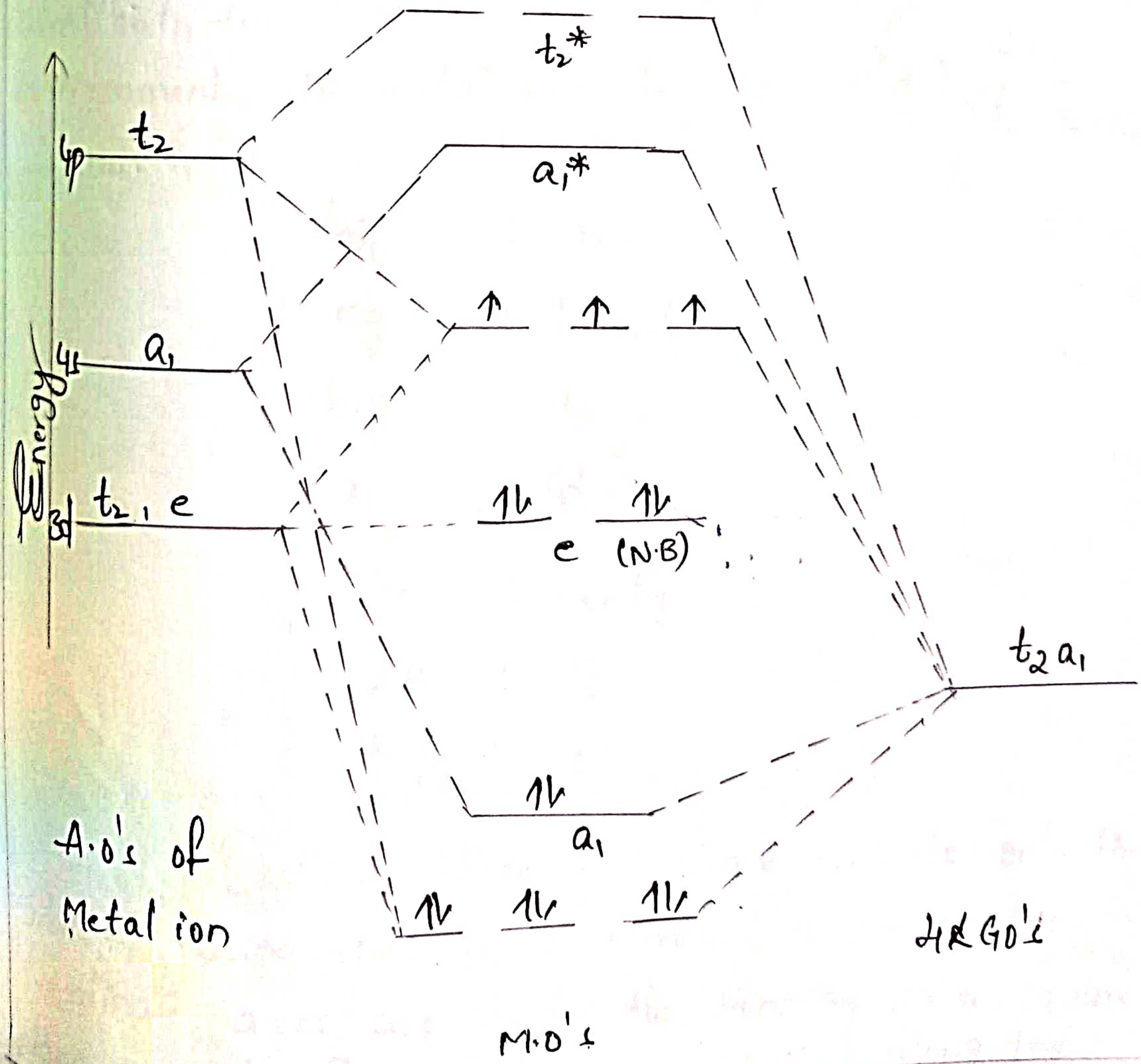


In $[CoCl_4]^{2-}$, Co in +2 state (d^7 system). the four chloride ligands provides 8 e's and a total of 15 e's (7+8).

Out of these 15 e's, the 12 e's will fill the six lowest energ. M.O's [upto e set]. The remaining 3 e's occupies the slightly-Anti-bonding t_2 M.O.

The energy gap between the e and the next highest t_2 orbital is labelled as Δ_t.

M.O diagram for square planar complexes:-

A no.of four coordinate complexes adopt a square planar geometry. If the four ligands, are identical, the complex belongs to D_{4h} symmetry. In this environment, the metal orbitals (viz.. s, p, d,) splits as follows.

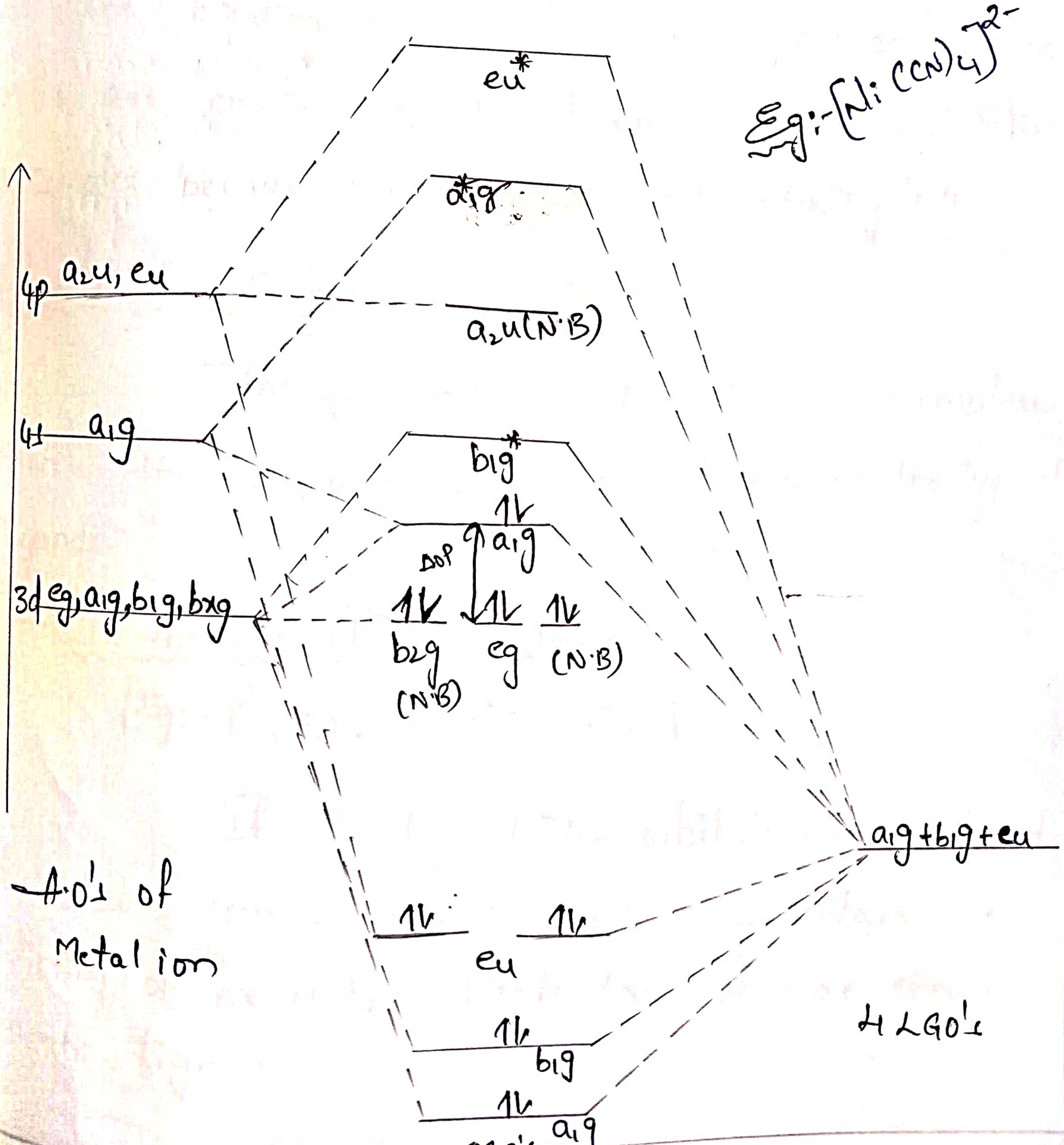
b_{2g} : d_{xy}
e_g : d_{xz}, d_{yz}
b_{1g} : $d_{x^2-y^2}$
a_{1g} : d_{z^2}
e_u : p_x, p_y
a_{2u} : p_z
a_{1g} : s

