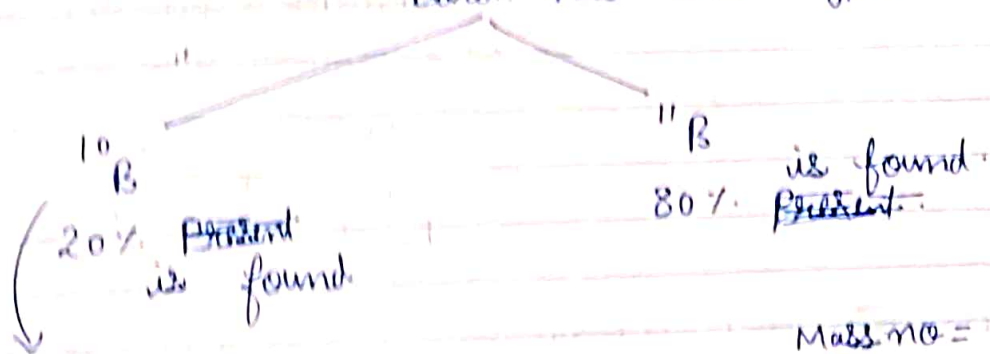


Chemistry of Boron

Boron has two types



They have tendency to accept a neutron that's why ^{11}B found more.

Mass no = $P + N$ increases mass increases

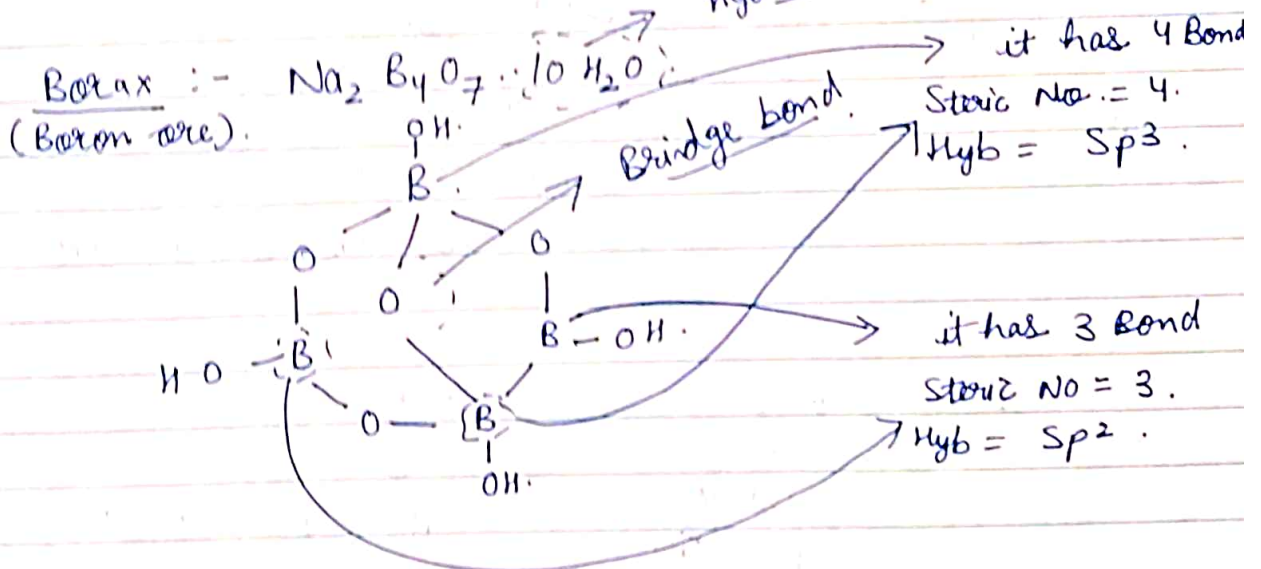
Boron ~~most~~ naturally found in two forms.

(1) icosahedron
 It has $\begin{bmatrix} 12 \text{ vertices} \\ 20 \text{ faces} \end{bmatrix}$

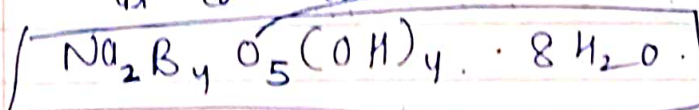
(2) Cuboctahedron.

Boron Extraction

we have two ores

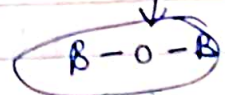
In $\text{Na}_2\text{B}_4\text{O}_7$ ore.2 Boron = Sp^3 hybridised.2 Boron = Sp^2 hybridised.

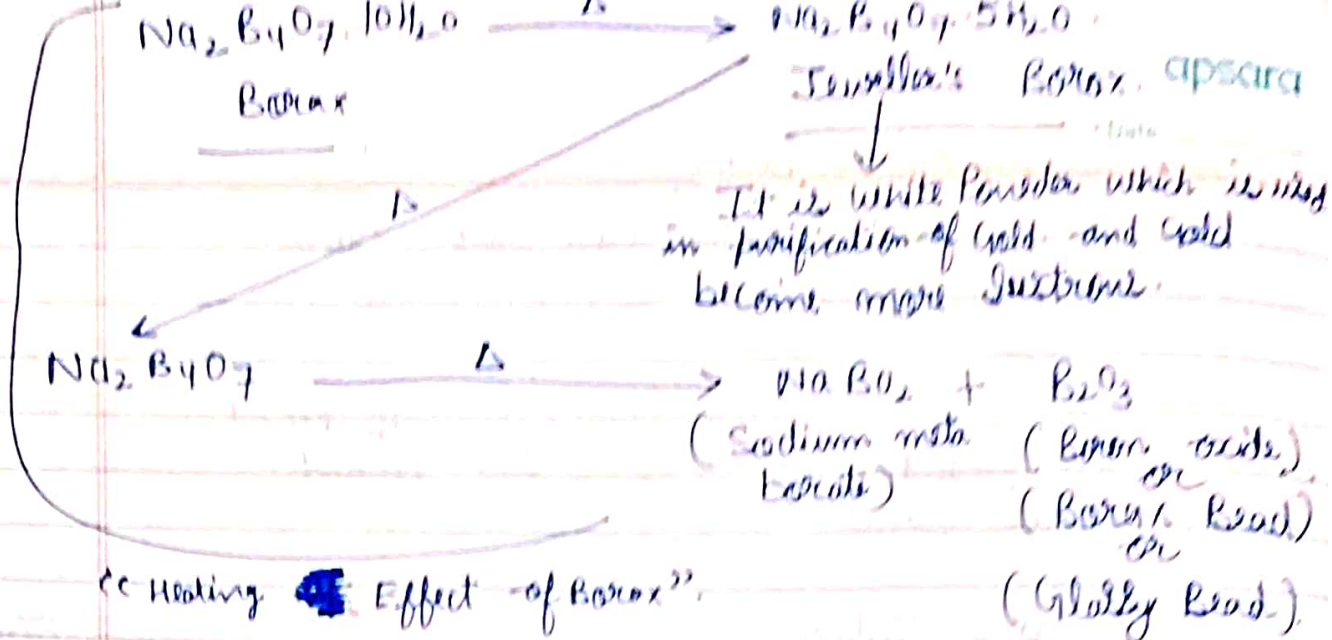
it can write like



Borax actual formula ↑

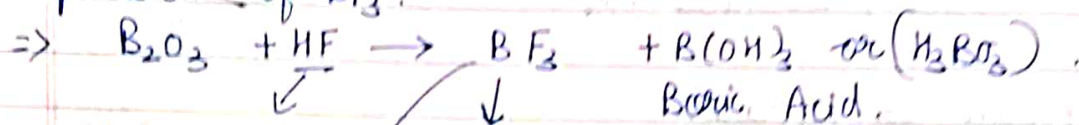
number of bridge bonds = 5.





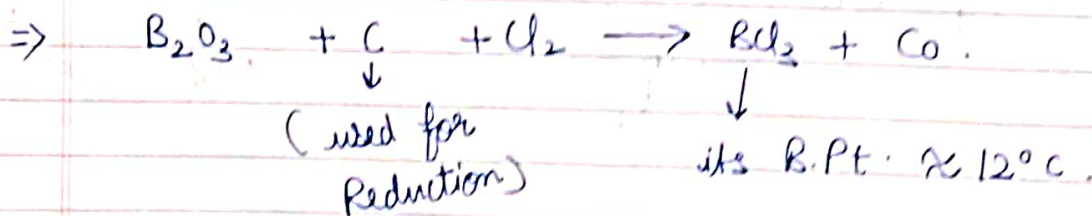
Boron halides :- BF_3 , BCl_3 , BBr_3 , BI_3 .

Preparation of BF_3 .

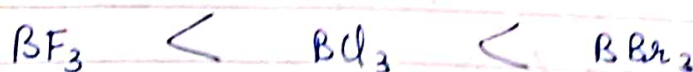


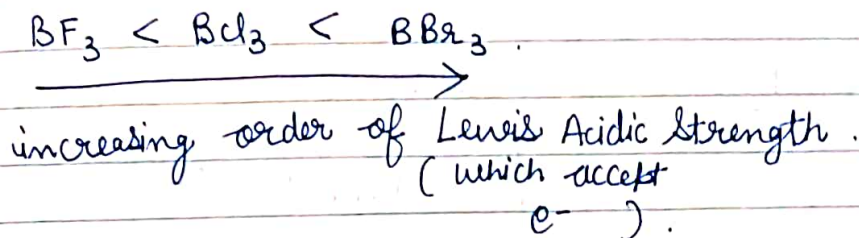
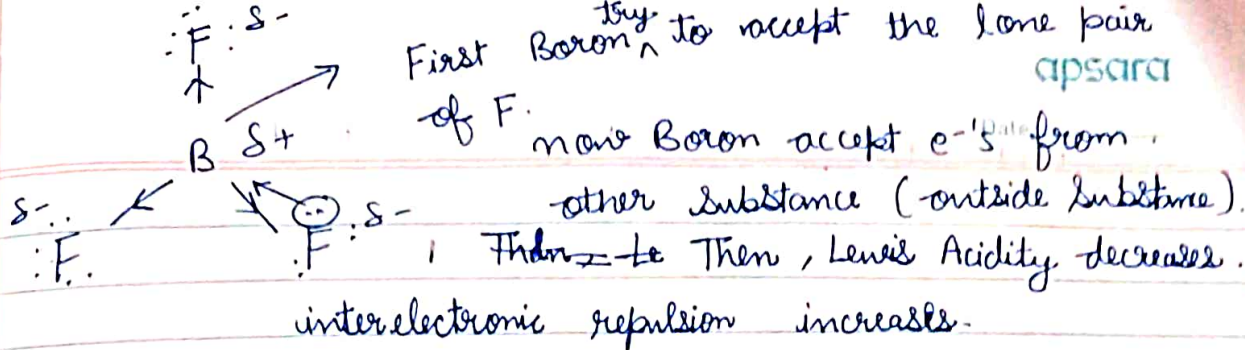
Strongly reacting agent
 (In anhydrous H_2O it reacts strongly)
 This is Lewis Acid.
 it has very low B.Pt
 B.Pt = -101.3°C .

This compound is gaseous at room temp.

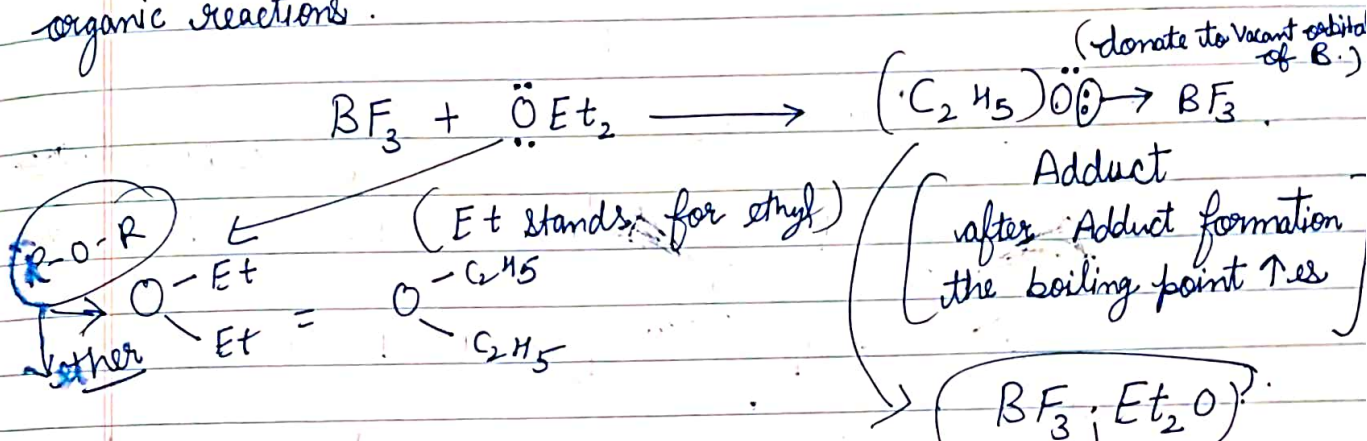


Lewis Acidic strength of Boron halides.





$\Rightarrow$ BF_3 ~~are~~ and BCl_3 used as Lewis acid in some organic reactions.



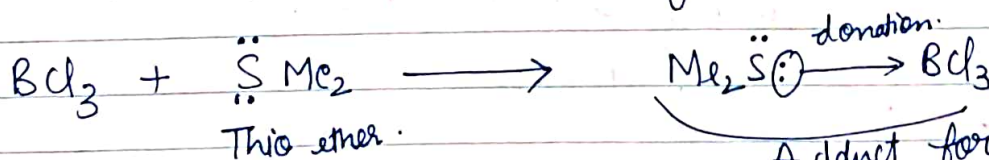
(most of time BF_3 ~~is~~ is in gaseous state)

we can easily use for reactions. Coordinate Bond.

So, we can make ~~adduct~~ adduct of BF_3 . i.e. $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Here the coordinate bond breaks. when we heat this compound then we get BF_3 which we can use in reactions.

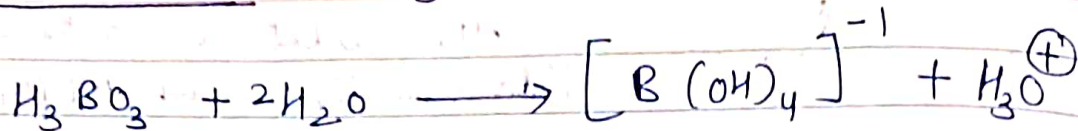
Most of time BCl_3 is also in gaseous state.



Now B. At δ will be. increase.

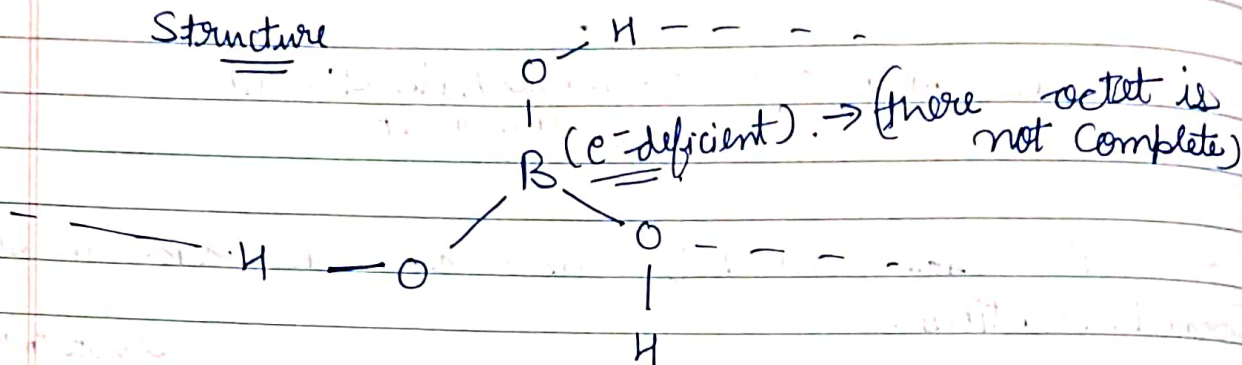
Now, we can use the Adduct $\text{BCl}_3 \cdot \text{Me}_2\text{S}$ in reactions.

