

BSc 2nd year Inorganic Chemistry

Complete Notes

(In English Medium)

BSc 2nd year Inorganic Chemistry

- 1. First Transition Series**
- 2. Second and Third Transition Series**
- 3. Coordination Compounds**
- 4. Chemistry of Lanthanides and Actenoid**
- 5. (a) Acids and Bases**
- (b) Oxidation and Reduction**

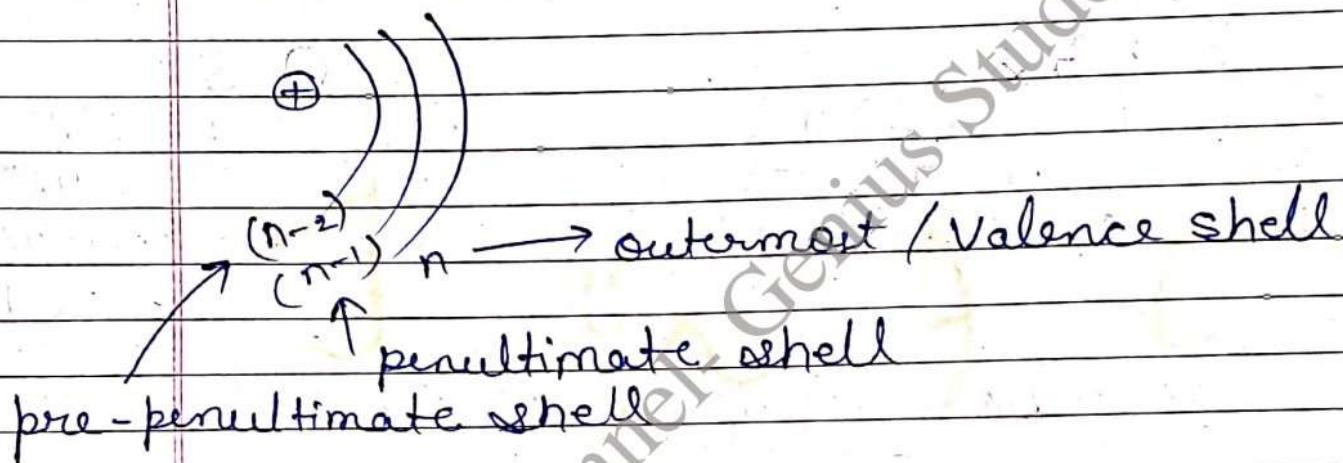
Chemistry of Elements of First Transition Series

Unit - 1

Chemistry of 1st Transition Series

D-Block element

The element in which last e⁻ enters in d-orbital of penultimate shell $n-1$.



Transition element →

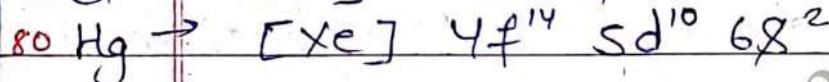
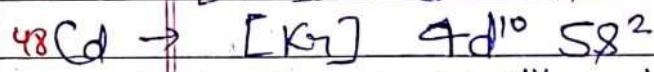
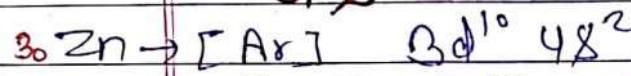
The d-block element which have partially filled $(n-1)$ d orbital in their ground state or in chemically significant oxidation state.

Note → All transition element are d-block element but all d-block element are not transition element.

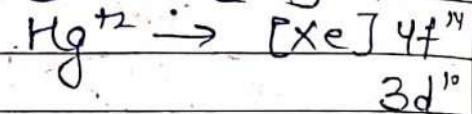
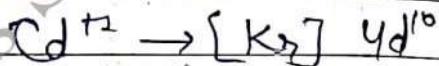
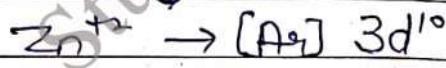
Ques Why Zn, Cd, Hg are not considered as transition elements? Explain reason.

Because they have completely filled d orbital in their ground state as well as in oxidation state.

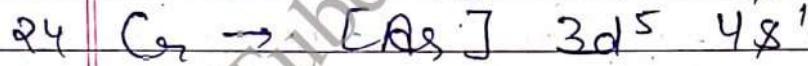
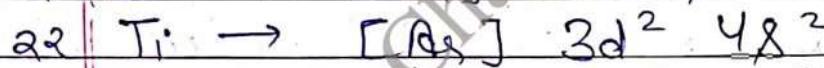
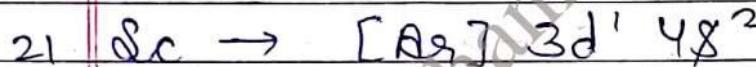
G.S



O.S



Electronic configuration of first transition series



(1) $3d^5$ and $4s^2$ subshell have very less energy difference hence exchange of e^- takes place easily

(2) Half filled orbitals are extra stable

General properties of transition element :-

* ① Metallic property →

All the transition elements have only 1 or 2 e^- in their outer most valence shell and consequently are metallic in nature.

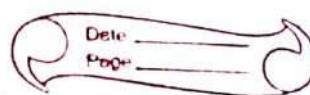
They have metallic luster, ductile in nature, high tensile strength and good conductors of heat and electricity.

* ② Atomic radii →

On moving left to right in 3rd transition series radius decreases. In initial elements Sc to Mn Z_{eff} is dominating over shielding effect so radius decreases.

In middle elements Z_{eff} and s.e. counteract each other so radius remains constant.

In last element (Cu, Zn) Z_{eff} no of electrons increased hence s.e. is dominating over Z_{eff} .



As a result radius decreases increases.

	Sc	1.62	radius (\AA)
Ti	V	1.47	
		1.34	
Cr		1.27	
Mn		1.26	
Fe		1.26	
Co		1.25	
Ni		1.24	
Cu		1.28	
Zn		1.38	

* ③ Ionisation potential \rightarrow

Due to small sizes of transition element they have high value of I.E.

When we move across a transition series very little change in I.P observed. This is becos tranⁿ metal does not have much more differences in sizes.

In other words we can say that increased z_{eff} is balanced by $\delta\cdot\epsilon$ of d electrons.

2nd I.P of Cr and Cu are greater
becoz after removal of one e^-
half filled and full filled ($3d^5$
and $3d^{10}$) e^- config'ns are obtain
which are extra stable and needs
much more amount of energy to
remove 2nd electron.

* (4) Reactivity →

2017

The I.E. of transition element are
fairly high because size of their
atoms is small. They also possess
high heat of sublimation due
to the existence of covalent
bonding due to d-d overlapping.

That's why trans' element are
less reactive than alkali and
alkaline earth metal.

And metal ions do not get hydro-
lysed easily.