Out of these 9 valence orbitals, only these orbitals having their lobes directed along x and y - coordinate axes are useful for bonding in a square planar geometry. [since ligands are pointed along the x and y axes].

Hence $s(a_{1g})$, $p_x, p_y (e_u)$ and $d_{x^2-y^2}(b_{1g})$ are capable for bonding and the remaining (a_{2u}, e_g, b_{2g}) are non-bonding orbitals.

The four ligands which will be oriental along the x and y axes will give rise to LGO's of a_{1g}, b_{1g} and e_u symmetry. These LGO's will interact with metal orbitals of some symmetry leading to the σ M.O diagram as shown in the fig.

Eg:- $[Ni(CN)_4]^{2-}$



The a_{1g} L.G.O overlaps with both a_{1g} metal orbitals, producing three M.O's of this symmetry.

The square planar geometry is common for complexes of d^8 metal ions. For such a complex, there will be sixteen electrons [eight from the metal and eight from four ligands].

These 16 e^-_s will occupy the 8 lowest energy M.O's and the complex is diamagnetic. [since there is no unpaired e^-_s].

From the diagram it is clear that, all the bonding M.O's are filled and all anti bonding M.O's are empty. Adding additional e^-_s will destabilise a complex because the e^-_s occupies Anti-bonding levels.

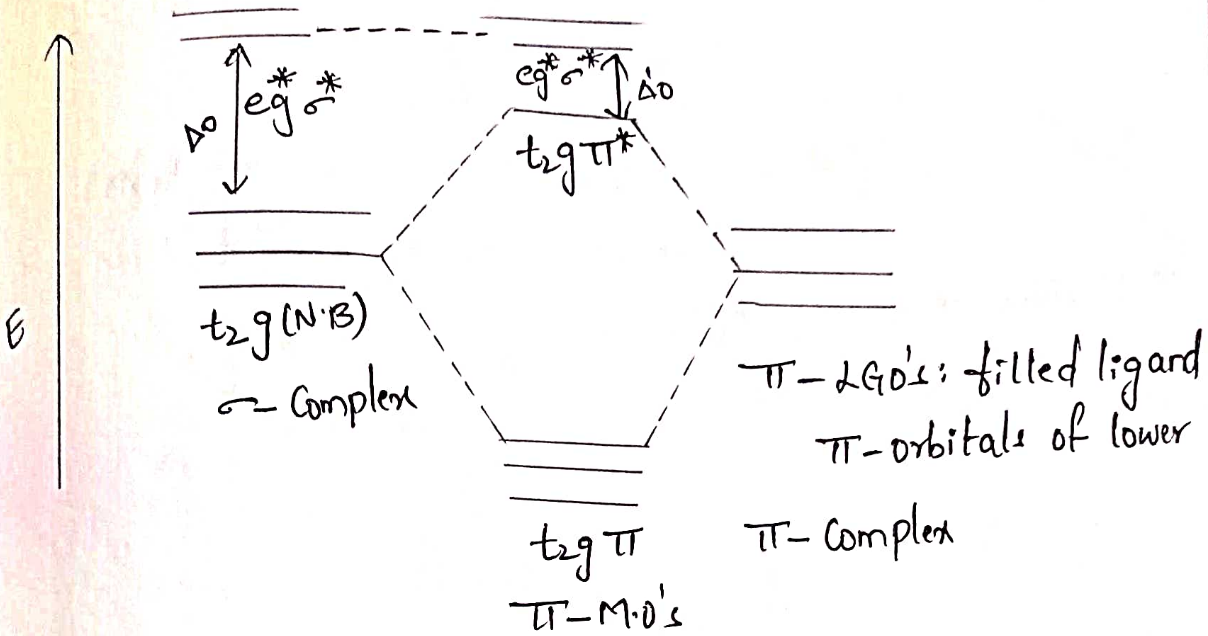
* Effects of π bonding on Δo :-

The formation of π- bonding in complexes effects the magnitude of Δo depending upon the type of ligands.

→ If the Ligand is π-donar:-

[Eg:- F^-, Br^-, Cl^-, O_2^{-2}, OH^- - - -]

If the ligand π- orbitals are filled and of lower energy than the metal t_{2g} orbitals, the splitting of metal t_{2g} orbitals takes place as shown in the fig.