⇒ Boric Acid :- H_3BO_3 or $B(OH)_3$.



→ it gain OH^- and loses H^+ .

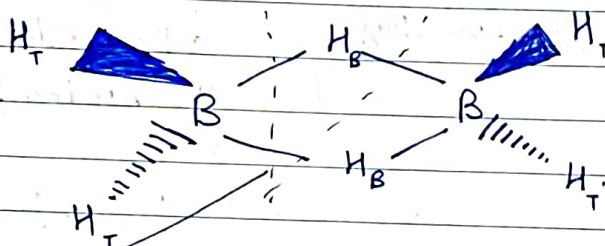
Structure



⇒ B_2H_6 :- Diborane

H_B = Bridge Hydrogen

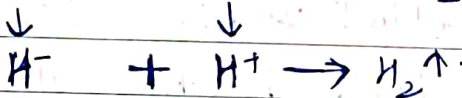
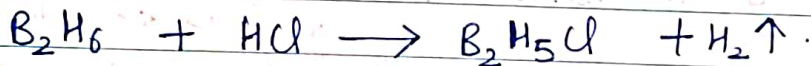
H_T = Terminal Hydrogen



Bond Strength :-



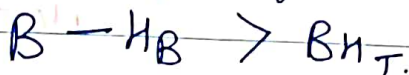
Here Breaking is not possible.
u can see in
reax. still
 B_2H_5 in
product.



it means the
released one H is
Terminal Hydrogen.

→ it Proves that Bond strength of $B-H_B$
is higher than $B-H_T$.

Bond Length of



Higher Borane [Boranes] :- Although boron does not combine directly with H to form hydrides. yet a large no. of hydrides of boron are known. these hydrides are covalent compounds and are called boranes by analogy with alkanes. These are electron-deficient compounds and are of two types.

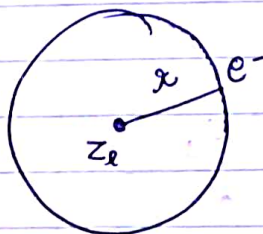
=> Boranes of $B_n H_{n+4}$ type :- Here.
 $n = 2, 5, 6, 8, 10$ and 18. These are quite stable and have melting points. Example $B_2 H_6$ (diborane), $B_5 H_9$ (Pentaborane), $B_6 H_{10}$ (Hexaborane), $B_8 H_{12}$ (Octaborane), $B_{10} H_{14}$ (Decaborane) etc.

Derive Bohr's theory of hydrogen atom?

A hydrogen atom consists of a tiny positively charged nucleus and an electron revolving in a stable circular orbital around the nucleus.

Let e = charge of the electron
 m = mass " " "
 v = velocity " " "
 r = Radius " " "

The Positive charge on the nucleus is Z_e .



The centripetal force on electron

$$F = \frac{mv^2}{r} \quad \text{--- (1)}$$

The Coulomb force of the system.

$$F = \frac{1}{4\pi\epsilon_0} \frac{Z_e e^-}{r^2} \quad \text{--- (2)}$$

From (1) and (2), we get.

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2}$$

or $mv^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$ — (3).

According to Bohr's Postulate.

(Angular momentum) $mv r = \frac{n h}{2\pi}$

or $v = \frac{n h}{2\pi m r}$ — (4).

using (4) in (3), we get.

$$m \frac{n^2 h^2}{4\pi^2 m^2 r^2} = \frac{Ze^2}{4\pi\epsilon_0 r}$$

or $Ze^2 = \frac{n^2 h^2 \epsilon_0}{\pi m r}$

or $r = \frac{n^2 h^2 \epsilon_0}{\pi m Ze^2}$ — (5).

(r = Radius)

~~or~~

For velocity using eqn. (4).

$$V = \frac{n h}{2 \pi m r}$$

(using (5), eqn. 2
for value of r)

$$V = \frac{n h}{2 \pi m \left(\frac{n^2 h^2 \epsilon_0}{4 \pi m z e^2} \right)}$$

or $V = \frac{\cancel{n h} z e^2}{2 n^2 \cancel{h^2} \epsilon_0}$

or $V = \frac{z e^2}{2 n h \epsilon_0}$ — (6)

For Energy

(using kinetic energy formula).

$$K.E = \frac{1}{2} m v^2$$

(using eqn. (3)
for mv)

$$K.E = \frac{1}{2} \left(\frac{1}{4 \pi \epsilon_0} \frac{z e^2}{r} \right)$$

$K.E = \frac{z e^2}{8 \pi \epsilon_0 r}$ — (7)

Potential energy

$U = - \frac{1}{4 \pi \epsilon_0} \frac{z e^2}{r}$ — (8)

apsara
Date: _____

Total Energy = K.E + P.E. (using 7, 8, we get)

$$E = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$E = - \frac{Ze^2}{8\pi\epsilon_0 r} \quad \text{--- (9)}$$

using λ , value from equ. (5), we get.

$$E = - \frac{Ze^2}{8\pi\epsilon_0 \left(\frac{n^2 h^2 \epsilon_0}{\pi m Z e^2} \right)}$$

$$E = - \frac{m Z^2 e^4}{8 \epsilon_0^2 n^2 h^2} \quad \text{--- (10)}$$

For 1st orbit λ energy $Z=1$.

$$E_1 = -13.6 \text{ eV}$$

Energy difference $\Delta E = E_2 - E_1$
(using equ (10))

$$\Delta E = - \frac{m Z^2 e^4}{8 \epsilon_0^2 n_2^2 h^2} + \frac{m Z^2 e^4}{8 \epsilon_0^2 n_1^2 h^2}$$

$$\frac{hc}{\lambda} = \frac{m Z^2 e^4}{8 \epsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \left[\frac{dE}{d\lambda} = \frac{hc}{\lambda^2} \right]$$

$$\frac{1}{\lambda} = \frac{m Z^2 e^4}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (11)} \quad R = \text{Rydberg Constant.} \\ R = \frac{m e^4}{8 \epsilon_0^2 h^3}$$

For hydrogen

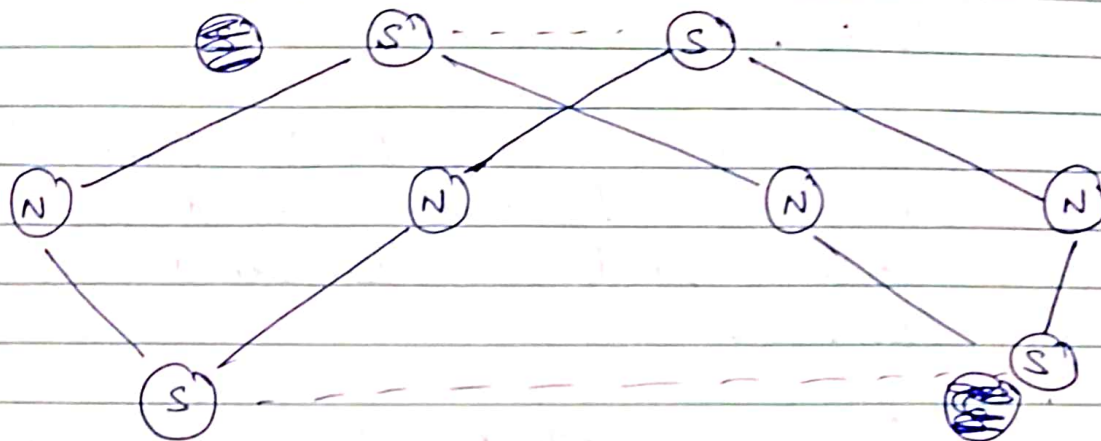
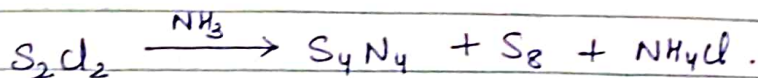
$\frac{Q}{\lambda}$

$Z = 1$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{--- (12)}$$

Ques 1> = Discuss the structure of S_4N_4 .

=> Preparation :-



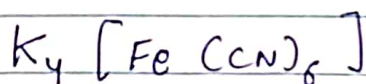
Structure of S_4N_4 .

[also called cradle shaped structure]

Ques 2> = what is Coordination compound.

=> A coordination complex is the product of Lewis Acid - base reaction in which, neutral molecules or anions (called ligands) bond to a central metal atom (or ion) by Coordinate Covalent bonds.

Example



Potassium hexacyano ferrate (II).

Ques 3> = Give the limitations of CFT.

=> 1> The assumption of the interaction b/w Metal-ligand is purely electrostatic and can not said to be realistic.

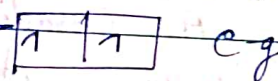
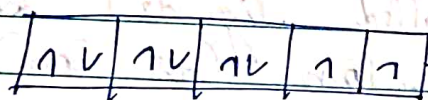
2> They theory study d-orbitals of a central metal atom but the s and p orbits are not considered for the study.

- 3) This theory could not explain the behaviour of some complexes about why some orbitals show large splitting and some show less splitting.
- 4) It cannot explain why H_2O is stronger ligand than OH^- .
- 5) The theory rules out the possibility of having p bonding. This is a serious drawback because p bonding is found in many complexes.
- 6) The theory gives no significance to the orbitals of the ligands.

Ques 4) Calculate the CFSE value of $[Ni(NH_3)_6]^{2+}$

$\Rightarrow Ni = 28$
 $Ni^{+2} = [Ar]^{18} 4s^0 3d^8$

$x + 6(0) = +2$
 $x = +2$



$+0.6$

Δ_o

-0.4



$NH_3 = \text{Strong ligand.}$

$\Delta_o = (0.6p - 0.4q) \Delta_o$

$= 0.6(2) - 0.4(6) \Delta_o$

$= (1.2 - 2.4) \Delta_o$

C.F.S.E = $-1.2 \Delta_o$

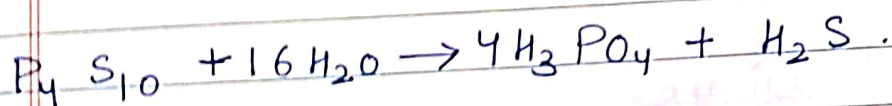
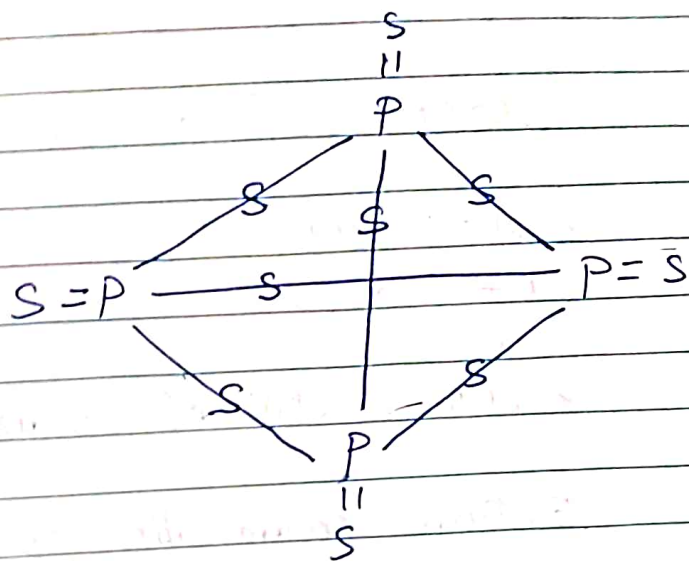
Ques 5) = Explain the structure of P_4S_{10} .

No. of P-S-P bonds = 6

No. of P-S bonds = 16.

No. of P=S bond = 4.

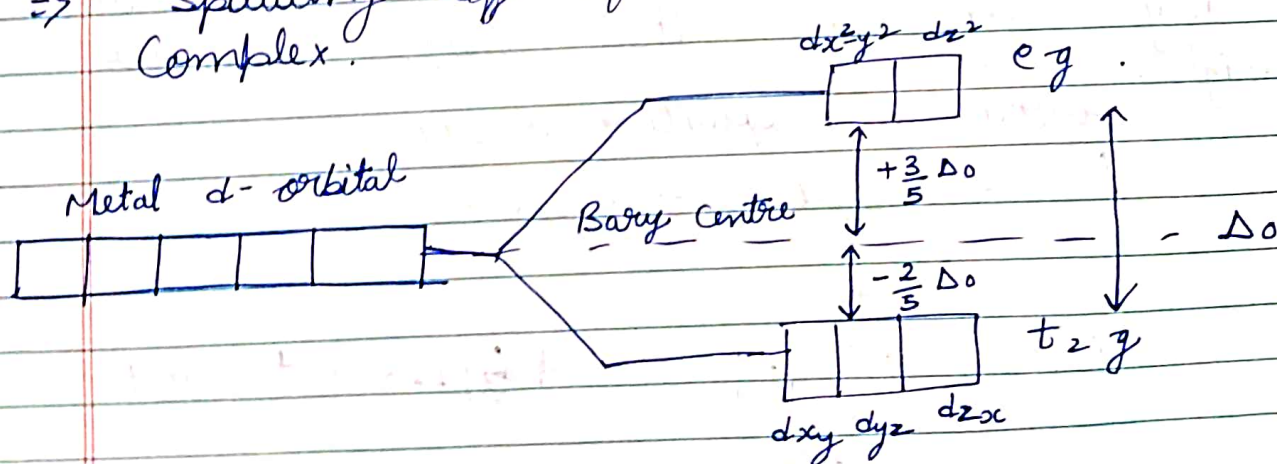
^3P - NMR Signals = 1



Ques 6) = Explain the splitting of d-orbitals under octahedral crystal field.

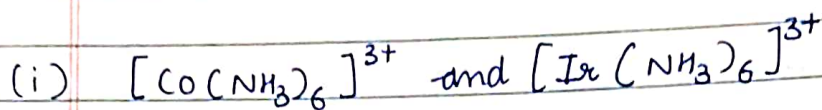
=> The difference of energy b/w the two sets of d-orbitals (in octahedral complexes) is called crystal field splitting energy [CFSE] or Δ_o .

=> Splitting of d-orbital in octahedral complex.



Crystal field splitting energy of octahedral

$$\Delta_o = \left(\frac{3}{5} \uparrow - \frac{2}{5} \downarrow \right) \Delta_o.$$



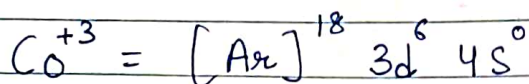
oxidation state of Co

$$x + 6(0) = 3$$

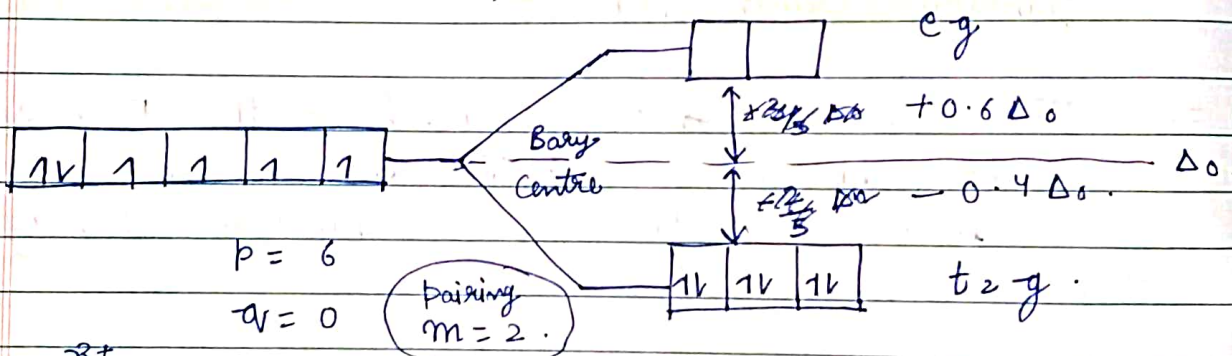
$$x = 3$$

oxidation state of Co is +3 in $[\text{Co}(\text{NH}_3)_6]^{3+}$

Electronic configuration of Co^{+3}



Crystal field splitting of $[\text{Co}(\text{NH}_3)_6]^{3+}$



In $[\text{Co}(\text{NH}_3)_6]^{3+}$, NH_3 is strong field ligand then the splitting is very large and its energy is also high.