* (5) Hardness →

2016 In trans' metal in add' to metallic
bonding (Metal ion is merged in
sea of free electron).

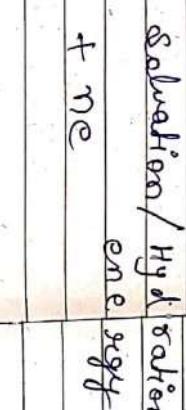
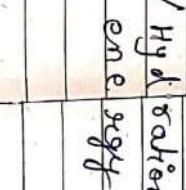
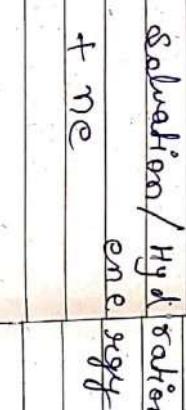
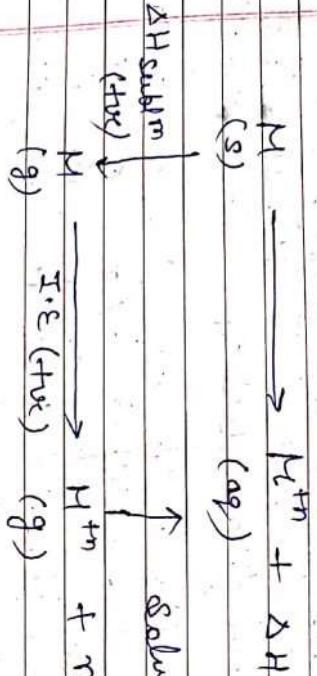
There must be some covalent
bonding due to d-d overlapping

The no. of such bonds are responsible for the hardness of transition metal. As no. of unpaired electron increases hardness increases.

But Zn, Cd, Hg are soft because they have completely filled d orbital.

Reducing property →

The reducing property of a metal depends on its tendency to be oxidized easily.



$$\Delta H = \Delta H_{\text{sub}} + I \cdot E + \Delta H_{\text{soln}}$$

The electrode potential are also measure of ΔH . The transition metals are weak reducing agent due to their high heat of sublimation.

Very few O.S are shown in bracket

\rightarrow Sc shows only +2 oxidn state due to stable inert gas config.

\rightarrow Zn shows only +2 oxidn state due to stable pseudo inert gas config.

high I.P., slow heat of hydration

Oxidation state →

Transition metal have very less energy difference b/w $(n-1)d$ and $n s$ orbital hence both e⁻'s can participate in bond formation that's why transition element shows variable oxidn state.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
No of unpaired -	1	2	3	5	5	4	3	2	0	0
4s e -	2	2	2	1	2	2	2	2	1	2
oxidn state,										
(+2)	(+2)	(+2)	(+1)	(+2)	(+2)	(+2)	(+2)	(+3)	(+2)	
+3	+3	+3	+2	+3	+3	+3	+3	(+3)	+2	
(+4)	(+4)	(+3)	(+4)	(+4)	(+4)	(+4)	(+4)	(+4)		
+5			+4	+5	+5	+5	+5			
(+6)			(+5)	(+6)	(+6)	(+6)	(+6)			
+6			(+6)	(+6)	(+6)	(+6)	(+6)			
+7										

→ As no. of unpaired e^- increase O.S also increase that's why Mn shows highest O.S (+7).

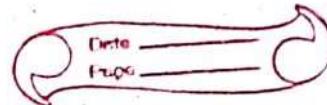
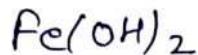
→ In the lower O.S. of the transition metal the character of the bond is ionic. As O.S increases polarisability increases and covalent character decreases.

→ With the decrease in ionic character of bond, the basic character of oxide also decreases.

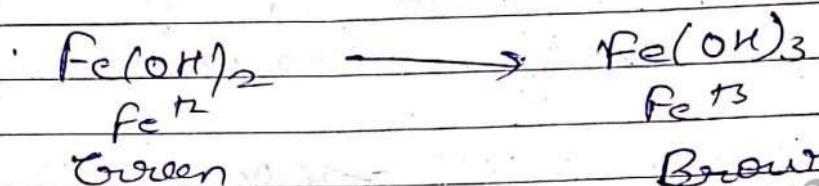
+2	+3	+4	+5	+6	+7
TiO		TiO ₂			
	V ₂ O ₃		V ₂ O ₅		
	Cr ₂ O ₃			CrO ₃	
MnO	Mn ₂ O ₃			MnO ₃	Mn ₂ O ₇
Basic	Less basic	Amphoteric	Very acidic	Acidic	Strongly acidic

→ In stability of O.S medium played an important role.

In stab. In acidic medium lower O.S more stable while in alkaline medium higher O.S more stable.

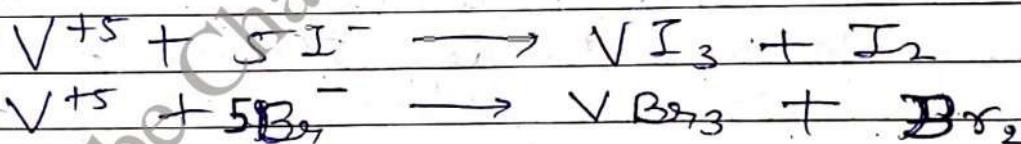


Eg \rightarrow Ferric hydroxide (brown color) oxidise into ferric hydroxide of brown color.



\rightarrow The existence of any particular O.S for a metal with a given ligand or anion depends on redox property of the metal ligand system.

for Eg \rightarrow VF_5 exist but with VI_5 and VB_{35} does not exist.



\rightarrow Trans metal shows their highest O.S in fluorides, Oxides bcoz F^- , O^{-2} have highest e⁻ negativity and small size.
due to which they does not oxidise easily.

★⑧ Catalytic Property

~~2019~~ Transition elements and their Comp'd behave as good catalyst becoz of following 2 reasons.

① → Transition metal show variable oxidation state.

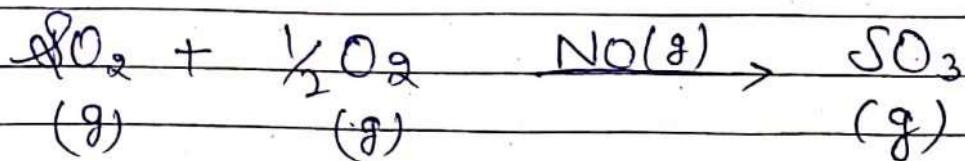
② → Transⁿ metal have partially filled $(n-1)d$ orbital.

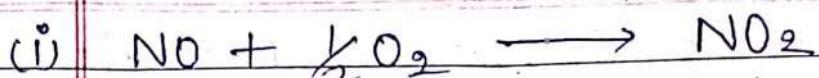
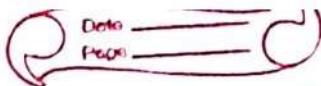
Theories of catalysis.

① Intermediate Theory

This theory is given for homogeneous catalysis. The transition element shows variable oxidation states due to presence of vacant d orbitals. They can form unstable intermediate products with catalyst reactant.