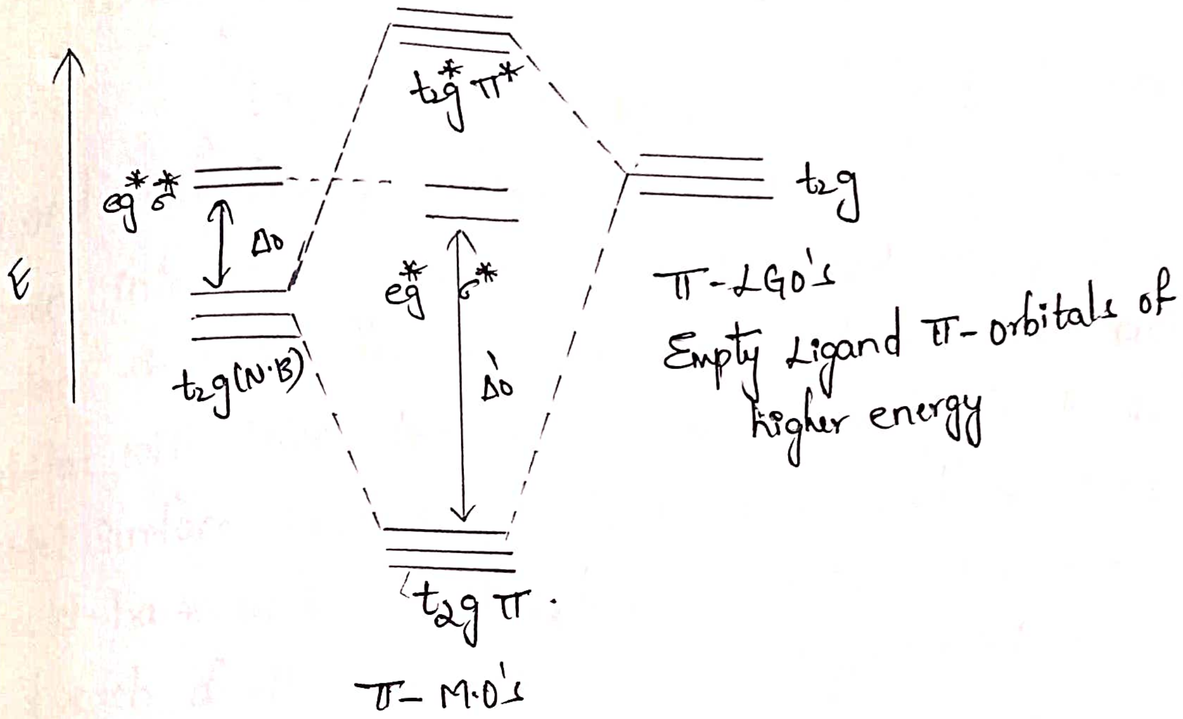
Since the π – interactions destabilises the t_2g metal orbitals relative to e_g^* M·O's, the value of Δo is reduced to Δo' as shown in fig. The Ligand in this case exerts a weaker field and is present at the weaker end of the spectrochemical series.

The π – bonding with this type is generally referred as ligand to Metal (L→M) π – bonding.

→ If the Ligand is π – Acceptor:-

[Eg:- PR_3, AsR_3, CO---]

If the ligand π – orbitals are empty and of higher energy than the metal 3d orbitals, the splitting of t_2g metal orbitals takes place as shown in fig.



In this case the net result of π-interaction is the metal t_{2g}-orbitals are stabilised relative to the e_g^* M.O's. i.e the metal t_{2g} electrons will go into the $t_{2g}\pi$ M.O's which are of lower energy than $t_{2g}^*\pi$ M.O's and thus the value of Δ_o will be increased to Δ_o'.

In this case the ligand exerts a strong field. The ligand of this type is referred to as an acceptor ligand because of the presence of π-orbitals in it and the π-bonding is referred as Metal to Ligand (M→L). π-bonding.

**Q. π- bonding and Molecular orbital theory.

In addition to formation of σ bonds, many ligands are having capable of forming π- bonding when interaction with a metal. π- bond has a nodal surface that includes the bond axes and that a π-bonding orbital will have lobes of +ve sign on each side of this nodal surface. From orbital symmetry an octahedral complex would have upto 12 such bonds - two between the metal and each of the 6 ligands. Metal and ligand orbitals participating in π bonds will lie perpendicular to the internuclear axes consider four potential metal-ligand π- interactions.

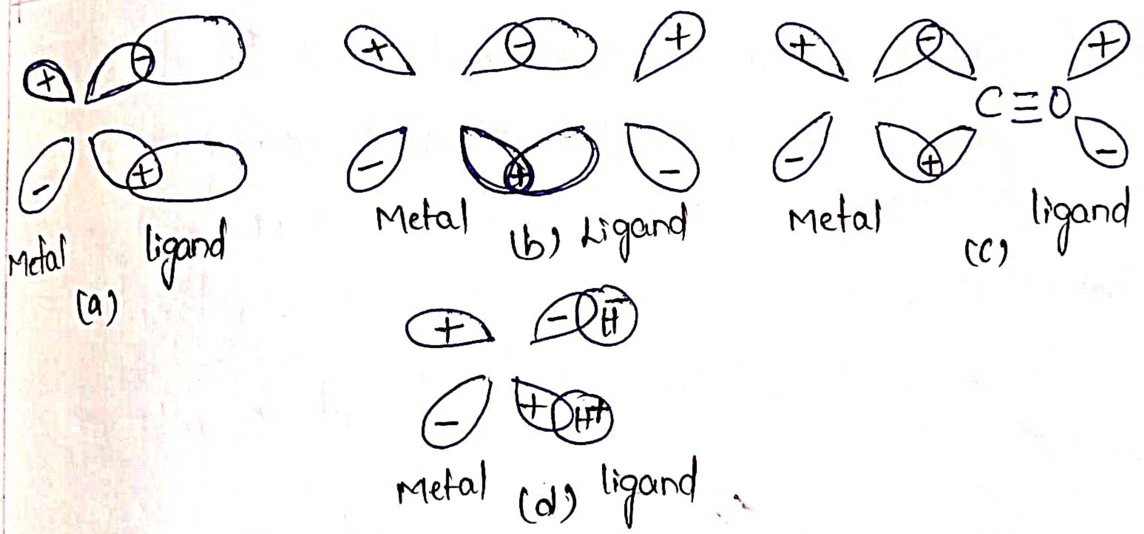
1. $d_\pi - p_\pi$ 2. $d_\pi - d_\pi$ 3. $d_\pi - \pi^*$ 4. $d_\pi - \sigma^*$

The examples of ligands capable of each type are shown in following table.

π- bonding in co-ordination compounds.

Type	Description	ligand examples.
$p_\pi - d_\pi$	Donation of e^-_s from filled p- orbital of ligand to empty d- orbital of metal.	RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N
$d_\pi - d_\pi$	Donation of e^-_s from filled d- orbital of metal to empty d- orbital of ligand.	R_3P, R_3As, R_3S.

$d\pi - \pi^*$	Donation of $\bar{e}_s$ from filled d-orbital of metal to empty π anti bonding orbital of ligand.	CO, RNC, CN^-, N_2, NO_2^-, Ethylene.
$d\pi - \sigma^*$	Donating of electrons from filled d-orbitals of metal to empty σ^* orbitals of ligand.	H_2, R_3P, alkanes.



π- overlap of metal d- orbital with various types of ligand orbitals (a) p, (b) d, (c) π^*, (d) σ^*,

Metal (or) ligand can ~~co~~ acts as a electron donar ' metal d-orbitals can donate electron density to an empty orbital on the ligand (or) an empty d- orbital on the metal can receive electron density from a filled orbital of ligand.

The ligand group orbitals capable of π- interactions in an octahedral complex fall into 4 symmetry categories t_{2g}, t_{1u}, t_{2u} & t_{1g}.

A transition metal will possess orbitals of only two of the types t_{2g} (d_{xy}, d_{yz}, d_{zx}) & t_{1u} (P_x, P_y, P_z) metal can use all of these orbitals for π bonds.

The members of t_{1u} set are directed towards the ligands and participate in strong σ bonds. Formation of π bonds using these orbitals will tend to weaken the σ system and hence will not be favoured. t_{2g} orbitals are directed b/w the ligands and they readily forms π-bond to LGO's of matching symmetry. The t_{2u} & t_{1g} ligand group orbitals must remain non-bonding. Since there is no orbitals of matching symmetry on the metal. π-bonding in octahedral complex is limited to orbitals of t_{2g} symmetry.