Crystal field splitting energy.

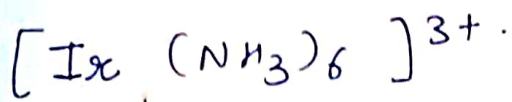
$$\Delta_o = +\frac{3}{5}\Delta_o - \frac{2}{5}\Delta_o$$

or

$$\Delta_o = \left[+0.6\Delta_o - 0.4\Delta_o \right] + mP$$

$$= \left[0.6(0)\Delta_o - 0.4(6)\Delta_o \right] + 2P$$

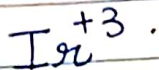
$$\text{C.F.S.E} = -2.4\Delta_o + 2P$$



oxidation state of Ir is

$$x + 6(0) = +3$$

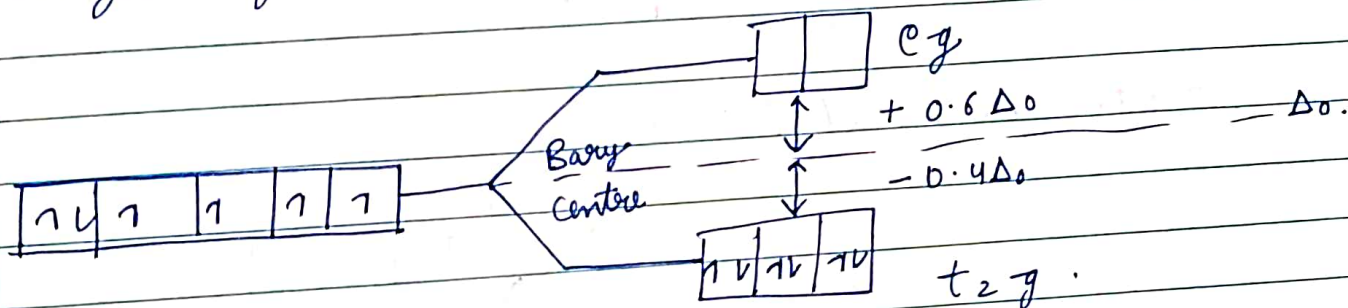
$$x = +3$$



Electronic Configuration of Ir^{+3} .



Crystal field splitting of $[\text{Ir}(\text{NH}_3)_6]^{3+}$ is.



here $p = 6$, $q = 0$ pairing $m = 2$

NH_3 is strong field ligand then the splitting is very large and its energy is also high.

C.F.S.E

$$\Delta_o = [+0.6q - 0.4p] \Delta_o + mp$$

$$= [+0.6(0) - 0.4(6)] \Delta_o + 2p$$

$$\text{C.F.S.E} = -2.4 \Delta_o + 2p$$

(ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ Date: _____

In $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Oxidation state of Co is

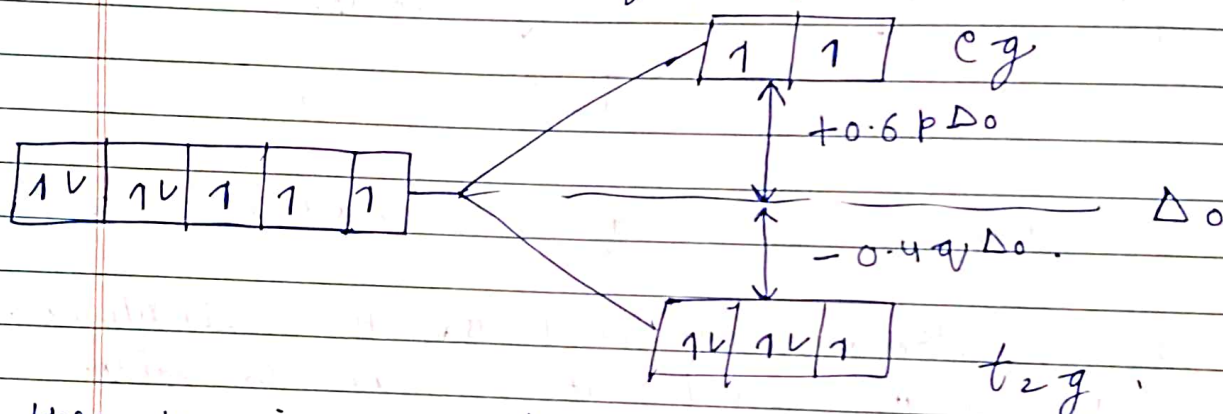
$$x + 6(0) = +2$$

$$x = +2$$

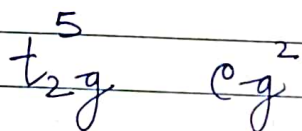
Then, Electronic configuration of Co^{+2}

$$\text{Co}^{+2} = [\text{Ar}]^{18} 3d^7 4s^0$$

Crystal field splitting.



Here, H_2O is weak ligand then splitting is less.



$$P = 5, q = 2$$

C.F.S.E value for d^7 complex ion (high spin).

$$= [-0.4P + 0.6q] \Delta_o$$

$$= [-0.4(5) + 0.6(2)] \Delta_o$$

$$= [-2.0 + 1.2] \Delta_o$$

$$= [-0.8 \Delta_o]$$

$$= -0.8 \Delta_o \text{ or } -8 Dq$$

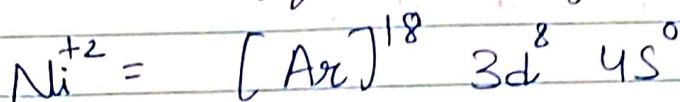
In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

oxidation state of Ni is

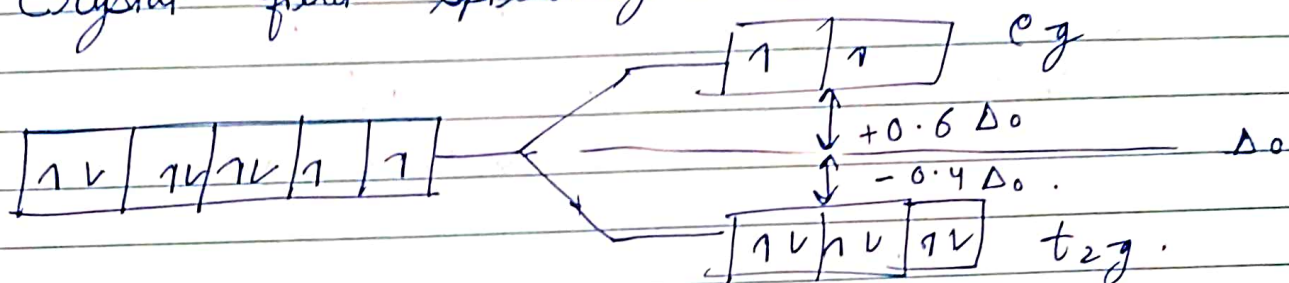
$$x + 6(0) = +2.$$

$$x = +2.$$

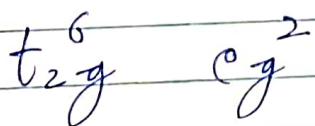
Then, Electronic Configuration of Ni^{+2} .



Crystal field splitting.



Here, H_2O is weak field ligand then splitting is less.



$$P = 6, \quad q = 2.$$

C.F.S.E value for d^8 Complex ion (high spin)

$$= [-0.4 p + 0.6 q] \Delta_o.$$

$$= [-0.4 (6) + 0.6 (2)] \Delta_o.$$

$$= [-2.4 + 1.2] \Delta_o.$$

$$\text{C.F.S.E} = -1.2 \Delta_o \quad \text{or} \quad -12 \Delta_q.$$

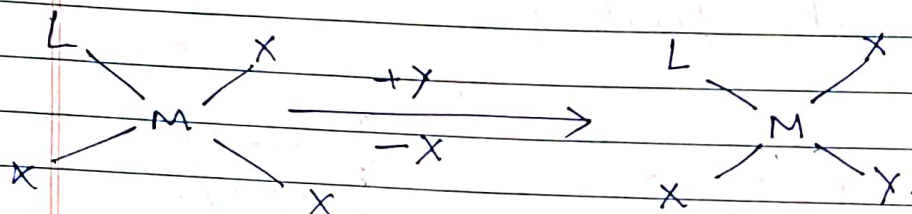
Ques^{7>} = what is meant by template effect?

unit-IV

Trans effect :-

Ability of the attached group to direct the substitution into a position trans to itself.

(It is in square planar complexes).



π -acceptors

CN^- , CO , NO , C_2H_4 > Ph_3 > H^- > CH_3^- , C_6H_5^- , NO_2^- , I^- , SCN^- , > Br^- > Cl^- > py > RNH_2 , NH_3 > F^- > OH^- > H_2O (σ donor).

CN^- , CO , NO , C_2H_4 $\rightarrow$ Highly π -acceptors

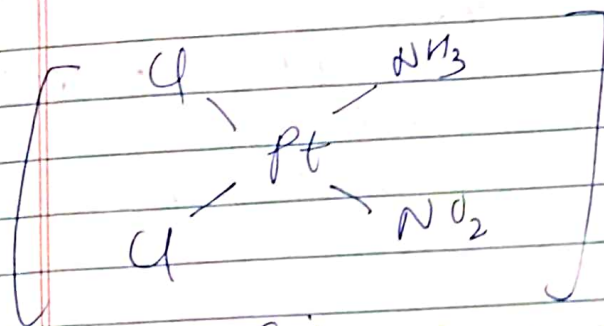
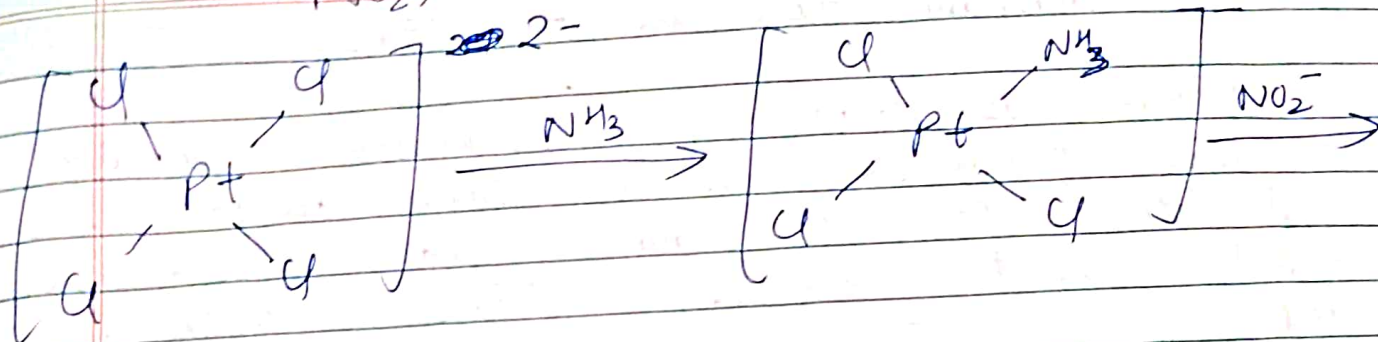
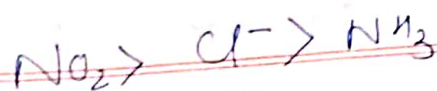
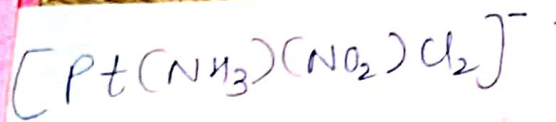
$\rightarrow$ empty π or π^* orbitals, form $d\pi-p\pi$ or $d\pi-d\pi$ bond with metal.

$\rightarrow$ Strong Trans directors.

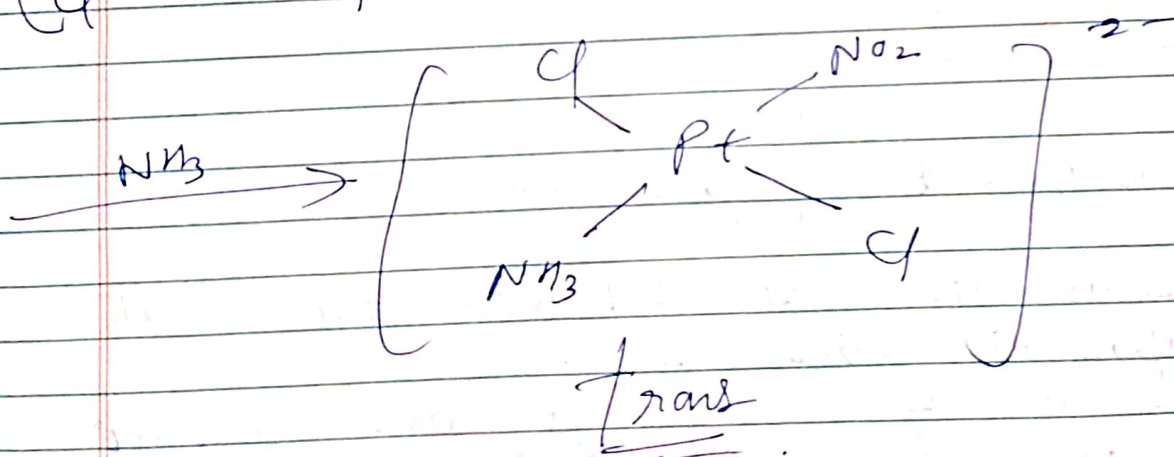
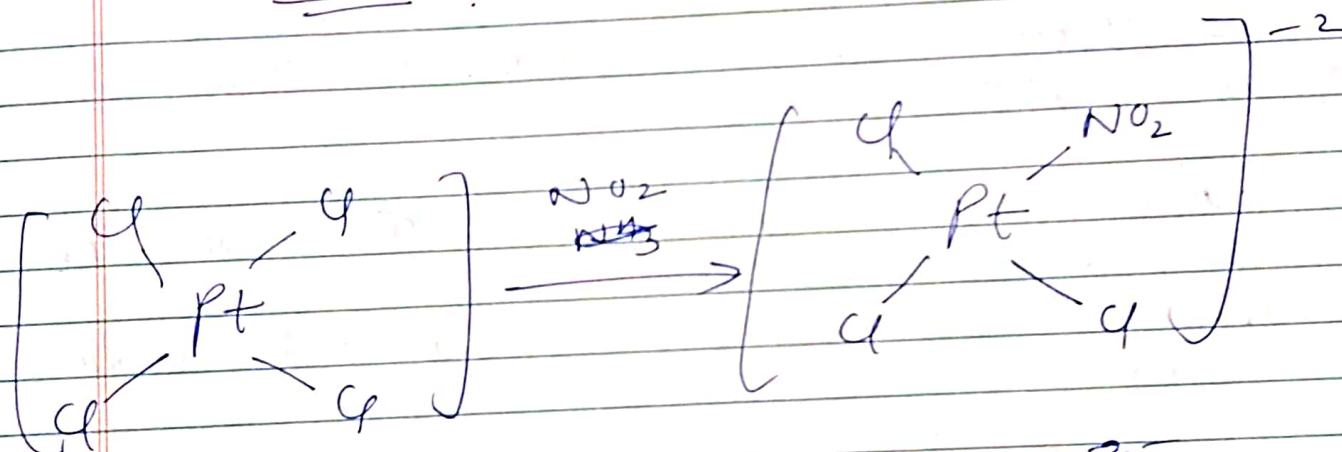
$\Rightarrow$ [strong trans directors promotes Rapid Substitution of ligand trans to itself than it does cis to itself.]

Application of Trans-effect.

$\rightarrow$ Most of Trans-effect done on square planar complexes of Pt(II) .



Cis



trans

Unit IV

Theories of trans effect :-

1) Polarisation theory, 2) π -Bonding Theory.

Polarization theory:-

Acc. to this theory the metal ligand bond polarization play a significant role in the trans effect.

This theory was forwarded by 'Grainberg' according to this theory: When a ligand approach centre metal atom. Then the leaving ligand show some polarity effect on the trans position. which leads the trans effect.

ligand with sigma donor or pi sep excepto produce the metal ligand bond polarity as a Result trans effect. observed.

Limitation of Polarization theory:-

- 1) This theory can not explain the formation of cis effect.
- 2) Bond Polarity Concept is not explain the trans effect successfully.
- 3) This theory cannot explain the formation of Back Bonding.

