

## d- Block Elements

### Short Answer Questions:

**\*\*1. Explain Werner's theory of coordination compounds with suitable examples**

**A: The important postulates of Werner's theory are:**

i) In coordination compounds the metal atom exhibit two types of valency

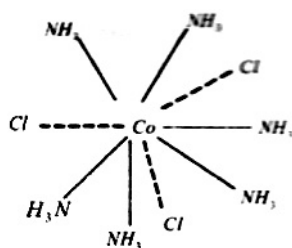
a) Primary valency b) secondary valency

Primary valency corresponds to oxidation state of the metal ion. This is also called principle (or) ionisable (or) ionic valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines. Primary valency is non directional, secondary valency is also termed as coordination number of the central metal ion. It is non ionic or non ionisable. This is satisfied by ligands. The ligands are directly attached to the central metal ion/atom and shown by thick line. Metal ion and ligands are placed in the coordination sphere. The ligands are directed towards the fixed positions in space about the central metal ion. This leads to definite geometry of the co-ordination compounds

ii) Every metal atom/ion has a fixed number of secondary valencies i.e. it has a fixed coordination number

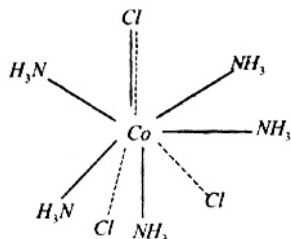
iii) The metal atom tends to satisfy both primary and secondary valencies. In order to meet this requirement a negative ion may show dual behavior i.e. it may satisfy both primary and secondary valencies.

a)  $CoCl_3 \cdot 6NH_3$  This compound on ionisation gives three chloride ions. Thus primary valency is satisfied by  $3Cl^-$ . It has six secondary valencies



b)  $CoCl_3 \cdot 5NH_3$ , This on ionisation gives two chloride ions

∴ Primary valency is two and is satisfied by  $2Cl^-$ . Secondary valency is six ( $5NH_3$  & one  $Cl^-$ ) this  $Cl^-$  ion exhibits dual character



**\*2. What is lanthanide contraction? What are the consequences of lanthanide contraction?**

A: The gradual decrease in the atomic and ionic sizes of lanthanides with increase in atomic number due to poor shielding effect of 4f-orbitals is called lanthanide contraction

Consequences of lanthanide contraction

i) There is similarity in the properties of second and third transition series

**Ex:** Zr and Hf have similar size

ii) Separation of lanthanides is difficult due to lanthanide contraction

iii) Due to lanthanide contraction the basic strength of lanthanide hydroxides decreases

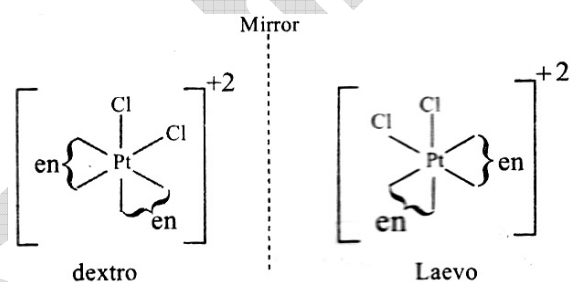
from  $La(OH)_3$  to  $Lu(OH)_3$

**\*3. Explain optical structural isomerism exhibited by coordination compounds, giving suitable examples?**

A:

**Optical Isomerism:** Some complexes which can have non-superimposable mirror image can exhibit optical isomerism. Dextro isomer rotates plane of polarised light towards right and laevo isomer rotates plane of polarised light towards left

Eg:  $[Pt(en)_2Cl_2]^{+2}$



## Structural Isomerism:

**1.Linkage isomerism;** Linkage isomerism arises in a coordination compound containing ambidentate ligand,  $NCS^-$  which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN.

**E.g.:**  $[Co(NH_3)_5(NO_2)]Cl_2$ , (red form) in this the nitrite ligand is bound through nitrogen ( $-NO_2$ )  
And  $[Co(NH_3)_5(ONO)]Cl_2$  (yellow form) in which the nitrite ligand is bound through oxygen, ( $-ONO$ ),

## 2. Coordination Isomerism?

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

**E.g.:**  $[Co(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_6][Co(CN)_6]$

## 3. Ionization Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

**E.g.:**  $[Co(NH_3)_5SO_4]Br$  and  $[Co(NH_3)_5Br]SO_4$  are ionization isomers.

## \*4. Explain geometrical isomerism in coordination compounds giving suitable examples?

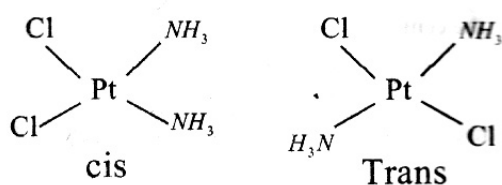
**A:** This type of isomerism arises due to different possible geometric arrangements of ligands. Complexes with co-ordination number '4' having tetrahedron geometry don't show geometrical isomerism