Unit-IV

Introduction:-

In studying the formation of complexes in Solution, two kinds of stability of complexes come in question. These are

Thermodynamic stability:-

This is a measure of extent to which, the complex will form (or) will be transferred into another species, when the system has reached equilibrium.

—Here we deal with stability constants, Metal-ligand bond energies, Thermodynamic variables like enthalpy, Entropy.

Kinetic stability:-

It refers to the (special) speed with which complex undergoes reactions like substitutions, interconversions, recemisation, Electro exchange reactions.

In terms of kinetic stability it is better to call the complexes as inert (or) Labile complexes.

Labile complexes:-

The complexes in which the ligands are "rapidly replaced" by others are called "Labile (or) Non-inert -Complexes."

(or)

The complexes in which the substitution of ligands takes place in "less than one minute" are called "Labile complex". The reactions conditions are specified as a temp of 25°c and 0.1 M solutions.

Inert Complexes:-

The complexes in which substitution, takes place "slowly" are called "Inert complexes."

*** Stepwise and overall formation constants :-

The formation of metal complexes is a reversible reaction. According to J. Bjerrum, the formatic of a complex in solution proceeds by the stepwise addition of ligands to the metal ion.

Consider the formation of the complex ML_n.

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + L \overset{K_n}{\rightleftharpoons} ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

The equilibrium constants $K_1, K_2 \cdots K_n$ are called as stepwise formation constants (or) stepwise stability constant.

The formation of the complex ML_n can be given by the overall reaction as

$$M + L_n \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

Where β_n is called overall formation constant ~~(for a complex ion, the greater)~~ (or) overall stability constant.

The higher the value of stability constant for a complex ion, the greater will be its stability.

The raciprocal of stability constant $(1/K)$ is called as instability constant.

Relation between overall stability constant (β_n) and stepwise stability constant (K_n) :-

Consider the formation of the complex ML_3 from metal and Ligands.

$$M + 3L \rightleftharpoons ML_3$$

$$\therefore \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

Multiplying both numerator and denominator by $[ML]\,[ML_2]$

$$\Rightarrow \beta_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML]\,[ML_2]}{[ML]\,[ML_2]}$$

$$= \frac{[ML_3]}{[ML_2][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML]}{[M][L]}$$

$$= K_3 \cdot K_2 \cdot K_1$$

$$\therefore \beta_n = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdots \frac{[ML_n]}{[ML_{n-1}][L]} \longrightarrow ①$$

$$= K_1 \cdot K_2 \cdot K_3 \cdots K_n$$

$$\boxed{\beta_n = \prod_{n=1}^{n} K_n}$$

Taking $\log_{10}$ on both sides of eq ①

$$\log_{10} \beta_n = \log_{10}\left[\frac{[ML]}{[M][L]} \cdots \frac{[ML_n]}{[ML_{n-1}][L]}\right]$$

$$= \log_{10}[K_1 \cdot K_2 \cdot K_3 \cdots K_n]$$

$$= \log_{10} K_1 + \log_{10} K_2 + \cdots + \log_{10} K_n$$

$$\boxed{\log_{10} \beta_n = \sum_{n=1} \log_{10} k_n}$$

*** Trends in stepwise stability constants:-

Consider the formation of the complex $[Cu(NH_3)_4]^{+2}$, which proceeds in four steps.

$$Cu^{+2} + NH_3 \xrightleftharpoons{K_1} [Cu(NH_3)]^{+2} \quad K_1 = 1.9\times10^4$$

$$[Cu(NH_3)]^{+2} + NH_3 \xrightleftharpoons{K_2} [Cu(NH_3)_2]^{+2} \quad K_2 = 3.6\times10^3$$

$$[Cu(NH_3)_2]^{+2} + NH_3 \xrightleftharpoons{K_3} [Cu(NH_3)_3]^{+2} \quad K_3 = 7.9\times10^2$$

$$[Cu(NH_3)_3]^{+2} + NH_3 \xrightleftharpoons{K_4} [Cu(NH_3)_4]^{+2} \quad K_4 = 1.5\times10^2.$$

The overall formation constant can be written as

$$Cu^{+2} + 4NH_3 \xrightleftharpoons{\beta_4} [Cu(NH_3)_4]^{+2} \quad \beta_4 = 8.1\times10^2.$$

The K values generally decrease gradually with increasing substitution by ligand.

The following factors is the reason for the steady decrease of the stability constants.

→ [Trends in K values]:-

i) Statistical factor:-

As the coordinated water molecules are replaced by ligand molecules (or) ions, the number of water molecules in the complex formed decreases. Hence the probability of replacing water molecules also decreases. As a result "K" values decreases gradually.

ii) Steric factor:-

This arises only when the incoming ligands are bulkier in ~~bi~~ size than the coordinated water molecules. As the small sized water molecules are replaced by bulkier ligand the steric crowding around the central metal ion increases. As a result of these steric repulsions the subsequent steps a. retarted. Hence the K values gradually decreases.

iii) Electrostatic factor (or) coulombic factor:-

In the 1st step of complex formation, one ligand (L) replaces one water molecule to give $[M(H_2O)_{n-1}L]$. In the second step another ligand (L) approaches the above complex. Now, there is an electrostatic repulsion between the ~~(incomplex)~~ incoming ligand and a similar ligand already present in the complex. As result of this electrostatic repulsion between the ligands, the subsequent steps are retarded. Hence "K" values decreases gradually.

∴ The general trend in K values is

$$K_1 > K_2 > K_3 > \cdots\cdots > K_n$$

*** Factors affecting the stability of metal complexes:-

A no. of factors affect the stability of complexes. Some of these factors depends on the nature of the central is while others depend on the nature of the Ligand.

→ I. Factors related to the nature of the metal ion:-

1. charge and size of the metal ion:-

Metal complexes with metal ion having high charge and small size are more stable.

A smaller and highly charged cation permits a more closer approach of the ligands and larger electrostatic attractions resulting from high charge on the cation gives a more stable complex.

Eg:- stability for Fe^{+3} and Fe^{+2} complexes is as follows

$[\overset{III}{Fe}(CN)_6]^{-3}$ – $\beta = 31.0$

$[\overset{II}{Fe}(CN)_6]^{-4}$ – $\beta = 8.3$

The charge/radius ratio for the central metal ion is called as polarising power of the cation. The larger the value of charge/radius ratio the more stable is the complex.

2. Natural order of stability [Iriving- Williains series]:-

The stabilities of the high spin complexes of the ions for a given ligand are according to the order.

$Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$

This order is called natural order of stability (or) Iriving- Williains series.

3. Electronegativity of the central metal ion:-

In General the bonding between the Central ion and a ligand due to the donation of electrons by the ligand to the central ion. Thus the high electronegative metal ions have Strong electron attracting tendency and give most stable complexes.

4. class a and class b metals:-

On the basis of their electron acceptor properties, metals, are divided into two categories.

class a	Class b
H, alkali and alkaline earth -metals, Sc, Ti, V, G, Zn, Im, Sn, Sb, lanthanides, & Actinides.	Rh, Pd, Ag, In, Pt, Au, Hg

The stability of the complexes formed by Class 'a' metals with the ligands with donar atoms is of the order.