π - Bonding Theory

was given by Proposed - Chatt and Orget.

This is the most important theory which explain the trans effect.

Acc. to this concept a ligand with pi C- always prefer the trans effect in the square planar complex under the Substitution Reax.

This is due to the associative mechanism i.e. Substituent Reax of square Planar complex involve the

apsara

Acceptor ligand always prefer the axial position and the result trans position formed.

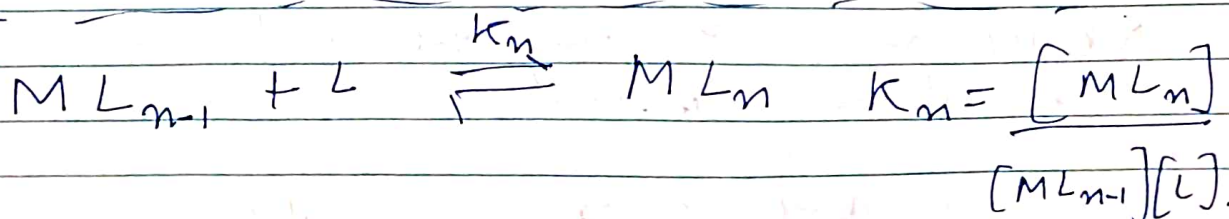
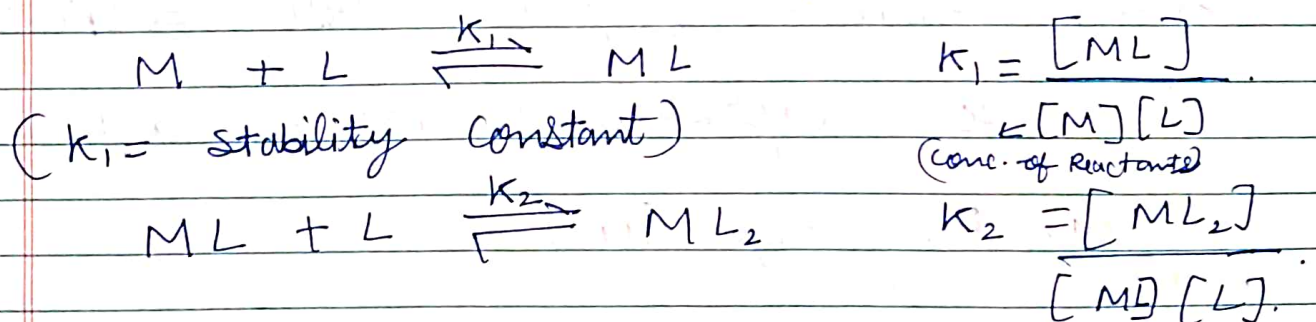
Evidence :-

① The Stereochemistry of the Reax.
favour the ~~pi~~ π bonded theory.

(2) This theory is also prefer the Reaction kinetics.

unit-2. (Formation Constant and its overall Stability Constant)
Stepwise and overall formation constants.

$\Rightarrow$ According to L. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n may take place by the following n consecutive steps and equilibrium constants.



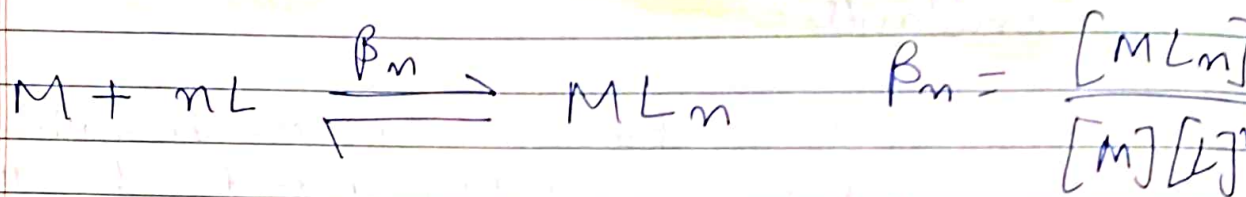
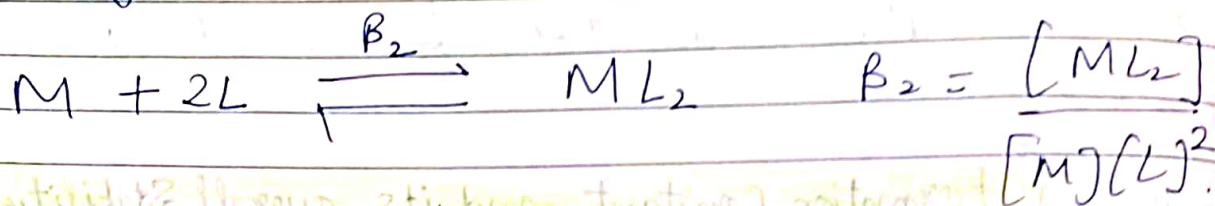
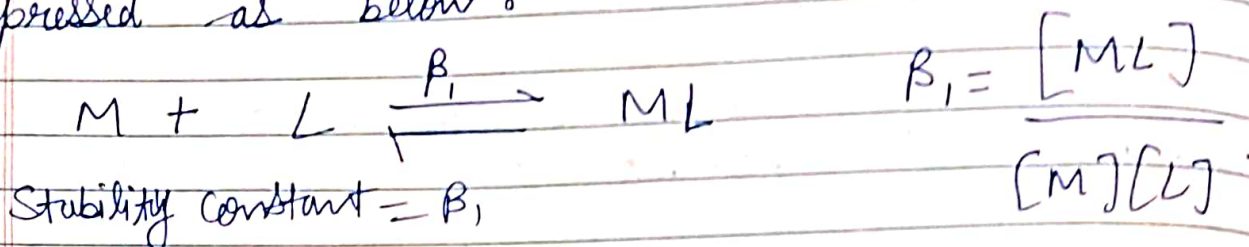
The equilibrium constants $k_1, k_2, \dots, k_n$ are called stepwise formation constants or stepwise stability constants. These constants are also

expressed as $\log_{10} K_1, \log_{10} K_2 \dots \log_{10} K_n$ respectively

Date: _____

overall formation constant.

The formation of complex ML_n may also be expressed as below :-



The equilibrium constants $\beta_1, \beta_2 \dots \beta_n$

are called overall formation constants or overall stability constants. These constants

are also expressed as $\log_{10} \beta_1, \log_{10} \beta_2 \dots \log_{10} \beta_n$ respectively.

Relation b/w stepwise and overall formation constant :-

Stepwise and overall formation constants are related to one another. for example let us consider the expression for β_3 viz.

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

Multip

⇒ Multiplying numerator and denominator by $[ML] [ML_2]$.

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

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

$$\Rightarrow \beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]}$$

$$\Rightarrow \beta_3 = K_1 \times K_2 \times K_3 \dots$$

or

$$\boxed{\beta_3 = K_1 \cdot K_2 \cdot K_3 \dots K_n} \quad \text{--- (1)}$$

$$\boxed{\log_{10} \beta_3 = \log_{10} K_1 + \log_{10} K_2 + \log_{10} K_3 \dots \log_{10} K_n} \quad \text{--- (2)}$$

From eqn (1) it is evident that the overall formation constant (β_n) is equal to the product of the stepwise formation constants.

Ques = Brief-out Various boranes.

=> Boranes are the type of cluster compound which are formed by the combination of boron and hydrogen.

=> ~~Hypercloso-boranes~~ :- ~~General formula is~~
 ~~$B_n H_n$~~ .

~~If $n=2$.~~



1> closo - Boranes :- Cage like structure.
General formula is $B_n H_{n+2}$.

2> Nido - Boranes :- Nest like structure.
General formula = $B_n H_{n+4}$.

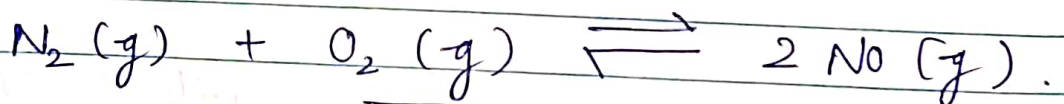
3> Arachno - Boranes :- Spider web like structure
General formula = $B_n H_{n+6}$.

4> Hypo - Boranes :- Net like structure
General formula = $B_n H_n$.

Ques = Define Le chatlier law:-

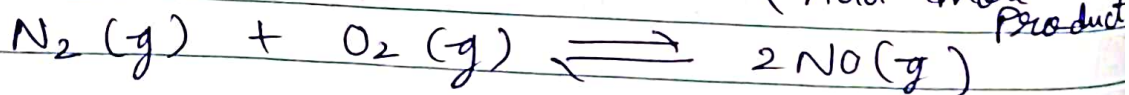
Ans = It states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.

Example :- (Add more Reactant)



Reaction shifts right. $\rightarrow$

(Add more Product)



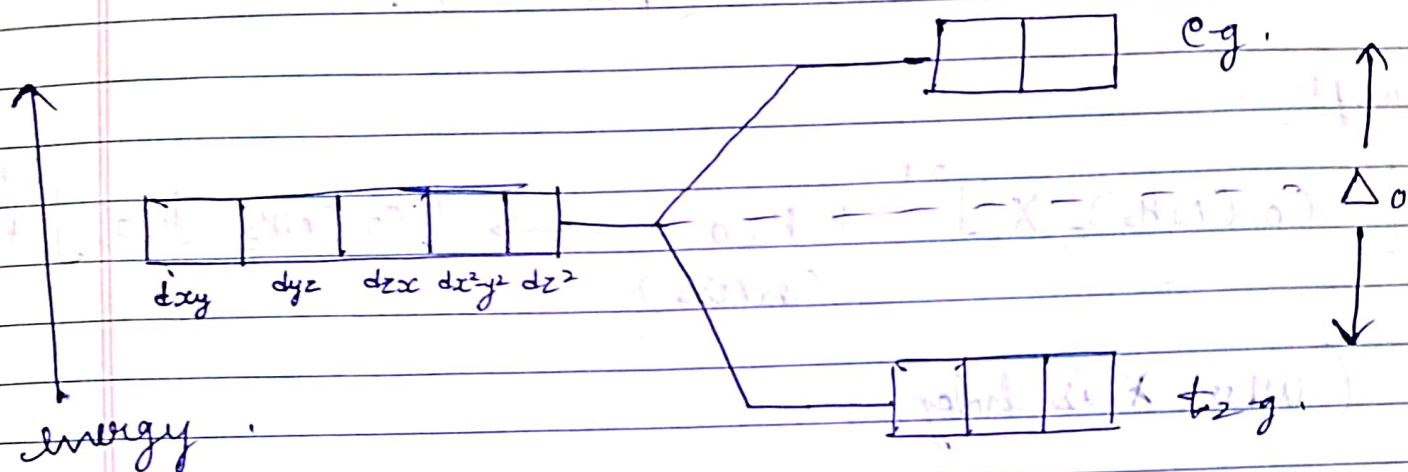
Reaction shifts left

$\leftarrow$

Ques = What is meant by CFT?

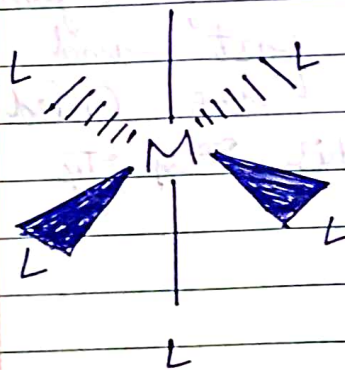
⇒ The CFT stands for Crystal field theory. It describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands.

Crystal field splitting in octahedral complex.

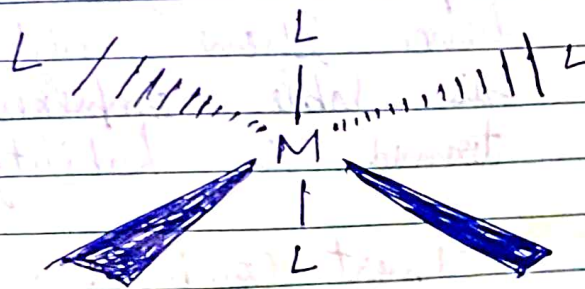


Ques = Explain Jahn-Teller distortion.

⇒ The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds.



Elongated



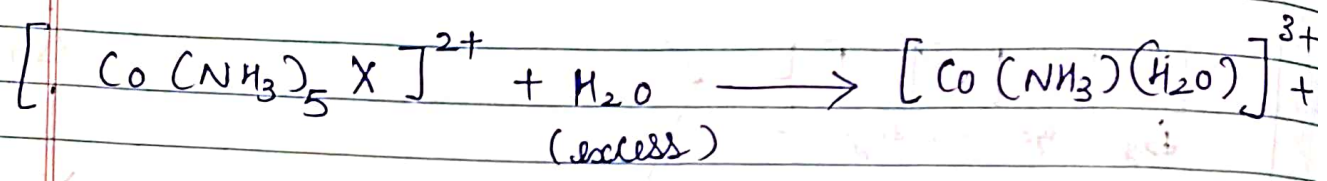
Compressed.

Ques. What is meant by Acid hydrolysis?

Ans = Acid hydrolysis reaction:-

In such reactions an aqua complex is formed by the replacement of a ligand by H_2O molecules. These reactions occur in neutral and Acid solution. ($pH < 3$).

Example:-



(where X is halogen).

#> Inert and Labile Complexes.

1> Labile Complexes:-

The Metal Complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile complexes. and this property is termed as Lability.

2> Inert Complexes:-

The Metal Complexes in which the rate of ligand displacement reactions is very slow and hence show low reactivity are called inert complexes. and this property

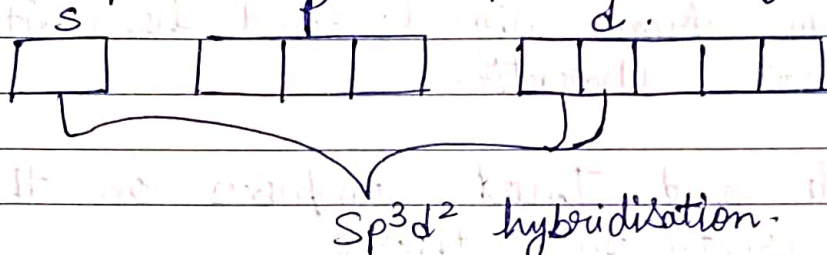
is termed as inertness.

⇒ Labile and inert complexes on the basis of Valence Bond theory (VBT).

According to the Valence Bond theory of chemical bonding octahedral metal complexes can be divided into two types:-

1) Outer orbital complexes:-

These complexes have sp^3d^2 hybridisation.

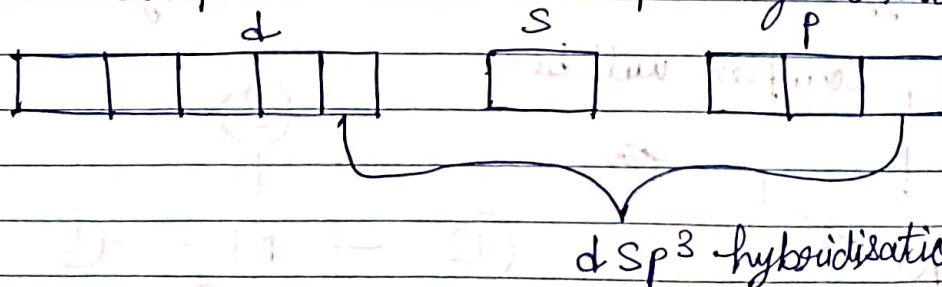


The bond in sp^3d^2 hybridisation complex is weak. therefore, they show labile character.

⇒ Example:- octahedral complexes of Mn^{2+} , Fe^{2+} show fast ligand displacement.

2) Inner orbital complexes:-

These complexes have d^2sp^3 hybridisation.



These ~~These~~ d^2sp^3 hybridized complex can form both inert and labile complexes.

$\Rightarrow$ d^2sp^3 hybridized Complex show Labile Complex.

when one orbital should be empty in dx, dy, dz . So that it can accept electron pair and can form seven coordinated intermediate. which is necessary step for ligand displacement.

$\Rightarrow$ d^2sp^3 hybridized Complex show inert Complex.

