

## d, f-BLOCK ELEMENTS & COORDINATION COMPOUNDS

### d-BLOCK ELEMENTS

#### INTRODUCTION

- \* In the long form of periodic table elements are classified based on electronic configuration. The elements which are classified between 's' & 'p' block are 'd' block elements or Transition elements. In these elements the differentiating electron enters in the 'd' orbitals of penultimate shell.
- \* General configuration for 'd' block elements is  $ns^{1-2} (n-1)d^{1-10}$ . i.e., in 'd' block elements the valence shell has constant number of electrons whereas the number of electron in penultimate shell go on increasing.
- \* Elements which have atleast one unpaired electron in their 'd' orbital in atomic or any oxidation state are called as Transition elements. Thus all transition elements are 'd' block elements but all 'd' block elements may not be transition elements or the elements having incompletely filled 'd' orbitals are called as transition elements.
- \* Transition elements are classified between 's' and 'p' blocks from fourth period onwards.
- \* Series of transition elements are four  
**1<sup>st</sup> Series** - They are classified in fourth period and are called as '3d' series of elements. Their atomic numbers are 21(Sc) to 30 (Zn).  
**2<sup>nd</sup> Series**- They are classified in fifth period and are called as '4d' series of elements. Their atomic numbers are 39(Y) to 48(Cd).  
**3<sup>rd</sup> series**- They are classified in sixth period and are called as '5d' series of elements. Their atomic numbers are 57(La), 72(Hf) to 80(Hg)  
**4<sup>th</sup> Series** - They are classified in the seventh period and are called as '6d' series of elements. This is an incomplete series. Their atomic numbers are 89(Ac), 104(Ku) to 112 (Uub).
- \* Electronic configuration of first series of transition elements.

Atomic number	Element	Symbol	Electronic configuration
21.	Scandium	Sc	$[\text{Ar}] 4s^2 3d^1$
22.	Titanium	Ti	$[\text{Ar}] 4s^2 3d^2$
23.	Vanadium	V	$[\text{Ar}] 4s^2 3d^3$
24.	Chromium	Cr	$[\text{Ar}] 4s^1 3d^5$
25.	Manganese	Mn	$[\text{Ar}] 4s^2 3d^5$
26.	Iron	Fe	$[\text{Ar}] 4s^2 3d^6$
27.	Cobalt	Co	$[\text{Ar}] 4s^2 3d^7$
28.	Nickel	Ni	$[\text{Ar}] 4s^2 3d^8$
29.	Copper	Cu	$[\text{Ar}] 4s^1 3d^{10}$
30.	Zinc	Zn	$[\text{Ar}] 4s^2 3d^{10}$

- \* Chromium and copper are elements having exceptional electronic configurations of  $[\text{Ar}] 4s^1 3d^5$  and  $[\text{Ar}] 4s^1 3d^{10}$  instead of  $[\text{Ar}] 4s^2 3d^4$  and  $[\text{Ar}] 4s^2 3d^9$
- \* Zn (30) is  $[\text{Ar}] 4s^2 3d^{10}$   
 Cd (48) is  $[\text{Kr}] 5s^2 4d^{10}$   
 Hg (80) is  $[\text{Xe}] 6s^2 4f^{14} 5d^{10}$   
 These three elements do not have any unpaired electrons in their 'd' orbitals in atomic as well as in ionic states. Therefore they are only classified as 'd' block elements and not as transition elements. Copper, Silver and Gold, the elements of IB group i.e., coinage metals, have  $ns^1 (n-1)d^{10}$  configuration. They are transition elements as in their higher oxidation state they have an unpaired electron in their 'd' orbitals.

#### GENERAL PROPERTIES OF D-BLOCK ELEMENTS

- \* All the elements of '3d' series are good reducing agents except copper.
- \* In general the reactivity of transition elements is less. Their reactivity decreases with increase in atomic number. The atomic radii of transition elements decrease by negligible amounts due to the shielding of valence shell electrons, provided by electrons of 'd' orbitals of penultimate shell.
- \* The ionisation potential of transition elements increase by negligible amounts due to shielding effect.

#### Metallic Character :

- \* All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- \* They are hard malleable and ductile. IB group elements Cu, Ag and Au are most ductile and soft.
- \* These are good conductor of heat and electricity (due to free  $e^-$ ) IB gp. elements are most conductive in nature. Their order of conductivity is :  $\text{Ag} > \text{Cu} > \text{Au} > \text{Al}$ .

#### Atomic size :

- \* Atomic and ionic radii of d-block elements is smaller than s-block elements
- \* Atomic radii depends on effective nuclear charge ( $Z_{\text{eff}}$ ) and screening effect (SE).
- \* In 3d series  
 $\text{Sc} \rightarrow \text{Cr} (Z_{\text{eff}} > \text{SE}) \therefore$  radius decreases  
 $\text{Mn} \rightarrow \text{Ni} (Z_{\text{eff}} = \text{SE}) \therefore$  radius remains constant  
 $\text{Cu} \rightarrow \text{Zn} (Z_{\text{eff}} < \text{SE}) \therefore$  radius increases
- \* In dipositive ions of 3d series  $\text{Cu}^{+2}$  is the smallest in size.
- \* The elements of 4d and 5d series belongs to a particular group have almost same atomic radii. This is due to Lanthanide contraction. e.g.  $\text{Zr} \approx \text{Hf}$ ,  $\text{Tc} \approx \text{Re}$ ,  $\text{Nb} \approx \text{Ta}$ ,  $\text{Ru} \approx \text{Os}$  etc.

- \* In d-block elements  
Largest atomic radii - La  
Smallest atomic radii - Ni
- \* In III B group order of atomic radii is  
Sc < Y < La (No lanthanide contraction)

**Density :**

- \* The atomic volume of the transition elements are low compared with s-block, so their density is comparatively high ( $D = M/V$ )
- \* Except Sc, Y and Ti, all the d-block elements have density greater than  $5 \text{ gm cm}^{-3}$
- \* Os ( $22.57 \text{ gm cm}^{-3}$ ) and Ir ( $22.61 \text{ gm cm}^{-3}$ ) have highest density.
- \* In all the groups there is normal increase in density from 3d to 4d series, and from 4d to 5d it increases just double it is due to lanthanide contraction.
- \* In 3d series : Sc  $\rightarrow$  Cr density increases  
Mn, Fe, Co, Ni  $\rightarrow$  almost constant ; Cu  $\rightarrow$  Zn decreases
- \* In 3d series highest density - Cu ; lowest density - Sc
- \* Some important orders of density  
Fe < Ni < Cu ; Fe < Cu < Au ; Fe < Hg < Au

**Melting and boiling points :**

- \* M.P. and b. p. of d-block > s-block (the reason is stronger metallic bond and presence of covalent bond formed by unpaired d-electrons.)
- \* In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond, their m.p. and b.p. are very low. (Volatile metals Zn, Cd, Hg)
- \* In 3d series  
Sc  $\rightarrow$  Cr m.p. b.p increases  
Mn  $\rightarrow$  Zn m.p. b.p decreases
- \* Mn and Tc possess comparatively low m.p., it due to stable configuration 'Half filled'
- \* Lowest mp Hg -  $38^\circ\text{C}$  ; Highest mp. W  $\approx 3400^\circ\text{C}$

**Trends in the  $M^{2+}/M$  Standard Electrode Potentials**

Electrode potentials ( $E^\circ$ ) : Standard electrode potentials of some half-cells involving 3d-series of transition elements and their ions in aqueous solution are given in table.

**Standard electrode potentials for 3d-elements**

Elements	Ion	Electrode reaction	$E^\circ$ / volt
Sc	$\text{Sc}^{3+}$	$\text{Sc}^{3+} + 3e^- \rightarrow \text{Sc}$	- 2.10
Ti	$\text{Ti}^{2+}$	$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	- 1.60
V	$\text{V}^{2+}$	$\text{V}^{2+} + 2e^- \rightarrow \text{V}$	- 1.20
Cr	$\text{Cr}^{3+}$	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	- 0.71
Mn	$\text{Mn}^{2+}$	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	- 1.18
Fe	$\text{Fe}^{2+}$	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	- 0.44
Co	$\text{Co}^{2+}$	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	- 0.28
Ni	$\text{Ni}^{2+}$	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	- 0.24
Cu	$\text{Cu}^{2+}$	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+ 0.34
Zn	$\text{Zn}^{2+}$	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	- 0.76

- \* The unique behaviour of Cu, having a positive  $E^\circ$ , accounts for its inability to liberate  $\text{H}_2$  from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to  $\text{Cu}^{2+}(\text{aq})$  is not balanced by its hydration enthalpy.
- \* The general trend towards less negative  $E^\circ$  values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.

**Trends in the  $M^{3+}/M^{2+}$  Standard Electrode Potentials**

- Standard electrode potential  $M^{3+}/M^{2+}$  : Ti = - 0.37, V = -0.26, Cr = -0.41, Mn = +1.57, Fe = +0.77, Co = +1.97.
- \* The low value for Sc reflects the stability of  $\text{Sc}^{3+}$  which has a noble gas configuration.
  - \* The highest value for Zn is due to the removal of an electron from the stable  $d^{10}$  configuration of  $\text{Zn}^{2+}$ .
  - \* The comparatively high value for Mn shows that  $\text{Mn}^{2+}(d^5)$  is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $\text{Fe}^{3+}(d^5)$ .

**Chemical Reactivity and  $E^\circ$  Values :**

- \* The metals of the first series with the exception of copper are relatively more reactive.
- \* The  $E^\circ$  values for  $M^{2+}/M$  indicate a decreasing tendency to form divalent cations across the series, general trend towards less negative  $E^\circ$  values is related to the increase in the sum of the first and second ionisation enthalpies.

**Characteristic properties of transition elements are**

- Variable oxidation state
- Coloured ions
- Paramagnetic properties
- Catalytic properties
- Formation of alloys
- Formation of interstitial compounds and
- Formation of complexes.

**(a) Variable valency or variable oxidation states:**

- \* The oxidation states of all transition elements of '3d' series are as follows

Sc	[Ar] $4s^2 3d^1$		+3		
Ti	[Ar] $4s^2 3d^2$	(+2)	+3	+4	
V	[Ar] $4s^2 3d^3$	+2	+3	+4	+5
Cr	[Ar] $4s^1 3d^5$	(+1)	+2	+3	(+4) (+5)
					+6
Mn	[Ar] $4s^2 3d^5$	+2	+3	+4	(+5) (+6)
					+7
Fe	[Ar] $4s^2 3d^6$	+2	+3	(+4)	(+5) (+6)
Co	[Ar] $4s^2 3d^7$	+2	+3	+4	
Ni	[Ar] $4s^2 3d^8$	+2	(+3)	(+4)	
Cu	[Ar] $4s^1 3d^{10}$	+1	+2		

[Oxidation States in brackets is/are unstable.]

- \* Highest oxidation state of transition elements can be calculated by =  $n + 2$  ( $n$  = no. of unpaired  $e^-$ ) (It is not applied for Cr and Cu).
- \* The transition metal ions having stable configuration are stable.

Metal ions of '3d' series having 3d<sup>0</sup> configuration Sc<sup>+3</sup>, Ti<sup>+4</sup> and V<sup>+5</sup> etc are stable.

Transition metal ions having 3d<sup>5</sup> configuration are stable like Mn<sup>+2</sup>, Fe<sup>+3</sup>

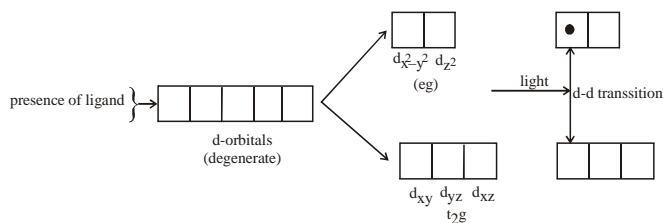
In aqueous medium Cr<sup>+3</sup> is stable.

Co<sup>+2</sup> and Ni<sup>+2</sup> are stable.

- \* Transition metal ion with 3d<sup>10</sup> configuration which is stable is Cu<sup>+1</sup>. In aqueous medium Cu<sup>+2</sup> is more stable than Cu<sup>+1</sup>.
- \* Most common oxidation state among the transition elements is +2.
- \* Highest oxidation state shown by transition elements of '4d' and '5d' series is +8. The elements showing this oxidation state are Ruthenium (44) and Osmium (76).
- \* The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.
- \* In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.  
e.g. in chromate ion CrO<sub>4</sub><sup>-2</sup>, the bonds between Cr and O are covalent.
- \* Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.  
e.g. – Ti<sup>+2</sup>, V<sup>+2</sup>, Fe<sup>+2</sup>, Co<sup>+2</sup> etc are reducing agents  
Cr<sup>+6</sup>, Mn<sup>+7</sup>, Mn<sup>+4</sup>, Mn<sup>+5</sup>, Mn<sup>+6</sup> etc are oxidising agents.

### Colour Property:

- \* Most of the transition metal ions exhibit colour property. This is due to the presence of unpaired electrons in their 'd' orbitals. They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.  
Ti<sup>+2</sup>[Ar]3d<sup>2</sup>, V<sup>+2</sup>[Ar]3d<sup>3</sup> etc.  
These are having unpaired electrons in their 'd' orbitals therefore they are coloured.
- \* Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like 3d<sup>0</sup> and 3d<sup>10</sup> configurations, do not exhibit any colour property.  
e.g., Sc<sup>+3</sup>[Ar]3d<sup>0</sup>, Cu<sup>+1</sup>[Ar]3d<sup>10</sup>, Ti<sup>+4</sup>[Ar]3d<sup>0</sup> etc. are colourless ions.
- \* A transition metal ion absorbs a part of visible region of light and emits rest of the six colours, the combination of which is the colour of emitted light. The colour of metal ion is the colour of the emitted light.
- \* In transition metal ion the 'd' orbitals split into lower energy set t<sub>2g</sub> orbitals and higher energy set eg orbitals. The electrons from t<sub>2g</sub> set get excited to higher energy set i.e., eg set. This excitation of electrons is called as 'd-d' transition. As d-d transition requires less amount of energy they absorb visible region of light. Due to this 'd -d' transition the transition metal ions exhibit colour property.  
Lower energy set = t<sub>2g</sub>  
Higher energy set = eg.



- \* KMnO<sub>4</sub> (dark pink), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (orange) having d<sup>0</sup> configuration are coloured due to charge transfer spectrum.

### Some of the coloured metal ions are as follows :

Ti <sup>+3</sup> - Purple	Cr <sup>+3</sup> - Green
Mn <sup>+2</sup> - Light pink	Fe <sup>+2</sup> - Pale green
Fe <sup>+3</sup> - yellow	Co <sup>+2</sup> - Blue
Ni <sup>+2</sup> - green	Cu <sup>+2</sup> - Blue

### Magnetic properties

- \* Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field.
- \* Ti<sup>+2</sup>[Ar]3d<sup>2</sup>, Ti<sup>+3</sup>[Ar]3d<sup>1</sup>, V<sup>+2</sup>[Ar]3d<sup>3</sup>, Cr<sup>+3</sup>[Ar]3d<sup>3</sup>  
As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having 3d<sup>0</sup> and 3d<sup>10</sup> configuration exhibit diamagnetic nature.
- \* An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning. Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature.
- \* The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using  

$$\mu = \sqrt{n(n+2)}$$
 Where 'n' is the number of unpaired electrons in the metal ion.  
 μ = Magnetic moment in Bohr Magnetons (B.M.)
- \* The magnetic moment of diamagnetic substances will be zero.
- \* As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- \* Transition metal ions having d<sup>5</sup> configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

### Catalytic Property :

- \* Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.

- \* When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- \* Transition metals and their compounds exhibiting catalytic properties in various processes are
  - (i) Fe is used in Haber's process for manufacture of  $\text{NH}_3$ .
  - (ii)  $\text{V}_2\text{O}_5$  is used in contact process for  $\text{H}_2\text{SO}_4$  manufacture
  - (iii) Pt is used in Ostwald's process of nitric acid
  - (iv) Ni is used in hydrogenation of oils
  - (v)  $\text{FeSO}_4$  is used in oxidation of Benzene with  $\text{H}_2\text{O}_2$
  - (vi) Cu is used in dehydrogenation of alcohols
  - (vii)  $\text{TiCl}_4$  is used as catalyst in Vinyl polymerisation.

#### Formation of Alloy :

- \* Transition elements have maximum tendency to form alloys.
- \* The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the Lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
- \* In the alloys ratio of component metals is fixed.
- \* These are extremely hard and have high M.P.

#### Some important Alloy :

1. Bronze - Cu (75 - 90 %) + Sn (10 - 25 %)
2. Brass - Cu (60 - 80 %) + Zn (20 - 40 %)
3. Gun metal - (Cu + Zn + Sn) (87 : 3 : 10)
4. German Silver - Cu + Zn + Ni (2 : 1 : 1)
5. Bell metal - Cu (80%) + Sn (20%)
6. Nichrome - (Ni + Cr + Fe)
7. Alnico - (Al, Ni, Co)
8. Type Metal - Pb + Sn + Sb
9. Alloys of steel
  - (a) Vanadium steel - V (0.2 - 1%)
  - (b) Chromium steel - Cr (2 - 4%)
  - (c) Nickel steel - Ni (3 - 5%)
  - (d) Manganese steel - Mn (10 - 18%)
  - (e) Stainless steel - Cr (12 - 14%) & Ni (2-4%)
  - (f) Tunguston steel - W (10 - 20%)
  - (g) Invar - Ni (36%)
10. 14 Carat Gold - 54% Au + Ag (14 to 30%) + Cu (12 - 28%)
11. 24 Carat Gold - 100% Au
12. Solder - Pb + Sn
13. Magnallium - Mg (10%) + Al (90%)
14. Duralumin - (Al + Mn + Cu)
15. Artificial Gold - Cu (90%) + Al (10%)
16. Constantan - Cu (60%) + Ni (40%)

#### Formation of Interstitial Compounds

- \* Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc. The smaller sized atoms get entrapped in between the interstitial spaces of the metal Lattices.
- \* These interstitial compounds are non stoichiometric in nature and hence cannot be given any definite formula.
- \* The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.

- \* The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.

#### COMPOUNDS OF TRANSITION ELEMENTS

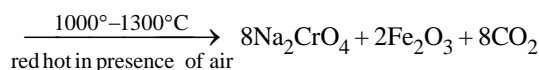
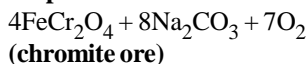
##### Oxides and Oxoanions of Metals

- \* These oxides are generally formed by the reaction of metals with oxygen at high temperatures.
- \* All the metals except scandium form MO oxides which are ionic.
- \* The highest oxidation number in the oxides, coincides with the group number and is attained in  $\text{Sc}_2\text{O}_3$  to  $\text{Mn}_2\text{O}_7$ . Beyond group 7, no higher oxides of iron above  $\text{Fe}_2\text{O}_3$  are known.
- \* As the oxidation number of a metal increases, ionic character decreases. In the case of Mn,  $\text{Mn}_2\text{O}_7$  is a explosive covalent green oil. The oxides of metals in high oxidation states are acidic. For example,  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ ,  $\text{Mn}_2\text{O}_7$  are acidic. Thus,  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$  and  $\text{CrO}_3$  gives  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ .  $\text{V}_2\text{O}_5$  is, however, amphoteric though mainly acidic and it gives  $\text{VO}_4^{3-}$  as well as  $\text{VO}_2^+$  salts. In vanadium there is gradual change from the basic  $\text{V}_2\text{O}_3$  to less basic  $\text{V}_2\text{O}_4$  and to amphoteric  $\text{V}_2\text{O}_5$ . The well characterised CrO is basic but  $\text{Cr}_2\text{O}_3$  is amphoteric. The basic and amphoteric oxides dissolve in one-oxidising acids forming hexaquo ions  $[\text{MCH}_2\text{O}_6]^{n+}$ . A few of these oxides dissolve in acids and bases to form important oxometallic salts. Potassium dichromate, chromate and permanganate are few of the examples.

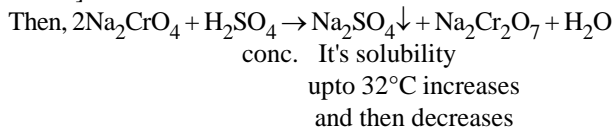
#### POTASSIUM DICHROMATE ( $\text{K}_2\text{Cr}_2\text{O}_7$ ):

Potassium dichromate is one of the most important compound of chromium, and also among dichromates. In this compound, Cr is in the hexavalent (+6) state.

##### Preparation:



[Lime (CaO) added with  $\text{Na}_2\text{CO}_3$  which keeps the mass porous so that air has access to all parts and prevents fusion]



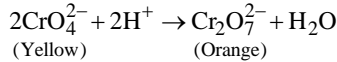
Hence, suitable temp. is to be employed to crystallise out  $\text{Na}_2\text{SO}_4$  first.

Then  $\text{Na}_2\text{Cr}_2\text{O}_7$  is crystallised out as  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (red crystal) on evaporation.

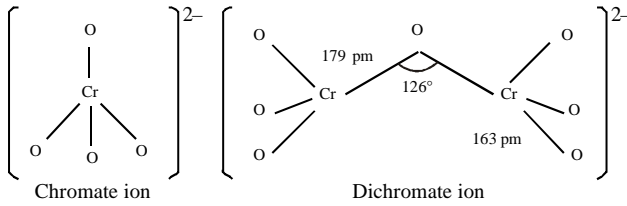
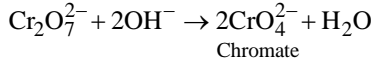
To get  $\text{K}_2\text{Cr}_2\text{O}_7$  :  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{KCl} \xrightarrow[\text{hot conc.}]{\text{double decomposition}} \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$   
NaCl crystallises out first and filtered off. Then  $\text{K}_2\text{Cr}_2\text{O}_7$  crystallised out on cooling.

**Properties :**

- (i) It is orange coloured solid.
- (ii) It is highly soluble in water.
- (iii) The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. In acidic pH, chromate ions get converted into dichromate ions and the colour of the solution becomes orange.

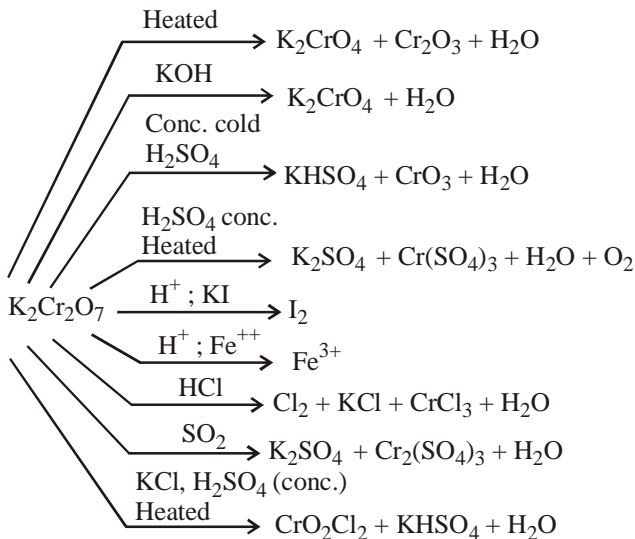
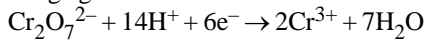
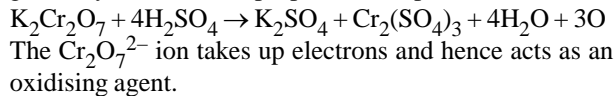


In basic pH, i.e., in presence of  $\text{OH}^-$ , orange coloured dichromate ion gets converted into chromate ion (yellow).

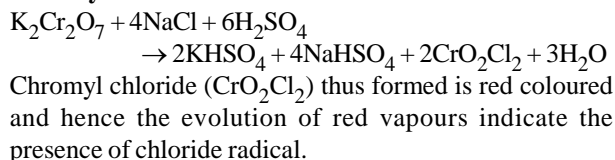


The structure of chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ions

- (iv) Potassium dichromate is a powerful oxidising agent and is generally used for this purpose in the presence of acids.



**\* Chromyl chloride test :**



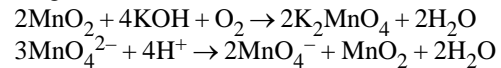
**Uses :** Potassium dichromate finds extensive use in dyeing, calico-printing and chrome-tanning (leather industry). It is used as an oxidising agent and in the preparation of various chromium compounds like  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ . It is also used in photography and in volumetric analysis for the estimation of ferrous salts. A mixture of  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc.  $\text{H}_2\text{SO}_4$ , usually known as chromic acid mixture, has strong oxidising properties and is used as a cleaning agent for glass ware etc.