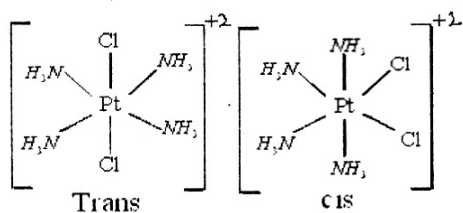
Square planar complexes with  $Ma_2b_2$ ,  $Ma_2bc$ ,  $Mabcd$  exhibits geometrical isomerism. Octahedron complexes like  $Ma_4b_2$ ,  $Ma_3b_3$ ,  $M(aa)_2b_2$  also exhibits geometrical isomerism

If similar ligands are adjacent to each other it is called as cis-isomer

If similar ligands are opposite to each other, it is called as trans-isomer

**E.g.:** i)  $[Pt(NH_3)_2Cl_2]$





**\*5. Write the characteristic properties of the transition elements?**

**Ans.** Transition elements exhibit the following characteristics due to presence of incomplete (n-1) d-orbitals

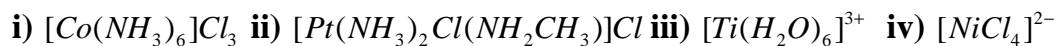
- 1) They are hard and show high melting and boiling points,
- 2) They are good conductors of heat and electricity,
- 3) They show Variable oxidation states,
- 4) They show Paramagnetic and ferromagnetic nature,
- 5) Formation of hydrated coloured ions and alloys
- 6) Formation of Complex compound forming ability,
- 7) They show Catalytic property.

**6. Using IUPAC norms write the formulas for the following**

- i) Tetra hydroxo zinacate (II)
- ii) Hexaammincobalt (III) sulphate
- iii) Potassium tetrachloropalladate (II) and
- iv) Potassium tri (oxalato) chromate (III)

- A:**
- i) Tetrahydrozincate (II) :  $[Zn(OH)_4]^{-2}$
  - ii) Hexaammincobalt (III) sulphate :  $[Co(NH_3)_6]_2(SO_4)_3$
  - iii) Potassium tetrachloro palladate (II):  $K_2[PdCl_4]$
  - iv) Potassium tri (oxalato) chromate (III):  $K_3[Cr(C_2O_4)_3]$

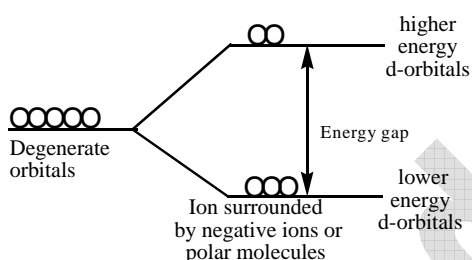
7. Using IUPAC norms write the systematic names of the following



- A: i)  $[Co(NH_3)_6]Cl_3$  ; hexaamine cobalt (III) chloride  
 ii)  $[Pt(NH_3)_2]Cl(NH_2CH_3)]Cl$  : diammine chloro methyl amine platinum (II) chloride  
 iii)  $[Ti(H_2O)_6]^{3+}$  : hexa aqua titanium (III) ion  
 iv)  $[NiCl_4]^{2-}$  : tetrachloro nickelate (II) ion

\*8. Why does the transition metal ions exhibit characteristic colours in aq. solution? Give example?

Ans. The colour of the hydrated transition metal ions and compounds may be attributed to the presence of unpaired d-electrons. In the gaseous state or isolated state of metal ion, all the five d-orbitals in a subshell are degenerate. But under the influence of anions in the compound or of water molecules in the hydrated metal ion, five degenerate orbitals are splitted into two sets of d-orbitals having different energies.

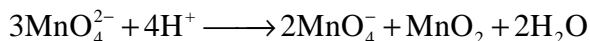
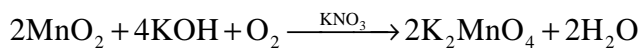


The excitation of electrons from a set of d-orbitals having less energy to another set of d-orbitals having high energy within the same d-subshell is called d-d transition. The amount of energy required for d-d transition is equal to the energy of any one of the colours in white light. Therefore, when white light falls on a hydrated transition metal ion having at least one unpaired d-electron, it absorbs a characteristic colour from visible region for d-d transition and transmit the complementary colour.