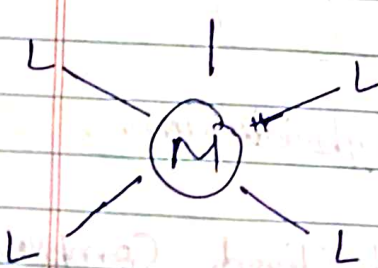
~~When one orbital should be empty in~~
when all dx, dy, dz, dxz orbitals contain at least one electron, it will not accept electron from ligand. and hence it shows inert character.

$\Rightarrow$ Labile and Inert Complexes on the bases of crystal field theory

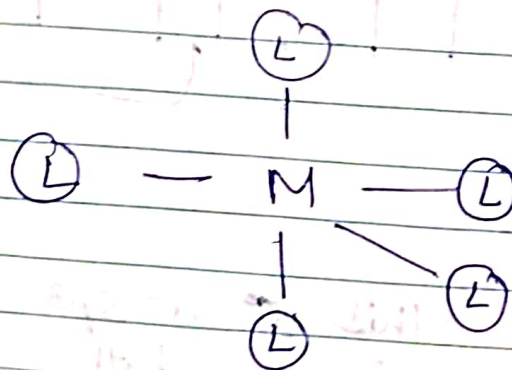
octahedral Complexes react either by SN^1 or SN^2 mechanism in which the intermediate are five and seven-coordinated species respectively.

In both cases, the symmetry of the complex is lowered down and due to this change in Crystal field symmetry, the crystal field stabilization energy (CFSE) value also changes.

For SN^1 Complex will be.

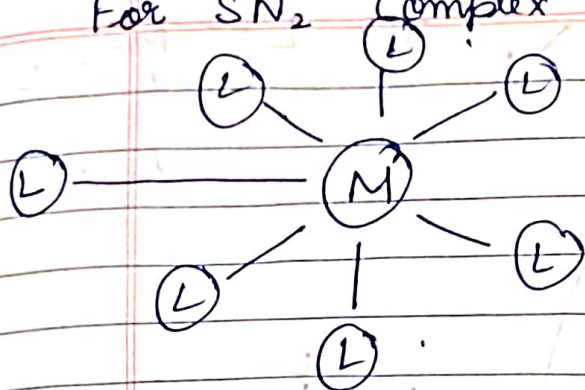


or



Coordination no. = 5.

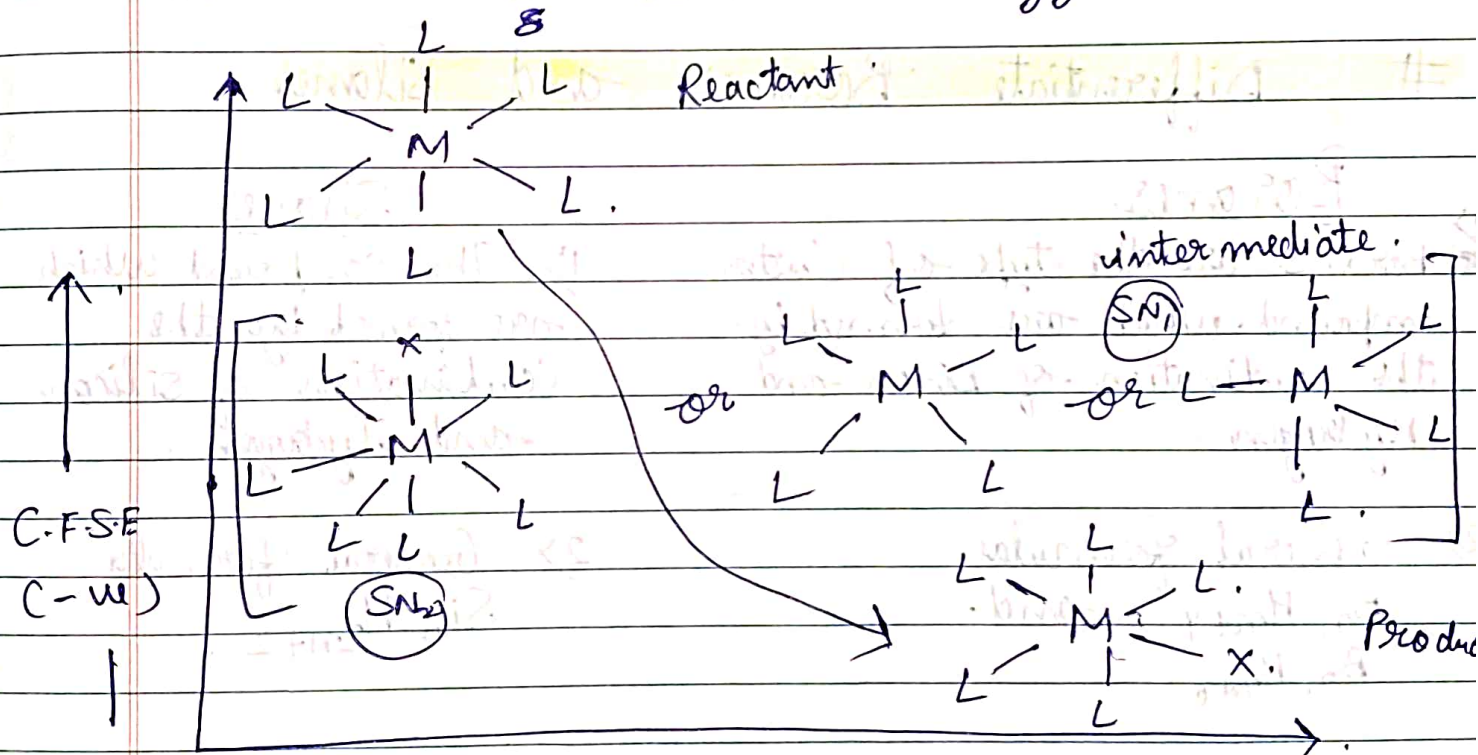
For SN_2 Complex will be .



Coordination no :- 7.

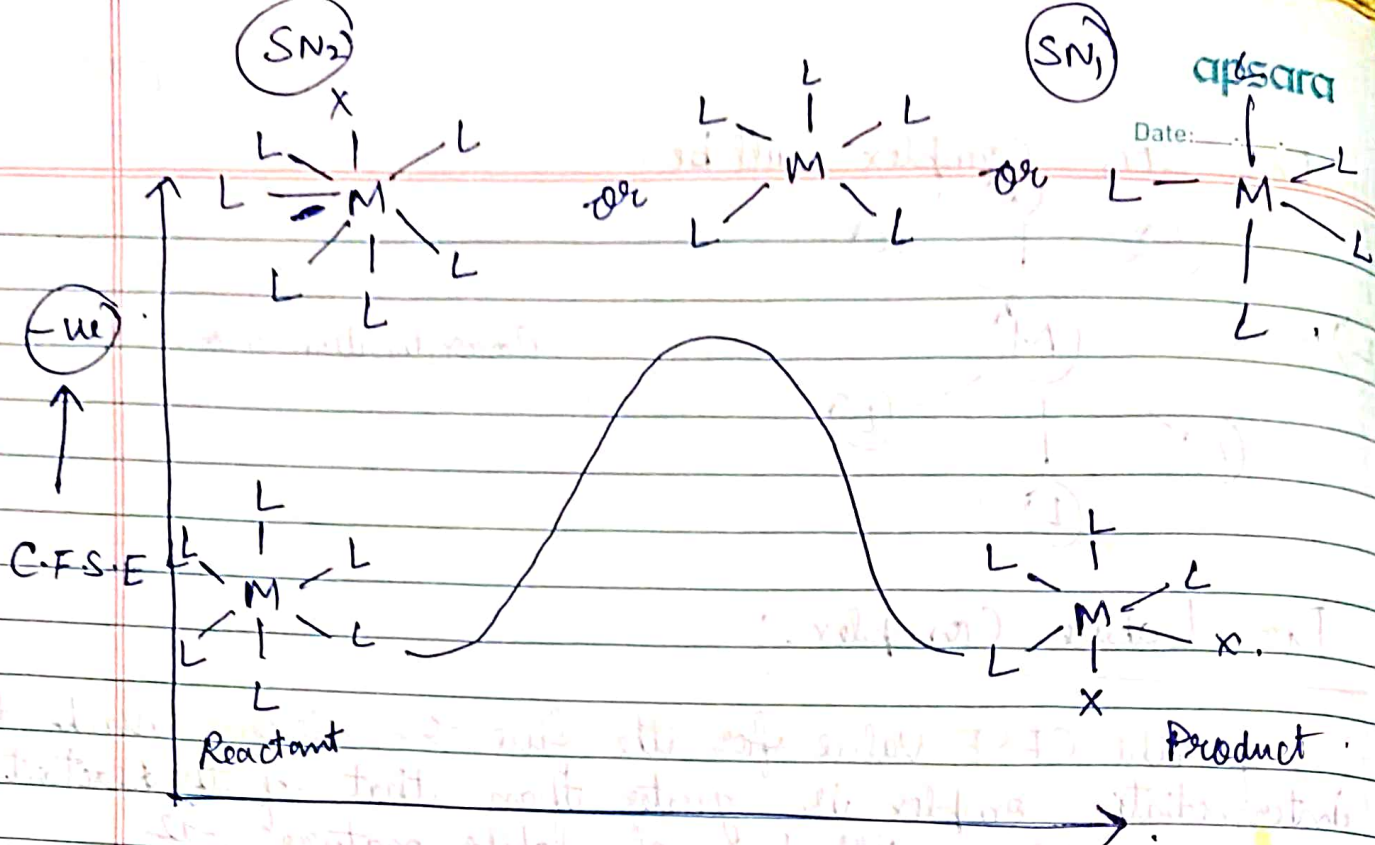
For Labile Complex :-

If the CFSE value for the five or Seven-membered intermediate complex is greater than that of the Reactant the complex will be of labile nature as there is zero activation energy barrier.



For inert Complex :-

If the CFSE value for the 5 or 7 membered intermediate complex is less than that of the Reactant, the metal complex will be of inert nature as loss of CFSE will become the activation energy barrier.



Differentiate Boranes and Silanes

Boranes

1) Boranes are the type of cluster compound which are formed by the combination of Boron and Hydrogen.

2) General formulae
 $B_n H_{n+4}$ and
 $B_n H_{n+6}$

3) Diboranes are toxic gases with sweet smell.

4) Diborane reacts with water to form Boric Acid.

5) Diborane is used as a Rocket Propellant.

Silanes

1) The compound which are formed by the combination of Silicon and Hydrogen.

2) General formula
 $Si_n H_{2n+2}$

3) Silane is toxic gas with repulsive smell.

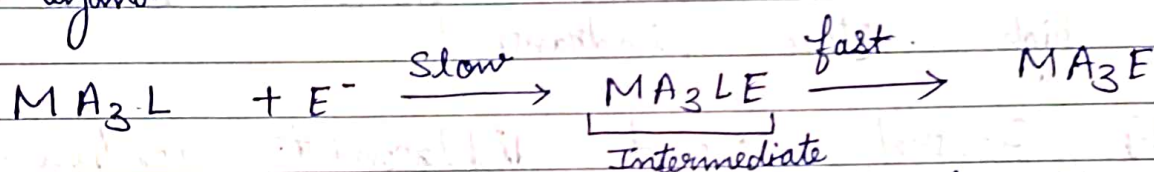
4) Silane does not react with water.

5) Silanes are used in fiberglass.

Ligand Displacement Mechanism in Square-Planar Complexes.

⇒ The ligand displacement reaction is nucleophilic substitution reaction in which the ligand of the complex is displaced by the another ligand.

⇒ The ligand displacement is favourable in square planar because the C.N.O is 4. it means the steric hindrance is low then the change of ligand of complex displaced by another ligand.



SN_2 mechanism is followed due to low steric hindrance.

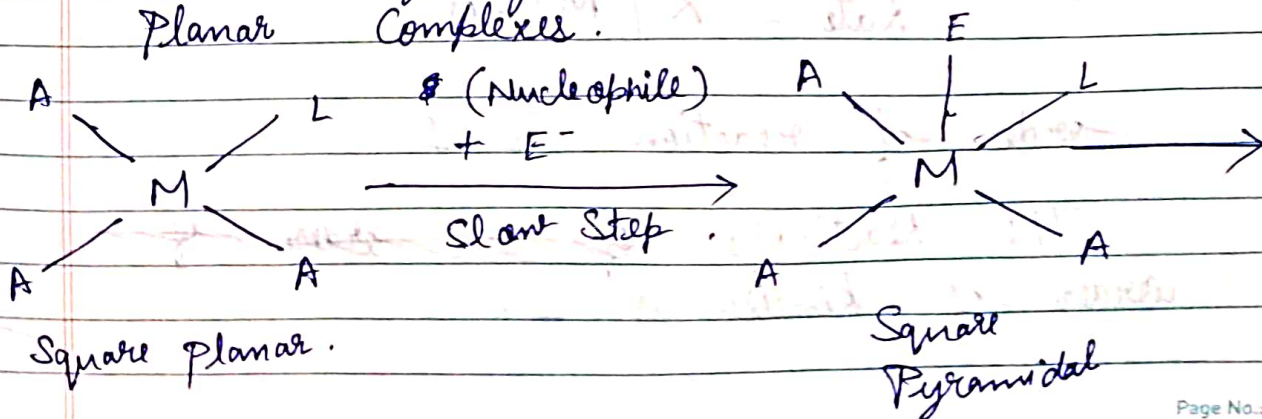
In ligand displacement reaction the Geometry of ~~MA₃L~~ Complex is same after nucleophilic substitution reaction

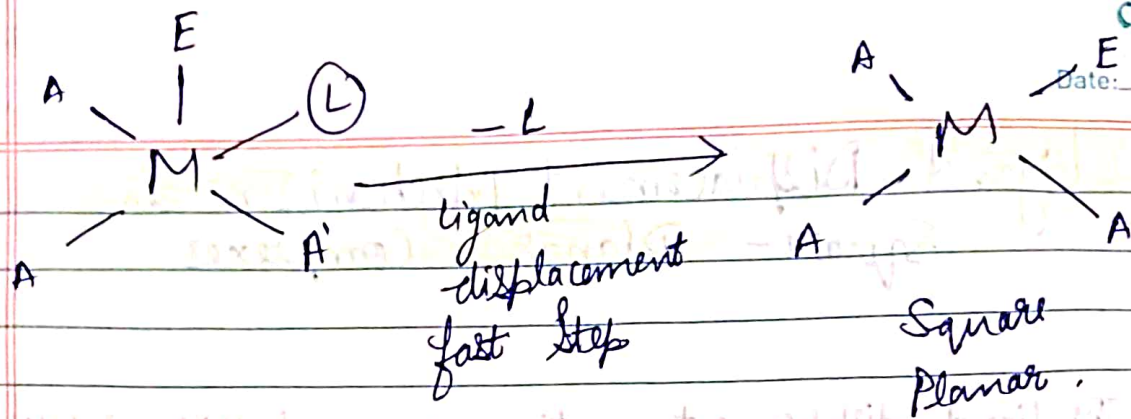
$$\text{Rate} = k [MA_3L][E]$$

order of reaction = 2.

It follows 2nd order kinetics.

⇒ Mechanism of ligand displacement in square-planar complexes.

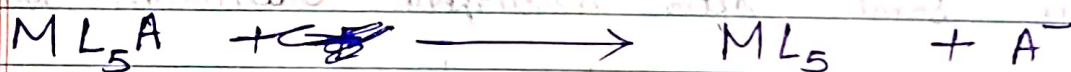




⇒ The ligand displacement reaction in octahedral complex is not much favourable because the C. No. of octahedral complex is 6. it means its steric hindrance is high. So, the ligand displacement reaction take place not easily. Here SN_1 mechanism follow because of high steric hindrance.

The General ligand displacement reaction. In SN_1 the reaction take place in two steps.