**POTASSIUM PERMANGANATE,  $\text{KMnO}_4$  :**

It is salt of an unstable acid Permanganic acid. The Mn is in +7 state in this compound.

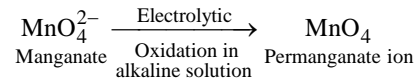
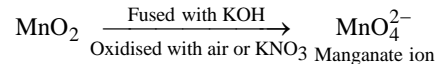
**Preparation :**

Potassium permanganate is prepared by fusion of  $\text{MnO}_2$  with an alkali metal hydroxy and an oxidising agent like  $\text{KNO}_3$ . This produces the dark green  $\text{K}_2\text{MnO}_4$  which disproportionates in a neutral or acidic solution to give permanganate.



**Commercial method of preparation :**

Commercially it is prepared by the alkaline oxidative fusion of  $\text{MnO}_2$  followed by the electrolytic oxidation of manganate (VI).



**Laboratory method of preparation :**

In the laboratory, a manganese (II) is oxidised by peroxodisulphate to permanganate

$$2\text{Mn}^{2+} + 5\text{S}_2\text{O}_8^{2-} + 8\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^- + 10\text{SO}_4^{2-} + 16\text{H}^+$$

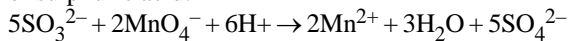
**Properties :**

- \* Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution.
- \* It is isomorphous with potassium perchlorate.
- \* Its solubility in water at  $20^\circ$  is only about 7%, whilst it dissolves more at higher temperatures (25% at  $63^\circ$ ).
- \* It is stored in dark coloured bottles because it gets decomposed in presence of sun light.
- \* Oxidising reaction of  $\text{KMnO}_4$

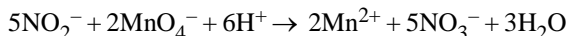
**In acid solutions:**

- (a) Iodine is liberated from potassium iodide :  $10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$
- (b)  $\text{Fe}^{2+}$  ion (green) is converted to  $\text{Fe}^{3+}$  (yellow):  $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
- (c) Oxalate ion or oxalic acid is oxidised at 333 K:  $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
- (d) Hydrogen sulphide is oxidised, sulphur being precipitated:  $\text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S}^{2-}$   
 $5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

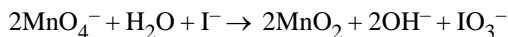


(f) Nitrite is oxidised to nitrate:

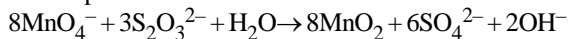


**In neutral or faintly alkaline solutions:**

(a) A notable reaction is the oxidation of iodide to iodate:



(b) Thiosulphate is oxidised almost quantitatively to sulphate:



(c) Manganous salt is oxidised to  $\text{MnO}_2$ ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:



**Uses :** Potassium permanganate is used as a disinfectant and as an oxidising agent. It is valuable volumetric reagent and is used for the estimation of ferrous salts, oxalic acid, hydrogen peroxide, etc. Alkaline  $\text{KMnO}_4$  is used in organic chemistry under the name of Baeyer's reagent.

#### NOTE

- \* Equivalent weight of  $\text{KMnO}_4$  in neutral and in alkaline medium is same i.e. one third of its molecular mass i.e.,  $158/3 = 52.6$
- \* Equivalent weight of  $\text{KMnO}_4$  in acidic medium is one fifth of its molecular mass i.e.,  $158/5 = 31.6$

#### Example 1 :

The transition metals are well-known for the formation of interstitial compounds. Explain.

**Sol.** This is because they have voids in which small atoms C and H can fit forming interstitial compounds.

#### Example 2 :

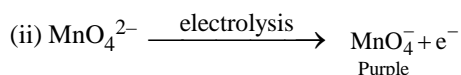
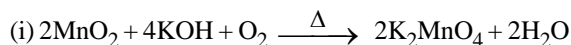
Which element in the first series of transition elements does not exhibit variable oxidation states and why ?

**Sol.** Scandium does not exhibit variable valency. It shows +3 oxidation state only. This is because after losing 3 electrons, it attains stable noble gas structure.

#### Example 3 :

Write chemical equations for the reactions involved in the manufacture of potassium permanganate from pyrolusite ore.

**Sol.** Relevant equations for the manufacture of  $\text{KMnO}_4$  from pyrolusite ore are :



#### Example 4 :

Of the ions  $\text{Co}^{2+}$ ,  $\text{Sc}^{3+}$  and  $\text{Cr}^{3+}$ , which one will give coloured aqueous solutions and how will each of them respond to a magnetic field and why ?

[Atomic numbers of Co = 27, Sc = 21, Cr = 24]

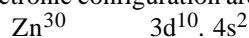
**Sol.**  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  are coloured and attracted in magnetic field whereas  $\text{Sc}^{3+}$  is colourless and repelled by magnetic field. It is because  $\text{Co}^{2+}$  ( $3d^7$ ) and  $\text{Cr}^{3+}$  ( $3d^3$ ) have unpaired electrons and can undergo d-d transitions by absorbing light from visible region.  $\text{Sc}^{3+}$  does not have unpaired electron and cannot undergo d-d transitions.

#### Example 5 :

Zn and Hg do not show variable valency like d-block elements because –

- (A) They are soft
- (B) Their d-shells are complete
- (C) They have only two electrons in the outermost subshell
- (D) Their d-shells are incomplete

**Sol.** (B). Zn and Hg do not show variable valency like d-block elements because their d-shell are complete their electronic configuration are :



The variable valency is shown by those elements which have got incompletely filled d orbital.

#### Example 6 :

The d-block elements easily form alloys because –

- (A) Their d-block are only partly filled.
- (B) They have very widely differing atomic sizes
- (C) They are very similar in their atomic sizes
- (D) They are highly electronegative in character.

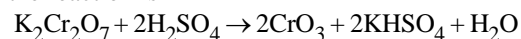
**Sol.** (C). In the case of the transition metals the atomic radii have values which are very close, that is they are of very similar size. Hence the atom of an element in a crystal lattice can easily be replaced by a metal atom of another transition elements. This makes metals form alloys very easily.

#### Example 7 :

A mixture of  $\text{K}_2\text{Cr}_2\text{O}_7$  and conc.  $\text{H}_2\text{SO}_4$  forms –

- (A) perchromic acid
- (B) chromic acid
- (C) chromium sulphate
- (D) chromium oxide

**Sol.** (B). When  $\text{K}_2\text{Cr}_2\text{O}_7$  is dissolved in concentrated  $\text{H}_2\text{SO}_4$ , the reaction is



The mixture is called chromic acid because  $\text{CrO}_3$  is highly acidic.

### TRY IT YOURSELF-1

- Q.1** The lowest melting point metals among transition metals belongs to –
- (A) Group 3
  - (B) Group 11
  - (C) Group 6
  - (D) Group 12
- Q.2** Which of the following oxide is basic?
- (A) CrO
  - (B)  $\text{Cr}_2\text{O}_3$
  - (C)  $\text{CrO}_3$
  - (D)  $\text{Cr}_2\text{O}_4$
- Q.3** d-block elements have tendency for complex formation because of –
- (A) Small size of metal ions

- (B) High ionic charges.  
 (C) Availability of vacant d-orbitals.  
 (D) All of these
- Q.4** The ions of d-block elements are mostly paramagnetic –  
 (A) Because their d-orbitals are complete.  
 (B) Because they have mostly paired electrons.  
 (C) Because they have mostly unpaired electrons.  
 (D) Because they form coloured ions.
- Q.5** The order of stability of complexes of ion  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Mn}^{+2}$  and  $\text{Fe}^{+2}$  decreases in the order –  
 (A)  $\text{Cu}^{+2} > \text{Ni}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$   
 (B)  $\text{Mn}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2}$   
 (C)  $\text{Ni}^{+2} > \text{Cu}^{+2} > \text{Fe}^{+2} > \text{Mn}^{+2}$   
 (D)  $\text{Fe}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Mn}^{+2}$
- Q.6** The elements which exhibit both vertical and horizontal similarities are  
 (A) Inert gas elements (B) Representative elements  
 (C) Rare elements (D) Transition elements
- Q.7** Which of the following statements is correct ?  
 (A) Iron belongs to third transition series of the periodic table.  
 (B) Iron belongs to f-block of the periodic table.  
 (C) Iron belongs to first transition series.  
 (D) Iron belongs to group VIII of the periodic table.
- Q.8** A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. How many unpaired electrons are expected to be present in the ion ?  
 (A) 1 (B) 2  
 (C) 3 (D) 4
- Q.9** Variable valency is generally shown by –  
 (A) s-block elements  
 (B) p-block elements  
 (C) Transition elements  
 (D) all elements in periodic table
- Q.10** Which of the following is the softest metals –  
 (A) Sc (B) Zn  
 (C) Ti (D) V
- Q.11** Which of the following cuprous compounds is not stable –  
 (A)  $\text{CuCl}_2$  (B)  $\text{Cu}_2(\text{CNS})_2$  (C)  $\text{Cu}_2\text{Cl}_2$  (D)  $\text{Cu}_2\text{SO}_4$
- Q.12** On addition of small amount of  $\text{KMnO}_4$  to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.  
 (A)  $\text{Mn}_2\text{O}_7$  (B)  $\text{MnO}_2$   
 (C)  $\text{MnSO}_4$  (D)  $\text{Mn}_2\text{O}_3$
- Q.13** When acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is added to  $\text{Sn}^{2+}$  salts then  $\text{Sn}^{2+}$  changes to  
 (A) Sn (B)  $\text{Sn}^{3+}$  (C)  $\text{Sn}^{4+}$  (D)  $\text{Sn}^+$

### ANSWERS

- (1) (D) (2) (A) (3) (D)  
 (4) (C) (5) (A) (6) (D)  
 (7) (C) (8) (B) (9) (C)  
 (10) (B) (11) (D) (12) (A)  
 (13) (C)

## f-BLOCK ELEMENTS

They were earlier called as rare earth metals as it was believed that they exist in earth's crust to a very less extent for e.g. : Pm, does not exist in the earth's crust. But this terminology is now not applicable as they exist in earth's crust to a sufficient extent.

The elements in which the additional electron enters in  $(n-2)f$  orbitals are called inner transition elements or f-block elements.

### Position in the periodic table

The lanthanides resemble yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanide series (Z = 58 - 71) (Ce – Lu)  
 Actinide series (Z = 90 - 103) (Th – Lw)

### Lanthanides (Lanthanones) :

Lanthanides are reactive elements so do not found in free state in nature. Most important minerals for lighter Lanthanides are - Monazite, cerites and orthite and for heavier lanthanides - Gadolinite and Xenotime.

### Electronic configuration :

The general configuration of lanthanides may be given as  $4f^{2-14}5s^25p^65d^{0/1}6s^2$ . Lanthanide have outer three shells incomplete.

### Atomic Element Symbol Outer electronic configuration

Number	Atomic	+3 ion
58 Cerium Ce	$4f^2 6s^2$	$4f^1$
59 Praseodymium Pr	$4f^3 6s^2$	$4f^2$
60. Neodymium Nd	$4f^4 6s^2$	$4f^3$
61. Promethium Pm	$4f^5 6s^2$	$4f^4$
62. Samarium Sm	$4f^6 6s^2$	$4f^5$
63. Europium Eu	$4f^7 6s^2$	$4f^6$
64. Gadolinium Gd	$4f^7 5d^1 6s^2$	$4f^7$
65. Terbium Tb	$4f^9 6s^2$	$4f^8$
66. Dysprosium Dy	$4f^{10} 6s^2$	$4f^9$
67. Holmium Ho	$4f^{11} 6s^2$	$4f^{10}$
68. Erbium Er	$4f^{12} 6s^2$	$4f^{11}$
69. Thulium Tm	$4f^{13} 6s^2$	$4f^{12}$
70. Ytterbium Yb	$4f^{14} 6s^2$	$4f^{13}$
71. Lutecium Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

It is to be noted here that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium ( $z = 64$ ) with an outer electronic configuration of  $4f^7 5d^1 6s^2$  (and not  $4f^8 6s^2$ ). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

On the other hand, the filling of f orbitals is regular in tripositive ions.

After losing outer electrons, the f orbitals shrink in size and became more stable. Pm is the only synthetic radioactive lanthanide.

### Oxidation states :

Lanthanides	Oxidation States
Ce <sub>58</sub>	+3,+4
Pr <sub>59</sub>	+3, (+4)
Nd <sub>60</sub>	+3
Pm <sub>61</sub>	+3
Sm <sub>62</sub>	(+2), +3
Eu <sub>63</sub>	+2,+3
Gd <sub>64</sub>	+3
Tb <sub>65</sub>	+3,+4
Dy <sub>66</sub>	+3; (+4)
Ho <sub>67</sub>	+3
Er <sub>68</sub>	(+2), +3
Tm <sub>69</sub>	(+2), +3
Yb <sub>70</sub>	+2,+3
Lu <sub>71</sub>	+3

- \* Oxidation states in brackets are unstable states
- \* The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.
- \* This corresponds to the use of two outermost electrons (6s<sup>2</sup>) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.
- \* All the lanthanides attains +3 oxidation state and only cerium, Praseodymium, and terbium exhibit higher oxidation state (+4).

Oxidation states +2 & +4 occur particularly when they lead to (i) A noble gas configuration e.g. Ce<sup>4+</sup> (f<sup>0</sup>)  
(ii) A half filled 'f' orbital e.g. Eu<sup>2+</sup>, Tb<sup>4+</sup>, (f<sup>7</sup>)  
(iii) A completely filled 'f' orbital e.g. Yb<sup>2+</sup> (f<sup>14</sup>)  
Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

### Magnetic properties

In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0). So lanthanum and lutecium ions which are diamagnetic, all other tripositive lanthanide ions are Paramagnetic.

**Colour** - The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorbs visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with 4f<sup>n</sup> configuration have similar colour to those ions having 4f<sup>14-n</sup> configuration.

Lanthanide ions having 4f<sup>0</sup>, 4f<sup>7</sup>, 4f<sup>14</sup> are colourless. Lanthanide ions 4f<sup>1</sup> and 4d<sup>13</sup> are also colourless.

### Other Properties

- (a) Highly dense metals with high m.pt. (do not show any regular trend).
  - (b) Ionisation Energies - Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
  - (c) Electro positive Character - High due to low I.P.
  - (d) Complex formation - Do not have much tendency to form complexes due to low charge density because of their large size.  
Lu<sup>+3</sup> is smallest in size can only form complex.
  - (e) Reducing Agent - They readily lose electrons so are good reducing agent.
- \* In +3 oxidation states, nitrates, perchlorates and sulphates of lanthanides and actinides are water soluble, while their hydroxides, fluorides and carbonates are water insoluble.
  - \* Alloys of lanthanides with Fe are called misch metals.
  - \* La(OH)<sub>3</sub> is most basic in nature while Lu(OH)<sub>3</sub> least basic.
  - \* Lanthanides form MC<sub>2</sub> type carbide with carbon, which on hydrolysis gives C<sub>2</sub>H<sub>2</sub>.

### LANTHANIDE CONTRACTION

- \* In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutecium or from La<sup>+3</sup> to Lu<sup>+3</sup>. This contraction in size is known as lanthanide contraction.
- \* The general electronic configuration of these elements is 4f<sup>0-14</sup>5s<sup>2</sup>6p<sup>6</sup>d<sup>0-1</sup>6s<sup>2</sup>. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- \* Such an electron cannot add to the size of the element and also because the intervening 5s<sup>2</sup>6p<sup>6</sup>d<sup>1</sup> electronic shells, it is very little screening effect on the outermost 6s<sup>2</sup> electrons. Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.
- \* The atomic volumes of europium and ytterbium are unexpectedly large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled, f<sup>7</sup>, and completely filled, f<sup>14</sup>), hence they utilise two electrons in metallic bonding as in the case with barium.

### EFFECTS OF LANTHANIDE CONTRACTION

- (i) **Close resemblace of Lanthanides** : The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu.  
This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability, solubility of their salts.
- (ii) **Similarity of yttrium with lanthanides** : The properties of yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.



(iii) **Anomalous behaviour of post-lanthanides** : The following anomalies may be observed in the behaviour of post-lanthanide elements.

(a) **Atomic size** : The ionic radii of  $Zr^{+4}$  is about 9% more than  $Ti^{+4}$ . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of  $Hf^{+4}$ , instead of increasing (because of inclusion of one more electronic shell). decreases (or is virtually equal to  $Zr^{+4}$ ) as a consequence of the lanthanide contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

(b) **Ionisation potential and electronegativity** : The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend.

Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

(c) **High density** : Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high. The densities of the third transition series elements are almost double to those of the second series elements.

#### APPLICATION OF LANTHANIDES

Cerium is most useful element in the lanthanides

- (a) Ceramic application -  $CeO_2$ ,  $La_2O_3$ ,  $Nd_2O_3$  and  $Pr_2P_3$  are used as decolorizing agents for glasses.
- (b)  $CeS$  (m.p. -  $2000^\circ C$ ) is used in the manufacture of a special type of crucibles and refractories.
- (c) Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- (d) In textile and leather industries ( $Ce$  salts).

#### ACTINIDES (5f-BLOCK ELEMENTS)

- \* The elements in which the extra electron enters 5f-orbitals of (n - 2)th main shell are known as actinides. Total no. = 14
- \*  $Th$ ,  $Pa$  and  $U$  first three actinides are natural elements and rest 11 are man-made.

#### Electronic configuration :

The general configuration of actinides may be given as  $5f^{1-14} 6d^{0/1} 7s^2$ .

Atomic No.	Elements	Symbol	Electronic Configuration
90	Thorium	Th	$6d^2 7s^2$
91	Protactinium	Pa	$5f^2 6d^1 7s^2$
92	Uranium	U	$5f^3 6d^1 7s^2$
93	Neptunium	Np	$5f^4 6d^1 7s^2$
94	Plutonium	Pu	$5f^6 7s^2$

95	Americium	Am	$5f^7 7s^2$
96	Curium	Cm	$5f^7 6d^1 7s^2$
97	Berkellium	Bk	$5f^9 7s^2$
98	Californium	Cf	$5f^{10} 7s^2$
99	Einsteinium	Es	$5f^{11} 7s^2$
100	Fermium	Fm	$5f^{12} 7s^2$
101	Mendelevium	Md	$5f^{13} 7s^2$
102	Nobelium	No	$5f^{14} 7s^2$
103	Lawrencium	Lw	$5f^{14} 6d^1 7s^2$

**Oxidation states** : In lanthanides and actinides +3 oxidation is the most common for both of the series of elements. This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

Actinides	Oxidation state
$Th_{90}$	+4
$Pa_{91}$	(+4), +5
$U_{92}$	(+3), (+4), (+5), +6
$Np_{93}$	(+3), (+4), +5, (+6), (+7)
$Pu_{94}$	(+3), +4, (+5), (+6), (+7)
$Am_{95}$	+2, (+3), (+4), (+5), (+6)
$Cm_{96}$	+3, (+4)
$Bk_{97}$	+3, (+4)
$Cf_{98}$	+3
$Es_{99}$	+3
$Fm_{100}$	+3
$Md_{101}$	+3
$No_{102}$	+3
$Lw_{103}$	+3

#### Example 8 :

Why do actinoids, in general, exhibit a greater range of oxidation states than the lanthanoids ?

**Sol.** The energies of 5f, 6d and 7s are comparable. So all of these electrons take part in bond formation. Therefore, actinoids, in general, exhibit a greater range of oxidation states.

#### Example 9 :

What is meant by 'lanthanoid contraction' ? State one use each of lanthanoid metals and their oxides.

**Sol.** The decrease in atomic and ionic size with increase in atomic number in lanthanoids is called lanthanoid contraction.

**Uses** : Lanthanoids are used for production of alloy steels for plates and pipes. Mixed oxides of lanthanoid metals are used as catalyst in petroleum cracking.

#### TRY IT YOURSELF-2

- Q.1** Correct electronic configuration of lanthanum is  
 (A)  $[Xe] 5d^1 6s^2$  (B)  $[Xe] 4d^1 5s^2$   
 (C)  $[Xe] 4f^1 5s^2$  (D)  $[Xe] 5f^1 6s^2$
- Q.2** Lanthanides and Actinides generally differ in –  
 (A) Oxoion formation  
 (B) Radioactive nature  
 (C) Tendency towards complex formation  
 (D) All of these

- Q.3** Which of the following oxidation state is common for all lanthanoids?  
 (A) +2 (B) +3  
 (C) +4 (D) +5
- Q.4** There are 14 elements in actinoid series. Which of the following elements does not belong to this series?  
 (A) U (B) Np  
 (C) Tm (D) Fm
- Q.5** Gadolinium belongs to 4f series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?  
 (A) [Xe] 4f<sup>7</sup>5d<sup>1</sup>6s<sup>2</sup> (B) [Xe] 4f<sup>6</sup>5d<sup>2</sup>6s<sup>2</sup>  
 (C) [Xe] 4f<sup>8</sup>6d<sup>2</sup> (D) [Xe] 4f<sup>9</sup>5s<sup>1</sup>
- Q.6** Which of the following actinoids show oxidation states upto +7?  
 (A) Am (B) Pu  
 (C) U (D) Np
- Q.7** Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?  
 (A) Ce (B) Eu  
 (C) Yb (D) Ho
- Q.8** Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because –  
 (A) it has variable ionisation enthalpy  
 (B) it has a tendency to attain noble gas configuration  
 (C) it has a tendency to attain f 0 configuration  
 (D) it resembles Pb<sup>4+</sup>

### ANSWERS

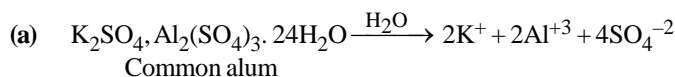
- (1) (A) (2) (D) (3) (B)  
 (4) (C) (5) (A) (6) (BD)  
 (7) (BC) (8) (BC)

## CO-ORDINATION CHEMISTRY

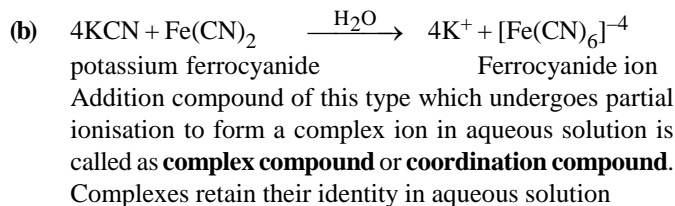
### COMPLEX FORMATION

- Transition metal ions have maximum tendency to form complexes. In the formation of complexes they form coordinate covalent bonds and act as electron pair acceptors.
- Transition metal ions have smaller size and have high positive charge i.e., high charge density. Due to this they have maximum tendency to accept electrons. They have vacant 'd' orbitals available on them hence they can accept lone pairs of electrons forming coordinate covalent bond.
- The greater the charge density on the transition metal ion, the greater they have tendency to form complexes. Thus Ti<sup>+2</sup> to Ni<sup>+2</sup> the stability of complexes formed goes on increasing.
- Compounds like NaCl, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> provide only two types of ions in aqueous solution i.e., cations and anions, are called as **simple salts**.
- When two or more simple salt solutions are mixed and then subjected for crystallisation, the crystals which are obtained are of addition compounds.

The addition compound formed may behave in one of the following ways



The addition compound which undergoes complete ionisation to form three types of ions i.e., two types of cations and one type of anions or vice versa, is called as **double salt**. These double salts lose their identity in aqueous solution.



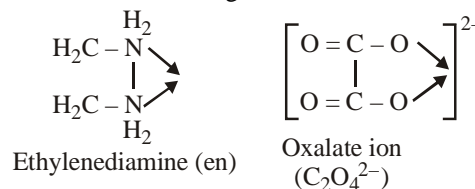
**Complex ion** : An aggregate of metal ion with anions cation or neutral molecules is called as complex ion. The metal ion which forms complex ion in combination with anions or neutral molecules is called as central metal ion. Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond.

The anions or neutral molecules which combine with central metal ion to form complex ion are called as **ligands**. They act as electron pair donors or Lewis bases.

Ligand may be neutral (NH<sub>3</sub>, H<sub>2</sub>O, C<sub>6</sub>H<sub>5</sub>N) or negatively charged species (: CN<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>). Sometimes positively charged species are also found as ligand (NO<sup>+</sup>).

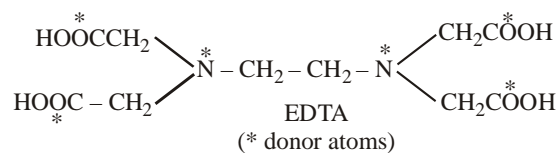
Ligand is said to be **unidentate** if it has only one pair of electrons that it can donate e.g., Cl<sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>O, etc.