This unstable product finally decompose. intermediate into product





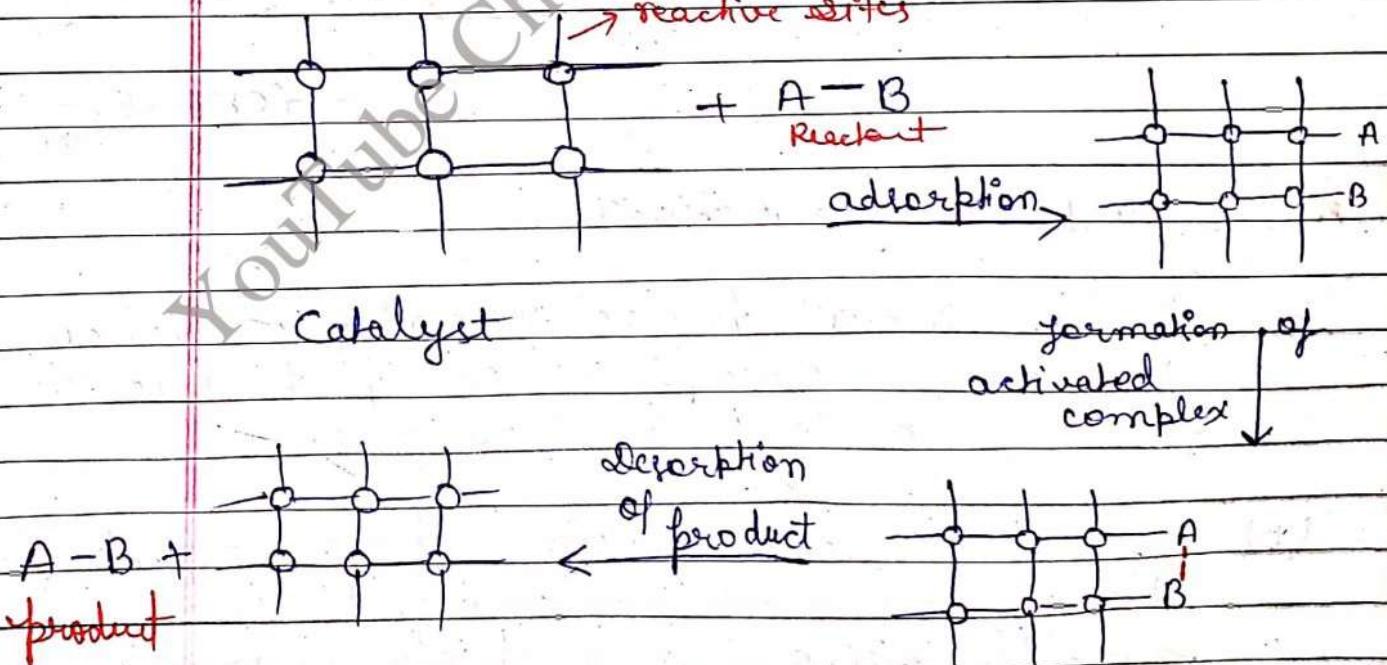
intermediate.
(unstable)

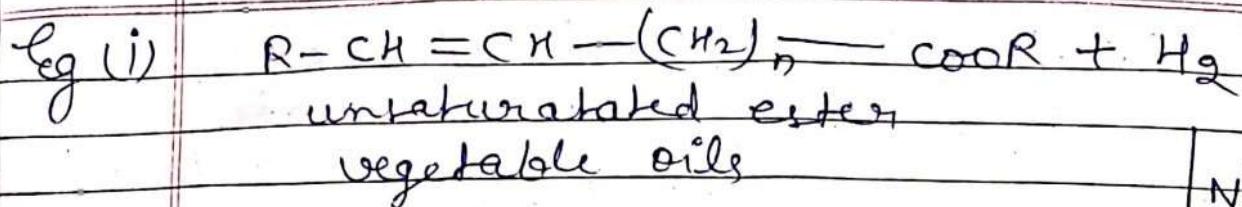


② Adsorption theory

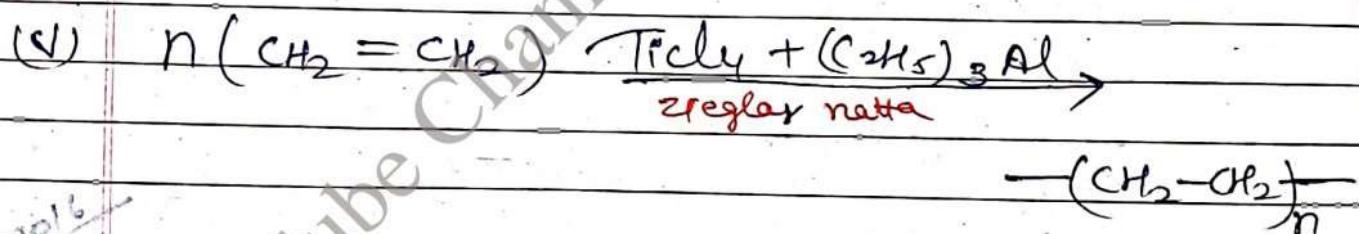
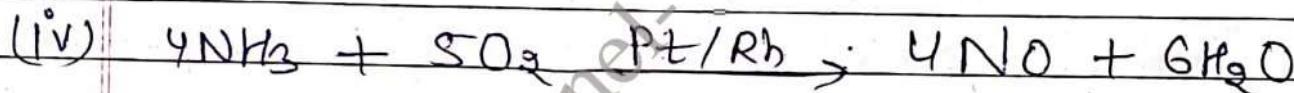
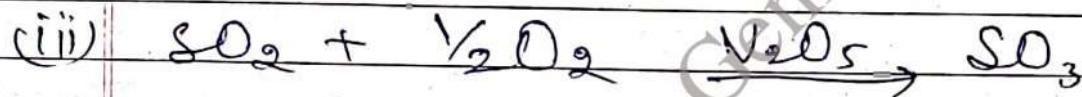
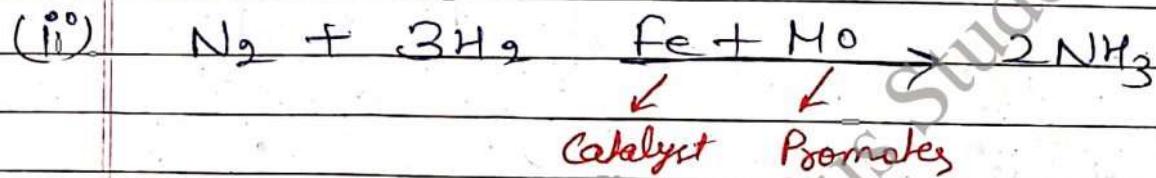
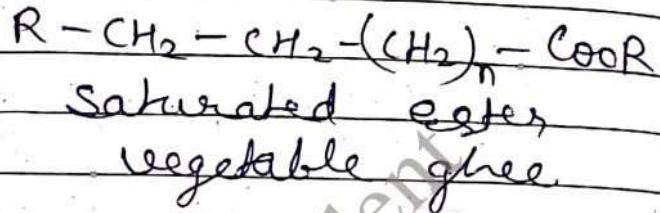
This Theory is given for heterogeneous catalyst. acc to This Theory Catalyst have reactive sites on their surface.

The reactant molecule adsorbed on the surface of catalyst and form a activated complex. This complex decompose into product giving back catalyst.





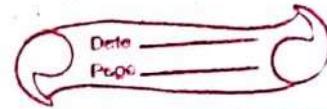
Ni/Pt/Pd



*⑨ Complex formation

Transⁿ metal have greater tendency to form complex compⁿd due to following 2 reasons.