~~Step~~ Step I



Step II



Rate of the reaction is

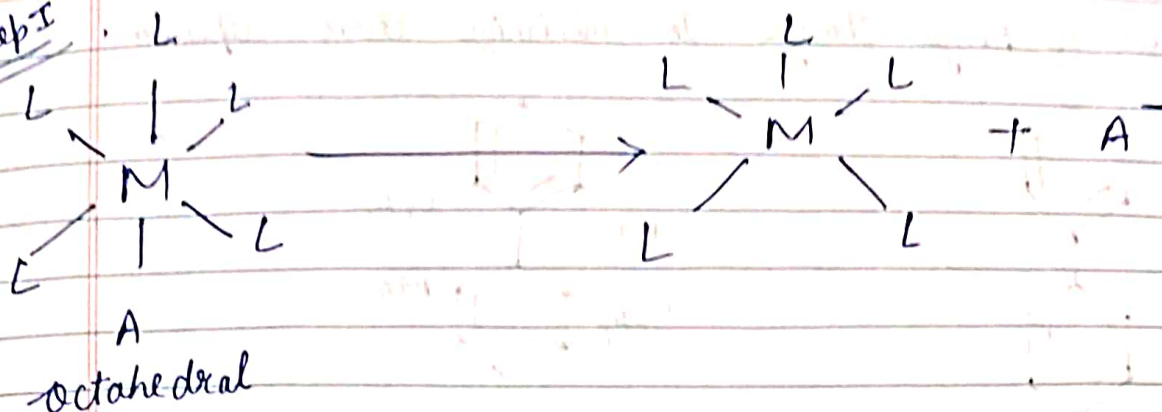
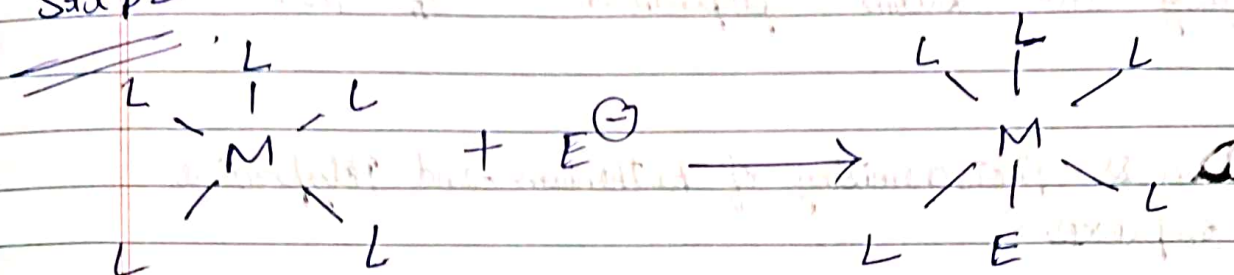
$$\text{Rate} = k [ML_5A]$$

order of reaction is 1.

The Reactivity ~~of ML_5A is~~ order of kinetics is 1.

The Mechanism of octahedral Complex

Date: _____

Step IStep II

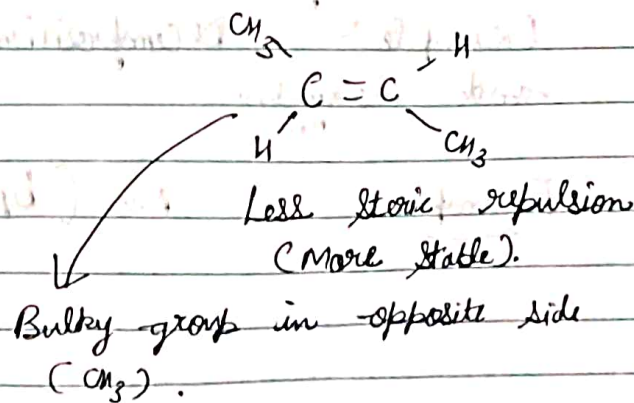
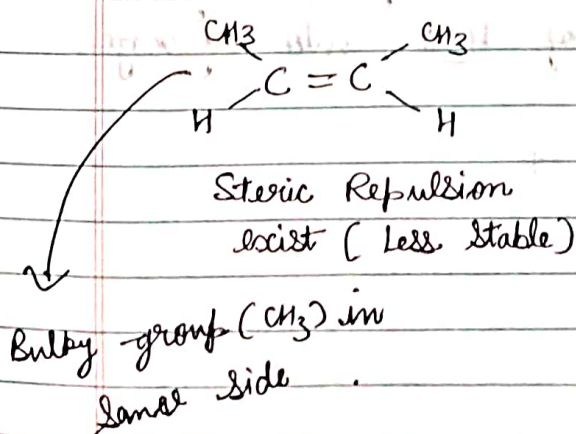
Steric effect:-

The substituent effect caused by σ -cloud repulsion of bulky groups when they are close to each other is called steric effect.

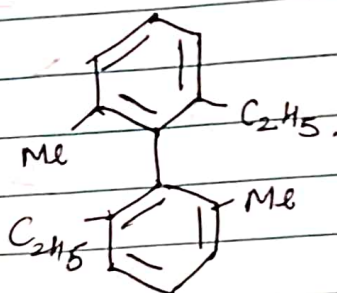
Some Examples of Cis and trans

(1) Stability of cis and trans:-

In general cis structure is less stable than trans structure due to more steric repulsion present in cis form.



② Plane of Rings Changes to minimize steric repulsion



To minimize steric repulsion one ring rotate about other ring and become perpendicular to its.

Discuss Photochemistry of Ruthenium and Polypyridine Complexes.

➤ / The Ruthenium (II) polypyridyls are the most

⇒ The Ruthenium (II) Polypyridine are the most popular systems.

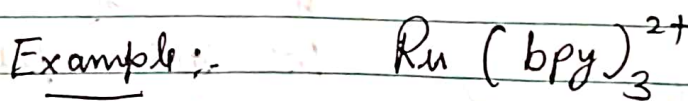
⇒ These compounds strongly emit visible light in fluid solution.

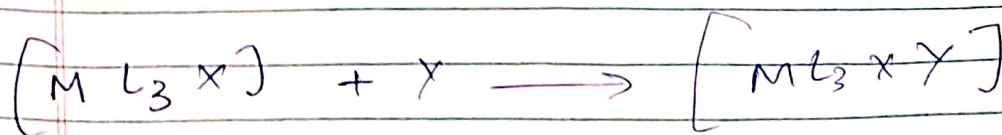
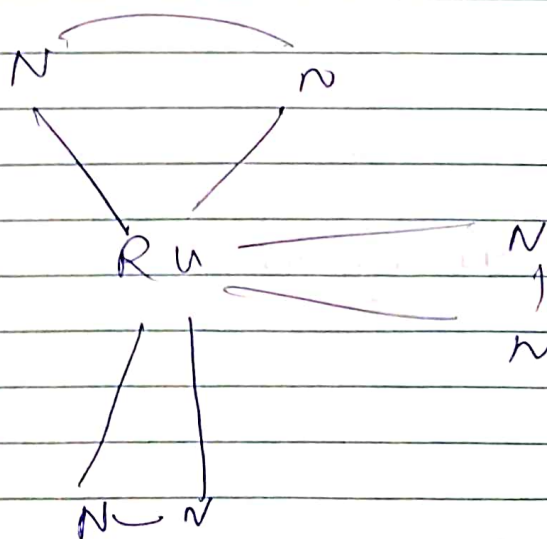
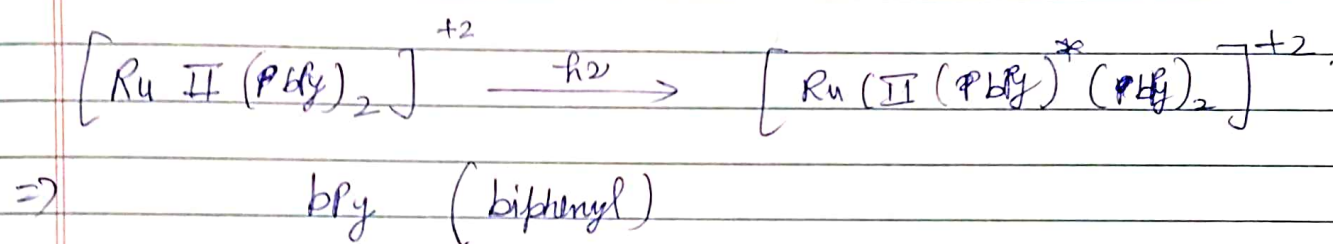
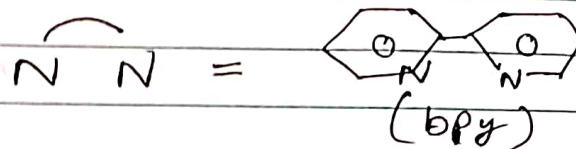
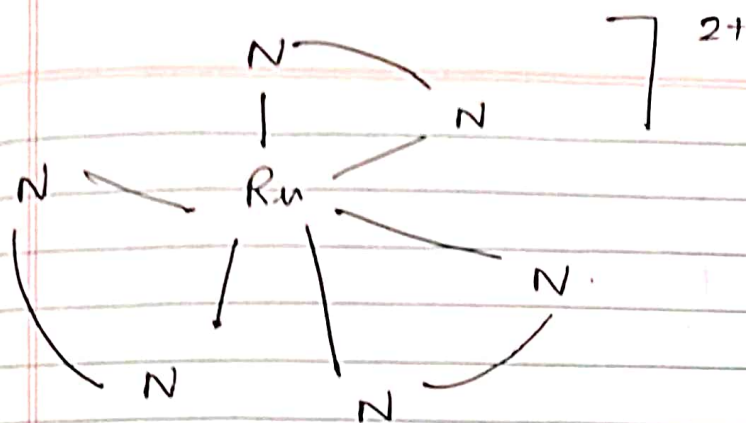
⇒ The compounds are thermally very stable in aqueous solutions.

⇒ These compounds are capable of participating in oxidation-reduction reactions (as both +2 and +3 oxidation states are stable in solution).

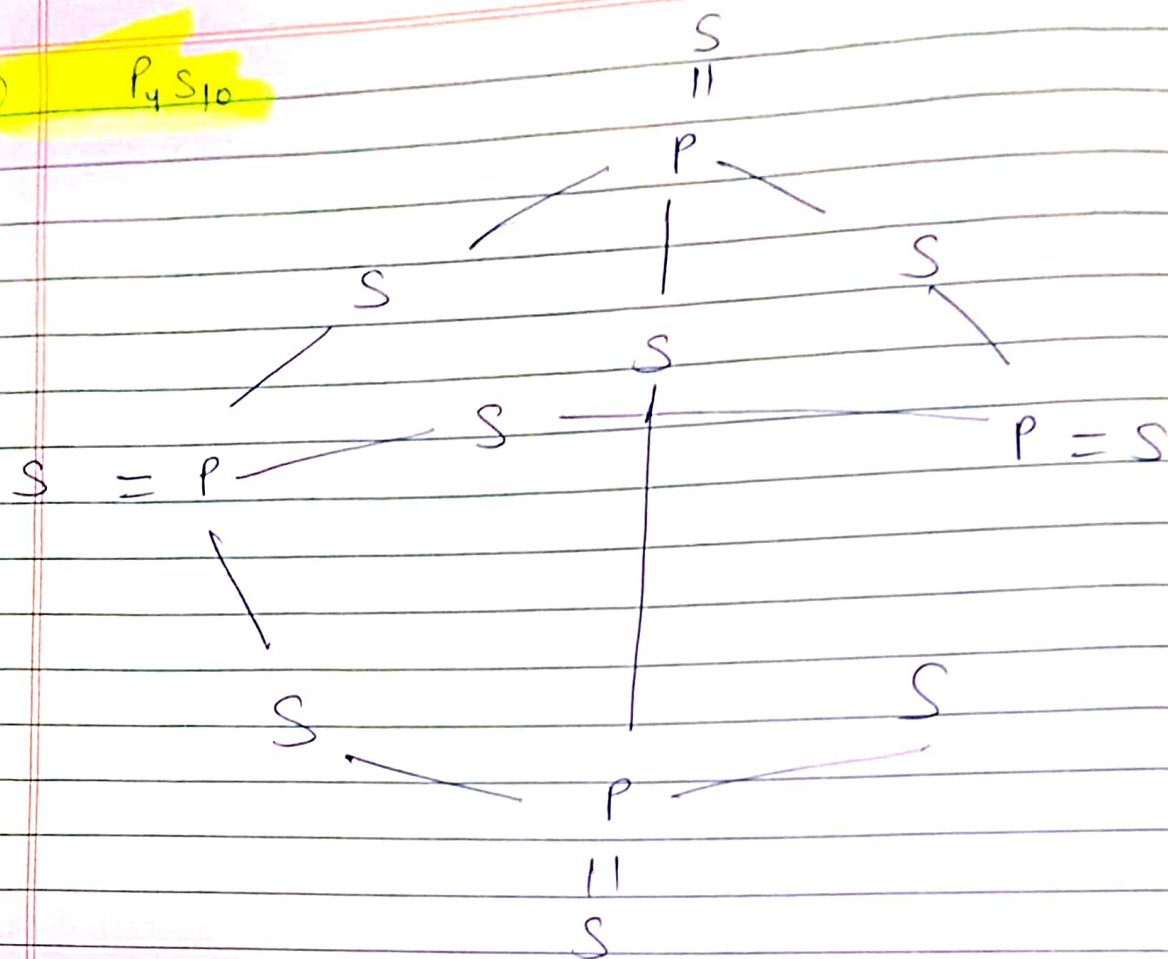
⇒ These compounds are used as photocatalyst.

Example:- Decomposition of H_2O into hydrogen and oxygen.





① P_4S_{10}



② Kapustinskii equation :-

- $\Rightarrow$ The Kapustinskii equation calculates the lattice energy U_L for an ionic crystal which is experimentally difficult to determine. It is named after Anatol Fedorovich Kapustinski who published the formula in 1956.
- $\Rightarrow$ It increases with increasing charge on the ions.
- $\Rightarrow$ It is larger for smaller ions.

$$U_L = \frac{CVZ^+Z^-}{r^+ + r^-}$$

V is the number of ions in the formula. (i.e., 2 for NaCl, 3 for MgF_2). C is a constant equal to 1.079×10^5 , radii in pm and U_L is in kJ mol^{-1} .

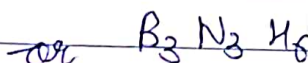
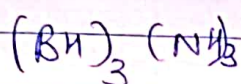
(3)

(4)

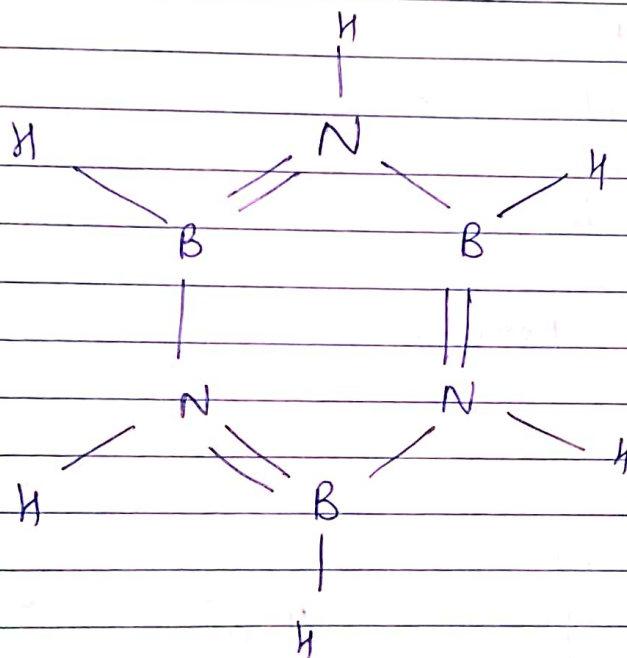
(5)

(6)

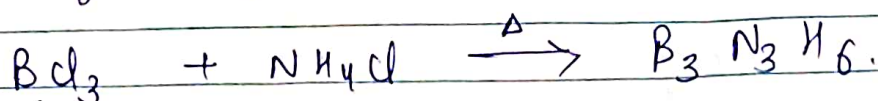
Borazine



⇒

⇒ Structure of Borazine.

- 1> In Borazine both Boron and Nitrogen are sp^2 hybridised
- 2> Each N-atom has one lone pair of electrons while each B-atom has an empty p-orbital

⇒ Preparation :-(1) Heating BCl_3 - with NH_4Cl .

(2) By heating a mix. of LiBH_4 and NH_4Cl .