For example,  $[Ti(H_2O)_6]^{3+}$  has one 3d electron. It absorbs green and yellow light from visible region and transmits a mixture of red and violet light. Hence hydrated  $Ti^{3+}$  ion has purple colour.

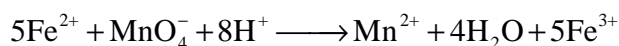
\*9. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron (II) ions; (ii) SO<sub>2</sub> (iii) oxalic acid?

**Ans. Preparation of KMnO<sub>4</sub>:** Potassium permanganate is prepared by the fusion of MnO<sub>2</sub> with an alkali metal hydroxide and an oxidising agent like KNO<sub>3</sub>. It forms dark green K<sub>2</sub>MnO<sub>4</sub> which disproportionates in a neutral or acidic solution to give permanganate.

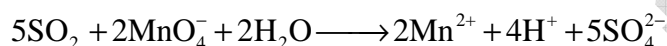


(b) Reactions of KMnO<sub>4</sub> in acidic medium

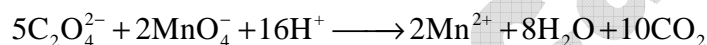
(i) **Iron (II) ions:** Ferrous is oxidised to ferric.



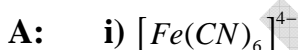
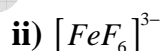
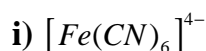
(ii) **SO<sub>2</sub> :** It is oxidised to SO<sub>4</sub><sup>2-</sup> by acidified KMnO<sub>4</sub>.



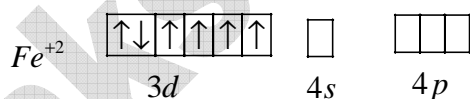
iii. **Oxalic acid:** It is oxidised to CO<sub>2</sub> by acidified KMnO<sub>4</sub>



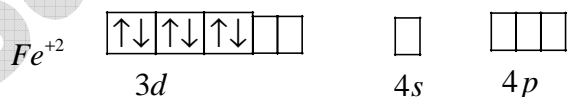
10. Discuss the nature of bonding and magnetic behavior in the following coordination entities on the basis of valence bond theory



In this complex, iron present as

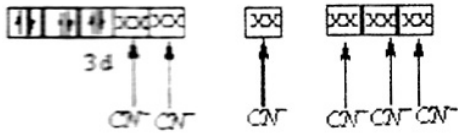


Under the influence of CN<sup>-</sup>, in 3d – of Fe<sup>+2</sup> rearranges as



One 4s, three 4p and two 3d empty orbitals of Fe<sup>+2</sup> intermixes and forms six d<sup>2</sup>sp<sup>3</sup> hybrid orbitals. These six hybrid orbitals arrange in octahedron manner around Fe<sup>+2</sup>

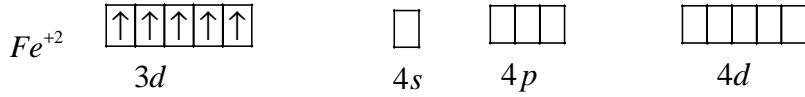
These empty hybrid orbitals overlaps axially with six orbitals of carbon of CN<sup>-</sup> having two e<sup>-</sup> forming six σ bonds



As there are no unpaired  $e^-$ , this complex is diamagnetic

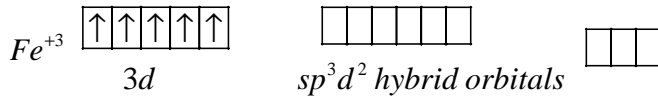
ii)  $[FeF_6]^{3-}$

In this complex iron present as



Approaching  $F^-$  can't make  $Fe^{+3}$  to rearrange it's  $d-e^-$

For providing six empty orbitals to accept lone pairs from six  $F^-$ ,  $Fe^{+3}$  intermixes one 4s, three 4p and two 4d empty orbitals to form six  $sp^3d^2$  hybrid orbitals



These empty hybrid orbitals overlaps with '2p' orbitals of  $F^-$  having two  $e^-$  axially to form six  $\sigma$  bonds

$[FeF_6]^{3-}$



Due to presence of 5 unpaired  $e^-$ , this complex is paramagnetic

## Very Short Answer Questions

**1. Calculate the 'spin only' magnetic moment of  $\text{Fe}^{2+}(\text{aq})$  ion ?**

**Ans.** Electronic configuration of Fe ( $Z = 26$ ) is  $[\text{Ar}] 3d^6 4s^2$ .

Electronic configuration of  $\text{Fe}^{2+} = [\text{Ar}] 3d^6$ .