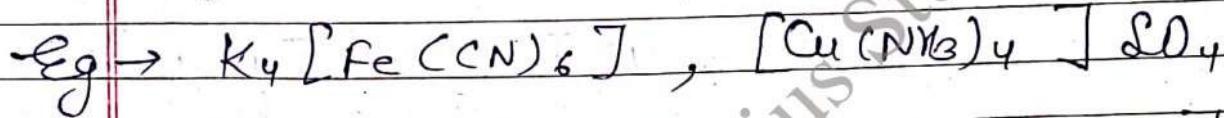
(i) Transⁿ metal cations have high charge density due to their small size and high charge.
 (z_{eff})



So they can accept l.p easily.

charge density = $\frac{\text{charge on cation}}{\text{size of cation}}$

(2) Trans metal have vacant d orbital
so they can accept l.p from ligands to form coordinate compd



★ 10 Magnetic property

(i) Intensity of Magnetisation

magnetic moment per unit volume is known as Intensity of Magnetism denoted by I.

It is defined as the pole strength induced per unit area.

m = pole strength

l = distance b/w poles

A = Area of pole

$$I = \frac{m}{A} = \frac{m \cdot l}{A \cdot l} = \frac{\text{magnetic moment}}{\text{Volume}}$$



(ii) Gauss law and total magnetic induction

If a substance is placed in magnetic field of magnitude (H), the magnetic flux (total no of magnetic lines of force per unit area) (B) is given by

$$B = H + 4\pi I \rightarrow \text{This is gauss law.}$$

(iii) Magnetic Permeability (μ)

The ratio of B is μ/μ_0 magnetic permeability.

$$\mu = \frac{B}{H} = \frac{H + 4\pi I}{H} = \frac{I + 4\pi I}{H}$$

$$\mu = \chi \leftarrow \text{chi}$$

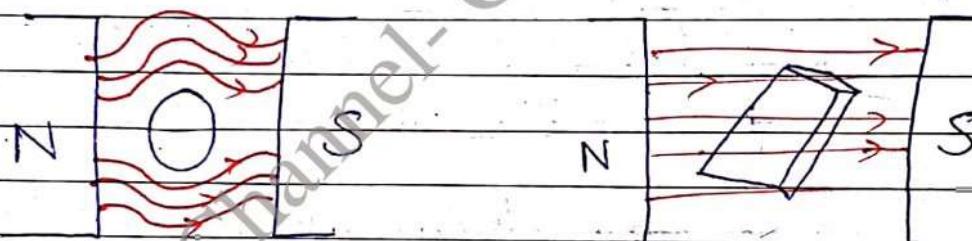
$\chi \rightarrow$ is called magnetic susceptibility per unit volume.

On the basis of magnetic property substances are of following 3 types :-

① Dimagnetic (strongly Repelled by Magnetic field)

The substance which when placed in magnetic field decrease the intensity of magnetic field than in vacuum are called dimagnetic substance. ex:- H₂O, NaCl, C₆H₆ etc.

Dimagnetic substance are repelled by the magnetic field and such substances sit themselves at right angles to the magnetic field.



Dimagnetism arises due to paired electron.

Dimagnetism does not depend on temp & and H but depends on ~~X~~.

for Dimagnetic substance $B < H$, $P < 1$ and X will be negative i.e I and H opposing to each other.

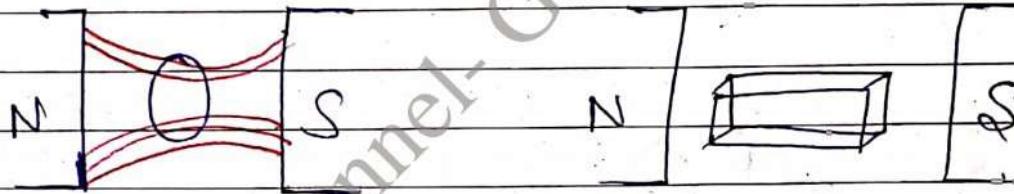
2019

②

Paramagnetic (e.g. Pt, Al)

The substance which when placed in a magnetic field increase the intensity of magnetic field than in vacuum are called paramagnetic substance.

Paramagnetic substance are attracted by the magnetic field and such substance set themselves at parallel to the magnetic field.



Paramagnetism arises due to unpaired electrons.

For paramagnetic substance $B \propto H$, $P > 1$ and $X = +ve$ i.e. I is acting in the direction of H .

③

Ferromagnetic (e.g. Fe, Co, Ni, CrO₂)

The substance which are strongly attracted by magnetic field are known as ferromagnetic substance.

They behave as magnet even in the absence of magnetic field.

Ques Fe, Co, Ni behave as ferromagnetic substance Why?

Ans (i) They have sufficient no of unpaired electron.

(ii) Due to high atomic number they have free exchange integral i.e. energy related with exchange of 2 electrons.

(iii) They have appropriate size.

Electron have 2 type of motion :-

① Orbital Motion

Due to this motion orbital magnetic moment is arises.

$$\mu_L = \sqrt{L(L+1)}$$

μ_L = orbital magnetic moment

L = sum of orbital angular quantum number.

② Spin motion

Due to this motion spin magnetic moment is arises.

$$\mu_s = \sqrt{4s(s+1)}$$

μ_s = Spin Magnetic moment

s = Sum of spin quantum no.

$$\mu_T = \mu_s + \mu_L$$

$$= \sqrt{4s(s+1)} + \sqrt{L(L+1)} B.M$$

for transition metals orbital magnetic moment is assumed negligible

$$\mu_T = \mu_s + \cancel{\mu_L}$$

$$= \mu_s$$

$$= \boxed{4s(s+1)}$$

$$s = \text{no of unpaired } e^- \times \frac{1}{2}$$

$$= \frac{1}{2} \times n$$

$$\mu_T = \sqrt{4 \times \frac{n}{2} \left(\frac{n}{2} + 1 \right)}$$

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

n	μ (B.M)
0	0
1	1.73
2	2.84
3	3.87
4	4.89
5	5.91

Calculate magnetic moment of Cr^{+3} and Fe^{+3} or any.

$$\text{Use } \rightarrow \mu = \sqrt{n(n+2)} \text{ BM}$$

* 11) Spectral property of Trans elemⁿt

2013
2017

Spectral property of complexes can be explained on the basis of CFT (Crystal field Theory) which have following postulates :-

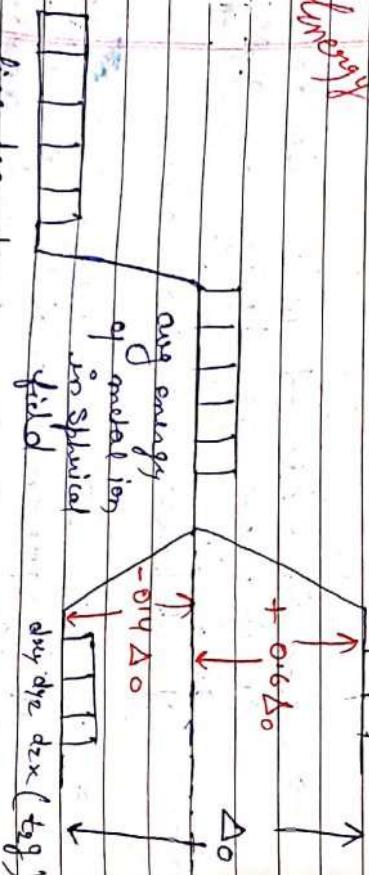
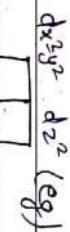
- Acc to this theory interaction b/w metal ion and ligand is purely ionic
- Acc to this theory ligands are considered as point charges and if ligand is neutral then it behave as dipole.
- In free state metal have five 'd' degenerate orbital but when complex is formed this degeneracy is lost and d orbitals splits into 2 parts.