$N >> P > As > Sb$
$O >> S > Se > Te$
$F > Cl > Br > I$
} Tendency to form complex with class (a) metal ions.

Similarly for class 'b' metal ions.

$N << P > As > Sb$
$O << S < Se \sim Te$
$F < Cl < Br < I$
} Tendency to form Complex with class (b) metal ions.

→ II. Factors related to the nature of the ligand :-

1. Size and charge of the ligand:-

A Ligand with Small Size and higher charge gives more stable complexes.

Eg:- Stability constants of

$[FeF]^{+2} = 10^6$

$[FeCl]^{+2} = 20$

Higher stability constant of $[FeF]^{+2}$ is due to the small size of flourine than chlorine.

For monodentate neutral ligands, the higher the dipole moment and smaller the size, the more stable are the complexes formed.

2. Basic character of Ligands:-

The more basic nature of the ligand implies that it can easily donate electron pairs to the central metal ion, forming more stable complexes. [Lewis theory

3. Chelate effect:-

polydentate ligands form chelated complexes which are very stable when compared to the ordinary metal complexes. This process of gaining stability by the formation of chelates is called "chelate effect."

Eg:- $[Ni(en)_3]^{+2}$ is more stable than $[Ni(NH_3)_6]^{+2}$.

Factors affecting the chelate effect:-

→ Ligands capable of exhibiting resonance forms more stable chelates.

→ Chelated complexes with more no.of rings are more stable.

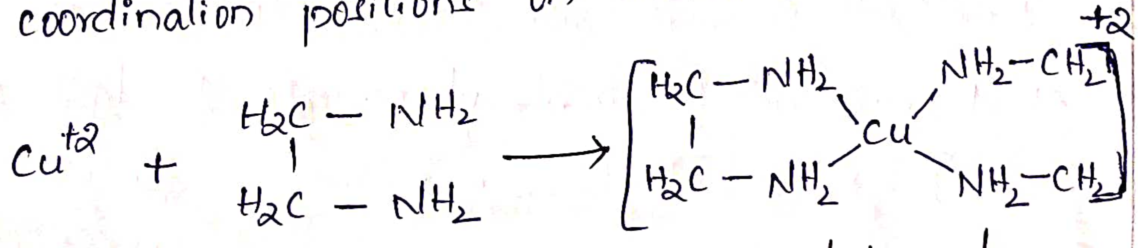
→ Five and six membered chelates are more stable.

→ Complexes having bulky groups on the chelate ring experiences some steric strain. This reduces the stability.

→ Transition metal forms more stable chelates when in more than chelate effect.

→ polydentate ligands complexes formed from these polydentate Ligands are called Metal Chelates.

Eg:- Ethylene diamine is a bidentate ligand, occupies two coordination positions on metal ion.



chelated complex

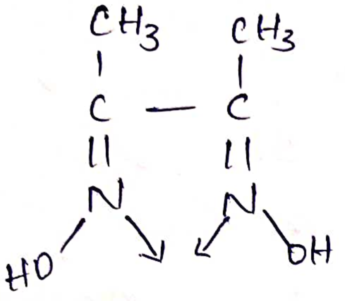
The metal chelates are more stable when compared to ordinary metal complexes. This is evident from the variation in formation constants β_n.

$[Ni(NH_3)_6]^{+2}$ — $\beta_6 = 8.3$ (No chelate rings)

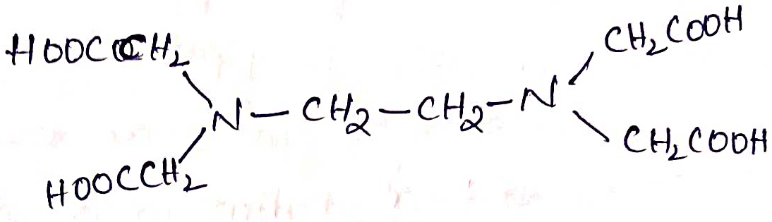
$[Ni(en)_3]^{+2}$ — $\beta_3 = 18.4$ (3 chelate rings)

"The extra stability enhanced by the formation of chelate rings is called chelated effect."

Eg's for polydentate ligands:-



Di-methyl glyoxime anion
(Bi-dentate ligand)



EDTA
(Hexadentate ligand)

The stability of metal chelates is due to

(i) If one of the two metal-ligand bonds of a bidental chelate complex is broken, the remaining bond still ring attached with the metal ion. So, that the broken bond can be re-established. This does not occur in a non-chelated complex.

ii) Consider the following reaction

$$[Ni(NH_3)_6]^{+2} + 3en \rightleftharpoons [Ni(en)_3]^{+2} + 6NH_3$$

If the reaction proceeds towards right, there is an increase in the no. of particles, hence there is an increase in entropy. This implies that during chelate formation, there is an increase in the entropy of the system. Hence metal chelates are more stable.

The increase of entropy ($\Delta S = +ve$) of the system during chelate formation results in a large value of stability constant (β_n)

$$\Delta G = -RT \ln \beta_n \rightarrow ①$$

$$\Delta G = \Delta H - T\Delta S \rightarrow ②$$

where ΔG = free Energy change

T = Absolute Temp

ΔS = Change in Entropy (+ve value)

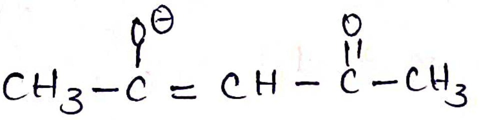
ΔH = Change in Enthalpy (−ve value)

Factors affecting the chelate Effect:-

1. Resonance:-

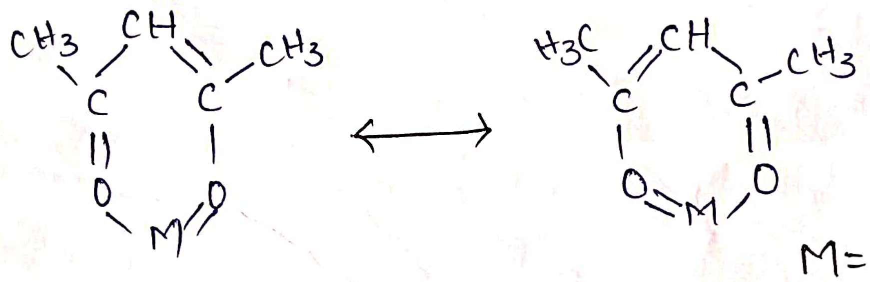
The ligands capable of exhibiting resonance form more stable metal chelates.

Eg:- Acetyl acetone coordinates as an anionic enolate ligand.



$$CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

As a result of resonance, the two M-O bond in these complexes are found to be equal in length.



M=Metal ion

Eg:- EDTA is a hexadentate ligand, forms more stable Complex.

③ Size of the Ring:-

(Five membered and six membered rings are more stable). When there is no double bond in chelate ring generally 5-membered ring will be the most stable. when there are double bonds, a six membered ring is most stable.

4. Transition metals form more stable chelates when Compared to non-transition metals.

5. Steric effect:-

Complexes having bulky groups on the chelate rings experience some steric strain. This reduces the stability of the complexes.

Eg:- Co(III) complexes with substituted - Ethylene diamine ligands are found to be less stable.