Ligand is said to be **bidentate** if it has two electron pairs available for donation. e.g.,

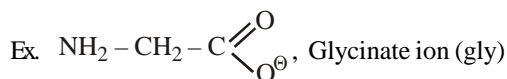


**Ambidentate ligand** : Some ligands can be coordinated to the metal or metal ion through either of the two atoms of the ligand, they are called as Ambidentate ligands.

**Flexidentate ligand** : These are those ligands which contains more than two donor sites but utilises less number of donating sites than actual number of sites, Ex. EDTA (Ethylene diamine tetra acetate).



**Polydentate ligand** : The ligands which contains two or more donor sites.



**Coordination number :**

- (i) The number of ligands that combine with the central metal ion to form the complex ion is called as coordination number.
- (ii) From every ligand central metal ion accepts lone pair of electrons. Thus the number of lone pair of electrons accepted by the central metal ion in the formation of a complex is called as coordination number.
- (iii) The total number of coordinate covalent bonds formed by central metal ion with Ligands is called as coordination number.

**Coordination sphere** - Central metal ion and the ligands attached to it, this aggregate which is written in square bracket is called as coordination sphere.

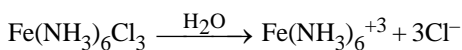
\* Werner's Theory of complexes - This was postulated by Alfred Werner in 1893. The postulates of Werner's Theory of complexes are

- (i)  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3 \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{NH}_3)_6]^{+3} + 3\text{Cl}^-$   
 $[\text{Fe}(\text{NH}_3)_5\text{Cl}_3] \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$   
 Every metal forming a complex exhibits two types of valencies - Primary valency and Secondary Valency. In the above complexes chlorines act as primary valencies and  $\text{NH}_3$  acts as secondary valency. Primary valency is equal to oxidation state of metal ion.
- (ii) Primary valency is ionisable in nature whereas secondary valency is nonionisable.
- (iii) The number of secondary valencies of a metal ion in the complex will remain constant and this is called as coordination number  
 e.g.  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Co}^{+3}$ ,  $\text{Pt}^{+4}$ ,  $\text{Cr}^{+3}$ ,  $\text{Ru}^{+2}$ ,  $\text{Os}^{+3}$  have a coordination number of six  
 $\text{Pt}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Au}^{+3}$ ,  $\text{Hg}^{+2}$  have a coordination number of four.  
 $\text{Ag}^{+1}$  which is an exceptional ion with coordination number of two.  
 $\text{Mo}^{+3}$  has the highest coordination number of eight.

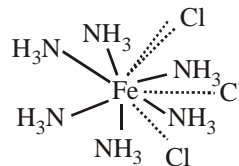
**Shapes and isomerism in complexes**

The shape of 6-coordinated complexes can be hexagonal planar or octahedral (more possible). The 6-coordinated complexes can exhibit geometrical or optical isomerism. The shape of 4-coordinated complexes can be square planar (exhibiting geometrical isomerism) or Tetrahedral (exhibiting optical isomerism).  
 Experimental evidence to werner's theory of complexes can be provided based on –

- (i) Precipitation of primary valencies on the addition of a suitable reagent.  
 e.g. -  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$  forms 3 moles of  $\text{AgCl}$  in the form of precipitate on addition of  $\text{AgNO}_3$  solution. This indicates that the complex ionises as

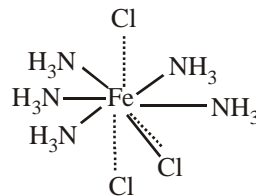


- (ii) Electrical conductance of complexes - More the number of ions provided greater is the electrical conductance of the complex in aqueous medium.  
 e.g. - The electrical conductance of aqueous  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$  is greater than that of aqueous solution of  $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .  $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Fe}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$  Total 3 ions  
 Representation of complexes– Werner's representation for  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$

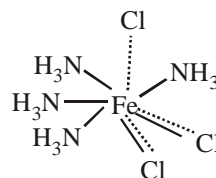


(Dotted lines indicate primary Valency and continuous lines indicate secondary valency of metal ion.) If the complex is

- (a)  $\text{Fe}(\text{NH}_3)_5\text{Cl}_3$  Then in this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation for this complex will be



- (b)  $\text{Fe}(\text{NH}_3)_4\text{Cl}_3$  In this complex 'c' groups act as primary valencies and two of the 'c' group act as secondary valencies also. Thus this complex is represented as



\* **Modern representation of complexes** - Central metal ion along with secondary valencies or ligands are written in square brackets and primary valencies outside the square bracket. For example :-  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$

**Coordination sphere or inner sphere** - This is written in square bracket. This constitutes the central metal ion along with ligands.

Outer sphere or ionisation sphere. This is written outside the square bracket. In aqueous solution the groups written outside the square bracket dissociate and are provided in the form of ions.

**MODERN THEORY OF COMPLEXES OR ELECTRONIC THEORY OF COMPLEXES-**

Sidgwick and Lowry in 1923 developed this theory, and modified Werner's Theory. According to sidgwick the primary valency is regarded to

be formed by transfer of electron and secondary valency is formed by the sharing of electron pair provided by the donor. During formation of primary valency the metal loses electrons. Thus the number of electrons decrease during primary valency formation. In the formation of secondary valency the metal ion gains electrons in pairs for the formation of coordinate bond. Thus during secondary valency formation the total number of electrons associated with the metal ion increase.

**Effective atomic number :** The total number of electrons associated with the metal ion in its complex may be equal to or nearly equal to the atomic number of inert gas of the same period. This total number of electrons is called 'Effective atomic number' (E.A.N.) of the metal.

For e.g. - E.A.N. of cobalt in  $(\text{Co}(\text{NH}_3)_6)^{3+}$  can be calculated as follows: Atomic number of cobalt = 27

In this complex, cobalt is in +3 oxidation state, thus the number of electrons in  $\text{Co}^{+3}$  ion are =  $27 - 3 = 24$

During secondary valency formation  $\text{Co}^{+3}$  ion gains 6 pairs of electrons during coordinate covalent bonding.

Thus E.A.N. of cobalt in

$$[\text{Co}(\text{NH}_3)_6]^{+3} = 24 + 12 = 36.$$

i.e., E.A.N. = (No. of electron in the metal ion)

$$+ (\text{No. of electrons gained from the ligands})$$

As the E.A.N. of cobalt is 36 in this complex, according to sidgwick, this complex will be stable. Though E.A.N. rule is applicable in many cases, there are several examples in which E.A.N. rule is not obeyed.

For example  $(\text{Cr}(\text{H}_2\text{O})_6)^{+3}$  EAN = 33

#### Example 10 :

Calculate the effective atomic number of the metal atoms in the following complexes/complex ions –

- (a)  $[\text{Cr}(\text{CO})_6]$  (b)  $[\text{Fe}(\text{CN})_6]^{3-}$   
 (c)  $[\text{Co}(\text{CN})_6]^{4-}$  (d)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

[Cr = 24, Fe = 26, Co = 27 and Ni = 28 as atomic numbers]

**Sol.** EAN = Number of electrons in metal atom or ion + Number of electrons donated by ligands to metal.

- (a)  $[\text{Cr}^0(\text{CO})_6]$  ; EAN =  $24 + 12 = 36$   
 (b)  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$  ; EAN =  $23 + 12 = 35$   
 (c)  $[\text{Co}^{\text{II}}(\text{CN})_6]^{4-}$  ; EAN =  $25 + 12 = 37$   
 (d)  $[\text{Ni}^{\text{II}}(\text{NH}_3)_6]^{2+}$  ; EAN =  $26 + 12 = 38$

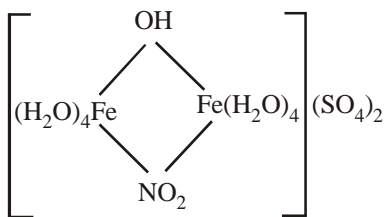
#### NOMENCLATURE OF COORDINATION COMPOUNDS -

The present system of nomenclature derived from the suggestions of Alfred Werner and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. is given. The main rules of naming of complexes are

- (i) Like simple salts, the positive part of the coordination compound is named first. For e.g.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  the naming of this complex starts with potassium.  
 (ii) The ligands of the coordination sphere are to be named.  
 (iii) The ligands can be neutral, anionic or cationic.  
 (a) The neutral ligands are named as the molecule e.g.  $\text{C}_5\text{H}_5\text{N}$  pyridine,  $(\text{C}_6\text{H}_5)_3\text{P}$  Triphenyl phosphine,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl,  $\text{H}_2\text{O}$  Aqua,  $\text{NH}_3$  amine.

- (b) The negative ligands end in - 'O'.  
 $\text{Cl}^-$  chloro,  $\text{SO}_4^{2-}$  sulphato  $\text{NO}_2^-$  Nitro  
 $\text{ONO}^-$  nitrito,  $\text{OH}$  Hydroxo,  $\text{NH}_2^-$  amido  
 $\text{NH}^-$  imido  $\text{NO}_3^-$  nitrato,  $\text{CO}_3^{2-}$  carbonato  
 $\text{CH}_3\text{COO}^-$  acetato,  $\text{CN}$  cyno  $\text{CNO}$  cyanato etc.  
 (c) Positive ligands naming ends in 'ium'  $\text{NH}_2-\text{NH}_3^+$  Hydrazinium,  $\text{NO}_2^+$  nitronium,  $\text{NO}^+$  nitrosonium
- (iv) If ligands are present more than once, then their repetition is indicated by prefixes like di, tri, tetra etc.  
 (v) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order. (prior to this naming of ligands was followed in the order - negative, neutral and positive ligands)  
 (vi) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets.  
 (vii) If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is. If the complex provides anionic complex ion then the name of central metal ion ends in 'ate'  
 (viii) After the naming of central metal ion anion which is in the outer sphere is to be named. The naming of some of the complexes is done as follows :- (as per IUPAC)
- $\text{K}_4[\text{Fe}(\text{CN})_6]$   
(anionic complex is present so suffix ate is added with metal's name) Potassium hexacyanoferrate (II)
  - $\text{K}_2[\text{PtCl}_6]$  Potassium hexachloroplatinate (IV)
  - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
(Cationic complex is present so metal is without any suffix) Hexamine cobalt (III) chloride
  - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$   
Tetra aqua di chloro chromium (III) chloride
  - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$   
Diamine tetra chloroplatinum (IV)
  - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (Neutral complex - hence no suffix is used with metal ion)  
Triammine trichloro cobalt (III)
  - $\text{K}_3[\text{Co}(\text{NO}_2)_6]$   
Potassium hexanitro cobaltate (III)
  - $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$   
Sodium pentacyano nitrosyl ferrate (II)
  - $[\text{NiCl}_4]^{2-}$  Tetrachloro nickelate (II) ion
  - $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$   
Pentammine chlororuthenium (III) ion
- (ix) When bidentate ligands are coordinated to the metal ion, their repetition is indicated by pre fixes like bis, tris, tetrakis etc. for example : (1)  $[\text{Fe}(\text{en})_3]\text{Cl}_3$   
Trisethylene diamine iron (III) chloride  
 (2)  $[\text{Ni}(\text{Gly})_2]$  - Bis glycinate nickel (II)
- (x) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as Bridging Ligand or Bridge group. A prefix of Greek letter  $\mu$ , is repeated before the name of each different kind of bridging group.



Octa aqua - $\mu$ -, hydroxo -  $\mu$ - nitro diiron (III) sulphate.

### ISOMERISM IN COMPLEXES

Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as Isomers. The phenomenon of exhibiting different structures is called as Isomerism. Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

**Structural isomerism** - It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere. The structural isomers are of following types

(1) **Ionisation isomers** - The type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere. This type of isomers yield different types of ions in solution,

**For e.g.:**

1.  $\text{Co}(\text{NH}_3)_4 \text{Br}_2 \text{SO}_4$  can represent  $[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$  (red violet) and  $[\text{Co}(\text{NH}_3)_4 \text{SO}_2] \text{Br}$  (red). These complexes give sulphate ion and bromide ion respectively
2.  $(\text{Pt}(\text{NH}_3)_4 \text{Cl}_2) \text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$
3.  $[\text{Co}(\text{NH}_3)_4 (\text{NO}_3)_2] \text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] (\text{NO}_3)_2$

(2) **Hydrate isomers** - The water molecules may be associated with metal ions or they may appear in lattice positions without being closely associated with the metallic cation.

The complexes which differ with respect to the number of water molecules attached to the metal ion as ligands are called as Hydrate isomers.

For e.g. -  $\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$  has three structures possible

- (i)  $[\text{Cr}(\text{H}_2\text{O})] \text{Cl}_3$  violet
- (ii)  $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$  green
- (iii)  $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$  dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. They also differ in their number of primary valencies i.e., chloride ions which are provided. Other hydrate isomers are  $[\text{Co}(\text{NH}_3)_4 \text{H}_2\text{O Cl}] \text{Cl}_2$   $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl} \cdot \text{H}_2\text{O}$

(3) **Linkage or salt isomers** - When a ligand has two different types of donor atoms but it is a monodentate ligand then this type of isomerism is exhibited. The ligand may get attached to the metal ion through either

of the two donor atoms. For e.g. -  $\text{NO}_2^-$  ligand. In this ligand the coordinating sites are nitrogen (i.e., - $\text{NO}_2$  Nitro ligand) or through oxygen (i.e.,  $\text{ONO}$  Nitrito ligand)

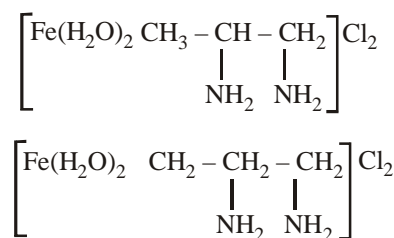
$[\text{Co}(\text{NH}_3)_5 \text{NO}_2]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5 \text{ONO}]^{+2}$  are linkage isomers of one another.

(4) **Coordination isomers :**

This type of isomerism occurs when both cation and anion are complex. The isomerism is caused by the interchange of ligands between the two complex ions of the same complex.

e.g.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  &  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

(5) **Ligand isomers** - Ligands with  $\text{C}_3\text{H}_6(\text{NH}_2)_2$  have two different structures i.e., 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine). Those complexes which have same molecular formula. but differ with respect to their ligands are called as Ligand isomers. For e.g. -  $[\text{Fe}(\text{H}_2\text{O})_2 \text{C}_3\text{H}_6(\text{NH}_2)_2 \text{Cl}_2]$  has two different structures



**Stereo isomers** - They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible are -

(i) Geometrical and (ii) optical.

(i) **Geometrical or cis-Trans isomer** - The ligands occupy different positions around the central metal ion. When two identical ligands are coordinated to the metal ion from same side then it is cis isomer. (in Latin, cis means same). If the two identical ligands are coordinated to the metal ion from opposite side then it is Trans isomer (in Latin, Trans means across). These geometrical isomers differ in physical as well as chemical properties.

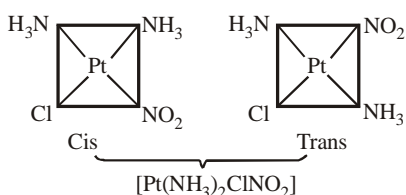
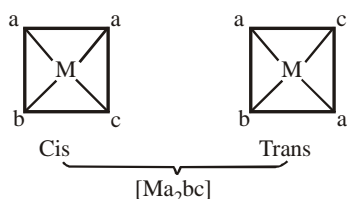
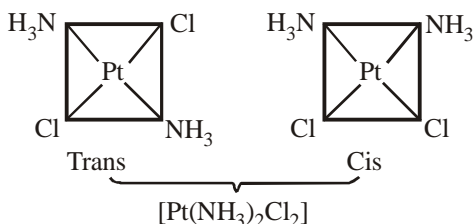
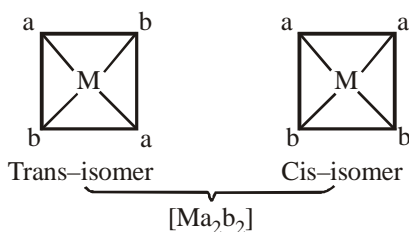
\* Geometrical isomerism is most important in compounds with coordination numbers 4 and 6. 4-coordinated complexes with tetrahedral geometry do not exhibit - cis-Trans isomerism.

\* It is exhibited by 4-coordinated complexes with square planar geometry.

\*  $\text{Ma}_2\text{b}_2$ ,  $\text{Ma}_2\text{bc}$  type of square planar complexes exhibit geometrical isomerism and gives two geometrical isomers each.

$\text{Mabcd}$  (Square planar) gives three isomers.

e.g.  $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_2]$



- \* Other 6-Coordinated geometrical isomers are
- | General formula                               | Total No. of geometrical isomers |
|---|----------------------------------|
| Mabcdef                                       | 15                               |
| Ma <sub>2</sub> b <sub>2</sub> c <sub>2</sub> | 5                                |
| Ma <sub>2</sub> bcd                           | 4                                |
| Ma <sub>4</sub> b <sub>2</sub>                |                                  |
| Ma <sub>4</sub> bc                            | 2                                |
| Ma <sub>3</sub> b <sub>3</sub>                |                                  |
| Ma <sub>6</sub> , Ma <sub>5</sub> b           | Nil                              |

Mabcdef

15

Ma<sub>2</sub>b<sub>2</sub>c<sub>2</sub>

5

Ma<sub>2</sub>bcd

4

Ma<sub>4</sub>b<sub>2</sub>Ma<sub>4</sub>bc

2

Ma<sub>3</sub>b<sub>3</sub>Ma<sub>6</sub>, Ma<sub>5</sub>b

Nil

Here M = central atom

a, b, c, d, e, f = ligands

- \* **Octahedral complexes** : (Coordination number = 6).

**MA<sub>4</sub>B<sub>2</sub> or MA<sub>2</sub>B<sub>4</sub> or MA<sub>4</sub>BC or MA<sub>3</sub>B<sub>3</sub> type:** An example of the type MA<sub>4</sub>B<sub>2</sub> or MA<sub>2</sub>B<sub>4</sub> is [CrCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> ion or [CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> ion or [Fe(CN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup>.

In cis-form, similar groups (trio of donor atoms) occupy the corners of one of the octahedral faces and hence is called **facial or fac-isomer** while in trans-form, the positions of trio of donor atoms are around the meridian of the octahedron. Hence it is called **meridional or mer-isomer**. Another example of this type is [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] or [Co(NO<sub>2</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>].

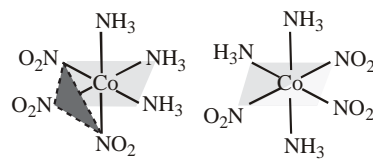
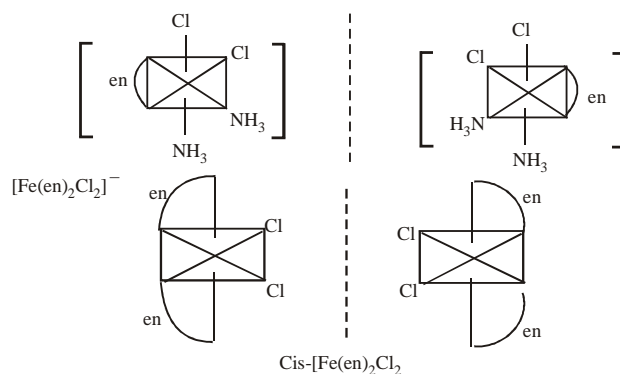
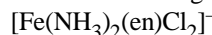


Figure : The facial (fac) and meridional (mer) isomers of [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>]

## (ii) Optical isomers

- \* Optically active complexes are those which are nonsuperimposable over the mirror image structure. An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- \* The complex which rotates plane polarised light to left hand side is laevo rotatory i.e., 'l' or '(-)', and if the complex rotates the plane polarised light to right hand side then it is dextro rotatory 'd'
- \* Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as optical isomers.
- \* The 'd' and 'l' isomers of a compound are called as Enantiomers or Enantiomorphs. 4-coordinated complexes with tetrahedral geometry exhibit optical activity
- \* Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isomerism. For e.g.



- \* Trans - [Fe(en)<sub>2</sub>Cl<sub>2</sub>] do not show optical activity due to superimposition of their mirror image.

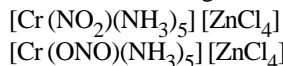
## Example 11 :

Select correct code about complex [Cr(NO<sub>2</sub>)(NH<sub>3</sub>)<sub>5</sub>][ZnCl<sub>4</sub>]

- (I) IUPAC name of compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)
- (II) It shows geometrical isomerism
- (III) It shows linkage isomerism
- (IV) It shows co-ordination isomerism.
- (A) III, IV      (B) I, III & IV
- (C) II, III & IV      (D) I, II, III & IV

- Sol.** (B). (I) [Cr(NO<sub>2</sub>)(NH<sub>3</sub>)<sub>5</sub>][ZnCl<sub>4</sub>]  
IUPAC name of compound is Pentaamminenitrito-N-chromium (III) tetrachloridozincate (II)

(III) It shows linkage isomerism due to presence of ambident ligands.



(IV) Because both complex ions have different ligands.

### BONDING THEORIES IN COMPLEXES

The main bonding theories of coordination compounds are : I. Valence Bond Theory II. Crystal field Theory

#### VALENCE BOND THEORY

This theory was mainly developed by Linus Pauling. The main features of this theory are

(i) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond. During this bond formation the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals. The number of vacant orbitals provided is equal to the coordination number of metal ion.

For e.g. - In the formation of  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ ,  $\text{Fe}^{3+}$  ion provides six vacant orbitals.

In  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Cu}^{2+}$  ion provides four vacant orbitals.

(ii) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.

(iii) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons. - The number of such overlapping is equal to the coordination number of metal ion.

(iv) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals. These complexes are called as Inner orbital complexes and outer orbital complexes respectively.

(v) If inner 'd' orbitals are involved in hybridisation, it is only through the pairing of unpaired electrons in the 'd' orbitals of metal ion. Then such type of complexes will be diamagnetic or less paramagnetic and will be called as Low spin complexes.

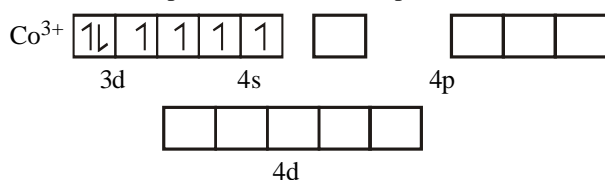
\* All outer orbital complexes have paramagnetic nature and they are called as High spin complexes.

#### APPLICATIONS OF VALENCE BOND THEORY

##### I To 6-coordinated complexes

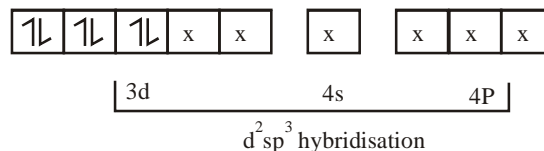
\*  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic whereas  $[\text{CoF}_6]^{3-}$  is paramagnetic.

\* In the two complex ions  $\text{Co}^{3+}$  ion is present



As  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic the unpaired electrons get paired up due to strong ligand and the metal ion provides vacant '3d' orbitals for hybridisation.

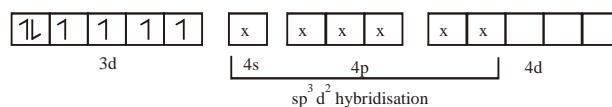
$\text{Co}^{3+}$  in  $[\text{Co}(\text{NH}_3)_6]^{3+}$



\* It is an octahedral complex.

\* This is a diamagnetic complex. As inner 'd' orbitals are involved in hybridisation, it is an inner orbital complex and it is a low spin complex.

As  $[\text{CoF}_6]^{3-}$  is paramagnetic, the unpaired electrons remain as it is. Thus  $\text{Co}^{3+}$  in  $[\text{CoF}_6]^{3-}$  will be



\* In this complex  $\text{F}^-$  is weak ligand therefore no pairing of e<sup>-</sup> occurred.

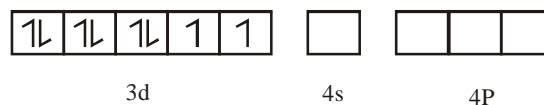
\* It is an octahedral complex.

This is a paramagnetic complex. The outer 'd' orbitals are involved in hybridisation, hence it is an outer orbital complex and a high spin complex.

##### II 4-coordinated complexes

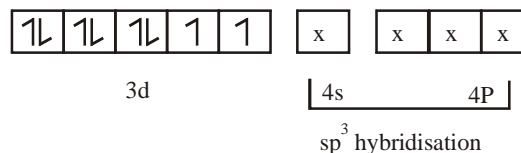
\*  $[\text{NiCl}_4]^{2-}$  is paramagnetic whereas  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.