$\Rightarrow$ NH_4Cl

$\Rightarrow \text{NH}_4\text{Cl} + \text{LiBH}_4 \rightarrow \text{B}_3\text{N}_3\text{H}_6$

(Ammonium chloride) (Lithium Borohydride)

$\Rightarrow$ Physical Property.

$\Rightarrow$ Physical Properties :-

(i) Colourless

(ii) Volatile liquid

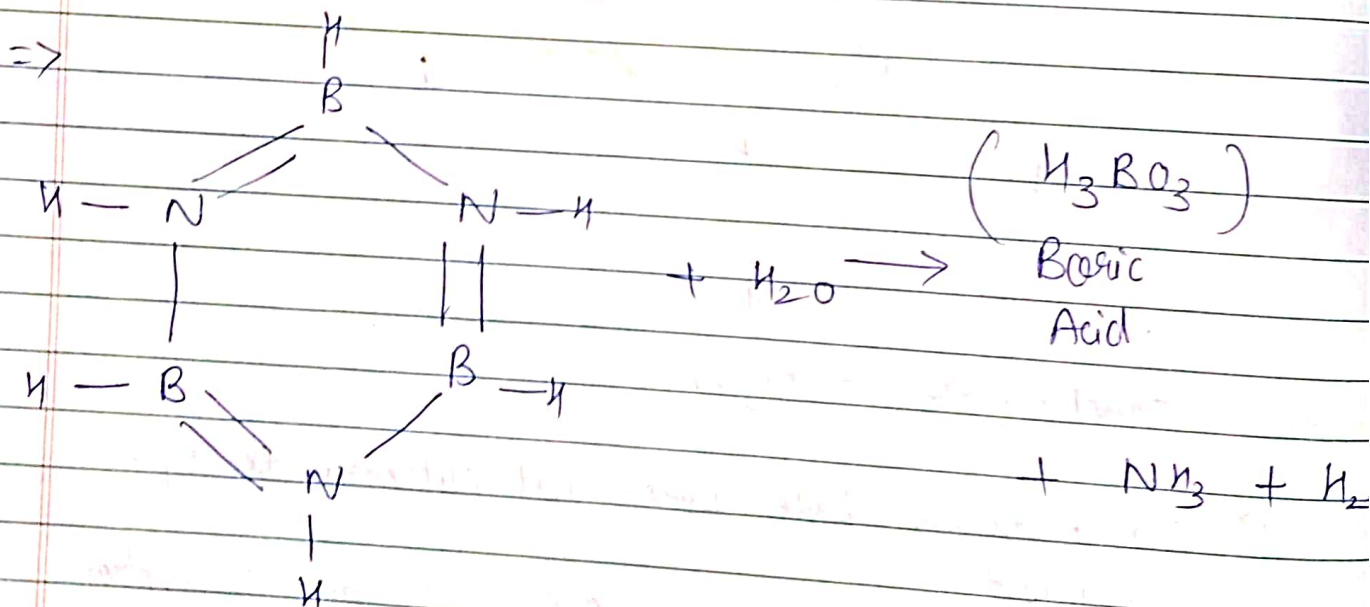
(iii) Boiling point Low.

(iv) Melting point Low.

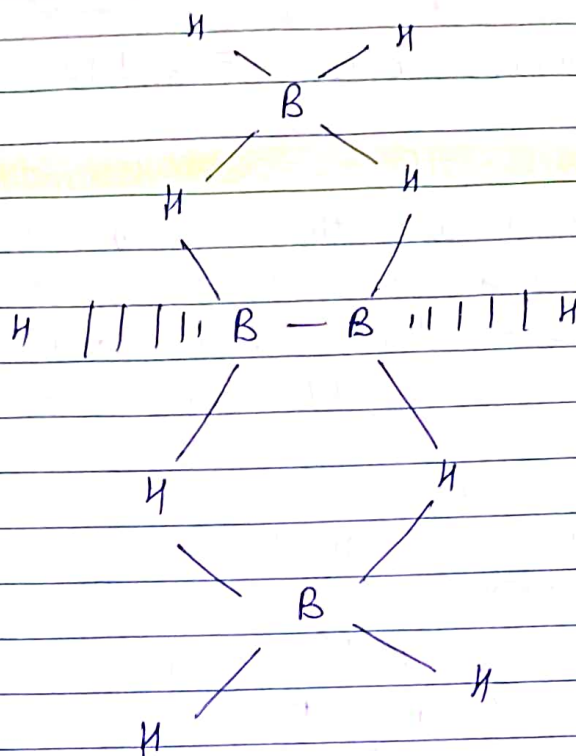
(v) Molecular weight = 78g.

$\Rightarrow$ Chemical Properties :-

 Hydrolysis of Borazine.



8) Structure of tetraborane



11) Born Lande's equation

The Born-Lande equation is a concept originally formulated in 1918 by the Scientist Born and Lande and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

$$U = \frac{N_A M Z^+ Z^- e^2}{4 \pi \epsilon_0 r} \left(1 - \frac{1}{n} \right)$$

Where N_A = Avogadro Constant

M = Madlung Constant

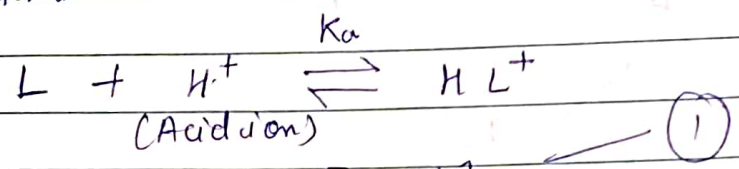
Z^+ = Numeric charge no. of cation.

Z^- = " " " " Anion.

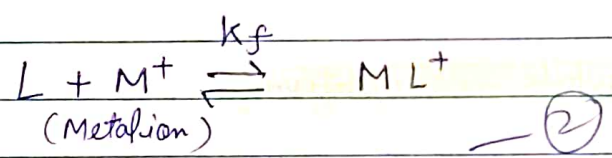
$e =$ Charge $1.6 \times 10^{-19} \text{ C}$.
 $\epsilon_0 =$ Permittivity of free space.
 $r_0 =$ Distance between ions.
 $n =$ a number b/w 5 and 12.

Photentiometric method or pH method / Photentiometric

$\Rightarrow$ When a ligand is either a weak acid or a weak base, there is a competition b/w H^+ ions and metal ions for the ligand and this can be used for the determination of the formation constant.



$$K_a = \frac{[\text{HL}^+]}{[\text{L}][\text{H}^+]} \quad \text{where } K_a = \text{Acid dissociation Constant.}$$



$$K_f = \frac{[\text{ML}^+]}{[\text{L}][\text{M}^+]} \quad \text{where } K_f = \text{Formation Constant}$$

Suppose C_H , C_m and C_L are the total amounts of acid H^+ , metal ion and basic ligand (L) respectively. we have :-

$$C_H = [\text{H}^+] + [\text{HL}^+]. \quad \text{--- (3)}$$

$$C_m = [\text{M}^+] + [\text{ML}^+]. \quad \text{--- (4)}$$

$$C_L = [\text{L}] + \overset{[\text{HL}^+]}{\cancel{[\text{M}^+]}} + [\text{ML}^+] \quad \text{--- (5)}$$

From eqn. (5), we get.

$$[\text{ML}^+] = C_m - [\text{M}^+]$$

From eqn (5), we have.

$$[ML^+] = C_L - [L] - [HL^+]. \quad \text{--- (6)}$$

Now, Substituting the value of $[HL^+]$ from equation (3) in (6), we get.

$$[ML^+] = C_L - [L] - C_H + [H^+]. \quad \text{--- (7)}$$

and from (1), we get.

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

$$[L] = \frac{[HL^+]}{K_a \cdot [H^+]} \quad \text{--- (8)}$$

Put value of (8) in (7), we get.

$$[ML^+] = C_L - \frac{[HL^+]}{K_a \cdot [H^+]} - C_H + [H^+]. \quad \text{--- (9)}$$

from eqn (4), we get.

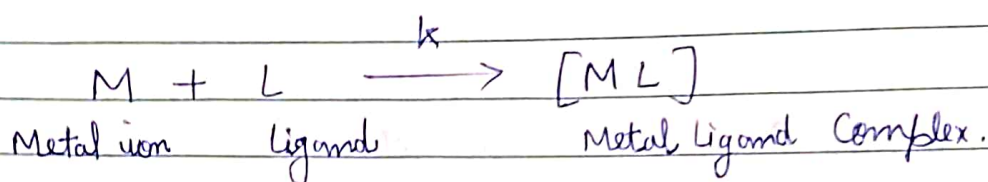
~~$$[M^+] = C_M - [ML^+] \quad \text{--- (10)}$$~~

Now Substituting the values of ~~(8)~~ $[L]$, $[ML^+]$ and $[M^+]$ in K_f we get

$$K_f = \frac{[ML^+]}{[L][M^+]}$$

II Stability of Metal Complexes and Factors affecting the formation Constant.

=> A Stability Constant is an equilibrium Constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents to form complexes.



$k =$ is formation Constant.

=> Factors affecting the stability of complexes:-
1> Nature of the central metal ion.



→ The nature of metal ion (like size) effect the stability constant

→ If the size of the metal ion increases the stability also increases.

② ~~Effect of size~~ charge on metal ion increases the stability also increases.

2> Ionic charge :-



Ionic charge

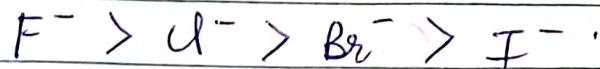
→ The Ionic charge effect the stability of the complex.

→ If the charge on metal ion increases the stability constant also increases.

3> Electronegativity of the central metal ion
 → If central metal ion have high electronegativity then it attracts more strongly the ligand to form a stable complexes.

4> Size and Charge of ligand :-

Ligand with small size form the stable complexes.



5> Basic nature of ligand :-

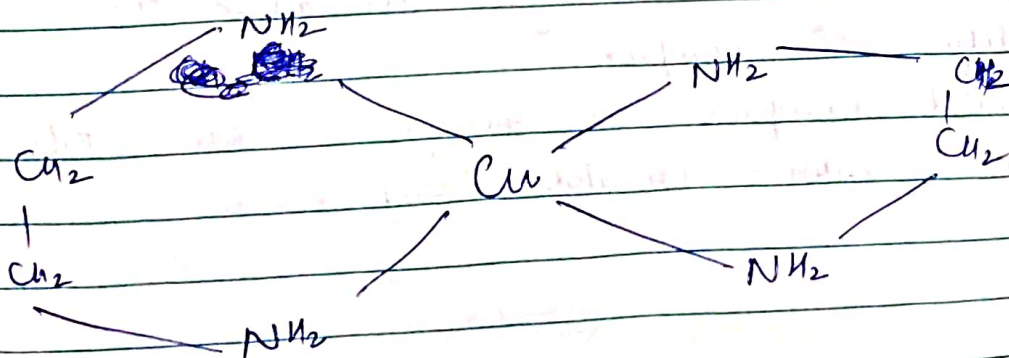
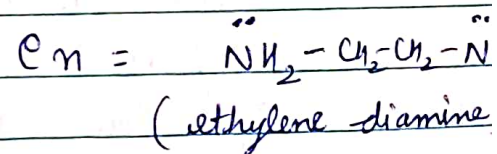
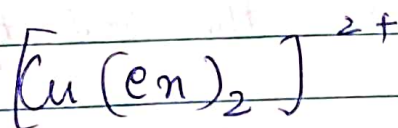
Which can donate lone pair of electrons easily form stable complexes.

Example :- F^- , and $\ddot{N}H_3$

6> Effect of chelation :-

→ In chelation the cyclic ring formation take place.

→ Stability increases with chelate ring formation.



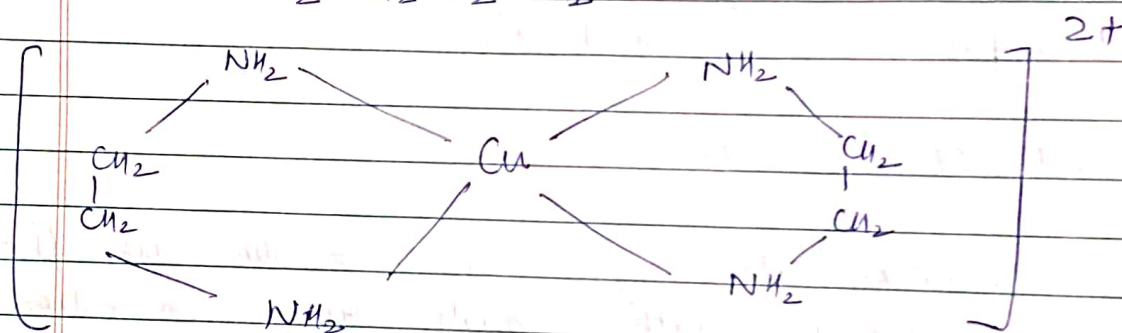
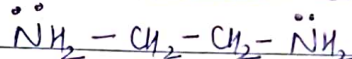
Chelate effect

=> When a bidentate or a polydentate ligand is attached by two or more atoms to the central atom forming a ring, the ligand is called chelating ligand and the complex is called chelate, the effect is called chelate effect.

Example:- $[\text{Cu}(\text{En})_2]^{2+}$

En is bidentate ligand

En is ~~tetra~~ ethylene diamine



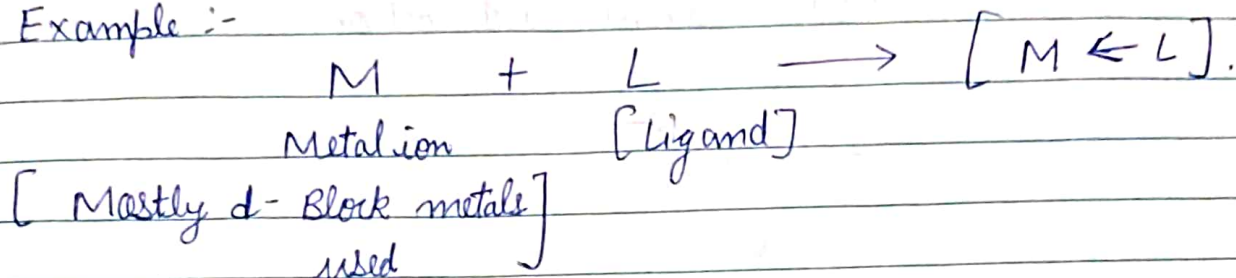
=> Chelate effect increases the stability of the complexes.

- 1> If the size ring formation increases the stability of complex.
- 2> The ~~size~~ number of rings increases the stability of complex.
- 3> The chelated complex is always more stable than the non-chelated complex.

Detection of complex formation - in solution.

⇒ The complex compound :- When the Metal ion accept a electron from a ligand a ligand it form a complex compound. and this complex compound cannot dissociate in water

Example :-



→ Ligand :- It is a substance which have extra electron. (it may be negative ligand or positive ligand or neutral ligand) these extra electron donated to central metal ion to form a complex.

→ Metal ion :- The metal ions are mostly d-block elements and they have vacant d-orbitals which accept electron from ligand to form complexes.

→ Metal ion act as Lewis Acid (electron acceptor).

→ Ligand act as Lewis Base (electron donor).

⇒ The formation of complex compounds can be detected by

(i) Change in color

(ii) Solubility

(iii) pH

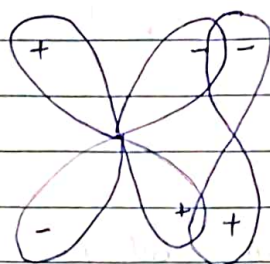
(iv) Electrical Conductivity.

#

MOT

MOT stands for molecular orbital theory
 it relates to ligand orbital theory.
 it is the distribution of electrons in atomic orbitals
 in a molecule.

Metal - ligand interaction.