*** Experimental Determination of stability constants.

1. Spectrophotometric Method:- [Job's Method]:-

This Method is used to determine the composition (formula) of a complex and stability constant of a complex and mainly used for solutions where only one type of a complex is formed from metal and ligands.

We know that the complexes absorb light difference than the metal ions. First for a complex whose stability constant is to be determined. find a Suitable wave length where the maximum absorbance is there (λ_{max}).

Procedure:-

10 Solutions of the complex containing metal ion and ligand are made, such that the total volume of each Solution is 10 ml.

Solution number	1	2	3	4	5	6	7	8	9	10
Vol. of Metal ion (ml)	0	1	2	3	4	5	6	7	8	9
Vol. of Ligand (ml)	10	9	8	7	6	5	4	3	2	1

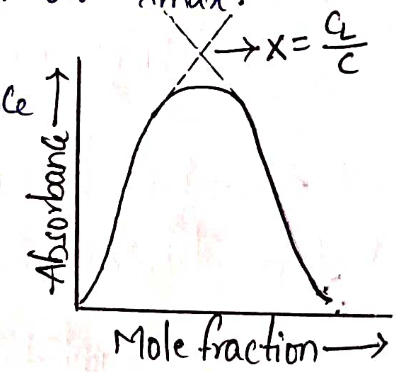
From this table it is evident that the Sum of the concentration of the metal ion (C_M) and Conc. of the Ligand (C_L) are constant.

$$\text{i.e } C_M + C_L = \text{Const}$$

$$C_M + C_L = C \rightarrow ①$$

Then the absorbance values of each Solution is measured by using spectrophotometer at λ_{max}.

- A Graph is drawn b/w Absorbance - of the complex and the mole fraction - of the ligand, as shown in fig.



$$\Rightarrow \frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C}$$

$$\Rightarrow \frac{C_M}{C} = 1 - \frac{C_L}{C}$$

$$= 1 - x \quad (\because \text{from } ②)$$

$$\therefore \boxed{\frac{C_M}{C} = 1 - x} \rightarrow ④$$

On dividing eq ② with Eq ④, we get

$$\frac{x}{1-x} = \frac{C_L/c}{C_M/c}$$

$$= \frac{C_L}{C_M} = n$$

$\therefore \boxed{n = \frac{x}{1-x}}$ By knowing the values of "n", the formula of complex is determined.

Let "A" be the true absorbance of the complex and "Aexpt" be the extrapolated absorbance (from graph)

For a 1:1 complex, the ratio of the true absorbance to the extrapolated absorbance is the mole fraction of the complex.

$$\therefore \frac{A}{A_{expt}} = \frac{[ML]}{c}$$

$$M + L \overset{KF}{\rightleftharpoons} ML$$

$$KF = \frac{[ML]}{[M][L]}$$

$$\Rightarrow [ML] = \left(\frac{A}{A_{expt}}\right)c \rightarrow ⑤$$

we know that

$$C_M = [M] + [ML] \rightarrow ⑥$$

$$C_L = [L] + [ML] \rightarrow ⑦$$

from Eq ⑥ $[M] = C_M - [ML] = C_M - \left(\frac{A}{A_{expt}}\right)c \rightarrow ⑧$

from Eq ⑦ $[L] = C_L - [ML] = C_L - \left(\frac{A}{A_{expt}}\right)c \rightarrow ⑨$

Substituting the values of [ML], [M], [L] in KF, we get

$$\boxed{K_F = \frac{\left(A/A_{expt}\right)c}{\left[C_M - \left(A/A_{expt}\right)c\right]\left[C_L - \left(A/A_{expt}\right)c\right]}}$$

//

*** Potentiometric Method [Bjerrum method]:-
(or)
pH method :-

When the ligand is a weak acid (or) a weak base, competition between Hydrogen ions & Metal ions for the ligand exists. This can be used for the determination of formation constant.

Procedure:-

Let us assume that

C_H be the concentration of an acid,

C_M be the concentration of the metal sol,

C_L be the concentration of the basic ligand.

The following equilibria exists in the solution

$$\underset{\text{(Basic ligand)}}{L} + \underset{\text{acid}}{H^+} \xrightleftharpoons{Ka} HL^+ , \quad Ka = \frac{[HL^+]}{[H^+][L]}$$

$$\underset{\text{(Basic Ligand)}}{L} + \underset{\text{(Metal ion)}}{M^+} \xrightleftharpoons{K_F} ML^+ , \quad K_F = \frac{[ML^+]}{[L][M^+]}$$

Where Ka = acid association constant of the ligand

K_F = Formation Constant.

The original concentrations of acid, Ligand, Metal ion can be written as

$$C_H = [H^+] + [HL^+] \longrightarrow ①$$

$$C_L = [L] + [ML^+] + [HL^+] \longrightarrow ②$$

$$C_M = [M^+] + [ML^+] \rightarrow ③$$

From Eq① $[HL^+] = C_H \mp [H^+] \rightarrow ④$

Substituting eq ④ in Ka

$$K_a = \frac{[HL^+]}{[H^+][L]}$$

$$\Rightarrow \boxed{[L] = \frac{C_H - [H^+]}{K_a [H^+]}} \rightarrow ⑤ \quad (\because \text{from eq } ①)$$

Substituting eq ⑤ & Eq ④ in eq's ② & ③

$$\Rightarrow [ML^+] = C_L - [HL^+] - [L]$$

$$= C_L - C_H + [H^+] - \frac{C_H - [H^+]}{[H^+] K_a}$$

$$\therefore \boxed{[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{[H^+] K_a}} \rightarrow ⑥$$

$$\boxed{[M^+] = C_M - [ML^+]} \rightarrow ⑦$$

The $[H^+]$ at equilibrium is determined potentiometrically using a pH meter. From the value of pH the $[H^+]$ can be caluclated using.

$$\boxed{pH = -\log_{10}[H^+]}$$

Substituting the values of C_H, C_L, C_M and $[H^+]$ in equations ⑤, ⑥ & ⑦ we can get the formation constant K_F.

Using the Formula, $K_F = \dfrac{[ML^+]}{[M^+][L]}$.

*** IRVING - WILLIAM Series.

Metal ions are classified in to 3 classes based on the stabilities of complexes formed by them with ligands having donar atoms from Groups VA, VIA, (&) VIIA.

Class A :-

Class A metal ions are those ions which form complexes of the greatest stability with the lightest element of each of these groups as the donar atom.

Examples of class a metal ions are

Li^+, Na^+, K^+

Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}

Al^{+3}, Ga^{+3}, Cr^{+3}, Fe^{+3}, Co^{+3} etc.

Class B :-

Class B metal ions are those which form least stable complexes with the lighest element of each group as donar atom.

Examples of class B metal ions are

Cu^+, Ag^+, Au^+, Tl^+

Hg^{+2}, Pd^{+2}, Pt^{+2}, Tl^{+3}.

Some metal ions form complexes whose stabilities cannot be predicted on the basis of the order which was observed for class a and class b metal ions. These ions are classific as "border line class."