$\text{Ni}^{2+}$  ion has configuration of  $[\text{Ar}] 3d^8$



The unpaired electrons remain as such, as it is a paramagnetic complex.

Thus  $\text{Ni}^{2+}$  in  $[\text{NiCl}_4]^{2-}$  will be



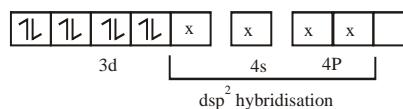
\* In this complex  $\text{Cl}^-$  is weak ligand.

\*  $[\text{NiCl}_4]^{2-}$  has tetrahedral geometry. It is an outer orbital complex and is a high spin complex.

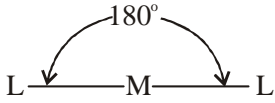
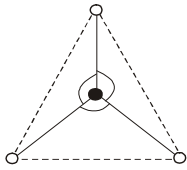
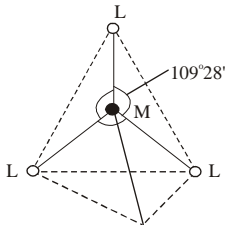
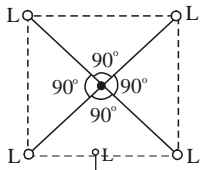
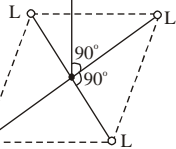
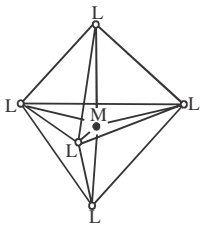
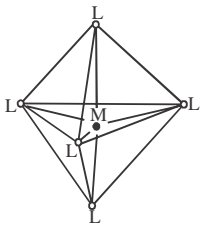
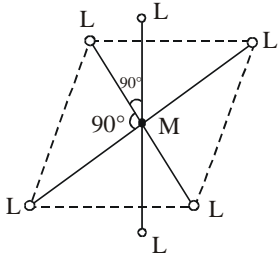
\*  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic in nature. Thus the unpaired electrons in '3d' orbitals of  $\text{Ni}^{2+}$  get paired up.

$\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$

\*  $\text{CN}^-$  is strong ligand.



## Coordination number and shapes of complex :

Coordination Number	Hybridised orbital	Geometrical shape of the complex	Examples of complex
2	$sp$	 Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$		$[\text{HgI}_3]^-$
4	$sp^3$	 Tetrahedral	$[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]^0$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$ $[\text{ZnCl}_4]^{-2}$ , $[\text{CuX}_4]^{-2}$ where X = CN $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , CNS
4	$dsp^2$ The d-orbital involved is $d_{x^2-y^2}$ orbital of the inner shell, i.e. it is $(n-1)d_{x^2-y^2}$ orbital	 	$[\text{Ni}(\text{CN})_4]^{-2}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$
5	$sp^3d$ , Square pyramidal	 Trigonal bipyramidal	$[\text{SbF}_5]^{2-}$
5	$dsp^3$ ; d-orbital is $n d_{x^2-y^2}$ orbital		$[\text{Fe}(\text{CO})_5]$ , $[\text{CuCl}_5]^{3-}$
6	$d^2sp^3$ When d-orbitals are $(n-1)d$ orbitals (Inner orbital complexes) or $sp^3d^2$ When d-orbitals are $nd$ orbitals (outer orbital complexes) In both cases d-orbitals are $d_{z^2}$ and $d_{x^2-y^2}$ orbitals		$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{-2}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{-2}$ , $[\text{CoF}_6]^{-3}$

L = Ligands indicated by white circles (same or different) M = Central metal indicated by black circles.



### CRYSTAL FIELD THEORY

This theory was proposed by Bethe and Vleck. According to this theory when a ligand approaches the metal ion, the 'd' orbitals of the metal ion undergo splitting forming two sets i.e., higher energy set, e.g. of  $d_{x^2-y^2}$  and  $d_{z^2}$  and a lower energy set,  $t_{2g}$  of  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ . If the ligand approaching is strongly basic then more splitting of 'd' orbitals is brought about i.e., the energy difference between 't<sub>2g</sub>' and 'e<sub>g</sub>' will be very high. Under these conditions

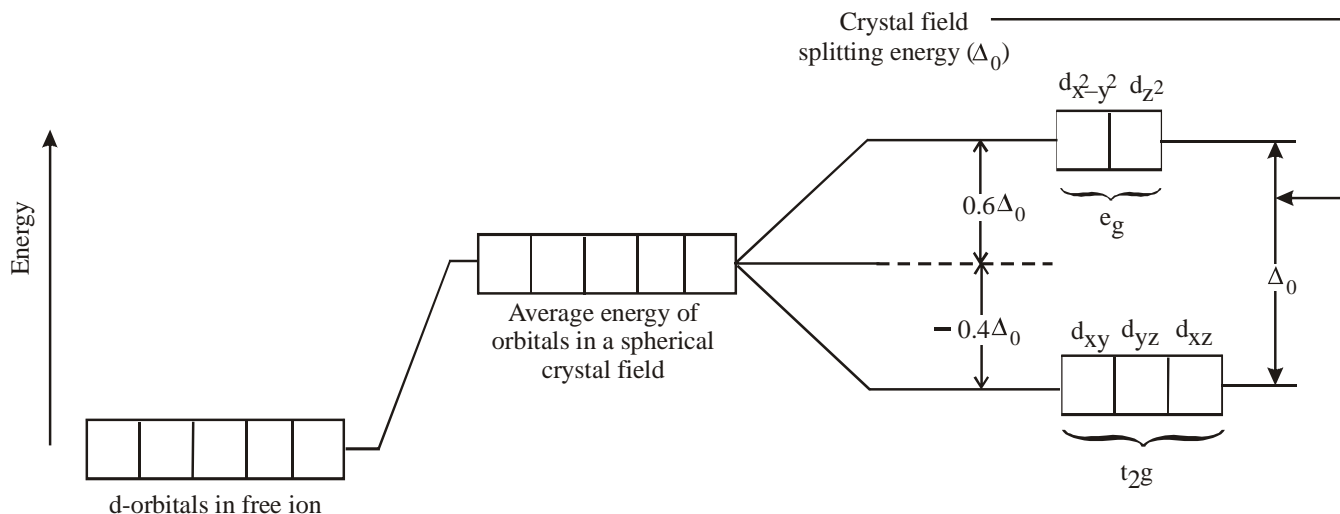
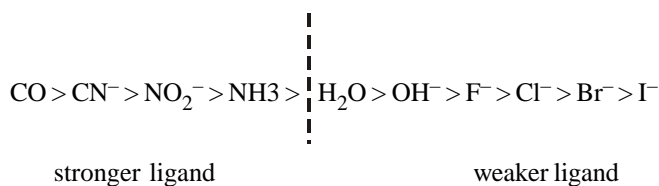


Figure : Splitting of d-orbitals in octahedral field

Order of decreasing splitting power is



- \* Strongly basic ligands are  $CN^-$ ;  $NH_3$ ,  $NO_2^-$  Ethylene diamine,  $CO$ ,  $NH_2$ . The effect of these ligands is they bring about pairing of unpaired electrons in the 'd' orbitals of metal ion during complex formation. According to crystal field Theory  $[Ni(CN)_4]^{2-}$  will be diamagnetic. As  $CN^-$  is a strongly basic ligand which brings about pairing of unpaired electrons in the  $3d^8$  configuration of  $Ni^{2+}$  ion. Whereas  $[NiCl_4]^{2-}$  will be paramagnetic, as  $Cl^-$  is a weakly basic ligand and under its influence no pairing of unpaired electrons can take place. Thus the magnetic nature of complexes can be easily predicted based on the crystal field theory.
- \* When a bidentate ligand like ethylene diamine, or Glycinate ion or oxalate ion combines with the metal ion in the formation of complexes, then the final complex resulted will be a cyclic complex. This type of cyclic complex formed is called as chelate.
- \* The process involving formation of a cyclic complex is called as chelation and the bidentate ligand is called as chelating agent.

the electrons of the 'd' orbitals of metal ion get paired up in the  $t_{2g}$  set of orbitals. This results in the formation of a diamagnetic or less paramagnetic complex. If the ligand approaching is weakly basic, then under its influence the 'd' orbitals of metal ion undergo less splitting i.e., the energy difference between  $t_{2g}$  and  $e_g$  orbitals will be less. Due to this the electrons of 'd' orbitals of metal ion get arranged in  $t_{2g}$  and  $e_g$  orbitals forming a paramagnetic complex ion.

### FACTORS AFFECTING THE STABILITY OF COMPLEXES

The stability of complexes depends on the following factors

(i) **Nature of the central metal ion :**

Greater the charge density on the metal ion greater the metal ion will have tendency to form the complex. Thus the complexes formed by metal ion with high charge density are more stable than complexes formed by metal ion with less charge density. For e.g. -  $Fe^{+3}$  ion forms a more stable complex than  $Fe^{+2}$ , Similarly  $Pt^{4+}$  complex is more stable than  $Pt^{2+}$  complex.

The stability of the complexes of some of the cations (having same charge but different ionic radii) decrease with the increase in ionic radii.

Ion	$Cu^{+2}$	$Ni^{+2}$	$CO^{+2}$	$Fe^{+2}$	$Mn^{+2}$
Ionic radii	0.69	0.78	0.82	0.83	0.91

(ii) **Nature of ligand**

A strongly basic ligand forms a more stable complex with the metal ion than a ligand which is weakly basic in nature. Thus a cyano complex will be more stable than a chloro complex.

(iii) When a bidentate ligand combines with the metal ion then a chelated complex is formed. This type of chelated complex will be more stable.

S. No.	Complex ions Form.	Metal ion	Coordination No	Configuration	Hybridisation	Geometry	U.E.	Magnetic Properties	Low spin High spin
01	$[\text{Ni}(\text{CN})_4]^{-2}$	$\text{Ni}^{+2}$	4	$d^8$	$dsp^2$	Sq. planar	0	Diamagnetic	L.S.
02	$[\text{Ni}(\text{CO})_4]$	Ni	4	$d^8s^2$	$sp^3$	Tetrahedral	0	Diamagnetic	L.S.
03	$[\text{Cu}(\text{NH}_3)_4]^{+2}$	$\text{Cu}^{+2}$	4	$d^9$	$dsp^2$	Sq. planar	1	Paramagnetic	L.S.
04	$[\text{Zn}(\text{NH}_3)_4]^{+2}$	$\text{Zn}^{+2}$	4	$d^{10}$	$sp^3$	Tetrahedral	0	Diamagnetic	L.S.
05	$[\text{CoCl}_4]^{-2}$	$\text{Co}^{+2}$	4	$d^7$	$sp^3$	Tetrahedral	3	Paramagnetic	L.S.
06	$[\text{NiCl}_4]^{-2}$	$\text{Ni}^{+2}$	4	$d^8$	$sp^3$	Tetrahedral	2	Paramagnetic	L.S.
07	$[\text{Pt}(\text{NH}_3)_4]^{+2}$	$\text{Pt}^{+2}$	4	$d^8$	$sp^3$	Tetrahedral	2	Paramagnetic	L.S.
08	$[\text{Fe}(\text{CN})_6]^{-3}$	$\text{Fe}^{+3}$	6	$d^5$	$d^2sp^3$	Octahedral	1	Paramagnetic	L.S.
09	$[\text{Fe}(\text{CN})_6]^{-4}$	$\text{Fe}^{+2}$	6	$d^6$	$d^2sp^3$	Octahedral	0	Diamagnetic	L.S.
10	$[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$	$\text{Fe}^{+2}$	6	$d^6$	$sp^3d^2$	Octahedral	4	Paramagnetic	H.S.
11	$[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$	$\text{Fe}^{+3}$	6	$d^5$	$sp^3d^2$	Octahedral	5	Paramagnetic	H.S.
12	$[\text{FeF}_6]^{-3}, [\text{FeCl}_6]^{-3}$	$\text{Fe}^{+3}$	6	$d^5$	$sp^3d^2$	Octahedral	5	Paramagnetic	H.S.
13	$[\text{Co}(\text{H}_2\text{O})_6]^{+3}$	$\text{Co}^{+3}$	6	$d^6$	$sp^3d^2$	Octahedral	4	Paramagnetic	H.S.
14	$[\text{Co}(\text{CN})_6]^{-4}$	$\text{Co}^{+2}$	6	$d^7$	$d^2sp^3$	Octahedral	1	Paramagnetic	L.S.
15	$[\text{CoF}_6]^{-3}$	$\text{Co}^{+3}$	6	$d^6$	$sp^3d^2$	Octahedral	4	Paramagnetic	H.S.
16	$[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$	$\text{Cr}^{+2}$	6	$d^4$	$sp^3d^2$	Octahedral	4	Paramagnetic	H.S.
17	$[\text{Cr}(\text{NH}_3)_6]^{+3}$	$\text{Cr}^{+3}$	6	$d^3$	$d^2sp^3$	Octahedral	3	Paramagnetic	L.S.
18	$[\text{Cr}(\text{Cl})_6]^{-3}$	$\text{Cr}^{+3}$	6	$d^3$	$d^2sp^3$	Octahedral	3	Paramagnetic	L.S.
19	$[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$	$\text{Ti}^{+3}$	6	$d^1$	$d^2sp^3$	Octahedral	1	Paramagnetic	L.S.
20	$[\text{V}(\text{H}_2\text{O})_6]^{+3}$	$\text{V}^{+3}$	6	$d^2$	$d^2sp^3$	Octahedral	2	Paramagnetic	L.S.
21	$[\text{Zn}(\text{NH}_3)_6]^{+2}$	$\text{Zn}^{+2}$	6	$d^{10}$	$sp^3d^2$	Octahedral	0	Diamagnetic	H.S.
22	$[\text{Pt}(\text{NH}_3)_6]^{+4}$	$\text{Pt}^{+4}$	6	$d^6$	$d^2sp^3$	Octahedral	0	Diamagnetic	L.S.
23	$[\text{Mn}(\text{CN})_6]^{-4}$	$\text{Mn}^{+2}$	6	$d^5$	$d^2sp^3$	Octahedral	1	Paramagnetic	L.S.

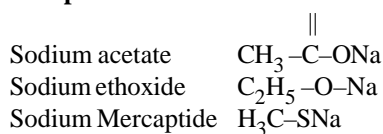
### PROPERTIES OF COMPLEX IONS

#### ORGANOMETALLIC COMPOUNDS

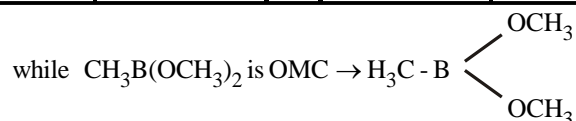
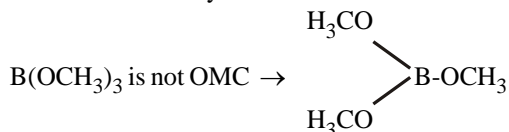
Compounds containing one or more metal carbon bonds.

- \* The compounds of metalloids (Ge, Sb) and non metals (B, Si, P, As etc.) which are less electro -ve than carbon are also categorised in this title. e.g : R - Zn - R dialkyl zinc (Frankland reagent); R-Mg-X Alkyl Mg halide (Grignards reagent)

- \* **Compounds like**



are not organometallic compd. as in these compounds metal is not directly attached with carbon atom.



- \* Cyanides, carbides and carbonates are not considered OMC because in these compounds metal is not attached to carbon of alkyl gp. or carbon of carbonyl group.

#### Classification of Organometallic Compounds

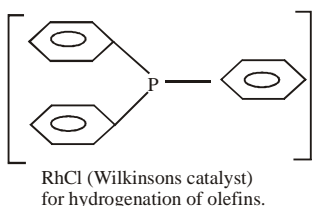
OMC can be classified into three main categories

- (a) **† - bonded OMC** : These compounds are formed mostly by non transition and metalloid elements.  
**eg.** R - Mg - X, (grignard's reagent)  
 $(\text{CH}_3)_2\text{Zn}$  (Dimethyl zinc or frankland's reagent)  
 $(\text{R})_2\text{Cd}$ , (dialkyl cadmium)  
 $(\text{C}_2\text{H}_5)_4\text{Pb}$  (Tetra ethyl lead)  
 $(\text{CH}_3)_3\text{Al}$ ,  $\text{TiCl}_4$  (Ziegler natta catalyst) etc.

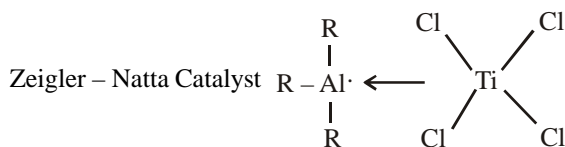
- (b) **f - bonded OMC** : These are usually formed by transition metals. eg. Ferrocene  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$  where  $\eta$ =No. of carbon atoms combined with metal atom.  
Zeise's salt  $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$   
Dibenzene chromium  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$
- (c) **† and f - bonded OMC** : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compds. of these metals have both  $\sigma$ , and  $\pi$  bonds. e.g.  $\text{INi}(\text{CO})_4$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Mn}_2(\text{CO})_{10}]$ ,  $[\text{M}(\text{CO})_6]$  where M is Cr, Mo, W.

**Application 'of Organometallic Compounds**

**(1) As homogeneous Catalyst**



**(2) As heterogenous catalyst**



Tri alkyl Al ← Titanium tetrachloride used for Polymerisation

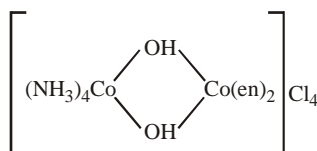
- (3) **Organic synthesis** - OMC like R - Mg - X,  $\text{R}_2\text{-Cd}$ ,  $\text{CH}_3\text{-Li}$  etc. are used for preparation of almost all type of organic compds. .
- (4) **As petrol additive** - TEL(Tetraethyl lead) is used as antiknock compd. in petrol.
- (5) **In medicine** - Organo arsenic compds are used as medicine for syphilis deases.
- (6) **In agriculture** - Seeds are treated with ethyl Hg Chloride to protect the plants against infection.

**TRY IT YOURSELF-3**

- Q.1** Predict which among the following properties given below belong to double salt and co-ordination compounds.
- The blue coloured solution prepared by  $\text{Cu}^{+2}(\text{aq})$  &  $\text{NH}_3(\text{NH}_4^+ \text{aq})$  does not show the presence of  $\text{Cu}^{+2}$
  - Compounds which are stable in the solid state but break up into its constituents in aqueous solution.
  - Aq. solution of carnallite.
  - The compounds in which central metal ion form dative bonds with species surrounding it.
  - Mohr's salt.
- Q.2** Write the systematic names of the following coordination entities and compounds.
- $[\text{CoCl}_2(\text{NH}_3)_4]^+$
  - $[\text{CrCl}_3(\text{NH}_3)_3]$
  - $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
  - $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - $[\text{PtCl}(\text{NH}_3)_5]\text{Cl}_3$

- Q.3** Consider the following complexes –
- $\text{K}_2\text{PtCl}_6$
  - $\text{PtCl}_4 \cdot 2\text{NH}_3$
  - $\text{PtCl}_4 \cdot 3\text{NH}_3$
  - $\text{PtCl}_4 \cdot 5\text{NH}_3$
- Their electrical conductances in aq. solutions are –
- 256, 0, 97, 404
  - 404, 0, 97, 256
  - 256, 97, 0, 404
  - 404, 97, 256, 0

- Q.4** Identify the complexes which are expected to be coloured and explain.
- $\text{Ti}(\text{NO}_3)_4$
  - $[\text{Cu}(\text{NCCH}_3)_4]^+\text{BF}_4^-$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$
  - $\text{K}_3[\text{VF}_6]$
- Q.5** Write the IUPAC name of the given compound.



- Q.6** As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is :
- Tetraaquadiamminocobalt(III) chloride
  - Tetraaquadiamminocobalt(III) chloride
  - Diaminetetraaquacobalt(III) chloride
  - Diamminetetraaquacobalt(III) chloride

- Q.7**  $\text{NiCl}_2[\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)]_2$  exhibits temperature dependent magnetic behavior (paramagnetic/diamagnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively :
- tetrahedral and tetrahedral
  - square planar and square planar
  - tetrahedral and square planar
  - square planar and tetrahedral

- Q.8** The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) –
- $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
  - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$
  - $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$
  - $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$
- Q.9** EDTA<sup>4-</sup> is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in  $[\text{Co}(\text{EDTA})]^{1-}$  complex ion is

- Q.10** Colourless species among the following is –
- $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Ni}(\text{CN})_4]^{2-}$
  - Both (A) and (C)

**ANSWERS**

- (a) Co-ordination, (b) Double salt (c) Double salt (d) Co-ordination, (e) Double salt
- (i) tetraamminedichloridocobalt (III)  
(ii) triaamminetrichloridochromium (III)  
(iii) potassiumtrioxalatochromate (III)  
(iv) potassium hexaacyanoferrate (II)  
(v) pentaamminechloridoplatinum (IV) chloride
- (A) (4) (CD)
- Tetraamine cobalt (III) di- $\mu$ -hydroxo bis ethylenediamine cobalt (III) Chloride.
- (6) (D) (7) (C) (8) (BD)
- (9) 8 (10) (C)

## USEFUL TIPS

- \* The doubly degenerate  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals ( $e_g$  orbitals) are of higher energy than triply degenerate  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  ( $t_{2g}$  orbitals), that are lower in energy.
- \* The tetrahedral crystal field splitting is only 4/9 of the octahedral splitting and there is no known low spin tetrahedral complex.
- \* In brown ring complex,  $\text{Fe}[(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ , the oxidation state of Fe is +1. In this complex, the hybridisation of Fe is  $d^2sp^3$ . Prussian blue is  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ . The hybridisation of Fe in  $[\text{Fe}(\text{CN})_6]^{2-}$  is  $d^2sp^3$ .  $\text{Fe}(\text{CO})_5$  has triangular bipyramidal shape ( $dsp^3$  hybridisation).
- \*  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoF}_6]^{3-}$  are high spin complexes.
- \* The strong field ligands produce low-spin complexes.
- \*  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  are low spin complexes.

## ADDITIONAL EXAMPLES

### Example 1 :

Which of the following statements is most likely to be incorrect –

- (1)  $\text{Ti}(\text{NO}_3)_4$  is a colourless compound
- (2)  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$  is a colourless compound
- (3)  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$  is a coloured compound
- (4)  $\text{K}_3[\text{VF}_6]$  is a colourless compound

### Sol. (4).

- (1)  ${}_{22}\text{Ti}^{4+}$  E.C. =  $3d^04s^0$  colourless
- (2)  ${}_{29}\text{Cu}^+$  E.C. =  $3d^{10}4s^0$  colourless
- (3)  ${}_{24}\text{Cr}^{3+}$  E.C. =  $3d^34s^0$  coloured (most likely)
- (4)  ${}_{23}\text{V}^{3+}$  E.C. =  $3d^24s^0$  coloured (most likely)

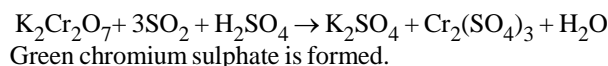
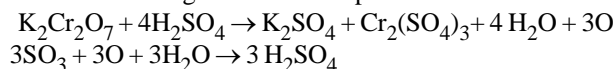
### Example 2 :

When  $\text{SO}_2$  is passed in acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution –

- (1) the solution turns blue
- (2) the solution is decolourised
- (3)  $\text{SO}_2$  is reduced
- (4) chromium sulphate is formed

### Sol. (4).

When  $\text{SO}_2$  gas is passed in acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution the following reaction takes place



### Example 3 :

In which of the following transition metal ions d-d transition is possible –

- (1)  $\text{Cu}^+$
- (2)  $\text{Zn}^{+2}$
- (3)  $\text{Ti}^{+3}$
- (4)  $\text{Sc}^{+3}$

### Sol. (3).

The d-d transition is possible in  $\text{Ti}^{+3}$  because it has got  $3d^1$  configuration, hence one electron can easily go from one orbital to another in degenerate levels.

### Example 4 :

Transition metals normally have unfilled 'd' orbitals which are degenerate. The colour of transition metal ions is due to absorption of light in visible region. Which of the following transition is responsible for providing the colour?

- (1) d-s transition
- (2) s-d transition
- (3) d-d transition
- (4) s-s transition

### Sol. (3).

Whenever a transition metal complex is formed, the approaching ligand removes the degeneracy of the 'd' orbitals. 'd' orbitals are split up into two sets having a different amount of energy. Absorption of light causes the promotion of electrons from lower energy set of orbitals to a higher energy set within the same 'd' subshell. This d-d transition is responsible for the colour of the ion.