This is t_{1g} Crystal field splitting.

CFT for Octahedral Complexes

d_{xy}, d_{yz}, d_{zx} orbitals (t_{2g}) have this lobe's lobe's along the axes, while $d_{x^2-y^2}, d_{z^2}$ (e_g) have their lobes on the axes.

In octahedral complex ligands approach towards the metal ion from axes, hence e_g orbital feels more repulsion compared to t_{2g} orbitals. Hence the ligand energy increases and orbital splits into 2 parts.



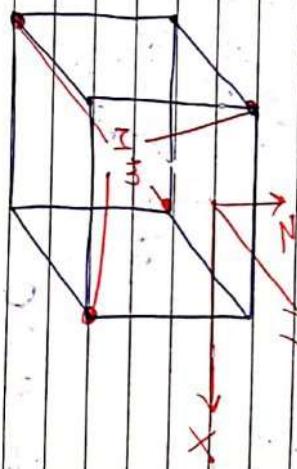
five degenerate orbitals in free metal

Metal ion in octahedral field

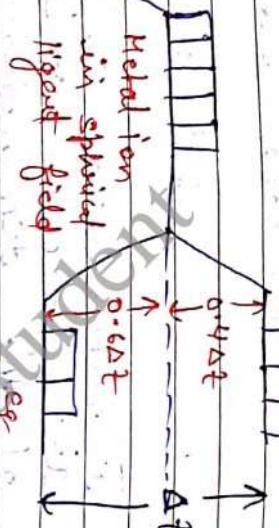
$\Delta_0 =$ crystal field splitting energy of octahedral complexes

CFT for tetrahedral complexes

In tetrahedral complex the 4 ligand are placed at the 4 corners of the tetrahedron located at axes, metal ion is in the centre and metal ion is in the centre of it.



Since lobes of t_{2g} orbitals are lying also on the axes, they lie directly in one pair of ligands. Therefore t_{2g} orbital feels greater repulsion compared to e_g orbital hence their energy is increased.



~~eg~~

free rotation

(E_g degenerate orbital)

splitting of d
orbital in
tetrahedral ligand
field

$\Delta t = \text{CFSE for tetrahedral}$
complexes

$$\Delta t = \frac{4}{9} \Delta O$$

color of absorbed light	Applied λ (nm)	Complementary color
Violet	400 - 435	Yellowish green
Blue	435 - 480	Yellow
Greenish blue	480 - 490	Orange
Bluish	490 - 500	Red
Green	500 - 560	Purple
Yellowish green	560 - 580	Violet
Yellow	580 - 595	Blue
Orange	595 - 605	Greenish blue
Red	605 - 700	Bluish Green

Colors of transition metal ion and complexes

~~no~~

When light of visible range (400nm to 700nm) is allow to fall on a complex, the complex may absorb some part of the light and reflect or transmit the remaining light.

When light of visible range (400nm to 700nm) is allow to fall on a complex, the complex may absorb some part of the light and reflect or transmit the remaining light.

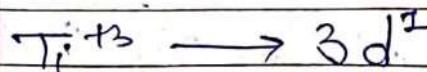
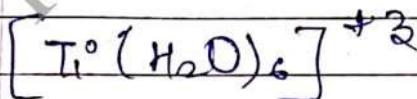
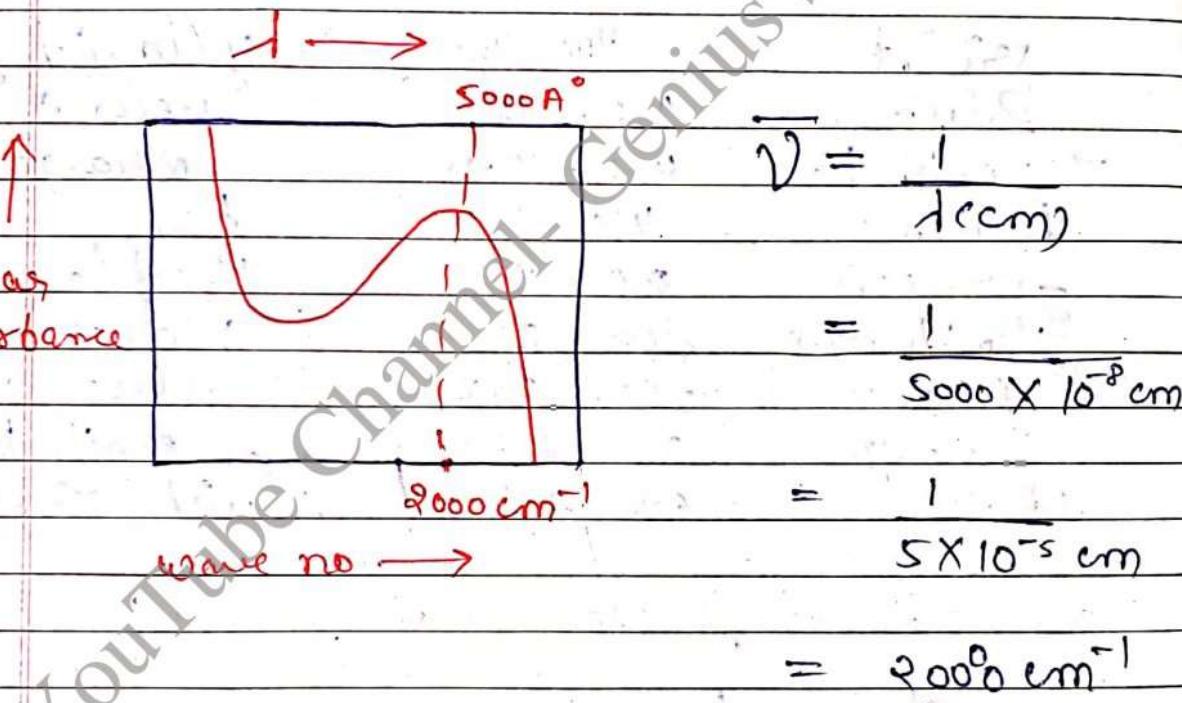
When light of visible range (400nm to 700nm) is incident on $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, this complex absorbs light at 540 nm. The energy associated with this wavelength is 157 kcal per mole which is sufficient

* compound form by Sc are colorless becoz no visible light is absorbed by Sc^{+3}

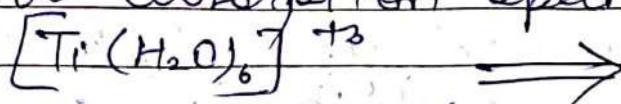
compd of Trans metal are colored becoz they absorb light for d-d transn.

to excite e^- from t_{2g} orbital
to e_g orbital this type of transⁿ is called d-d transⁿ or ligand filled transⁿ.