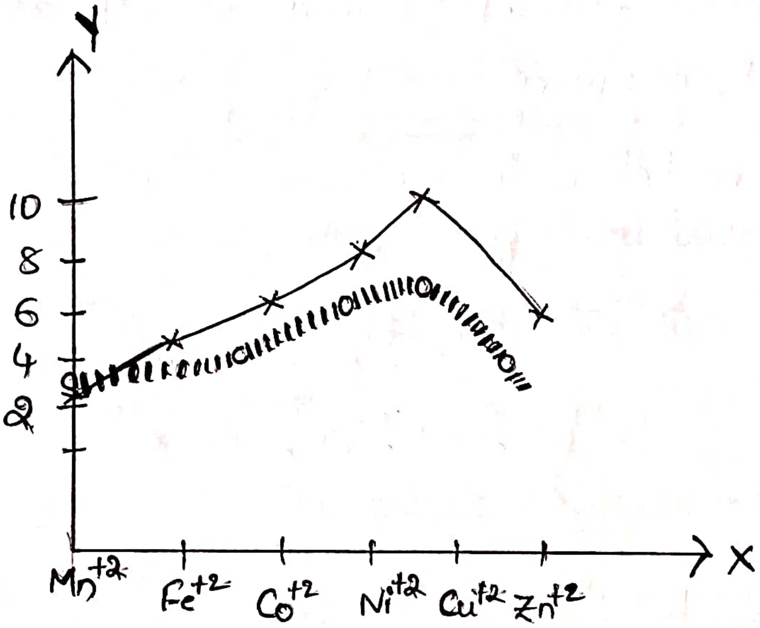
Examples of border line class are Mn^{+2}, Fe^{+2}, Co^{+2},

Ni^{+2}, Cu^{+2}, Zn^{+2} etc. For these metal ions, the stability of complexes with a given ligand is almost in the order

$$Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$$

This order is known as Irving- William Series

Although, the fig. shows the trend in K_1 values the Irving-william series generally holds good for K_2 and K_3 also.



Trends in K_1 values as Mn^{+2} is altered, illustrating Irving- William series.

*** Acid- Base Strength and HSAB:-

Hardness and softness refer to special stability of hard- hard and soft-soft interactions & should be distinguished from (~~inherent aci~~) inherent acid (or) base strength.

For example, both $OH^{\ominus}$ and $F^{\ominus}$ are hard bases. Now, the basicity of $OH^{\ominus}$ is about 10^{13} times that of

$F^{\ominus}$ ion. Similarly, both SO_3^{-2} and Et_3P may be considered Soft bases. However the latter is 10^7 times as strong.

It is possible for a strong acid (or) base to displays a weaker one, even though this appears to violate the principle of hard and soft acids & bases.

For example, the stronger, softer base surfite ion can displace the weak hard base $F^{\ominus}$ ion. from hard acid the proton H^+.

$$SO_3^{-2} + HF \rightleftharpoons HSO_3^- + F^- . \quad K_{eq} = 10^4$$

Like wise, very strong hard base $\overset{\ominus}{O}H$ ion can displace the weaker Soft base SO_3^{-2} ion from soft acid, Methyl mercury cation.

$$\overset{\ominus}{O}H + CH_3HgSO_3^- \rightleftharpoons CH_3HgOH + SO_3^{-2} \quad K_{eq} - 10.$$

In these cases, the strengths of bases ($SO_3^{-2} > F^-$, $\overset{\ominus}{O}H > SO_3^{-2}$) are Sufficient to force these reactions to the right inspite of hard-soft considerations.

~~(Nevertheless, it a co)~~

Never the less, if a competitive situation is set up in which both strength and hardness-softness are considered, the hard-soft rule works.

$$\underset{\text{Soft-Hard}}{CH_3HgF} + \underset{\text{Hard-soft}}{HSO_3^-} \rightleftharpoons \underset{\text{Soft-Hard}}{CH_3HgSO_3^-} + \underset{\text{Hard-soft}}{HF} . \quad K_{eq} \sim 10^3.$$

$$CH_3HgOH + HSO_3^- \rightleftharpoons CH_3HgSO_3^- + HOH \quad K_{eq} > 10^7$$

*** Macrocyclic Ligands.

Macrocyclic ligands are special type of polydentate ligands in which the ligating atoms are in a large ring encircling the metal atom.

Eg:- Crown ethers, cryptates.

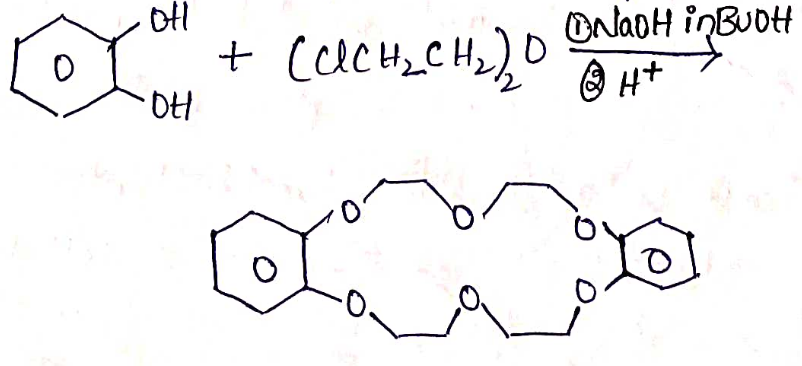
The macrocycles have the unusual property of forming stable complexes with alkali metals.

This exceptional stability is due to the close fitting of the alkalimetal into the hole in the centre of the ligand.

→ Crown Ethers :-

Crown ethers are macrocyclic ethers in which the oxygen atoms are seperated by two methylene groups each lie in a nearly planar arrangement about the central metal atom and the remainder of the molecule lies in a crown arrangement.

Crown ethers were 1st synthesized by C.T pedersen in 1967 by the following reaction.



Dibenzo-18-crow-6.

The general formula of crown ethers is

n-Crown-m.

Where "n" is the ring size.

"m" is the no.of oxygen atoms.

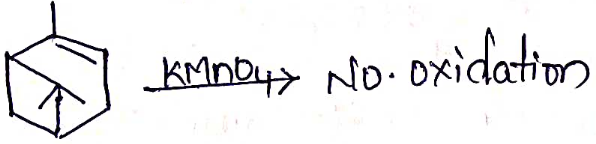
~~For~~ Eg:-

18-C-6 (C-crown)

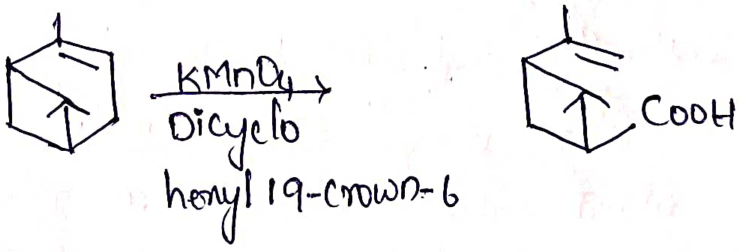
[Dibenzo-18-crown-6]

Crown ethers reactions generally occur in organic reactions.

Eg:- α-pinene.