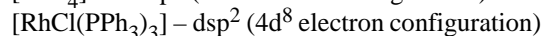
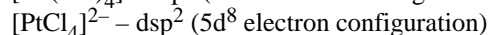
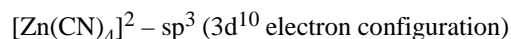
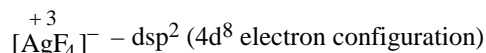
### Example 5 :

All the following complexes show decreases in their weights when placed in a magnetic balance then the group of complexes having tetrahedral geometry is

- (i)  $\text{Ni}(\text{CO})_4$
  - (ii)  $\text{K}[\text{AgF}_4]$
  - (iii)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$
  - (iv)  $\text{K}_2[\text{PtCl}_4]$
  - (v)  $[\text{RhCl}(\text{PPh}_3)_3]$
- (1) (ii), (iii), (v)
  - (2) (ii), (ii), (iii)
  - (3) (i), (ii), (iv)
  - (4) None of these

### Sol. (4).

$\text{Ni}(\text{CO})_4 - sp^3$  (CO strong field ligand)



All complexes are diamagnetic in nature which show decrease in their weights in magnetic field.

### Example 6 :

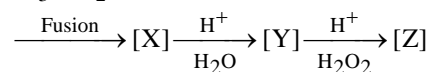
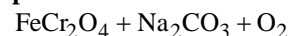
Amongst  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$  (At. No. Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are

- (1)  $\text{TiF}_6^{2-}$  &  $\text{Cu}_2\text{Cl}_2$
- (2)  $\text{Cu}_2\text{Cl}_2$  &  $\text{NiCl}_4^{2-}$
- (3)  $\text{TiF}_6^{2-}$  &  $\text{CoF}_6^{3-}$
- (4)  $\text{CoF}_6^{3-}$  &  $\text{NiCl}_4^{2-}$

### Sol. (1).

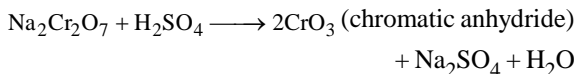
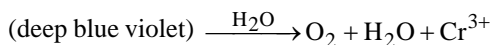
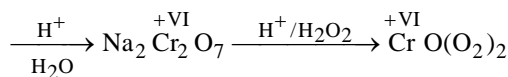
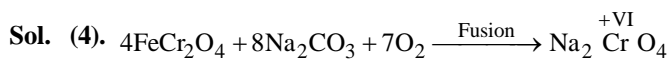
Due to the absence of unpaired electron  $\text{TiF}_6^{2-}$  &  $\text{Cu}_2\text{Cl}_2$  colourless species.

### Example 7 :



Which of the following statement is true for the compounds [X], [Y] and [Z] ?

- (1) In all three compounds, the chromium is in + 6 oxidation state.
- (2) [Z] is a deep blue-violet coloured compound which decomposes rapidly in aqueous solution into  $\text{Cr}^{3+}$  and dioxygen.
- (3) Saturated solution of [Y] gives bright orange compound, chromic anhydride. with concentrated  $\text{H}_2\text{SO}_4$
- (4) All of these.

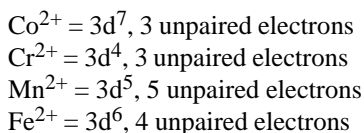


**Example 8 :**

The pair in which both species have same magnetic moment (spin only value) is –

- (A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{CoCl}_4]^{2-}$   
 (B)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (C)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   
 (D)  $[\text{CoCl}_4]^{2-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

**Sol. (B).** Same magnetic moment = Same number of unpaired electrons =  $\sqrt{n(n+2)}$ , Where n = no. of unpaired electrons



**Example 9 :**

All the following complexes show a decreases in their weights when placed in a magnetic balance. Then which of these has square planar geometry ?

- (A)  $\text{Ni}(\text{CO})_4$  (B)  $\text{K}[\text{AgF}_4]$  (C)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  (D) None

**Sol. (B).** In  $\text{K}[\text{AgF}_4]$ , Ag (III) has  $4d^8$  configuration. This has higher CFSE which favours pairing of electrons and thus complex is diamagnetic and square planar.

**Example 10 :**

Which of the following statements is not correct ?

- (a)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  &  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  have same value of CFSE.  
 (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  have same value of magnetic moment.

- (A) only a (B) only b  
 (C) Both a and b (D) None of these

**Sol. (A).** (a) Ammonia is a stronger field ligand than water. So,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  will have higher CFSE than  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ .  
 (b) Both complexes  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  have  $sp^3d^2$  hybridisation with two unpaired electrons. So, they possess same magnetic moment (spin only).

**Passage (Ex.11-Ex.13)**

(T) imparts violet colour  $\xrightarrow{\text{Compd (U)+conc. H}_2\text{SO}_4}$  (V)

Red gas  $\xrightarrow{\text{NaOH+AgNO}_3}$  (W) Red ppt.

$\xrightarrow{\text{NH}_3 \text{ soln.}}$  (X)

(W) Red ppt.  $\xrightarrow{\text{dil HCl}}$  (Y) white ppt.

(U)  $\xrightarrow[\Delta]{\text{NaOH}}$  (Z) gas (gives white fumes with HCl)

**Example 11 :**

The compound W is –

- (1)  $\text{CrO}_3$  (2)  $\text{Ag}_2\text{CrO}_4$   
 (3)  $\text{HgI}_2$  (4)  $\text{AgNO}_2$

**Example 12 :**

The compound T and U are –

- (1)  $\text{KMnO}_4$ , HCl (2)  $\text{K}_2\text{Cr}_2\text{O}_7$ , HCl  
 (3)  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{NH}_4\text{Cl}$  (4)  $\text{K}_2\text{CrO}_4$ , KCl

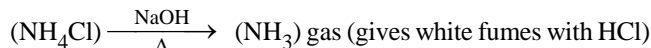
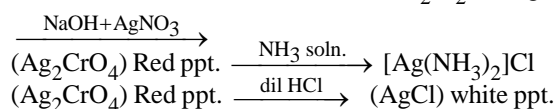
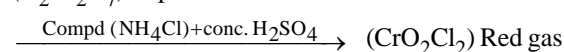
**Example 13 :**

The compound 'V' is –

- (1)  $\text{CrO}_3$  (2)  $\text{Cl}_2$   
 (3)  $\text{Br}_2$  (4)  $\text{CrO}_2\text{Cl}_2$

(11) (2), (12) (3), (13) (4).

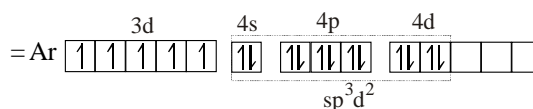
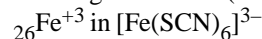
( $\text{K}_2\text{Cr}_2\text{O}_7$ ) imparts violet colour



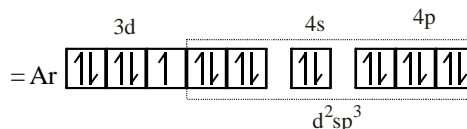
**Example 14 :**

For the octahedral complexes of  $\text{Fe}^{3+}$  in  $\text{SCN}^-$  (thiocyanato-S) and in  $\text{CN}^-$  ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Atomic number of Fe = 26]

**Sol. 4.**  $\text{SCN}^-$  is weak field effect (WFE) ligand whereas  $\text{CN}^-$  is strong field effect (SFE) ligand.



$$\text{Spin only magnetic moment} = \sqrt{5(5+2)} = \sqrt{35} \text{ BM}$$



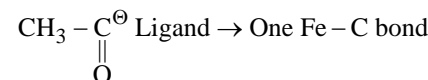
$$\text{Spin only magnetic moment} = \sqrt{1(1+2)} = \sqrt{3} \text{ BM}$$

$$\text{Difference} = \sqrt{35} - \sqrt{3} \approx 4$$

**Example 15 :**

In the complex acetyl bromidodicarbonylbis(triethyl phosphine)iron(II), the number of Fe–C bond(s) is

**Sol. 3.**  $[\text{Fe}(\text{CH}_3\text{CO})\text{Br}(\text{CO})_2\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]$



CO Ligand  $\rightarrow$  two Fe – C bond

## QUESTION BANK

## CHAPTER 8 : d, f-BLOCK ELEMENTS &amp; COORDINATION COMPOUNDS

## EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

**PART 1 : POSITION IN THE PERIODIC****TABLE (d-BLOCK)**

- Q.1** Which element belongs to d – block  
(A) Na (B) Ca  
(C) Cu (D) Ar
- Q.2** Choose the correct statement related to transition metals series,  
(A) 3d series is from Sc to Zn  
(B) 4d series is from Y to Cd  
(C) 5d series is from La to Hg omitting Ce to Lu.  
(D) All of these
- Q.3** Which of the following elements does not belong to the first transition series?  
(A) Fe (B) Ag  
(C) V (D) Cu
- Q.4** Choose the correct statement –  
(A) Zinc, cadmium and mercury are not regarded as transition metals.  
(B) Zinc, cadmium and mercury are regarded as transition metals.  
(C) Zinc, cadmium and mercury have full  $d^{10}$  configuration in their ground state.  
(D) Both (A) and (C)

**PART 2 : ELECTRONIC CONFIGURATIONS OF THE d-BLOCK ELEMENTS**

- Q.5** The element having general electronic configuration  $3d^4 4s^1$  is  
(A) Noble gas (B) Non-metal  
(C) Metalloid (D) Transition metal
- Q.6** The placement of Zn, Cd and Hg along with d-block elements is not proper because  
(A) Their d orbitals are completely filled.  
(B) Their d orbitals are empty.  
(C) They do not form complex compounds.  
(D) They do not form coloured compounds.
- Q.7** Which of the following electronic configuration is that of a transition element  
(A)  $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6$  (B)  $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^1$   
(C)  $1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$  (D)  $1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
- Q.8** The electronic configuration of Tantalum (Ta) is  
(A)  $6s^25d^14f^0$  (B)  $6s^25d^24f^{14}$   
(C)  $6s^25d^34f^{14}$  (D)  $6s^25d^44f^{14}$
- Q.9** The last electron in d-block elements goes to  
(A)  $(n-1)d$  (B) nd  
(C) np (D)  $(n-1)s$
- Q.10** Choose the correct statement related to electronic configurations of Cr and Cu –  
(a) Cr :  $3d^5 4s^1$  (b) Cr :  $3d^4 4s^2$   
(c) Cu :  $3d^{10} 4s^1$  (d) Cu :  $3d^9 4s^2$

- (A) (a) and (c) (B) (b) and (d)  
(C) (b) and (c) (D) (a) and (d)

- Q.11** The highest oxidation state is exhibited by the transition metals with configuration:  
(A)  $(n-1)d^3 ns^2$  (B)  $(n-1)d^5 ns^1$   
(C)  $(n-1)d^5 ns^2$  (D)  $(n-1)d^8 ns^2$
- Q.12** Atomic size of these elements is almost same because pairing of electrons takes place in d orbitals causing repulsion and effective nuclear charge does not increase appreciably  
(A) Sc, Ti, V (B) Ni, Cu, Zn  
(C) Fe, Co, Ni (D) V, Ni, Cu
- Q.13** Which of the following is a 'd-block element'?  
(A) Gd (B) Hs  
(C) Es (D) Cs
- Q.14** General electronic configuration of transition metals is  
(A)  $(n-1)d^{1-10} ns^2$  (B)  $nd^{10} ns^2$   
(C)  $(n-1)d^{10} ns^2$  (D)  $(n-1)d^{1-5} ns^2$
- Q.15** The atomic number (Z) of an element is 25. In its ground state, how many electrons are present in the  $n^{\text{th}}$  shell ?  
(A) 13 (B) 2  
(C) 15 (D) 3

**PART 3 : GENERAL PROPERTIES OF THE TRANSITION ELEMENTS (d-BLOCK)**

- Q.16** Which statement is true about the transitional elements  
(A) They are highly reactive.  
(B) They show variable oxidation states.  
(C) They have low melting point.  
(D) They are highly electropositive.
- Q.17** Which forms coloured salts  
(A) Metals (B) Non-metals  
(C) p-block elements (D) Transition elements
- Q.18** Which of the following transition metal has lowest boiling point (B.P.)  
(A) Zn (B) Sc  
(C) Ti (D) V
- Q.19** Which of the following element has maximum first ionisation potential  
(A) V (B) Ti  
(C) Cr (D) Mn
- Q.20** Transition metals show paramagnetism  
(A) Due to characteristic configuration  
(B) High lattice energy  
(C) Due to variable oxidation states  
(D) Due to unpaired electrons
- Q.21** Which of the following is expected to form colourless complex  
(A)  $Ni^{2+}$  (B)  $Cu^+$   
(C)  $Ti^{3+}$  (D)  $Fe^{3+}$
- Q.22** The most stable oxidation state of Mn is  
(A) +2 (B) +4 (C) +5 (D) +7

- Q.23** Atomic radii from Cr to Cu is almost identical because of  
 (A) Increasing nuclear charge from Cr to Cu.  
 (B) Repulsion among increased electrons.  
 (C) Increased screening effect to nullify increased nuclear charge.  
 (D) All the above
- Q.24** In the series Sc(Z = 21) to Zn(Z = 30), the enthalpy of atomisation of which element is least?  
 (A) Sc (B) Mn  
 (C) Cu (D) Zn
- Q.25** Identify the species in which the metal atom is in +6 oxidation state.  
 (A)  $\text{MnO}_4^-$  (B)  $\text{Cr}(\text{CN})_6^{3-}$   
 (C)  $\text{NiF}_6^{2-}$  (D)  $\text{CrO}_2\text{Cl}_2$
- Q.26** In which of the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other ?  
 (A)  $\text{Ti}^+$ ,  $\text{Ti}^{3+}$  (B)  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$   
 (C)  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$  (D)  $\text{V}^{2+}$ ,  $\text{VO}^{2+}$  ( $\text{V}^{4+}$ )
- Q.27** Which of the following compounds is not coloured  
 (A)  $\text{Na}_2[\text{CuCl}_4]$  (B)  $\text{Na}_2[\text{CdCl}_4]$   
 (C)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (D)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- Q.28** Which one of the following transition metal ions has the lowest density ?  
 (A) Copper (B) Nickel  
 (C) Scandium (D) Zinc
- Q.29** Colour of transition metal ions are due to absorption of some wavelength. This results in  
 (A) d-s transition (B) s-s transition  
 (C) s-d transition (D) d-d transition
- Q.30** The first ionisation energies of the elements of the first transition series (Ti to Cu) :  
 (A) Increases as the atomic number increases.  
 (B) Decreases as the atomic number increases.  
 (C) Do not show any change as the addition of electrons takes place in the inner (n - 1) d-orbitals.  
 (D) Increases from Ti to Mn and then decreases from Mn to Cu.
- Q.31** In context with the transition elements, which of the following statements is incorrect ?  
 (A) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.  
 (B) In the highest oxidation states, the transition metals show basic character and form cationic complexes.  
 (C) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.  
 (D) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
- Q.32** The catalytic activity of the transition metals and their compounds is described to –  
 (A) their chemical reactivity.  
 (B) their magnetic behaviour.  
 (C) their filled d-orbitals.  
 (D) their ability to adopt multiple oxidation state and their complexing ability.
- Q.33** Metallic radii of some transition elements are given below. Which of these elements will have highest density ?  

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

 (A) Fe (B) Ni  
 (C) Co (D) Cu
- Q.34** For Sc(III), Ti(IV), Pd(II) and Cu(II) ions, correct statements are –  
 (A) All are paramagnetic.  
 (B) All are diamagnetic.  
 (C) Sc(III), Ti(IV) are paramagnetic and Pd(III), Cu(II) are diamagnetic.  
 (D) Sc(III), Ti(IV) are diamagnetic and Pd(II), Cu(III) are paramagnetic.
- Q.35** The common oxidation states of Ti are  
 (A) +2, +3 (B) +3, +4  
 (C) -3, -4 (D) +2, +3, +4
- Q.36**  $\text{Fe}^{3+}$  compounds are more stable than  $\text{Fe}^{2+}$  compounds because  
 (A)  $\text{Fe}^{3+}$  has smaller size than  $\text{Fe}^{2+}$   
 (B)  $\text{Fe}^{3+}$  has  $3d^5$  configuration (half-filled)  
 (C)  $\text{Fe}^{3+}$  has higher oxidation state  
 (D)  $\text{Fe}^{3+}$  is paramagnetic in nature.
- Q.37**  $\text{Ti}^{2+}$  is purple while  $\text{Ti}^{4+}$  is colourless, because  
 (A) There is no crystal field effect in  $\text{Ti}^{4+}$ .  
 (B)  $\text{Ti}^{2+}$  has  $3d^2$  configuration.  
 (C)  $\text{Ti}^{4+}$  has  $3d^2$  configuration.  
 (D)  $\text{Ti}^{4+}$  is a very small cation when compared to  $\text{Ti}^{2+}$  and hence, does not absorb any radiation.
- Q.38** Which of the following d-block element has half-filled penultimate as well as valence subshell ?  
 (A) Cu (B) Au  
 (C) Ag (D) Cr
- Q.39** Which of the following is arranged in order of decreasing thermal stability ?  
 (A)  $\text{Zn} > \text{Hg} > \text{Cd}$  (B)  $\text{Cd} > \text{Hg} > \text{Zn}$   
 (C)  $\text{Zn} > \text{Cd} > \text{Hg}$  (D)  $\text{Hg} > \text{Cd} > \text{Zn}$
- Q.40** Which of the following statement is not true?  
 (A) Transition elements form the complex compounds.  
 (B) Coloured compounds of transition elements are paramagnetic.  
 (C) Colourless compounds of transition elements are diamagnetic.  
 (D) Colour less compounds of transition elements are paramagnetic.
- Q.41** Reactivity of transition elements decreases almost regularly from Sc to Cu because of  
 (A) Lanthanoid contraction  
 (B) Regular increase in ionisation enthalpy  
 (C) Regular decrease in ionisation enthalpy  
 (D) Increase in number of oxidation states.
- Q.42** Elements which generally exhibit multiple oxidation states and whose ions are usually coloured are  
 (A) Metalloids (B) Non-metals  
 (C) Transition elements (D) Gases

**PART 4 : SOME IMPORTANTS  
COMPOUNDS OF TRANSITION  
ELEMENTS**

- Q.43** Acidified potassium dichromate reacts with potassium iodide and oxidises it to  $I_2$ . What is the oxidation state of chromium in the products of the reaction ?  
(A) +4 (B) +6  
(C) +3 (D) +2
- Q.44** One of the products formed due to the reaction between  $KMnO_4$  and  $HCl$  is  
(A) Red liquid (B)  $MnO_2$   
(C) Greenish yellow gas (D)  $HClO_4$
- Q.45** Which of the following compounds is used as the starting material for the preparation of potassium dichromate -  
(A)  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$  (Chrome alum)  
(B)  $PbCrO_4$  (Chrome yellow)  
(C)  $FeCr_2O_4$  (Chromite)  
(D)  $PbCrO_4 \cdot PbO$  (Chrome red)
- Q.46** On heating potassium permanganate, one of the following compound is not obtained.  
(A)  $O_2$  (B)  $MnO$   
(C)  $MnO_2$  (D)  $K_2MnO_4$
- Q.47** Compound that is both paramagnetic & coloured is  
(A)  $K_2Cr_2O_7$  (B)  $(NH_4)_2[TiCl_6]$   
(C)  $VO_2$  (D)  $K_3[Cu(CN)_4]$
- Q.48** Potassium dichromate is prepared from  
(A) Chromate obtained by the fusion of chromite ore with sodium carbonate in free access of air.  
(B) Pyrolusite which is fused with potassium hydroxide in the presence of air.  
(C) Iron pyrite by the fusion with potassium carbonate in presence of moisture.  
(D) None of these
- Q.49** What happens when potassium iodide reacts with acidic solution of potassium dichromate ?  
(A) it liberates iodine  
(B) Potassium sulphate is formed  
(C) Chromium sulphate is formed  
(D) All the above products are formed
- Q.50** Which of the following is correct representation of reaction of acidified permanganate solution with sulphurous acid ?  
(A)  $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$   
(B)  $MnO_4^- + SO_3^{2-} + 2H_2O \rightarrow S + Mn^{2+} + 4H^+$   
(C)  $2MnO_4^- + 5SO_3^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + S + 2Mn^{2+} + 4H^+$   
(D)  $3MnO_4^- + 2SO_3^{2-} + 2H_2O \rightarrow 2S + 3Mn^{2+} + 4H^+$
- Q.51** On addition of small amount of  $KMnO_4$  to concentrated  $H_2SO_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following  
(A)  $Mn_2O_7$  (B)  $MnO_2$   
(C)  $MnSO_4$  (D)  $Mn_2O_3$
- Q.52** Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in the three conditions are, respectively  
(A)  $MnO_2$ ,  $MnO_2$ ,  $Mn^{2+}$  (B)  $MnO_4^{2-}$ ,  $Mn^{3+}$ ,  $Mn^{2+}$   
(C)  $Mn_2$ ,  $MnO_4^{2-}$ ,  $Mn^{3+}$  (D)  $Mn$ ,  $MnO_4$ ,  $Mn^{2+}$
- Q.53** Which of the following statements is correct about equivalent weight of  $KMnO_4$ ?  
(A) It is one third of its molecular weight in alkaline medium.  
(B) It is one fifth of its molecular weight in alkaline medium.  
(C) It is equal to its molecular weight in acidic medium.  
(D) It is one third of its molecular weight in acidic medium.
- Q.54** The colour of potassium dichromate depends upon pH of solution. The chromate and dichromate are inter convertible in aqueous solution depending upon pH. In acidic pH, chromate ions get converted into ions whose colour is  
(A) Blue (B) Orange  
(C) Red (D) Colourless
- Q.55** The number of moles of  $KMnO_4$  that are needed to react completely with one mole of ferrous oxalate in acidic solution is  
(A)  $3/5$  (B)  $2/5$   
(C)  $4/5$  (D) 1
- Q.56** Which of the following statement is true about dichromate ion structure?  
(A) It consists of two tetrahedra sharing one corner with Cr – O – Cr bond angle of  $126^\circ$ .  
(B) It has one Cr–Cr bond.  
(C) It has two Cr–Cr bond.  
(D) None of these
- Q.57** Which of the following compounds has colour but no unpaired electrons ?  
(A)  $KMnO_4$  (B)  $K_2MnO_4$   
(C)  $MnSO_4$  (D)  $MnCl_2$

**PART 5 : THE LANTHANOIDS**

- Q.58** Lanthanoid contraction is due to increase in  
(A) Atomic number  
(B) Effective nuclear charge  
(C) Atomic radius  
(D) Valence electrons
- Q.59** Which of the following oxidation state is common for all lanthanoids ?  
(A) +2 (B) +3  
(C) +4 (D) +5
- Q.60** Choose the correct statement  
(A) The lanthanoids are silvery white soft metals.  
(B)  $La^{3+}$  and  $Lu^{3+}$  ions are colourless.  
(C) Zr and Hf have almost identical radii.  
(D) All of these
- Q.61** Lanthanoid contraction is responsible for the fact that  
(A) Zr and Y have about the same radius.  
(B) Zr and Nb have similar oxidation state.  
(C) Zr and Hf have about the same radius.  
(D) Zr and Zn have similar oxidation state.



- Q.62** Which of the following lanthanide is commonly used?  
 (A) Lanthanum (B) Nobelium  
 (C) Thorium (D) Cerium
- Q.63** Although zirconium belongs to 4d transition series and Hafnium to 5d transition series even then they show similar physical and chemical properties because –  
 (A) Both belong to d-block.  
 (B) Both have same number of electrons.  
 (C) Both have similar atomic radius.  
 (D) Both belong to the same group of the periodic table.
- Q.64** Which of the following lanthanide ion is paramagnetic ?  
 (A)  $Ce^{4+}$  (B)  $Yb^{2+}$   
 (C)  $Lu^{3+}$  (D)  $Eu^{2+}$
- Q.65** Which is the non-lanthanide element ?  
 (A) La (B) Lu  
 (C) Pr (D) Pm
- Q.66** Across the lanthanide series, the basicity of the lanthanoid hydroxides:  
 (A) increases  
 (B) decreases  
 (C) first increases and then decreases  
 (D) does not change
- Q.67** Composition of mischmetal is  
 (A) 5% of a lanthanoid metal, 95% of iron and traces of S, C, Ca and Al.  
 (B) 95% of an actinoid metal, 5% of iron and traces of S, C, Ca and Al.  
 (C) 95% of a lanthanoid metal, 5% of iron and traces of S, C, Ca and Al.  
 (D) 95% of a transition metal, 5% of iron and traces of S, C, Ca and Al.