Complementary colors of absorbed green light is purple hence this complex appears purple in colour.



Visible absorption spectrum of



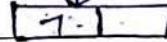


d-d transⁿ

eg



eg

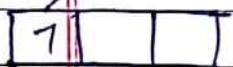


light absorbed

$$d = 5000 \text{ \AA}$$

(green color)

$$\Delta_0 = 57 \text{ kcal/mole}$$



$$E = 57 \text{ kcal/mole}$$



t_{2g}

t_{2g}

Ground state

excited state

$$1 \text{ cm}^{-1} = 2.85 \times 10^{-3} \text{ kcal/mole}$$

$$20000 \times 2.85 \times 10^{-3} = 57 \text{ kcal/mole}$$

② Charge transfer

2014

Another reason for colour of the complexes is charge transfer spectra.

In this phenomena trⁿ of e⁻ take place b/w molecular orbitals of metal ion and ligand.

In this trⁿ e⁻ absorbs light of visible range hence they appear colour. And colours are more intense due to charge transfer spectra compared to d-d transⁿ.

As charge increasing on metal ion colour becomes more intense bcz possibility of charge transfer increases. That's why K_3MnO_4 appears purple and $\text{K}_2\text{Cr}_2\text{O}_7$ appears orange in colours.

Ques Mn^{+2} comp'd have pink colour Why

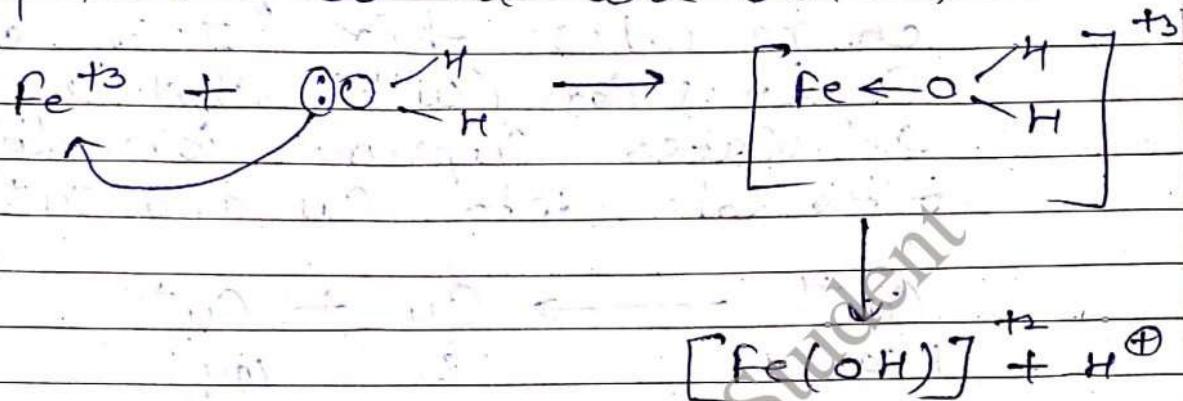
2012

Mn^{+2} ion have $3d^5$ E.C which is extra stable due to half filled This E.C opposes d-d trans. Hence higher energy or low wavelength is require. That's why it appear pale pink color.

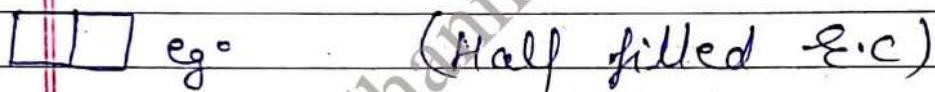
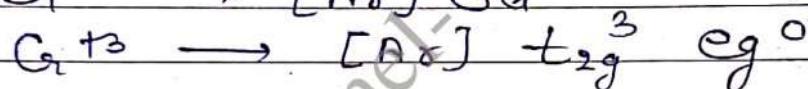
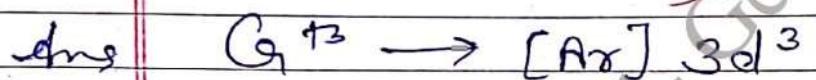
★ 12 Hydrolytic tendency of ions

Transition metal ions are highly charged and their $(m-1)d$ orbital are partially filled - Thus when one salt of transition metal ion are dissolved in water then the metal ion attract water molecules ultimately the cations form a bond by accepting one dip from oxygen.

Consequently the ppt of hydroxide of transition element are obtain.



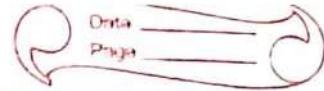
Ques Cr_2O_3 is neither oxidising agent
~~nor~~²⁰¹⁶ nor a reducing agent.



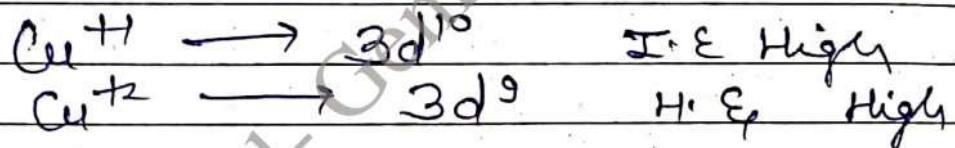
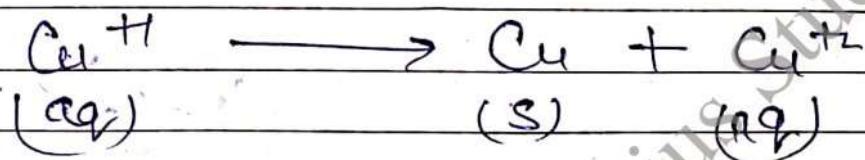
$[\text{t}\text{t}\text{t}\text{t}] t_{2g}^3$ which is more extractable due to which e's are not accepted or lost.

Ques Cuprous salt are strong R.A
~~and~~²⁰¹⁵ and unstable in water
 OR

(Cu^{+1}) Cuprous ion is less stable than Cupric ion in water.



Ans In water cupric ions (Cu^{+2}) more stable due to high H.E. which compensates high I.E. of Cuprous ion (Cu^{+}). That's why in water Cuprous ion dissociates into Cu and Cu^{+2} .



Chemistry of Elements of Second and Third Transition Series

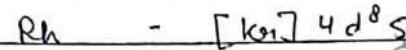
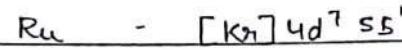
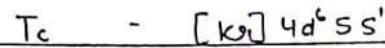
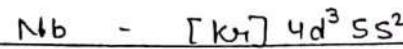
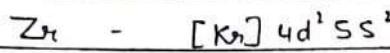
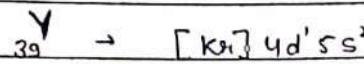
Unit-II Chemistry of 2nd and 3rd T.S.