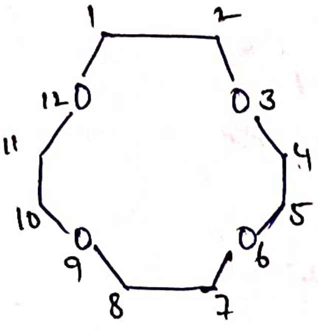
α-pinene



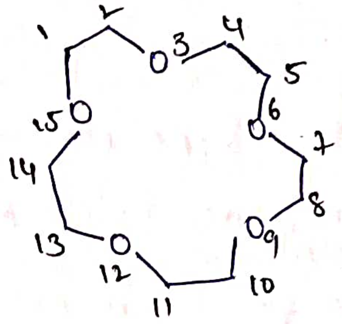
In nature, they are used for trapping of between crown ether and metal is Guest-Host relation.

Experimental studies shows that the stability of of metal ions with crowns is determined by the ratio of metal ion size to the dimensions of the inner space of the crown.

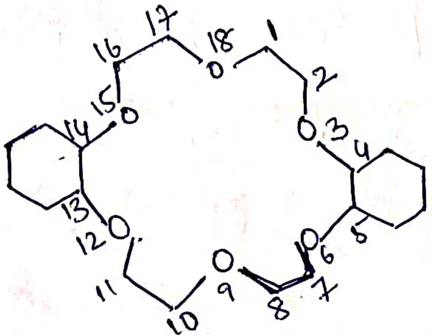
Some Eg's of Crown ethers:-



12- crown -4



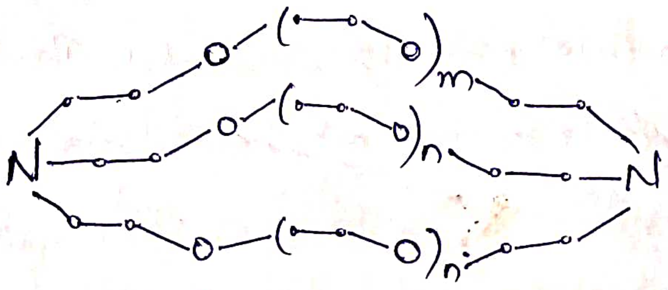
15- crown -5



Dicyclo hexyl -18- crown - 6

→ Cryptates (or) cryptands:-

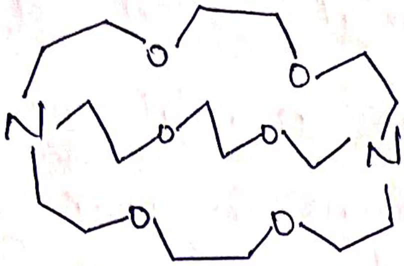
The macrocyclic Ligands in which the Complex of metal ion takes place are called cryptates. These are 3- dimensional Ligands with an innerspace Confined by three carbon chains including hetero atoms. These are represented by general formula.



Thus cryptates may be regarded as bicyclic oxygen-donar ligands with terminal nitrogen atoms.

Eg:- $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$

This is also represented as (cryptand - 222)



Cryptates are highly selective to bio-metals. for Eg:- The naturale macrocyclic ligand valinomycin is selective to K^+ ions.

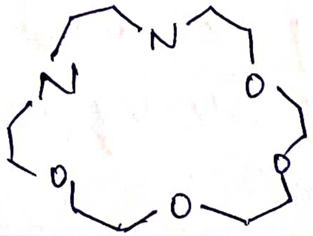
An unusal compound $[Na(cryptand\text{-}222)]^+ Na^-$ can be formed by cooling a sol. of Na in ethylamine with cryptand-222.

This is a golden yellow diamagnetic solid, which is only stable below -10°c. The interesting feature is that it contains Na^- ion (sodide ion).

Other alkalide compounds containing K^-, Rb^- (Rubidid) Cs^- (caeside) ions have been made in a similar way. If the reaction is carried out with an excess of cryptand, some unusal compounds are formed called as "Electrides;" These are black solids and paramagnetic.

Their formula is $[Cs^+ (cryptand\text{-}222)]$ [cryptand-222 in which an electron is trapped in a hole of radius 2.4Å.

cryptands are bicyclic crown ethers containing nitrogen also, generally used as phase transfer catalysts [usually crown ethers are monocyclic in nature].



HARD and SOFT ACIDS and BASES ①

HSAB principle (or) PEARSON principle.

X, [Certain ligands tend to form most stable complex with heavier ions such as Ag^{+}, Hg^{+2}, Pd^{+2}, Pt^{+2}, with nearly full d electrons, others prefer to form complexes with lighter ions, such as Be^{+2}, Al^{+3}, Ti^{4+} with no d electrons (or) number of d-electrons].

Based on the preferential bonding metal ion as well as ligands have been classified into two classes.

Class a:- class a metal ions (or) Hard acids:-

Alkali metal ions, alkaline earth metal ions, lighter transition metals with no d e^{-}s or lesser no. of d e^{-}s (i.e in higher oxidation states) are classified as Hard acids (or) class a metal ions.

Eg:- Ti^{+4}, Fe^{+3}, Cr^{+3}, Co^{+3}, H^{+}, Cl^{+}, Na^{+}, K^{+}, Ba^{+2}, Mg^{+2}, Cm^{+2}, Sn^{+2}, Al^{+3}, These ions have the following characteristic features.

→ They have small size, high polarizing power & higher oxidation states.

→ Their outer electrons (or) orbitals are not distorted.

Class b:- Class b metal ions (or) Soft acids:-

Heavier transition metal ions with nearly full d electrons (or) metal ions in lower oxidations states (or) metal ions with bigger size are classified as class b metal ion (or) soft acids.

Eg:- Pd^{2+}, Pt^{+2}, Ag^{+}, Au^{+}, Cd^{+2}, Hg^{+2}, Hg_2^{2+}, Metal atoms (M^0)

Class a ligands (or) Hard bases:-

The ligands which prefers to form most stable complexes with light metal ions (hard acids) are classified as hard bases.

These are anions (or) neutral molecules which are not easily polarizable.

Eg:- NH_3, H_2O, OH^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, F^-, Cl^-

Class b ligands (or) Soft bases:-

The ligands which prefer to form most stable complexes with heavy metal ions (soft acids) are classified as soft bases.

Bonding in Hard-Hard and Soft-Soft Combination:-

Since hard acids have generally vaccant d- orbital they can accept electrons from hard bases. So, that the bonding between hard acids and hard bases is ionic.

Interaction between Soft acids and Soft bases occurs mostly through pi bonding. So, that the bonding between Soft acids and Soft bases is largely covalent.

HSAB principle :- [pearson's principle]

~~The~~ typical Lewis acid-base reaction Can be represented as.

$$\underset{\text{Lewis acid}}{A} + \underset{\text{Lewis base}}{:B} \longrightarrow \underset{\text{Adduct (or) complex.}}{A:B}$$

The HSAB (SHAB) principle is very helpful in making a prediction of the stability of the complex A:B..

According to this principle the complex A:B is most stable when A and B are either both Soft (or) both Hard.

The complex is least stable when one of the reactants (namely A & B) is very hard & the other one is very Soft.

This principle also means that if there is a choice of reaction between an acid & two bases (or) between a base and two acids, a hard acid will prefer combine with a hard base and a soft acid will prefer combine with soft base & thus a more stable product will be obtained.