### **PART 6: THE ACTINOIDS**

- Q.68** What is the total number of inner transition elements in the periodic table ?  
 (A) 10 (B) 14  
 (C) 30 (D) 28
- Q.69** The electronic configuration of actinoids cannot be assigned with degree of certainty because of  
 (A) Small energy difference between 5f and 6d levels.  
 (B) Overlapping of inner orbitals.  
 (C) Free movement of electrons over all the orbitals.  
 (D) None of the above.
- Q.70** There are 14 elements in actinoid series. Which of the following elements does not belong to this series?  
 (A) U (B) Np  
 (C) Tm (D) Fm
- Q.71** Which elements is not an actinide?  
 (A) Terbium (B) Californium  
 (C) Uranium (D) Curium
- Q.72** In human body if necessary, the plate, screw or wire used for surgery are made up of  
 (A) Ni (B) Au  
 (C) Pt (D) Ta
- Q.73** Hypo is used in photography to  
 (A) Reduce AgBr grains to metallic silver.  
 (B) Convert metallic silver to silver salt.  
 (C) Remove undecomposed silver bromide as a soluble complex.  
 (D) Remove reduced silver.

### **PART 8: WERNER'S THEORY OF COORDINATION COMPOUNDS**

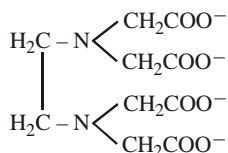
- Q.74** The primary valence of the metal ion in the co-ordination compound  $K_2[Ni(CN)_4]$  is –  
 (A) Four (B) Zero  
 (C) Two (D) Six
- Q.75** When one mole of each of the following complexes is treated with excess of  $AgNO_3$ , which will give maximum amount of  $AgCl$  ?  
 (A)  $[Co(NH_3)_6]Cl_3$  (B)  $[Co(NH_3)_5Cl]Cl_2$   
 (C)  $[Co(NH_3)_4Cl_2]Cl$  (D)  $[Co(NH_3)_3Cl_3]$
- Q.76** Which one is the most likely structure of  $CrCl_3 \cdot 6H_2O$ , if 1/3 of total chlorine of the compound is precipitated by adding  $AgNO_3$  to its aqueous solution ?  
 (A)  $CrCl_3 \cdot 6H_2O$  (B)  $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$   
 (C)  $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$  (D)  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
- Q.77** Which of the following is not a double salt but is a complex salt ?  
 (A)  $KCl \cdot MgCl_2 \cdot 6H_2O$   
 (B)  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$   
 (C)  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$   
 (D)  $4KCN \cdot Fe(CN)_2$
- Q.78** According to the postulates of Werner's theory for coordination compounds  
 (A) Primary valence is ionizable.  
 (B) Secondary valence is ionizable.  
 (C) Primary and secondary valences are non-ionizable.  
 (D) Only primary valence is non-ionizable.
- Q.79** Primary valence of binary compounds  $CrCl_3$ ,  $CoCl_2$  and  $PdCl_2$  are –  
 (A) 2, 2 and 3 respectively. (B) 2, 3 and 2 respectively.  
 (C) 3, 3 and 2 respectively. (D) 3, 2 and 2 respectively.
- Q.80** Copper sulphate dissolves in ammonia due to the formation of  
 (A)  $Cu_2O$  (B)  $[Cu(NH_3)_4]SO_4$   
 (C)  $[Cu(NH_3)_4]OH$  (D)  $[Cu(H_2O)_4]SO_4$
- Q.81** Choose the correct statement related Werner's theory –  
 (A) It does not explain the magnetic spectral properties.  
 (B) The secondary valence is equal to the coordination number.  
 (C) The primary valences are satisfied by negative ions.  
 (D) All of these

### **PART 7: SOME APPLICATIONS OF d-AND f-BLOCK ELEMENTS**

- Q.72** The substance used in cancer therapy is  
 (A) Rn (B) Ni  
 (C) Fe (D) Co

**PART 9 : IMPORTANT TERMS OF  
PERTAINING COORDINATION  
COMPOUNDS**

- Q.83** The ligand in potassium ferricyanide is  
(A)  $K^+$  (B)  $CN^-$   
(C)  $Fe^{3+}$  (D)  $(CN)_6$
- Q.84** Co-ordination number of aluminum is  
(A) 8 (B) 6  
(C) 12 (D) 4
- Q.85** The oxidation number of Cr in  $[Cr(NH_3)_6]Cl_3$  is  
(A) 8 (B) 6  
(C) 4 (D) 3
- Q.86** The ligand  $N(CH_2CH_2NH_2)_3$  is  
(A) Bidentate (B) Tridentate  
(C) Tetradentate (D) Pentadentate
- Q.87** The oxidation number of Pt in  $[Pt(C_2H_4)Cl_3]^-$  is:  
(A) +1 (B) +2  
(C) +3 (D) +4
- Q.88** Which of the following statement(s) is/are true about  $[EDTA^{4-}]$  ?  
I. It is ethylenediaminetetracetate ion.  
II. It is a hexadentate ligand.  
III. It can bind through two nitrogen and four oxygen atoms to a central metal ion.  
IV. Its structure is



The correct set of statements is –

- (A) I, II and III (B) II and IV  
(C) I, III and IV (D) I, II, III and IV
- Q.89** Which of the following ligands will not show chelation?  
(A) EDTA (B) DMG  
(C) Ethene-1, 2-diamine (D)  $SCN^-$
- Q.90** Identify the statement which is not correct ?  
(A) Coordinate compounds are mainly known for transition metals.  
(B) Coordination number and oxidation state of a metal are same.  
(C) Tetrahedra complexes do not show geometrical isomerism.  
(D) A ligand donates at least one electron pair to the metal atom to form a bond.
- Q.91** Ligands in a complex salt are  
(A) Anions linked by coordinate bonds to a central metal atom or ion.  
(B) Cations linked by coordinate bonds to a central metal atom or ion  
(C) Molecules linked by coordinate bonds to a central metal atom or ion.  
(D) Ions or molecules linked by coordinate bonds to a central metal atom or ion.

- Q.92** In the compound lithium tetrahydridoaluminate, the ligand is :  
(A)  $Al^+$  (B) H  
(C)  $H^-$  (D) None of these
- Q.93** Which of the following has a square planar geometry ?  
(A)  $[PtCl_4]^{2-}$  (B)  $[CoCl_4]^{2-}$   
(C)  $[FeCl_4]^{2-}$  (D)  $[NiCl_4]^{2-}$   
(At. nos. : Fe = 26, Co = 27, Ni = 28, Pt = 78)
- Q.94** Which one is not a ligand ?  
(A)  $PH_3$  (B)  $NO^+$   
(C)  $BF_3$  (D)  $Cl^-$
- Q.95** Which of the following species is not expected to be a ligand ?  
(A) NO (B)  $NH_4^+$   
(C)  $NH_2CH_2CH_2NH_2$  (D) CO
- Q.96** The oxidation state of Fe in brown complex  $[Fe(H_2O)_5NO]SO_4$  is  
(A) +1 (B) +2  
(C) +3 (D) +4
- Q.97** Which of the following is not a neutral ligand ?  
(A)  $H_2O$  (B)  $NH_3$   
(C) ONO (D) CO
- Q.98** A group of atoms can function as ligand only when –  
(A) It is small molecule.  
(B) It has an unshared electron pair.  
(C) It is a negatively charged ion.  
(D) It is positively charged ion.
- Q.99** Which of the following are ambidentate ligands?  
(i)  $SCN^-$  (ii)  $NO_3^-$  (iii)  $NO_2^-$  (iv)  $C_2O_4^{2-}$   
(A) i and iii (B) i and iv  
(C) ii and iii (D) ii and iv

**PART 10 : NOMENCLATURE OF  
COORDINATION COMPOUNDS**

- Q.100** IUPAC name of  $K_3[Fe(CN)_6]$  is  
(A) Potassium ferrocyanide (II)  
(B) Potassium hexaferrocyanate (III)  
(C) Potassium ferrohexacyanate (II)  
(D) Potassium hexacyanoferrate (III)
- Q.101** The IUPAC name of  $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$  is  
(A) Potassium ammine dicyanodioxoperoxochromate (VI)  
(B) Potassium ammine cyano peroxo dioxochromium (VI)  
(C) Potassium ammine cyano peroxo dioxo chromium (VI)  
(D) Potassium ammine cyano peroxo dioxochromate (IV)
- Q.102** IUPAC name of the coordination compound  $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$   
(A) Diamminechlorido(methylamine) platinum(II) chloride  
(B) Diamminechlorido(methylamine) platinum(III) chloride  
(C) Tetraamminechlorido(methylamine) platinum(II) chloride  
(D) None of these
- Q.103** The correct IUPAC name of the following compound is  $[Cr(NH_3)_5(NCS)] [ZnCl_4]$   
(A) Pentaammineisothiocyanatochromium(III) tetrachlorozincate(II)  
(B) Pentammineisothiocyanatezincchloride chromate(III)

- (C) Pentaammineisothiocyanatochromate(II)  
(D) Isothiocyanatopentaamminechromium(II) zinc chloride (IV)
- Q.104** The formula of the complex potassium trichloroethylene platinate(II) is  
(A)  $K[PtCl_3(C_2H_4)]$  (B)  $K_2[PtCl_3(C_2H_4)_3]$   
(C)  $K_4[PtCl_3(C_2H_4)]$  (D)  $K_3[Pt_2Cl_3(C_2H_4)_3]$
- Q.105** A complex cation is formed by Pt (in same oxidation state) with ligands (in proper number so that coordination number of Pt becomes six). Which of the following can be its correct IUPAC name ?  
(A) Diammineethylenediamminedithiocyanato -S-platinum(II) ion  
(B) Diammineethylenediamminedithiocyanato -S-platinate(IV) ion  
(C) Diammineethylenediamminedithiocyanato -S-platinum(IV) ion  
(D) Diamminebis(ethylenediammine)dithiocyanate-S-platinum(IV) ion
- Q.106** Which of the following rules is not correct regarding IUPAC nomenclature of complex ions?  
(A) Cation is named first and then anion.  
(B) In coordination sphere, the ligands are named alphabetically.  
(C) Positively charged ligands have suffix 'ate'.  
(D) More than one ligand of a particular type are indicated by using di, tri, tetra, etc.
- Q.107** The IUPAC name of  $K_3[Ir(C_2O_4)_3]$  is  
(A) Potassium trioxalatoiridium(III)  
(B) Potassium trioxalatoiridate(III)  
(C) Potassium tris(oxalato)iridium(III)  
(D) Potassium tris(oxalato)iridate(III)
- Q.108** The IUPAC name for  $K[SbCl_5(C_6H_5)_3]$  is  
(A) Luteroantimonate (V)  
(B) Potassium pentachlorophenylantimonite(IV)  
(C) Potassium phenylchloroantimonate(V)  
(D) Potassium benzalantimony(III) chloride.
- Q.109** Which of the following does not depict the correct name of the compound ?  
(A)  $K_2[Zn(OH)_4]$ ; Potassium tetrahydrozincate(II)  
(B)  $[Co(NH_3)_5CO_3]Cl$   
: Pentaammine carbonatochlorocobaltate(III)  
(C)  $Na_3[Co(NO_2)_6]$ : Sodium hexanitrocobaltate(III)  
(D)  $K_3[Cr(CN)_6]$ : Potassium hexacyanochromate(III)
- Q.110** The IUPAC name for  $[Co(NH_3)_6][Cr(CN)_6]$  is  
(A) Hexaamminecobalt(III)hexacyano-chromium(VI)  
(B) Hexaamminecobalt(III)hexacyano-chromate(III)  
(C) Hexacyanochromium(III)hexaammine-cobalt(III)  
(D) Hexacyanochromiumcobalthexa-ammine(VI)
- Q.111** The correct IUPAC name of  $[Pt(NH_3)_2Cl_2]$  is  
(A) Diamminedichloridoplatinum(II)  
(B) Diamminedichloridoplatinum(IV)  
(C) Diamminedichloridoplatinum(0)  
(D) Dichloridodiammineplatinum(IV)
- Q.112** The hypothetical complex chlorodiaquatetraamminecobalt(III) chloride can be represented as  
(A)  $[CoCl(NH_3)_3(H_2O)_2]Cl_2$  (B)  $[Co(NH_3)_3(H_2O)Cl_3]$   
(C)  $[Co(NH_3)_3(H_2O)_2Cl]$  (D)  $[Co(NH_3)_3(H_2O)_3]Cl_3$
- Q.113** Correct formula of tetraamminechloronitroplatinum (IV) sulphate can be written as  
(A)  $[Pt(NH_3)_4(ONO)Cl]SO_4$  (B)  $[Pt(NH_3)_4Cl_2NO_2]_2SO_4$   
(C)  $[Pt(NH_3)_4(NO_2)Cl]SO_4$  (D)  $[PtCl(ONO)NH_3(SO_4)]$

### PART 11: ISOMERISM IN COORDINATION COMPOUNDS

- Q.114** Which one of the following octahedral complexes will not show geometric isomerism (A and B are monodentate ligands)  
(A)  $[Ma_5b]$  (B)  $[Ma_2b_4]$   
(C)  $[Ma_3b_3]$  (D)  $[Ma_4b_2]$
- Q.115** Coordination isomerism is caused by the interchange of ligands between the  
(A) Cis and Trans structure  
(B) Complex cation and complex anion  
(C) Inner sphere and outer sphere  
(D) Low oxidation and higher oxidation states
- Q.116** Which of the following compounds exhibits linkage isomerism  
(A)  $[Co(en)_3]Cl_3$  (B)  $[Co(NH_3)_6][Cr(CN)_6]$   
(C)  $[Co(en)_2NO_2Cl]Br$  (D)  $[Co(NH_3)_5Cl]Br_2$
- Q.117** The number of isomers possible for square planar complex  $K_2[PdClBr_2(SCN)]$  is  
(A) 2 (B) 3  
(C) 4 (D) 6
- Q.118** Which one of the following is expected to exhibit optical isomerism [en = ethylenediamine] –  
(A) Trans- $[Co(en)_2Cl_2]$  (B) Cis- $[Pt(NH_3)_2Cl_2]$   
(C) Cis- $[Co(en)_2Cl_2]$  (D) Trans- $[Pt(NH_3)_2Cl_2]$
- Q.119** Identify the geometrical isomers of  $[Pt(NH_3)_2Cl_2]$
- I.

II.
- III.

IV.
- Choose the correct option –  
(A) I and II (B) II and III  
(C) I and III (D) II and IV
- Q.120** A similarity between optical and geometrical isomerism is that  
(A) Each gives equal number of isomers for a given compound.  
(B) If in a compound, one is present then so is the other.  
(C) Both are included in stereoisomerism.  
(D) They have no similarity.

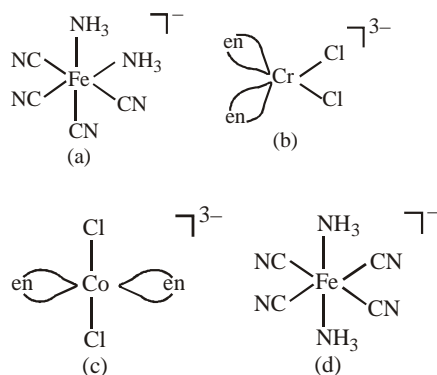
**Q.121** The two compounds, sulphatopentaamminecobalt(III) bromide and sulphatopentaamminecobalt(III) chloride represent which isomerism –

- (A) Linkage (B) Ionisation  
(C) Coordination (D) No isomerism.

**Q.122** Few isomers are given below. Mark the correct statement regarding them

- (i)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$   
(ii)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
(iii)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
(A) i, ii and iii are hydrate isomers  
(B) i, ii and iii are coordination isomers  
(C) i, ii and iii are ionisation isomers  
(D) i and ii are stereoisomers.

**Q.123** In the given structures identify the cis- and trans-isomers.



- (A) cis-isomers : (b), (c) ; trans-isomers : (a), (d)  
(B) cis-isomers : (a), (d) ; trans-isomers : (b), (c)  
(C) cis-isomers : (a), (b) ; trans-isomers : (c), (d)  
(D) cis-isomers : (a), (c) ; trans-isomers : (b), (d)

**Q.124** Which of the following pairs represents linkage isomers?

- (A)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  &  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$   
(B)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$   
(C)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$  and  $(\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$   
(D)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

**Q.125** Which of the following complexes will have four isomers?

- (A)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$   
(B)  $[\text{Co}(\text{PPh}_3)_2(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$   
(C)  $[\text{Co}(\text{en})_3]\text{Cl}_3$   
(D)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ .

**Q.126** The name of the linkage isomer of

$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  is –

- (A) Pentaamminonitrocobalt(II) chloride  
(B) Pentaamminenitrochloridocobaltate(III)  
(C) Pentaamminenitritocobalt(III) chloride  
(D) Pentanitrosoamminechlorocobaltate(III).

**Q.127** Which type of isomerism arises when didentate ligands (L–L) are present in complexes of formula  $[\text{MX}_2(\text{L–L})_2]$ ?

- (A) Optical (B) Geometrical  
(C) Linkage (D) Solvate

**Q.128** What type of isomerism exists in the following pairs of complexes ?

- (i)  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$   
(ii)  $[\text{Co}(\text{en})(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$  and  $[\text{Co}(\text{en})(\text{H}_2\text{O})\text{Cl}_3]\text{H}_2\text{O}$   
(A) (i) Ionisation (ii) Hydrate  
(B) (i) Linkage (ii) Hydrate  
(C) (i) Ionisation (ii) Linkage  
(D) (i) Linkage (ii) Coordination

**Q.129** Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type

- $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$  &  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$  are:  
(A) Linkage (B) Coordination  
(C) Ionisation (D) Geometrical

**Q.130** Consider the following statements about solvate isomerism

- I. It is also known as 'hydrate isomerism' where water is involved as a solvent.  
II. It is also similar to ionisation isomerism.  
III. Aqua complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) is an example of solvate isomerism. Its solvate isomer is  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ .

The correct set of statements is

- (A) I and II (B) II and III  
(C) I and III (D) I, II and III

**Q.131**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$  &  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$  exhibit which type of isomerism ?

- (A) Geometrical (B) Optical  
(C) Linkage (D) Ionisation

**Q.132** What kind of isomerism exists between  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (greyish-green) ?

- (A) Linkage (B) Solvate  
(C) Ionisation (D) Coordination

**Q.133** Which of the following will not show geometrical isomerism ?

- (A)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (B)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
(C)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  (D)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

**Q.134**  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$  and  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  are known as

- (A) Ionisation isomers (B) Coordination isomers  
(C) Linkage isomers (D) Polymerisation isomers

**Q.135**  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  exists in different isomeric forms which show different colours like violet and green. This is due to which isomerism

- (A) Ionisation (B) Coordination  
(C) Optical (D) Hydrate

## PART 12 : BOUNDING IN COORDINATION COMPOUNDS

**Q.136** The increasing order of crystal field splitting strength of the given ligands is

- (A)  $\text{NH}_3 < \text{Cl}^- < \text{CN}^- < \text{F}^- < \text{CO} < \text{H}_2\text{O}$   
(B)  $\text{F}^- < \text{Cl}^- < \text{NH}_3 < \text{CN}^- < \text{H}_2\text{O} < \text{CO}$   
(C)  $\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- < \text{CO}$   
(D)  $\text{CO} < \text{CN}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{F}^- < \text{Cl}^-$

- Q.137** Which is the strongest field ligand ?  
 (A)  $\text{NO}_2^-$  (B)  $\text{CN}^-$   
 (C)  $\text{NH}_3$  (D) En
- Q.138** Which of the following statements is/are correct?  
 (i) In octahedral complexes,  $t_{2g}$  orbitals possess low energy as compared to  $e_g$  orbitals.  
 (ii) In tetrahedral complexes,  $t_{2g}$  orbitals possess high energy as compared to  $e_g$  orbitals.  
 (iii) In octahedral complexes,  $e_g$  orbitals possess low energy as compared to  $t_{2g}$  orbitals.  
 (A) ii only (B) iii only  
 (C) i and ii (D) i and iii
- Q.139** An octahedral complex is formed when hybrid orbitals of the following type are involved  
 (A)  $sp^3d$  (B)  $sp^3d^2$   
 (C)  $dsp^2$  (D)  $sp^3$
- Q.140** Of the following complexes, the one with the largest value of crystal field splitting energy is  
 (A)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Ru}(\text{CN})_6]^{3-}$   
 (C)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Fe}(\text{NH}_3)_6]^{3+}$
- Q.141** The magnitude of CFSE (Crystal Field Splitting Energy,  $\Delta_0$ ) can be related to the configuration of d-orbitals in a coordination entity as  
 (A) If  $\Delta_0 < P$ , the configuration is  $t_{2g}^3 e_g^1$   
 = weak field ligand and high spin complex  
 (B) If  $\Delta_0 > P$ , the configuration is  $t_{2g}^3 e_g^1$   
 = strong field ligand and low spin complex  
 (C) If  $\Delta_0 > P$ , the configuration is  $t_{2g}^4 e_g^0$   
 = strong field ligand and high spin complex  
 (D) If  $\Delta_0 = P$ , the configuration is  $t_{2g}^4 e_g^0$   
 = strong field ligand and high spin complex.
- Q.142** The CFSE for octahedral  $[\text{CoCl}_6]^{4-}$  is  $18,000 \text{ cm}^{-1}$ . The CFSE for tetrahedral  $[\text{CoCl}_4]^{2-}$  will be  
 (A)  $18,000 \text{ cm}^{-1}$  (B)  $16,000 \text{ cm}^{-1}$   
 (C)  $8,000 \text{ cm}^{-1}$  (D)  $20,000 \text{ cm}^{-1}$
- Q.143** Which of the following are the limitations of VBT?  
 I. It does not give quantitative interpretation of magnetic data.  
 II. It does not distinguish between weak and strong ligands.  
 III. It does not explain the colour exhibited by coordination compounds.  
 IV. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.  
 Identify the correct option from the choices given  
 (A) I, II, III and IV (B) II, III and IV  
 (C) I, III and IV (D) II, III and IV
- Q.144** Hexafluorocobaltate(III) ion is found to be high spin complex, the probable hybrid state of cobalt in it is  
 (A)  $d^2 sp^3$  (B)  $sp^3$   
 (C)  $sp^3d$  (D)  $sp^3d^2$
- Q.145** Which order is correct in spectrochemical series of ligands ?  
 (A)  $\text{Cl}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{NO}_2^- < \text{CN}^-$   
 (B)  $\text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{Cl}^- > \text{NO}_2^- < \text{F}^-$   
 (C)  $\text{C}_2\text{O}_4^{2-} < \text{F}^- < \text{Cl}^- > \text{NO}_2^- < \text{CN}^-$   
 (D)  $\text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-}$
- Q.146** The correct structure of  $\text{Fe}(\text{CO})_5$  is ( $Z = 26$  for Fe)  
 (A) Octahedral  
 (B) Tetrahedral  
 (C) Square pyramidal  
 (D) Trigonal bipyramidal
- Q.147** Which of the following is correct ?  
 (A) Valence bond theory explains the colour of the coordination compounds.  
 (B)  $[\text{NiCl}_4]^{2-}$  is diamagnetic in nature.  
 (C) Ambident ligands can show linkage isomerism  
 (D) A bidentate ligand can have four coordination sites.
- Q.148** Which of the following facts are related to CFT?  
 I. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate.  
 II. If a spherically symmetrical field of negative charges surrounds the metal atom/ion, the degeneracy is maintained.  
 III. When this negative field is due to ligands in a complex, it becomes asymmetrical and the degeneracy of the d-orbitals is lifted.  
 IV. It results in splitting of d-orbitals. This pattern of splitting depends upon the nature of the crystal field.  
 The correct set of statements is  
 (A) I, II, III and IV (B) II, III and IV  
 (C) I, II and III (D) I, III and IV
- Q.149** Mark the incorrect statement  
 (A) Inner orbital (low spin) complexes involve  $d^2sp^3$  hybridisation.  
 (B) Outer orbital (high spin) complexes involve  $sp^3d^2$  hybridisation.  
 (C) Tetrahedral complexes generally involve  $dsp^2$  hybridisation.  
 (D) Stereoisomerism involves geometrical and optical isomerism.
- Q.150** Mark the correct statements regarding the geometry of complex ions.  
 (i) The geometry of the complex ion depends upon the coordination number.  
 (ii) If coordination number is 6, the complex is octahedral.  
 (iii) If coordination number is 4, the geometry of the complex may be tetrahedral or square planar.  
 (A) i, ii and iii (B) i and ii only  
 (C) i and iii only (D) ii and iii only
- Q.151** In an octahedral crystal field, the  $t_{2g}$  orbitals are  
 (A) Raised in energy by  $0.4 \Delta_0$   
 (B) Lowered in energy by  $0.4 \Delta_0$   
 (C) Raised in energy by  $0.6 \Delta_0$   
 (D) Lowered in energy by  $0.6 \Delta_0$
- Q.152** Which will form an octahedral complex ?  
 (A)  $d^4$  (low spin) (B)  $d^8$  (high spin)  
 (C)  $d^6$  (low spin) (D) None of these

- Q.153** Low spin tetrahedral complexes are not formed because
- (A) For tetrahedral complexes, the CFSE is lower than pairing energy.
- (B) For tetrahedral complexes, the CFSE is higher than pairing energy.
- (C) Electrons do not go to  $e_g$  in case of tetrahedral complexes.
- (D) Tetrahedral complexes are formed by weak field ligands only.
- Q.154** Which of the following sets of examples and geometry of the compounds is not correct ?
- (A) Octahedral -  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$
- (B) Square planar -  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- (C) Tetrahedral -  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{ZnCl}_4]^{2-}$
- (D) Trigonal bipyramidal -  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ,  $[\text{CuCl}_4]^{2-}$

### PART 13: BOUNDING IN METAL CARBONYLS

- Q.155** Homoleptic carbonyls formed by most of the transition metals, have
- (A) simple, well-defined structures
- (B) only carbonyl ligands.
- (C) Both (A) and (B)
- (D) None of the above
- Q.156** In which of the following compounds, the transition metal is in oxidation state of zero ?
- (A)  $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]$       (B)  $[\text{Ni}(\text{CO})_4]$
- (C)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$       (D)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- Q.157** Among the following metal carbonyls, the C–O bond order is the lowest in
- (A)  $[\text{Mn}(\text{CO})_6]^+$       (B)  $[\text{Fe}(\text{CO})_5]$
- (C)  $[\text{Cr}(\text{CO})_6]$       (D)  $[\text{V}(\text{CO})_6]^-$

- Q.158** The M – C  $\pi$  bond is formed by the
- (A) donation of a pair of electrons.
- (B) sharing of a pair of electrons.
- (C) receiving a pair of electrons.
- (D) None of the above

### PART 14: STABILITY OF COORDINATION COMPOUNDS

- Q.159** The reciprocal of the formation constant is called
- (A) instability constant      (B) dissociation constant
- (C) Both (A) and (B)      (D) stability constant
- Q.160** Mark the incorrect statement regarding the stability of the complexes.
- (A) Higher the charge density on the central ion, greater is the stability of the complex.
- (B) Higher the oxidation state of metal, higher is the stability of the complex.
- (C) Higher the basicity of the ligand, higher is the stability of the complex.
- (D) More the chelation tendency of ligand, lower is the stability of the complex.