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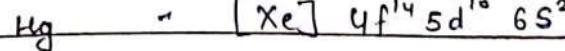
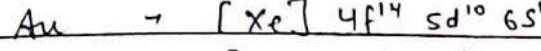
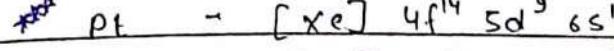
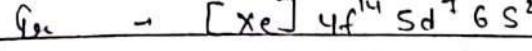
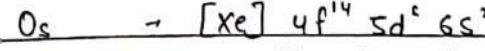
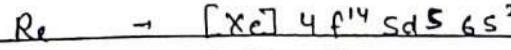
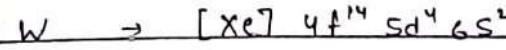
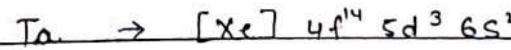
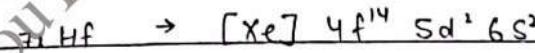
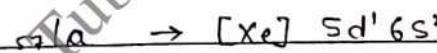
Electronic Configuration :-

4d Series :-



Note: Te (Technetium) does not found on earth.

5d Series :-



3) Atomic Radius:- On moving left to right in transition series radius is decreases but in last element it increases slightly.

Atomic Radius

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1.62	1.45	1.34	1.29	-	1.24	1.25	1.28	1.34	1.41
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1.69	1.44	1.94	1.30	1.28	1.26	1.26	1.29	1.34	1.44

Comparative Study :-

① B/w 3d and 4 d transition series sizes of 4d series elements are greater than 3d series elements becoz on moving top to bottom in a grp, no. of shells increases

② B/w 4d and 5d Ts elements both have similar size because after lanthanum e⁻ enters in 4f subshell and 4f e⁻ have poor shielding effect due to which radius decreases. This phenomenon is known as lanthanoid contraction.

Sizes

$$4d > 3d$$

$$4d \approx 5d$$

	III B	IV B	V B	
3d	Sc	Ti	V	$r_{La} > r_Y > r_{Sc}$ ($n \uparrow, r \uparrow$)
4d	Y	Zr	Nb	$r_{Zn} > r_{Ti}$ ($n \uparrow, r \uparrow$)
5d	La	Hf	Ta	$r_{Zn} \approx r_{Hf}$ (due to lanthanoid contraction)

③ Oxidation State :-

4f Series :

V	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3 (+3)	(+2)	+2	-	+2	+2	+2	+2	+1	
+1 (+3)	+3	-	+3	+3	(+3)	(+2)		+2	
(+4)	+4	(+4)	+4	+4	+4	+4			
+5	+5	(+5)	(+5)						
+6 (+6)		(+6)							
+7 (+7)									
(+8)									

5d Series :

La	Hf	Ta	W	Ru	Ox	Cr	Pr	Tc	Hg
+3 (+3)	(+2)	+2	(+1)	+2	+2	+2	+2	+1	+1
+4 (+3)	(+3)	(+3)	(+2)	+3	+3	(+3)	+4	+4	+2
(+4)	+4	+3	+3	+4	+4	+4	+4	+3	
+5 +5	+5	+4	+4	+6	(+6)				
+6 (+6)				+8					

() Rare Oxidation state

IInd and IIIrd T.S. shows higher O.S. This can be explained on the basis of that 4d and 5d orbitals are more spread out in space than the 3d orbital. This leads to smaller inter electronic repulsion and increasing nuclear charge makes closer approach.

the ligand orbital or metal orbital in complexes
that's why these ~~as~~ elements shows higher O.S.

	IV B	V B	VI B	VII B	VIII		IB	
3d	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	+4	+5	+3	+2	+2, +3	+2, +3	+2	+2
4d	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Rh
	+4	+5	+6	+4, +7	+3	+3	+2	+1
5d	Hf	Ta	W	Re	Os	Ir	Pt	Au
	+4	+5	+6	+3, +4, +7	+8	+3 +4	+2 +4	+3

For 1st T.S. +2, +3 or O.S are important but for 4d & 5d series higher O.S are important hence element form complex anion of higher O.S which are highly stable and have less tendency to undergo reduction while simple anions of 1st T.S elements are easily reduced for e.g. Molybdate (MoO_4^{2-}), Tungstate (WO_4^{2-}) are sufficient stable while chromate ion behave as a strong O.S agent (greater tendency to reduce in Cr^{+3})

2 Perchlorate $[\text{TcO}_4]^-$, Peroxate $[\text{ReO}_4]^-$ ion are stable but per manganate ion MnO_4^- act as strong Oxidising agent (greater tendency to reduce in Mn^{+2})

Stereochemistry of ~~1st~~ 2nd and 3rd T.S Elements:-

In stereochemistry we deal with the relative arrangement of atoms or groups in 3-d space around a central atom. such type of arrangement is mainly deter-

missed by C.N. For a particular C.N. some specific arrangement are prefer becos for such arrangement repulsion b/w the grp. is minimum.

for 1st T.S. 4, 6 co-ordination no. is common whereas for the 2nd and 3rd T.S. 7 & 8 is common.

C.N.

Geometry (Arrangement of atoms
of atom around central)

2

Linear

3

Trigonal planar

4

Tetrahedral / Square planar

5

Trigonal bipyramidal

6

Square bipyramidal

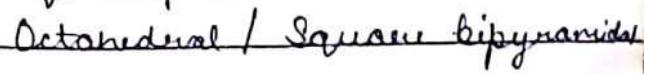
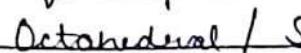
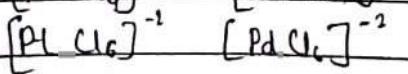
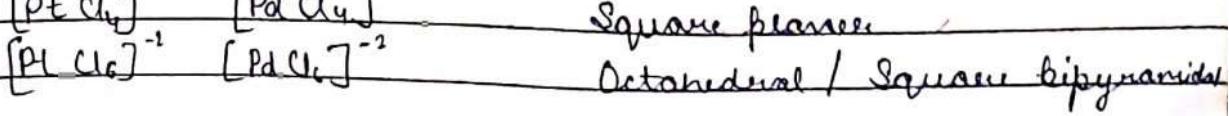
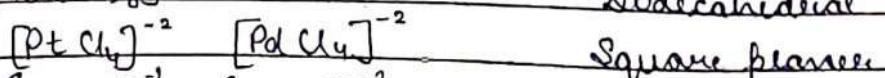
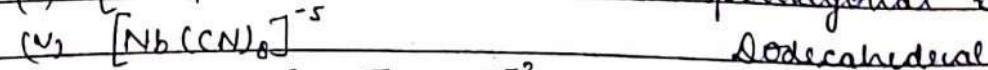
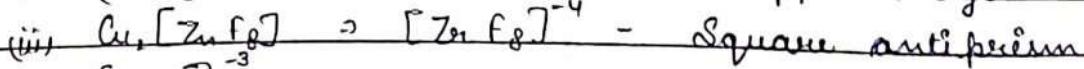
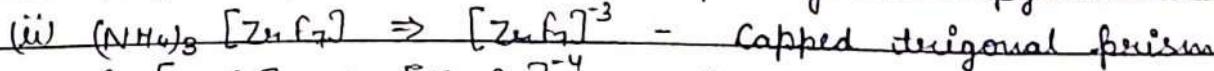
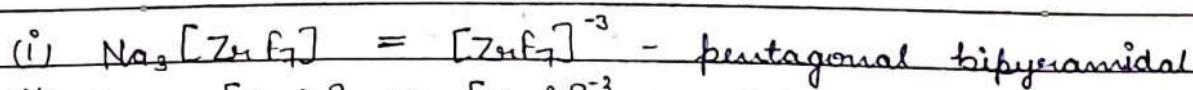
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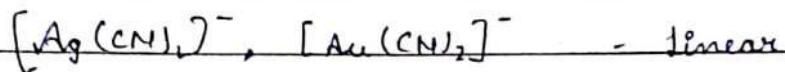
Pentagonal bipyramidal