Four unpaired electrons are present in  $\text{Fe}^{2+}(\text{aq})$  ion, i.e.,  $n = 4$ . Applying 'spin only' formula for magnetic moment.

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.83 \text{ BM}$$

**2. Write the electronic configuration of chromium and copper?**

**Ans.** Electronic configuration of Cr ( $Z=24$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$  or  $[\text{Ar}] 3d^5 4s^1$ .

Electronic configuration of Cu ( $Z=29$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  or  $[\text{Ar}] 3d^{10} 4s^1$ .

**3. Why are  $\text{Mn}^{+2}$  compounds more stable than  $\text{Fe}^{+2}$  towards oxidation to their +3 state?**

**Ans.**  $\text{Mn}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$  (half-filled d-orbital)

$\text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

$\text{Mn}^{2+}$  compounds are more stable due to half-filled d-orbitals.  $\text{Fe}^{2+}$  compounds are comparatively less stable as they have six electrons in their 3d-orbital. So, they tend to lose one electron (form  $\text{Fe}^{3+}$ ) and get stable  $3d^5$  configuration.

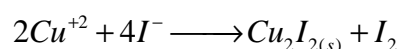
**4. Why do transition elements exhibit more than one oxidation state?**

**Ans.** Transition elements exhibit more than one oxidation state because the inner d-electrons

i.e.  $(n-1)d$  involve in bonding along with outer i.e.  $nS$  electrons as the energy gap between  $(n-1)d$  and  $nS$  is less.

**5.  $\text{Cu}^{II}$  forms halides like  $\text{CuF}_2$ ,  $\text{CuCl}_2$ ,  $\text{CuBr}_2$  but not  $\text{CuI}_2$ . Why?**

**Ans.** All  $\text{Cu}^{II}$  halides are known except the iodide because  $\text{Cu}^{+2}$  oxidises  $\text{I}^-$  to  $\text{I}_2$ .





**6. Why  $Zn^{+2}$  is diamagnetic while  $Mn^{+2}$  is paramagnetic?**

**Ans.** Electronic configuration of  $Zn^{+2}$  is  $1s^22s^22p^63s^23p^63d^{10}$

Electronic configuration of  $Mn^{+2}$  is  $1s^22s^22p^63s^23p^63d^5$

$Zn^{+2}$  has no unpaired electrons while  $Mn^{+2}$  has 5 unpaired electrons. Hence  $Zn^{+2}$  is diamagnetic and  $Mn^{+2}$  is paramagnetic.

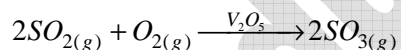
**7. Aqueous  $Cu^{+2}$  are blue in colour where as  $Zn^{+2}$  ions are colourless?**

**Ans.** Electronic configuration of  $Cu^{+2}$  is  $1s^22s^22p^63s^23p^63d^9$ . It has one unpaired electron. Thus hydrated cupric ion ( $Cu^{2+}$ ) absorbs orange red light from visible region and transmits its complementary colour greenish blue during d-d transition. Hence aqueous  $Cu^{+2}$  ions are in blue colour.  $Zn^{+2}$  ions are colourless as there is no unpaired electron.

**8. How do transition elements exhibit catalytic activity?**

**Ans.** The catalytic activity of transition metals is due to their ability to adopt multiple oxidation states and to form complexes.

**E.g.:** In contact process for the manufacture of sulphuric acid, vanadium pent oxide is used as catalyst to oxidise sulphur dioxide to sulphur trioxide.



This reaction takes place in two steps. In the first step  $SO_2$  is oxidised to  $SO_3$  and  $V^{5+}$  is reduced to  $V^{4+}$ . In the second step  $V^{4+}$  oxidised to  $V^{5+}$ .

**9. What is an alloy? Give an example?**

**Ans.** An intimate mixture having physical properties similar to that of the metal, formed by a metal with other metals or metalloid or sometimes a nonmetal, is called an alloy.

**E.g.:** Brass (copper and zinc), bronze (Cu+Sn)

**10. What is mischmetal? Give its composition and uses?**

**Ans.** An alloy containing lanthanide metal (~95%), iron (~5%), traces of S, C, Ca and Al is mischmetal. It is **used** in Mg-based alloy to produce bullets, shell and lighter flint.



15.  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. Why?

**Ans.** In both the complex compounds, Fe is in +2 oxidation state with configuration  $3d^6$ , i.e., it has four unpaired electrons. In the presence of weak  $\text{H}_2\text{O}$  ligands, the unpaired electrons do not pair up. But in the presence of strong ligand  $\text{CN}^-$ , they get paired up. Then no unpaired electron is left. Due to this difference in the number of unpaired electrons, both complex ions have different colours.

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