### PART 15: APPLICATIONS OF COORDINATION COMPOUNDS

- Q.161** Mark the incorrect match
- (A) Insulin - Zinc      (B) Haemoglobin - Iron
- (C) Vitamin B<sub>12</sub> - Cobalt      (D) Chlorophyll - Chromium
- Q.162** In quantitative analysis of second group in laboratory, H<sub>2</sub>S gas is passed in acidic medium for precipitation. When Cu<sup>2+</sup> and Cd<sup>2+</sup> react with KCN, then for product true statement is –
- (A)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  more soluble
- (B)  $\text{K}_2[\text{Cd}(\text{CN})_4]$  less stable
- (C)  $\text{K}_2[\text{Cd}(\text{CN})_3]$  more soluble
- (D)  $\text{K}_2[\text{Cu}(\text{CN})_2]$  less soluble

## EXERCISE - 2 [LEVEL-2]

### PART A (d AND f BLOCK ELEMENTS)

Choose one correct response for each question.

- Q.1** Light green crystals of ferrous sulphate lose water molecule and turn brown on exposure to air. This is due to its oxidation to
- (A)  $\text{Fe}_2\text{O}_3$       (B)  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- (C)  $\text{Fe}(\text{OH})\text{SO}_4$       (D)  $\text{Fe}_2\text{O}_3 + \text{FeO}$
- Q.2** Which is mild oxidising agent
- (A)  $\text{Ag}_2\text{O}$       (B)  $\text{KMnO}_4$
- (C)  $\text{K}_2\text{Cr}_2\text{O}_7$       (D)  $\text{Cl}_2$
- Q.3** Choose the correct statement –
- (a) Transition metals and many of their compounds show paramagnetic behaviour.
- (b) The enthalpies of atomisation of the transition metals are low.
- (A) only (a)      (B) only (b)
- (C) Both (a) and (b)      (D) None of these
- Q.4** Which of the following metals corrodes readily in moist air
- (A) Gold      (B) Silver
- (C) Nickel      (D) Iron
- Q.5** Silver nitrate is mainly used
- (A) In photography.      (B) In model formation.
- (C) Reducing agent.      (D) Dehydrating agent.
- Q.6** Iron is dropped in dil.  $\text{HNO}_3$ , it gives
- (A) Ferric nitrate.
- (B) Ferric nitrate and  $\text{NO}_2$ .
- (C) Ferrous nitrate and ammonium nitrate.
- (D) Ferrous nitrate and nitric oxide,
- Q.7** A metal which is 'not' affected by conc.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  or alkalis forms a compound X. This compound X can be used to give a complex which finds its application (for toning in photography). The metal is
- (A) Au      (B) Ag
- (C) Hg      (D) Cu

- Q.8** An aqueous solution of  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  and chrome alum is heated with excess of  $\text{Na}_2\text{O}_2$  and filtered. The materials obtained are  
 (A) A colourless filtrate and a green residue  
 (B) A yellow filtrate and a green residue  
 (C) A yellow filtrate and a brown residue  
 (D) A green filtrate and a brown residue
- Q.9** The melting point of copper is higher than that of zinc because  
 (A) Copper has a bcc structure.  
 (B) The atomic volume of copper is higher.  
 (C) The 'd' electrons of copper are involved in metallic bonding.  
 (D) The 's' as well as 'd' electrons of copper are involved in metallic bonding.
- Q.10** When acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is added to  $\text{Sn}^{2+}$  salts, then  $\text{Sn}^{2+}$  changes to  
 (A) Sn (B)  $\text{Sn}^{3+}$   
 (C)  $\text{Sn}^{4+}$  (D)  $\text{Sn}^+$
- Q.11** In which of the following the stability of two oxidation states is correctly represented?  
 (A)  $\text{Fe}^{2+} > \text{Fe}^{3+}$  (B)  $\text{Ti}^{3+} > \text{Ti}^{4+}$   
 (C)  $\text{Mn}^{2+} > \text{Mn}^{3+}$  (D)  $\text{Cu}^+ > \text{Cu}^{2+}$
- Q.12** Consider the following statements  
 I.  $\text{La}(\text{OH})_3$  is least basic among hydroxides of lanthanides.  
 II.  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  possess almost the same ionic radii  
 III.  $\text{Ce}^{4+}$  can act as an oxidising agent.  
 Which of the above is/are true ?  
 (A) I and III (B) II and III  
 (C) II only (D) I and II
- Q.13** Mercury sticks to the surface of the glass when it comes in contact with  
 (A)  $\text{Hg}_2\text{O}$  (B)  $\text{HNO}_3$   
 (C)  $\text{O}_3$  (D) Grease
- Q.14**  $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$  is highly positive than that of  $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  or  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  because :  
 (A)  $\text{Mn}^{2+}$  ( $d^5$ ) can be easily oxidised to  $\text{Mn}^{3+}$  ( $d^4$ ) due to low ionisation enthalpy.  
 (B) Third ionisation enthalpy of Mn is much larger due to stable half filled  $d^5$  electronic configuration of  $\text{Mn}^{2+}$ .  
 (C)  $\text{Mn}^{3+}$  is more stable than  $\text{Mn}^{2+}$  due to higher oxidation state.  
 (D) Second ionisation enthalpy of Mn is higher than third ionisation enthalpy.
- Q.15** In the aqueous solution,  $\text{Cu}^{(+1)}$  salts are unstable because –  
 (A)  $\text{Cu}^{(+1)}$  has a  $3d^{10}$  configuration.  
 (B) The change in free energy of the overall reaction is zero.  
 (C) They disproportionate easily to the Cu and  $\text{Cu}^{(+2)}$  states.  
 (D) They disproportionate easily to the  $\text{Cu}^{(+2)}$  and  $\text{Cu}^{(+3)}$  states.
- Q.16** Which of the following transition metal ions is colourless  
 (A)  $\text{V}^{2+}$  (B)  $\text{Cr}^{3+}$   
 (C)  $\text{Zn}^{2+}$  (D)  $\text{Ti}^{3+}$
- Q.17** Which of the following ions has the highest magnetic moment?  
 (A)  $\text{Ti}^{3+}$  (B)  $\text{Mn}^{2+}$   
 (C)  $\text{Sc}^{3+}$  (D)  $\text{Zn}^{2+}$
- Q.18** Transition elements form binary compounds with halogens. Which of the following elements will form  $\text{MF}_3$  type compounds ?  
 (A) Cr (B) Cu  
 (C) Ni (D) All of these
- Q.19**  $\text{KMnO}_4$  acts as an oxidising agent in alkaline medium. When alkaline  $\text{KMnO}_4$  is treated with KI, iodide ion is oxidised to  
 (A)  $\text{I}_2$  (B)  $\text{IO}^-$   
 (C)  $\text{IO}_3^-$  (D)  $\text{IO}_4^-$
- Q.20** The ionic radii of Group-12 metals Zn, Cd and Hg are smaller than those of Group-2 metals because Zn, Cd and Hg have  
 (A) 10 d-electrons which shield the nuclear charge poorly.  
 (B) 10 d-electrons which shield the nuclear charge strongly.  
 (C) 10 d-electrons which have a large radius ratio.  
 (D) 10 d-electrons which have a large exchange energy.
- Q.21** +4 ion of which of these has half-filled 4f subshell?  
 (A) Nd (B) Tb  
 (C) Sc (D) Tu
- Q.22** All  $\text{Cu}(\text{II})$  halides are known except the iodide. The reason for it is that  
 (A) Iodide is a bulky ion.  
 (B)  $\text{Cu}^{2+}$  oxidizes iodide to iodine.  
 (C)  $\text{Cu}^{2+}(\text{aq})$  has much more negative hydration enthalpy.  
 (D)  $\text{Cu}^{2+}$  ion has smaller size.
- Q.23** When KCN is added to  $\text{CuSO}_4$  solution  
 (A) KCN acts as reducing agent  
 (B) KCN acts as complexing agent  
 (C)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  is formed  
 (D) All are correct
- Q.24** The correct statement(s) among the following is/are –  
 (i) All the d- and f-block elements are metals  
 (ii) All d- and f-block elements form coloured ions.  
 (iii) All d- & f-block elements are paramagnetic.  
 (A) (i) only (B) (i) and (ii)  
 (C) (ii) and (iii) (D) (i), (ii) and (iii)
- Q.25** The melting points of Cu, Ag and Au follow the order  
 (A)  $\text{Cu} > \text{Ag} > \text{Au}$  (B)  $\text{Cu} > \text{Au} > \text{Ag}$   
 (C)  $\text{Au} > \text{Ag} > \text{Cu}$  (D)  $\text{Ag} > \text{Au} > \text{Cu}$
- Q.26** Which of the following ions is paramagnetic?  
 (A)  $\text{Sc}^{+++}$  (B)  $\text{Cu}^+$   
 (C)  $\text{Zn}^{++}$  (D)  $\text{Ni}^{++}$

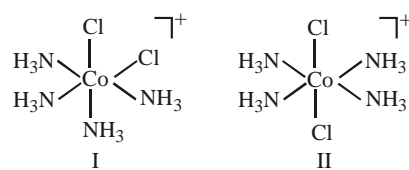
- Q.27** Which one of the following ionic species will impart colour to an aqueous solution ?  
 (A)  $Ti^{4+}$  (B)  $Cu^+$   
 (C)  $Zn^{2+}$  (D)  $Cr^{3+}$
- Q.28** Yellow coloured aqueous solution of sodium chromate changes to orange when acidified with sulphuric acid because  
 (A)  $H^+$  ions convert chromate ions to dichromate ions.  
 (B)  $H^+$  ions react with sodium chromate to give sodium ions which turn solution orange.  
 (C)  $Cr^{3+}$  ions are liberated in the solution which turn the solution orange.  
 (D) Sodium hydroxide is formed during the reaction which imparts orange colour to the solution.
- Q.29** The highest magnetic moment is shown by the transition metal ion with outer electronic configuration  
 (A)  $3d^2$  (B)  $3d^5$   
 (C)  $3d^7$  (D)  $3d^9$
- Q.30** Which one of the following shows highest magnetic moment ?  
 (A)  $V^{3+}$  (B)  $Cr^{3+}$   
 (C)  $Fe^{3+}$  (D)  $Co^{3+}$
- Q.31**  $4K_2Cr_2O_7 \xrightarrow{\text{Heat}} 4K_2CrO_4 + 3O_2 + X$ .  
 In the above reaction X is –  
 (A)  $CrO_3$  (B)  $Cr_2O_7$   
 (C)  $Cr_2O_3$  (D)  $CrO_5$
- Q.32** A scarlet red precipitate is obtained on treating mercuric chloride solution with  
 (A)  $H_2S$  (B)  $KI$   
 (C)  $NaOH$  (D)  $NH_4OH$
- Q.33** Transition metals make the most efficient catalysts because of their ability to –  
 (A) Adopt multiple oxidation states and to form complexes.  
 (B) Form coloured ions.  
 (C) Show paramagnetism due to unpaired electrons.  
 (D) form a large number of oxides.
- Q.34** Acidified solution of chromic acid on treatment with hydrogen peroxide yields –  
 (A)  $CrO_3 + H_2O + O_2$  (B)  $CrO_5 + H_2O$   
 (C)  $Cr_2O_3 + H_2O + O_2$  (D)  $H_2Cr_2O_7 + H_2O + O_2$
- Q.35** Arrange the oxides of manganese according to increasing acidic strength.  
 (A)  $MnO < Mn_3O_4 < Mn_2O_3 < MnO_2 < Mn_2O_7$   
 (B)  $Mn_2O_7 < MnO_2 < Mn_2O_3 < Mn_3O_4 < MnO$   
 (C)  $MnO_2 < Mn_2O_7 < Mn_3O_4 < Mn_2O_3 < MnO$   
 (D)  $Mn_3O_4 < Mn_2O_3 < Mn_2O_7 < MnO_2 < MnO$
- Q.36** When  $SO_2$  is passed through acidified  $K_2Cr_2O_7$  solution  
 (A) The solution turns blue  
 (B) The solution is decolorised  
 (C)  $SO_2$  is reduced  
 (D) Green  $Cr_2(SO_4)_3$  is formed.
- Q.37** The common oxidation state shown by lanthanides in their compounds is  
 (A) +1 (B) +3  
 (C) +5 (D) +6
- Q.38** Which of the following dissolves in hot concentrated  $NaOH$  solution ?  
 (A) Fe (B) Zn  
 (C) Cu (D) Ag
- Q.39** Which of the following reactions are disproportionation reactions ?  
 (I)  $Cu^+ \rightarrow Cu^{2+} + Cu$   
 (II)  $3MnO_4^- + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$   
 (III)  $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$   
 (IV)  $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$   
 (A) I, II (B) I, II, III  
 (C) II, III, IV (D) I, IV
- Q.40** Which one of the following is reduced by hydrogen peroxide in acid medium?  
 (A) Potassium permanganate  
 (B) Potassium iodide  
 (C) Ferrous sulphate  
 (D) Potassium ferrocyanide
- Q.41** Which of the following has no unpaired electrons but is coloured ?  
 (A)  $K_2Cr_2O_7$  (B)  $K_2MnO_4$   
 (C)  $CuSO_4 \cdot 5H_2O$  (D)  $MnCl_2$
- Q.42** Which of the following statements concerning lanthanide elements is false ?  
 (A) Lanthanides are separated from one another by ion-exchange method.  
 (B) Ionic radii of trivalent lanthanides steadily increase with increase in the atomic number.  
 (C) All lanthanides are highly dense metals.  
 (D) More characteristic oxidation state of lanthanides elements is +3.
- Q.43** Which of the following pairs of ions have the same electronic configuration ?  
 (A)  $Cu^{2+}, Cr^{2+}$  (B)  $Fe^{3+}, Mn^{2+}$   
 (C)  $Co^{3+}, Ni^{3+}$  (D)  $Sc^{3+}, Cr^{3+}$
- Q.44** Choose the correct statement –  
 (a) The transition metals generally form coloured compounds.  
 (b) Transition metals and their many compounds act as good catalyst.  
 (A) only (a) (B) only (b)  
 (C) Both (a) and (b) (D) None of these
- Q.45** Number of electrons transferred in each case when  $KMnO_4$  acts as an oxidising agent to give  $MnO_2$ ,  $Mn^{2+}$ ,  $Mn(OH)_3$  and  $MnO_4^{2-}$  are –  
 (A) 3, 5, 4 and 1 (B) 4, 3, 1 and 5  
 (C) 1, 3, 4 and 5 (D) 5, 4, 3 and 1
- Q.46** The correct order of ionic radii of Ce, La, Pm and Yb in +3 oxidation state is  
 (A)  $La^{3+} < Pm^{3+} < Ce^{3+} < Yb^{3+}$   
 (B)  $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$   
 (C)  $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$   
 (D)  $Yb^{3+} < Ce^{3+} < Pm^{3+} < La^{3+}$



- Q.47** The reason for the stability of  $Gd^{3+}$  ion is  
 (A) Half filled 4f subshell.  
 (B) Completely filled 4f subshell.  
 (C) Possesses the general electronic configuration of noble gases.  
 (D) Empty 4f subshell.
- Q.48** Zn does not show variable valency because of  
 (A) Complete 'd' subshell (B) Inert pair effect  
 (C)  $4s^2$  subshell (D) 5 unpaired electrons.
- Q.49** In which of the following compounds manganese has oxidation number equal to that of iodine in  $KiO_4$ ?  
 (A) Potassium manganate  
 (B) Potassium permanganate  
 (C) Manganous chloride  
 (D) Manganese chloride
- Q.50** Which of the following compounds is used as the starting material for the preparation of potassium dichromate?  
 (A)  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$  (Chrome alum)  
 (B)  $PbCrO_4$  (Chromite yellow)  
 (C)  $FeCr_2O_4$  (Chromite)  
 (D)  $PbCrO_4 \cdot PbO$  (Chrome red)
- Q.51** Which is colourless in water?  
 (A)  $Ti^{3+}$  (B)  $V^{3+}$   
 (C)  $Cu^{3+}$  (D)  $Sc^{3+}$
- Q.52** Which of the following is not correctly matched with the given example?  
 (A) An element of first transition series which has highest second ionisation enthalpy-Cu.  
 (B) An element of first transition series with highest third ionisation enthalpy-Zn.  
 (C) An element of first transition series with lowest enthalpy of atomisation-Zn.  
 (D) Last element of third transition series-Cd.

### PART B (COORDINATION COMPOUNDS)

- Q.1** The co-ordination number of copper in cuprammonium sulphate is  
 (A) 2 (B) 6  
 (C) 4 (D) -4
- Q.2** Which of the following acts as a bidentate ligand in complex formation  
 (A) Acetate (B) Oxalate  
 (C) Thiocyanate (D) EDTA
- Q.3** The coordination number of Cu in complex  $[Cu(H_2O)_4]^{++}$  is  
 (A) 4 (B) 3  
 (C) 2 (D) 1
- Q.4** Which one is organometallic compound  
 (A) Lithium methoxide (B) Lithium dimethyl amide  
 (C) Lithium acetate (D) Methyl lithium
- Q.5** In which of the following complexes oxidation state of metal is zero  
 (A)  $[Pt(NH_3)_2Cl_2]$  (B)  $[Cr(CO)_6]$   
 (C)  $[Cr(NH_3)_3Cl_3]$  (D)  $[Cr(en)_2Cl_2]$
- Q.6** Oxidation state of Fe in  $K_3[Fe(CN)_6]$   
 (A) 2 (B) 3  
 (C) 0 (D) None
- Q.7** In the complex  $[SbF_5]^{2-}$ ,  $sp^3d$  hybridisation is present. Geometry of the complex is  
 (A) Square pyramidal (B) Square bipyramidal  
 (C) Tetrahedral (D) Square
- Q.8**  $[Pt(NH_3)_4]Cl_2$  is  
 (A) Square planar (B) Tetrahedral  
 (C) Pyramidal (D) Pentagonal
- Q.9** The neutral ligand is  
 (A) Chloro (B) Hydroxo  
 (C) Ammine (D) Oxalato
- Q.10** A strong ligand gives a complex which is generally called  
 (A) High spin (B) High energy  
 (C) Low spin (D) Stable
- Q.11** A person suffering from lead poisoning should be fed with—  
 (A) Hypo (B) Cis-platin  
 (C)  $[Ca(EDTA)]^{2-}$  (D) DMG
- Q.12** Which complex is an outer orbital complex—  
 (A)  $[Ni(NH_3)_6]^{2+}$  (B)  $[Mn(CN)_6]^{4-}$   
 (C)  $[Co(NH_3)_6]^{3+}$  (D)  $[Fe(CN)_6]^{4-}$
- Q.13** The value of the 'spin only' magnetic moment for one of the following configurations is 2.84BM. The correct one is  
 (A)  $d^4$  (in strong ligand field)  
 (B)  $d^4$  (in weak ligand field)  
 (C)  $d^3$  (in weak as well as in strong fields)  
 (D)  $d^5$  (in strong ligand field)
- Q.14** Which of the following statement is correct regarding the complex  $[CuL_6]^{2+}$ , one solution is blue and another is green.  
 (A) Blue solution will have higher value of  $\Delta_0$   
 (B) Green solution will have higher value of  $\Delta_0$   
 (C) Both have same value of  $\Delta_0$   
 (D) No prediction can be done regarding  $\Delta_0$
- Q.15** The two forms dextro and laevo  
 I. depend upon the direction they rotate the plane of polarised light in a polarimeter.  
 II.  $\ell$ -rotates to the right.  
 III. d-rotates to the left.  
 The correct statement(s) is/are  
 (A) Both II and III (B) I, II and III  
 (C) Only I (D) None of these
- Q.16** Which of the following primary and secondary valence are not correctly marked against the compound?  
 (A)  $[Cr(NH_3)_6]Cl_3$ , p = 3, s = 6  
 (B)  $K_2[PtCl_4]$ , p = 2, s = 4  
 (C)  $[Pt(NH_3)_2Cl_2]$ , p = 2, s = 4  
 (D)  $[Cu(NH_3)_4]SO_4$ , p = 4, s = 4
- Q.17**  $AgCl$  is soluble in  $NH_4OH$  solution. The solubility is due to the formation of  
 (A)  $AgOH$  (B)  $Ag_2O$   
 (C)  $[Ag(NH_3)_2]^+$  (D)  $[AgCl(NH_3)]$