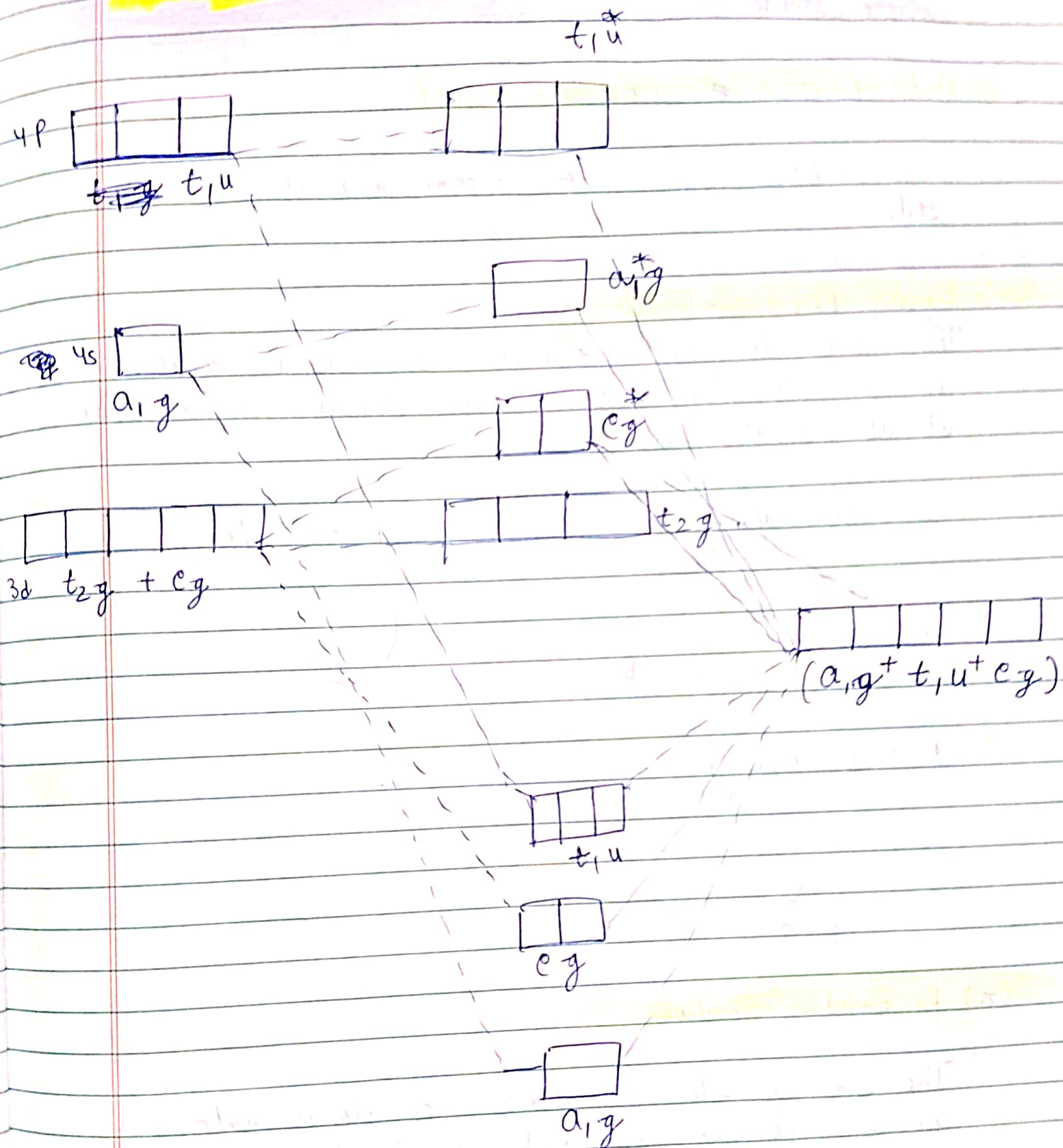
Metal ligand

π -Bonding in octahedral complexes.

orbitals.	Representation
S	a_{1g}
P_x, P_y, P_z	t_{1u}
d_{xy}, d_{yz}, d_{zx}	t_{2g}
$d_{x^2-y^2}, d_{z^2}$	e_g

Where a = non-degenerate
 e = doubly degenerate
 t = triply degenerate

⇒ The generation of π and σ molecular orbitals in octahedral complexes.



Bonding orbitals = t_{1u} , e_g , a_{1g} , t_{2g} .
 Anti Bonding orbitals = t_{1u}^* , e_g^* , a_{1g}^* , t_{2g}^* .

Bonding ^{molecular} orbital

These orbitals have less energy and they are more stable.

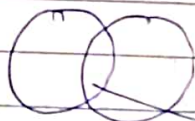
Anti-Bonding ^{molecular} orbital

These orbitals have more energy and they are less stable.

(6) Sigma Bond formation

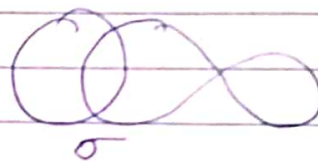
The end to end overlap of atomic orbital in a complex molecule is called sigma bond. it is denoted by σ .

S-S overlapping

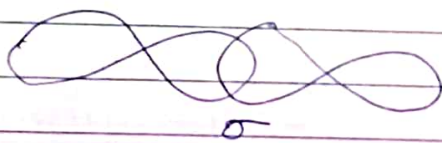


Sigma Bond
(σ)

S-P overlapping



P-P overlapping

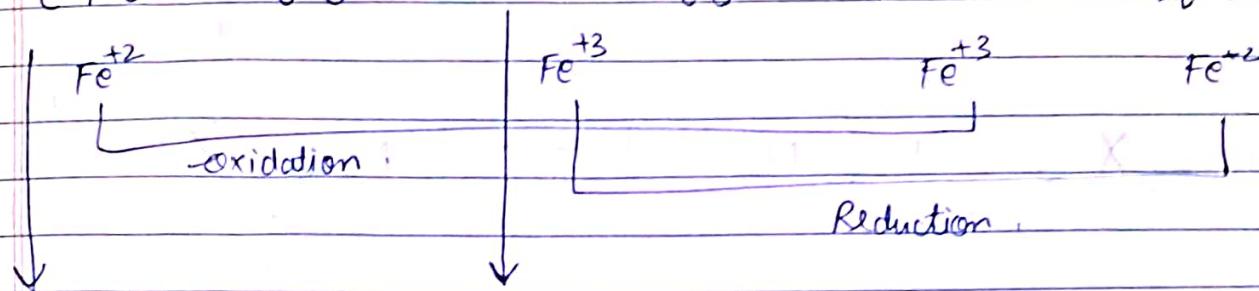
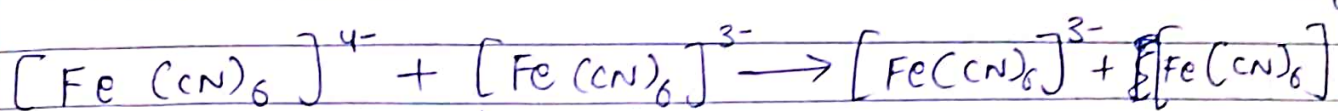


(7) Pi Bond formation

The side by side overlapping of atomic orbitals in a complex compound is called pi bond. it is denoted by π .

Electron transfer Reactions / Redox Reax.

⇒ Transfer of an electron from one complex to another.



Reducing agent
(Reductant)

oxidizing agent
(oxidant).

⇒ Electron transfer reactions take place in two mechanisms

(i) outer sphere mechanism.

(ii) Inner sphere mechanism.

⇒ Inner sphere mechanism:-

⇒ oxidant and Reductant use a ligand in coordination sphere to form a bridged complex, the electron is then transferred through bridging ligand.

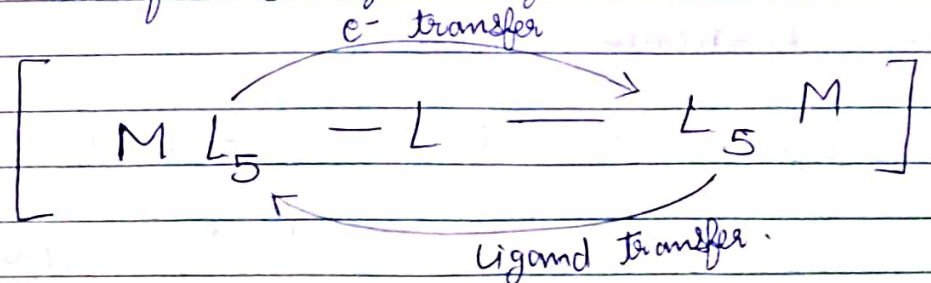
⇒ Condition:-

1) one complex should be labile.

2) other " " " Inert.

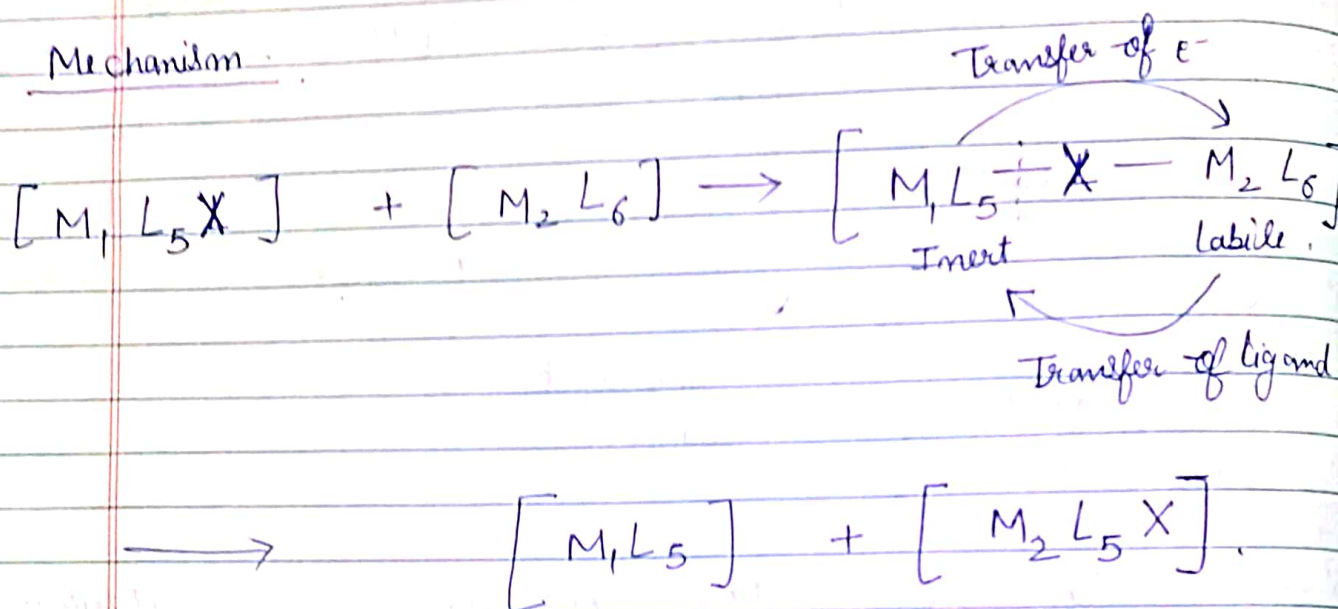
(Because electron transfer from inert to labile).

3) e^- transfer through Bridge intermediate.



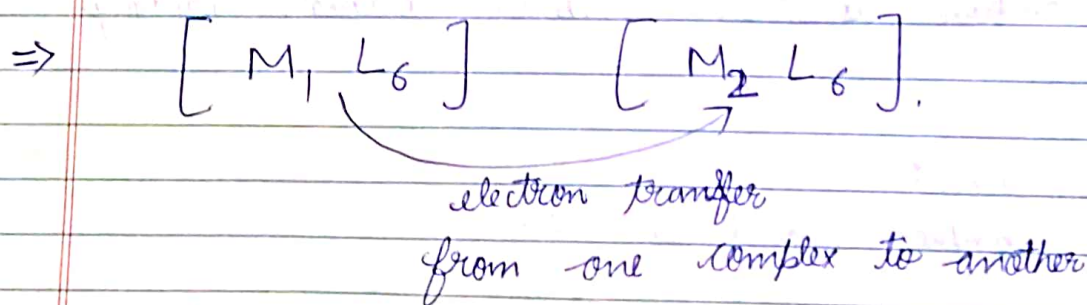
⇒ In Inner orbital Complex, both electron and ligand transfer in ~~to~~ one coordinate sphere of a complex.

Mechanism

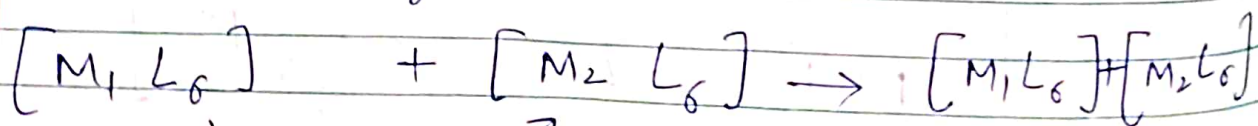


⇒ outer orbital Complex:-

⇒ In outer orbital Complex, the electron transfer from one complex to another complex is called outer orbital Complex.



⇒ In outer orbital Complex both reactants are kinetically inert.

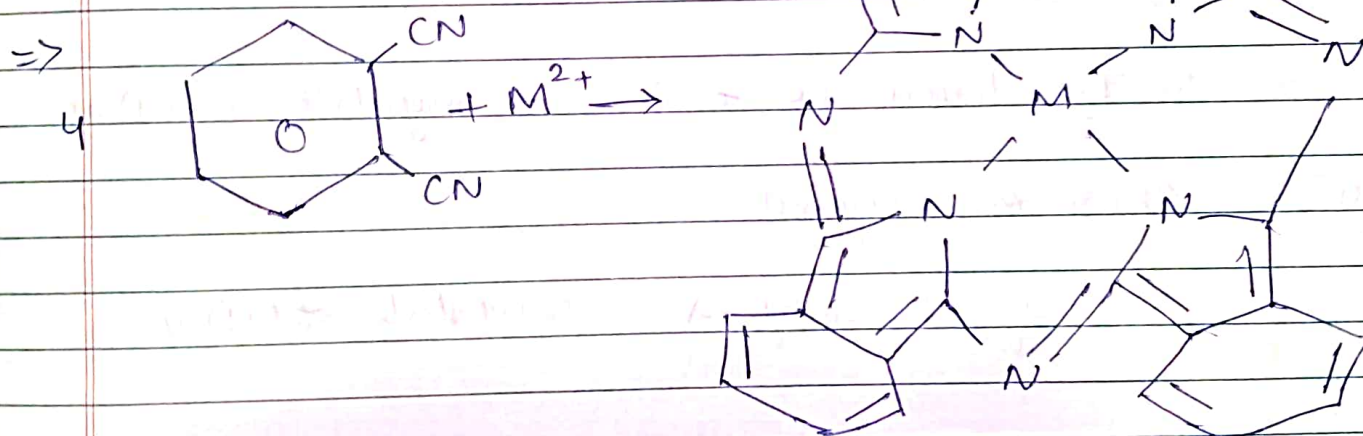


Due to oxidation and Reduction take place. e^- transfer take place. → Metal ions oxidation state changes.

Template effect :-

- $\Rightarrow$ In template reactions, macrocyclic ligands are generated in the presence of metal ions.
- $\Rightarrow$ In the absence of the metal ion, the same organic reactants produce different, often polymeric products.
- $\Rightarrow$ Template reactions term is mainly used in Coordination Chemistry.

A template reaction is any of a class of ligand-based reactions that occur between two or more adjacent coordination sites on a metal center.



$\Rightarrow$ Synthesis of Macrocyclic ligands.

$\Rightarrow$ Application :-

- 1> The Production of Macrocyclic ligands
- 2> They are used in dye pigments.
- 3> They are used in Semiconductors.
- 4> They are used in biological macrocycles.

Factors affecting magnitude of $10 Dq$ (Δ).

(1) Charge on the Metal ion

The crystal field theory is based on electrostatic model, the ionic charge on metal affects the magnitude of $10 Dq$ (Δ).

If charge of metal increases it attracts the ligand towards more closely.

(2) Radius of the Metal ion :-

$$\text{Radius of the Metal ion} \propto \frac{1}{10 Dq}$$

(3) Period no. of the Metal ion

$\Rightarrow$ The ~~eff~~ period no. $\propto$ magnitude of $10 Dq$.

(4) Charge on Ligand

$$\text{Ligand charge} \propto \text{magnitude of } 10 Dq.$$

(5)