8

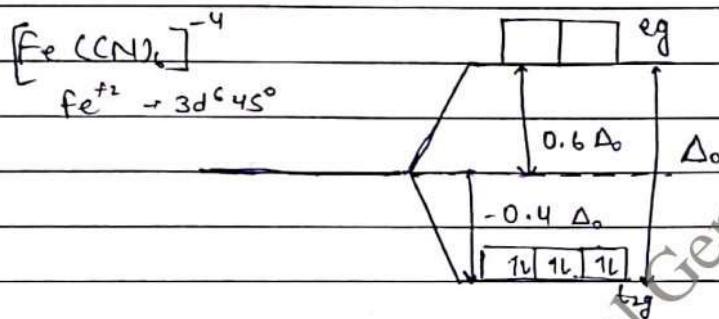
Dodecahedral

As we knew that size decreases with the increase in atomic no. that's why the elements present in the beginning of a series have higher co-ordination no. and the elements present on the right side becomes so small that the structure of lower co-ordination no. becomes more stable.



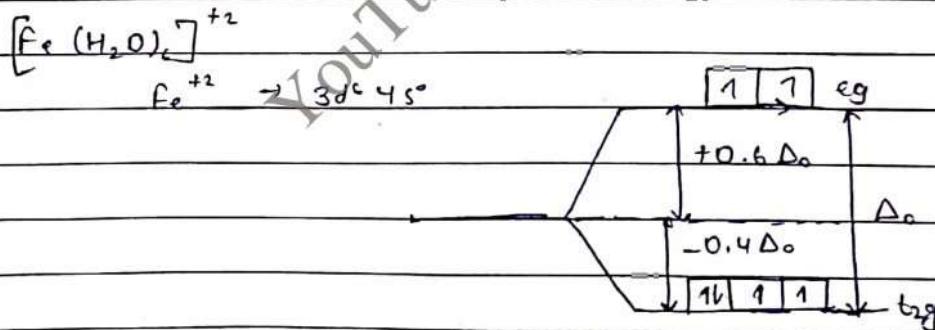


Magnetic Property :- For 1st T.S. in complex formation ligand field is highly important if ligand is SFL then pairing of e⁻ take place and low spin complex will be formed and if ligand is WFL then pairing of e⁻ can't take place and high spin complex will be form.



CN⁻ is SFL $\Delta_o > \pi$ (pairing Energy)

No. of unpaired e⁻ is zero (low spin complex)
Complex is diamagnetic



H₂O is WFL

$$\Delta_o < \pi$$

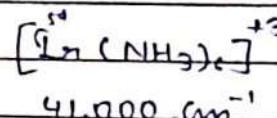
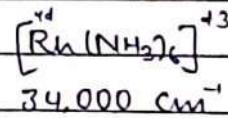
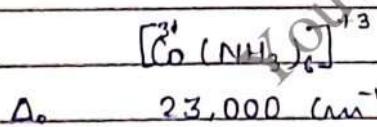
No. of unpaired e⁻ 4 (High spin Complexes)
Complex is paramagnetic

Low spin complexes are those in which no. of unpaired e^- are minimum, while high spin complexes are those in which no. of unpaired e^- are maximum.

2^{nd} and 3^{rd} T.S elements does not have effect of ligand field and always form low spin complexes due to following two reasons-

① pairing energy (π) is lower for 2^{nd} and 3^{rd} Transition elements than that of 1^{st} T.S. This is because $4d$ & $5d$ orbitals are larger than $3d$ orbitals. Due to more space the inter-electronic repulsion between e^- is significantly less as a result pairing energy is lower.

② The splitting of d-orbital due to the field produced by a given set of ligand is larger for $5d$ orbital than that of $4d$ orbital and in both cases larger splitting than for $3d$ orbitals.



For the 2^{nd} and 3^{rd} Transition element the orbital contribution is not only significant and in addition spin orbit coupling may occur and more complicated eqn must be used. Thus the simple interpretation of Magnetic moments in terms of the no. of unpaired e^- can not be applied for 2^{nd} and 3^{rd} T.S elements.

The 2nd and 3rd Transition series elements also show expensive temp. dependent paramagnetism. This is explain by the spin orbit coupling which removes the degeneracy from the lower energy level in the ground state.

Metal-Metal Bonding and Clusture Compounds:

Metal-Metal bonding take place not only in the metal but also in some compounds. Metal-Metal bonding is quite rare in the 1st T.S. elements. It occurs only in few carbonyl compounds like as $[\text{Mn}(\text{CO})_{10}]$, $[\text{Co}_2(\text{CO})_8]$, $[\text{Fe}(\text{CO})_5]$, $[\text{Co}_3(\text{CO})_8]$, $[\text{Fe}_3(\text{CO})_{12}]$ and in carboxylate complexes such as chromium $[\text{Cr}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})]$ etc.

But in the 2nd and 3rd T.S elements metal-Metal bond are much more common.

1] They form carbonyls with M-M bonds similar to those from the 1st T.S such as $[\text{Ru}_2(\text{CO})_{12}]$, $[\text{Os}_2(\text{CO})_{12}]$, $[\text{Rh}_2(\text{CO})_{12}]$ or $[\text{Ir}_2(\text{CO})_{12}]$, $[\text{Rh}_4(\text{CO})_{12}]$ and a type not formed by 1st T.S. is $[\text{Rh}_6(\text{CO})_{16}]$.

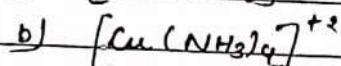
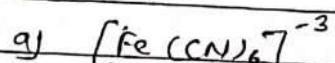
2] The metals Mo, Ru and Rh form binuclear carboxylate complexes such as $[\text{Mo}_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2]$

3] $[\text{ReCl}_6]^{3-}$ and $[\text{Mo}_2\text{Cl}_9]^{3-}$ also have M-M bond. The lower halides of several elements have a group of 3 or 6 metal atom bonding together and are known as clusture compound. These elements are following.

Nb, Mo, Ta, W, Re

Eg.: $[Nb_6 Cl_{10}]^{+5}$ and $[Ta_6 Cl_{10}]^{+5}$ have uncommon structures. Both contains 6 metal atom arranged in a clusters at the corners of an octahedron with 1 \times bridging halogen atom across the corners and there is expensive σ -M-M bonding with in the octahedron.

Q) Calculate the no. of unpaired e^- in the following ions



Ans) $[Fe(CN)_6]^{-3}$



in free state

1	1	1	1	1	4s	4p
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in complex form

3d

d²sp³



in free state

3d

4s

4p

1L	1L	1L	1L	1L	1	1	1	1
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in complex

dsp²

one unpaired e^-