- Q.18** Which complex has square planar structure ?  
 (A)  $\text{Ni}(\text{CO})_4$  (B)  $[\text{NiCl}_4]^{2-}$   
 (C)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- Q.19** How many moles of  $\text{AgCl}$  is precipitated, when excess of  $\text{AgNO}_3$  is added to the one mole of  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (green) mixed with  $\text{NH}_3$  ?  
 (A) 1 (B) 2  
 (C) 3 (D) 4
- Q.20** Which of the following has largest paramagnetism?  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (C)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- Q.21** Iron has lowest oxidation state in  
 (A)  $\text{Fe}(\text{CO})_5$  (B)  $\text{Fe}_2\text{O}_3$   
 (C)  $\text{K}_2\text{FeO}_4$  (D)  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$
- Q.22** The overall complex dissociation equilibrium constant for the complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion will be ( $\beta$  for this complex is  $2.1 \times 10^{13}$ )  
 (A)  $4.7 \times 10^{-14}$  (B)  $2.1 \times 10^{13}$   
 (C)  $11.9 \times 10^{-2}$  (D)  $2.1 \times 10^{-13}$
- Q.23** Optical isomers  
 I. are mirror images.  
 II. cannot be superimposed on one another.  
 III. are also called as enantiomers.  
 The correct statement(s) is/are  
 (A) Only I and II (B) Only II and III  
 (C) Only I and III (D) I, II and III
- Q.24** Which is high spin complex ?  
 (A)  $[\text{CoF}_6]^{3-}$  (B)  $[\text{Fe}(\text{CN})_6]^{3-}$   
 (C)  $[\text{Fe}(\text{CN})_6]^{4-}$  (D) None of these
- Q.25** Which of the following isomers will give white precipitate with  $\text{BaCl}_2$  solution ?  
 (A)  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  (B)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$   
 (C)  $[\text{Co}(\text{NH}_3)_4(\text{SO}_4)_2]\text{Br}$  (D)  $[\text{Co}(\text{NH}_3)_4\text{Br}(\text{SO}_4)]$
- Q.26** Which of the following is not correctly matched?  
 (A) Coordination compound containing cationic complex ion :  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]_2\text{SO}_4$   
 (B) Coordination compound containing anionic complex ion :  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$   
 (C) Non-ionic coordination compound :  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$   
 (D) Coordination compound containing cationic and anionic complex ion :  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
- Q.27** Arrange the following complexes in increasing order of conductivity of their solutions.  
 (i)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (iii)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (iv)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (A)  $i < ii < iv < iii$  (B)  $ii < i < iii < iv$   
 (C)  $i < iii < ii < iv$  (D)  $iv < i < ii < iii$
- Q.28** The formula of sodium nitroprusside is  
 (A)  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$  (B)  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$   
 (C)  $\text{NaFe}[\text{Fe}(\text{CN})_6]$  (D)  $\text{Na}_2[\text{Fe}(\text{CN})_6\text{NO}_2]$
- Q.29** In any ferric salt, on adding potassium ferro-cyanide a Prussian blue colour is obtained, which is mainly due to the formation of  
 (A)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (B)  $\text{KFe}[\text{Fe}(\text{CN})_6]$   
 (C)  $\text{FeSO}_4 \cdot \text{Fe}(\text{CN})_6$  (D)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- Q.30** Which of the following complexes will show maximum paramagnetism ?  
 (A)  $3d^4$  (B)  $3d^5$   
 (C)  $3d^6$  (D)  $3d^7$
- Q.31** Which of the following shows maximum number of isomers ?  
 (A)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  (B)  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$   
 (C)  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]^{2-}$  (D)  $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$
- Q.32** Given the molecular formula of the hexacoordinate complex (a)  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (b)  $\text{CoCl}_3 \cdot 5\text{NH}_3$  (c)  $\text{CoCl}_3 \cdot 4\text{NH}_3$ . If the number of coordinated  $\text{NH}_3$  molecules in a, b and c respectively are 6, 5 and 4, the primary valency in (a), (b) and (c) are  
 (A) 3, 3, 3 (B) 0, 1, 2  
 (C) 3, 2, 1 (D) 6, 5, 4
- Q.33**  $\text{NH}_2 \cdot \text{NH}_2$  serves as  
 (A) Monodentate ligand (B) Chelating ligand  
 (C) Bridging ligand (D) (A) and (C) both
- Q.34** Which ligand is capable for forming low spin as well as high spin complexes ?  
 (A)  $\text{CO}$  (B)  $\text{NO}_2^-$   
 (C)  $\text{CN}^-$  (D)  $\text{NH}_3$
- Q.35** Indicate the complex ion which shows geometrical isomerism.  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  (B)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]$   
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (D)  $[\text{Co}(\text{CN})_5(\text{NCl})]^{3-}$
- Q.36** Among the following compounds which is both paramagnetic and coloured ?  
 (A)  $\text{K}_2\text{Cr}_2\text{O}_7$  (B)  $[\text{Co}(\text{SO}_4)]$   
 (C)  $(\text{NH}_4)_2[\text{TiCl}_6]$  (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$
- Q.37** Ammonia acts as a very good ligand but ammonium ion does not form complexes because  
 (A)  $\text{NH}_3$  is a gas while  $\text{NH}_4^+$  is in liquid form.  
 (B)  $\text{NH}_3$  undergoes  $sp^3$  hybridisation while  $\text{NH}_4^+$  undergoes  $sp^3d$  hybridisation.  
 (C)  $\text{NH}_4^+$  ion does not have any lone pair of electrons.  
 (D)  $\text{NH}_4^+$  ion has one unpaired electron while  $\text{NH}_3$  has two unpaired electrons.
- Q.38**  $\text{CH}_3 - \text{Mg} - \text{Br}$  is an organometallic compound due to  
 (A)  $\text{Mg} - \text{Br}$  bond (B)  $\text{C} - \text{Mg}$  bond  
 (C)  $\text{C} - \text{Br}$  bond (D)  $\text{C} - \text{H}$  bond.
- Q.39**

  
 Here, I and II are  
 (A) geometrical isomers (B) optical isomers  
 (C) linkage isomers (D) None of these
- Q.40** The formula of the complex diamminechloro (ethylenediamine) nitroplatinum(IV) chloride is  
 (A)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{en})\text{NO}_2]\text{Cl}_2$   
 (B)  $\text{Pt}[\text{Pt}(\text{NH}_3)_2(\text{en})\text{Cl}_2\text{NO}_2]$   
 (C)  $[\text{Pt}(\text{NH}_3)_2(\text{en})\text{NO}_2]\text{Cl}_2$   
 (D)  $\text{Pt}[(\text{NH}_3)_2(\text{en})\text{NO}_2\text{Cl}_2]$

- Q.41** Consider the following reaction
- $$\text{Fe}^{3+}_{(\text{aq})} \xrightarrow{\text{Excess SCN}^-} \text{Blood red colour (A)}$$
- $$\xrightarrow{\text{Excess of F}^-} \text{Colourless (B)}$$
- The magnetic moment of complex B is
- (A)  $\sqrt{8}$  (B)  $\sqrt{15}$   
 (C)  $\sqrt{24}$  (D)  $\sqrt{35}$
- Q.42** Change in composition of coordination sphere yields which type of isomers ?
- (A) Ionization (B) Optical  
 (C) Geometrical (D) None of these
- Q.43** Atomic number of Cr and Fe are respectively 24 and 26. Which of the following is paramagnetic with the spin of the electron
- (A)  $[\text{Cr}(\text{CO})_6]$  (B)  $[\text{Fe}(\text{CO})_5]$   
 (C)  $[\text{Fe}(\text{CN})_6]^{4-}$  (D)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- Q.44** The EAN of iron is  $[\text{Fe}(\text{CN})_6]^{3-}$  is
- (A) 34 (B) 36  
 (C) 37 (D) 35
- Q.45** The fraction of chlorine precipitated by  $\text{AgNO}_3$  solution from  $[\text{Co}(\text{NH}_3)_3\text{Cl}]_2\text{Cl}_2$  is
- (A) 1/2 (B) 2/3  
 (C) 1/3 (D) 1/4
- Q.46** The coordination number and the oxidation state of the element E in the complex  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)]\text{NO}_2$  (where (en) is ethylene diamine) are, respectively
- (A) 6 and 3 (B) 6 and 2  
 (C) 4 and 2 (D) 4 and 3
- Q.47**  $\text{CuSO}_4$  dissolves in  $\text{NH}_3$  due to formation of
- (A)  $\text{Cu}(\text{OH})_2$  (B)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
 (C)  $[\text{Cu}(\text{NH}_3)_4(\text{OH})_2]$  (D)  $\text{CuO}$
- Q.48** The IUPAC name for  $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$  is
- (A) Tetrakis (pyridine) platinum(II) tetrachloroplatinate(II)  
 (B) Tetrapyridine tetrachlorodiplatinum(IV)  
 (C) Tetrachlorotetrapyridine diplatinum(II)  
 (D) Tetrakis (pyridine) platinum(IV) tetrachloroplatinum(IV)
- Q.49** A substance appears coloured because
- (A) It absorbs light at specific wavelength in the visible part and reflects rest of the wavelengths.  
 (B) Ligands absorb different wavelengths of light which gives colour to the complex.  
 (C) It absorbs white light and shows different colours at different wavelength.  
 (D) It is diamagnetic in nature.
- Q.50** A complex of platinum, ammonia and chlorine produces four ions per molecule in the solution. The structure consistent with the observation is
- (A)  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$  (B)  $[\text{Pt}(\text{NH}_3)_2]\text{Cl}_4$   
 (C)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}_3$  (D)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$
- Q.51** If  $\Delta_0 < P$ , the correct electronic configuration for  $d^4$  system will be
- (A)  $t^4_{2g} e^0_g$  (B)  $t^3_{2g} e^1_g$   
 (C)  $t^0_{2g} e^4_g$  (D)  $t^2_{2g} e^2_g$
- Q.52** When 0.1 mol  $\text{CoCl}_3(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$ , 0.2 mol of  $\text{AgCl}$  are obtained. the conductivity of solution will correspond to :
- (A) 1 : 3 electrolyte (B) 1 : 2 electrolyte  
 (C) 1 : 1 electrolyte (D) 3 : 1 electrolyte
- Q.53** Which of the following compounds exhibits linkage isomerism ?
- (A)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  (B)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{en})_3]$   
 (C)  $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{Br}$  (D)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$
- Q.54** For the reaction of the type  $\text{M} + 4\text{L} \rightleftharpoons \text{ML}_4$
- (A) larger the stability constant, lower the proportion of  $\text{ML}_4$  that exists in solution.  
 (B) larger the stability constant, higher the proportion of  $\text{ML}_4$  that exists in solution.  
 (C) smaller the stability constant, higher the proportion of  $\text{ML}_4$  that exists in solution.  
 (D) None of the above
- Q.55** Which of the following is not a simple salt ?
- (A)  $\text{FeSO}_4$  (B)  $\text{KCl.MgCl}_2.6\text{H}_2\text{O}$   
 (C)  $\text{Al}_2(\text{CO}_3)_3$  (D)  $\text{NH}_4\text{Br}$
- Q.56** Which will not give the usual test for iron ?
- (A)  $\text{K}_2\text{Fe}_2(\text{SO}_4)_4.24\text{H}_2\text{O}$  (B)  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2.6\text{H}_2\text{O}$   
 (C)  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (D)  $\text{Fe}_2(\text{SO}_4)_3$
- Q.57** Consider transition metal ions which have  $d^1$  to  $d^{10}$  electrons. Which of these can form high spin and low spin complexes in octahedral geometry.
- (A)  $d^3, d^5, d^6, d^9$  (B)  $d^4, d^5, d^6, d^7$  (C)  $d^2, d^5, d^7, d^9$  (D)  $d^4, d^6, d^7, d^{10}$
- Q.58** The crystal field splitting energy for  $\text{Cr}^{+3}$  ion in an octahedral field increases for the ligands  $\text{I}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$  and the order is such that
- (A)  $\text{I}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$   
 (B)  $\text{CN}^- < \text{I}^- < \text{H}_2\text{O} < \text{NH}_3$   
 (C)  $\text{CN}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{I}^-$   
 (D)  $\text{NH}_3 < \text{H}_2\text{O} < \text{I}^- < \text{CN}^-$
- Q.59** The correct IUPAC name of the coordination compound  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$  is
- (A) Potassium pentacyanonitrosylferrate(II)  
 (B) Potassium pentacyanonitroferrate(III)  
 (C) Potassium nitritopentacyanoferrate(IV)  
 (D) Potassium nitritepentacyanoiron(II).
- Q.60** On treatment of 100 mL of 0.1 M solution of the complex  $\text{CrCl}_3.6\text{H}_2\text{O}$  with excess of  $\text{AgNO}_3$ , 4.305 g of  $\text{AgCl}$  was obtained. The complex is
- (A)  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3].3\text{H}_2\text{O}$   
 (B)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}.2\text{H}_2\text{O}$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2.\text{H}_2\text{O}$   
 (D)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- Q.61** Which of the following is a tridentate ligand ?
- (A)  $\text{EDTA}^{4-}$  (B)  $(\text{COO})_2^{2-}$   
 (C) Dien (D)  $\text{NO}_2^-$
- Q.62** The spin magnetic moment of cobalt in  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is
- (A)  $\sqrt{3}$  BM (B)  $\sqrt{8}$  BM  
 (C)  $\sqrt{15}$  BM (D)  $\sqrt{24}$  BM

**EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)**

**NOTE:** The answer to each question is a NUMERICAL VALUE.

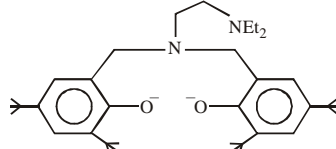
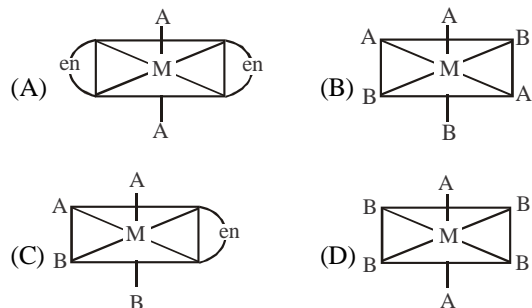
- Q.1** Total number of geometrical isomers for the complex  $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is
- Q.2**  $\text{EDTA}^{4-}$  is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in  $[\text{Co}(\text{EDTA})]^{1-}$  complex ion is
- Q.3** A list of species having the formula  $\text{XZ}_4$  is given :  $\text{XeF}_4$ ,  $\text{SF}_4$ ,  $\text{SiF}_4$ ,  $\text{BF}_4^-$ ,  $\text{BrF}_4^-$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{FeCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$ . Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is –
- Q.4** The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is :
- Q.5** The charge on cobalt in  $[\text{Co}(\text{CN})_6]^{3-}$  is-
- Q.6** How many pairs of enantiomers are possible for following complex compound.  
 $[\text{M}(\text{AB})(\text{CD})\text{ef}]^{n\pm}$  (where AB, CD– Unsymmetrical bidentate ligand, e,f–Monodentate ligands)
- Q.7** Hexafluoro ferrate (III) ion is an outer orbital complex. The number of unpaired electrons present in it is –
- Q.8** The hybridisation of Mn in hexacyano-manganate (II) is  $\text{sp}^3\text{d}^2$ . The number of unpaired electrons in it is –
- Q.9** The EAN of nickel in  $\text{Ni}(\text{CO})_4$  is-
- Q.10** Hexafluoroferrate (III) ion is an outer orbital complex. The number of unpaired electrons present in it is.

**EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]**

- Q.1** Arrange  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Pm}^{3+}$ , and  $\text{Yb}^{3+}$  in increasing order of their ionic radius - [AIEEE-2002]  
 (A)  $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$   
 (B)  $\text{Ce}^{3+} > \text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+}$   
 (C)  $\text{Yb}^{3+} > \text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+}$   
 (D)  $\text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+} < \text{Yb}^{3+}$
- Q.2** In  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , the isomerism shown is [AIEEE-2002]  
 (A) Ligand (B) Optical  
 (C) Geometrical (D) Ionization
- Q.3** In the complexes  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3+}$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{FeCl}_6]^{3-}$ , more stability is shown by [AIEEE-2002]  
 (A)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Fe}(\text{CN})_6]^{3+}$   
 (C)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (D)  $[\text{FeCl}_6]^{3-}$
- Q.4** One mole of the complex compound  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ , gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(\text{s})$ . The structure of the complex is [AIEEE-2003]  
 (A)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$  (B)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{Cl} \cdot \text{NH}_3$   
 (C)  $[\text{Co}(\text{NH}_3)_4\text{Cl}] \text{Cl}_2 \cdot \text{NH}_3$  (D)  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$
- Q.5** In the coordination compound  $\text{K}_4[\text{Ni}(\text{CN})_4]$ , the oxidation state of nickel is - [AIEEE-2003]  
 (A) 0 (B) +1  
 (C) +2 (D) -1
- Q.6** The number of 3d-electrons remained in  $\text{Fe}^{2+}$  (At. no. of Fe = 26) is - [AIEEE-2003]  
 (A) 4 (B) 5  
 (C) 6 (D) 3
- Q.7** Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion with copper ions in alkaline solutions but not in acidic solution. What is the reason for it - [AIEEE-2003]  
 (A) In acidic solution hydration protects copper ions.  
 (B) In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available.  
 (C) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali.  
 (D) Copper hydroxide is an amphoteric substance.
- Q.8** What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - [AIEEE-2003]  
 (A)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed  
 (B)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (C)  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to +3 state of Cr  
 (D)  $\text{Cr}_2\text{O}_7^{2-}$  is oxidised to +7 state of Cr
- Q.9** The atomic number of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are 23, 24, 25 and 26 respectively. Which one of these may be expected to have the highest second ionisation enthalpy - [AIEEE-2003]  
 (A) V (B) Cr  
 (C) Mn (D) Fe
- Q.10** The radius of  $\text{La}^{3+}$  is 1.06 Å, which of the following given values will be closest to the radius of  $\text{Lu}^{3+}$  (At no. of Lu = 71, La = 57) [AIEEE-2003]  
 (A) 1.6 Å (B) 1.4 Å  
 (C) 1.06 Å (D) 0.85 Å
- Q.11** Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statement about cerium is incorrect [AIEEE-2004]  
 (A) Cerium (IV) acts as an oxidising agent.  
 (B) The +3 oxidation state of cerium is more stable than the +4 oxidation state.  
 (C) The +4 oxidation state of cerium is not known in solutions.  
 (D) The common oxidation states of cerium are +3 and +4
- Q.12** Excess of KI reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is incorrect for this reaction - [AIEEE-2004]  
 (A) Evolved  $\text{I}_2$  is reduced (B)  $\text{CuI}_2$  is formed  
 (C)  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised (D)  $\text{Cu}_2\text{I}_2$  is formed
- Q.13** Calomel on reaction with  $\text{NH}_4\text{OH}$  gives - [AIEEE-2004]  
 (A)  $\text{HgNH}_2\text{Cl}$  (B)  $\text{NH}_2\text{-Hg-Hg-Cl}$   
 (C)  $\text{Hg}_2\text{O}$  (D)  $\text{HgO}$
- Q.14** Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by  $\text{CN}^-$  ion towards metal species is - [AIEEE-2004]  
 (A) c, a (B) b, c  
 (C) a, b (D) a, b, c
- Q.15** The coordination number of a central metal atom in a complex is determined by - [AIEEE-2004]  
 (A) The number of ligands around a metal ion bonded by sigma and pi-bonds both.  
 (B) The number of ligands around a metal ion bonded by pi-bonds.  
 (C) The number of ligands around a metal ion bonded by sigma bonds.  
 (D) The number of only anionic ligands bonded to the metal ion.
- Q.16** Which one of the following complexes in an outer orbitals complex - [AIEEE-2004]  
 (A)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (B)  $[\text{Mn}(\text{CN})_6]^{4-}$   
 (C)  $[\text{Fe}(\text{CN})_6]^{4-}$  (D)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
 (Atomic nos. : Mn = 25; Fe = 26; Co = 27; Ni = 28)
- Q.17** Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect ? [AIEEE-2004]  
 (A) Cyanocobalamin is vitamin  $\text{B}_{12}$  and contains cobalt.  
 (B) Haemoglobin is the red pigment of blood and contains iron.  
 (C) Chlorophylls are green pigments in plants and contain calcium.  
 (D) Carboxypeptidase-A is an enzyme and contains zinc.

- Q.18** The correct order of magnetic moments (spin only values in B.M. among is) – [AIEEE-2004]  
 (A)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$   
 (B)  $[\text{MnCl}_4]^{4-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$   
 (C)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$   
 (D)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$   
 (Atomic nos : Mn = 25 ; Fe = 26 ; Co = 27 ; Ni = 28)
- Q.19** The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM . The correct one is – [AIEEE-2005]  
 (A)  $d^4$  (in strong ligand field)  
 (B)  $d^4$  (in weak ligand field)  
 (C)  $d^3$  (in weak as well as in strong field)  
 (D)  $d^5$  (in strong ligand field)
- Q.20** The lanthanoid contraction is responsible for the fact that [AIEEE-2005]  
 (A) Zr and Y have about the same radius.  
 (B) Zr and Nb have similar oxidation state.  
 (C) Zr and Hf have about the same radius.  
 (D) Zr and Zn have similar oxidation state.
- Q.21** Lanthanoid contraction is caused due to – [AIEEE-2006]  
 (A) the same effective nuclear charge from Ce to Lu.  
 (B) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge.  
 (C) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge.  
 (D) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge.
- Q.22** The IUPAC name for the complex  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5] \text{Cl}_2$  is [AIEEE-2006]  
 (A) pentaammine nitrito-N-cobalt (II) chloride  
 (B) pentaammine nitrito-N-cobalt (III) chloride  
 (C) nitrito-N-pentaamminecobalt (III) chloride  
 (D) nitrito-N-pentaamminecobalt (II) chloride
- Q.23** Nickel (Z = 28) combines with a ninegative monodentate ligand  $X^-$  to form a paramagnetic complex  $[\text{NiX}_4]^{2-}$ . The number of unpaired electron in the nickel and geometry of this complex ion are respectively – [AIEEE-2006]  
 (A) one, square planar (B) two, square planar  
 (C) one, tetrahedral (D) two, tetrahedral
- Q.24** In  $\text{Fe}(\text{CO})_5$ , the Fe–C bond possesses [AIEEE-2006]  
 (A) ionic character (B)  $\sigma$ -character only  
 (C)  $\pi$ -character (D) both  $\sigma$  and  $\pi$  character
- Q.25** How many EDTA (ethylenediaminetetraacetate ion) molecules are required to make an octahedral complex with a  $\text{Ca}^{2+}$  ion ? [AIEEE-2006]  
 (A) One (B) Two  
 (C) Six (D) Three
- Q.26** The "spin-only" magnetic moment [in units of Bohr magneton] of  $\text{Ni}^{2+}$  in aqueous solution would be (At. No. Ni = 28) – [AIEEE-2006]  
 (A) 0 (B) 1.73  
 (C) 2.84 (D) 4.90
- Q.27** Which one of the following has a square planar geometry (Co = 27, Ni = 28, Fe = 28, Fe = 26, Pt = 78) [AIEEE-2007]  
 (A)  $[\text{CoCl}_4]^{2-}$  (B)  $[\text{FeCl}_4]^{2-}$   
 (C)  $[\text{NiCl}_4]^{2-}$  (D)  $[\text{PtCl}_4]^{2-}$
- Q.28** Identify the incorrect statement among the following – [AIEEE-2007]  
 (A) d-block elements show irregular and erratic chemical properties among themselves.  
 (B) La and Lu have partially filled d-orbitals and no other partially filled orbitals.  
 (C) The chemistry of various lanthanoids is very similar  
 (D) 4f and 5f-orbitals are equally shielded.
- Q.29** The actinoids exhibits more number of oxidation states in general than the lanthanoids. This is because – [AIEEE-2007]  
 (A) The 5f-orbitals are more buried than the 4f-orbitals.  
 (B) There is a similarity between 4f-and-5f in the their angular part of the wave function.  
 (C) The actinoids are more reactive than the lanthanoids.  
 (D) The 5f-orbitals extend further from the nucleus than the 4f-orbitals.
- Q.30** The coordination number and the oxidation state of the element 'E' in the complex  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)] \text{NO}_2$  (where en) is ethylene diamine) are, respectively – [AIEEE-2008]  
 (A) 6 and +2 (B) 4 and +2  
 (C) 4 and +3 (D) 6 and +3
- Q.31** In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of  $\Delta_0$  be the highest [AIEEE-2008]  
 (A)  $[\text{Co}(\text{CN})_6]^{3-}$  (B)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (D)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Q.32** Which of the following has an optical isomer ? [AIEEE-2009]  
 (A)  $[\text{CO}(\text{en})(\text{NH}_3)_2]^{2+}$  (B)  $[\text{CO}(\text{H}_2\text{O})_4(\text{en})]^{3+}$   
 (C)  $[\text{CO}(\text{en})_2(\text{NH}_3)_2]^{3+}$  (D)  $[\text{CO}(\text{NH}_3)_3\text{Cl}]^+$
- Q.33** Which of the following pairs represents linkage isomers [AIEEE-2009]  
 (A)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$   
 (B)  $[\text{CO}(\text{NH}_3)_5\text{NO}_3] \text{SO}_4$  and  $[\text{CO}(\text{NH}_3)_5\text{SO}_4] \text{NO}_3$   
 (C)  $[\text{PtCl}_2(\text{NH}_3)_4] \text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4] \text{Cl}_2$   
 (D)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
- Q.34** In context with the transition elements, which of the following statements is incorrect ? [AIEEE-2009]  
 (A) In the highest oxidation states, the transition metal show basic character and form cationic complexes.  
 (B) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and electrons are used for bonding.  
 (C) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.  
 (D) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

- Q.35** Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? [AIEEE-2009]  
 (A) The ionic sizes of Ln (III) decrease in general with increasing atomic number.  
 (B) Ln (III) compounds are generally colourless.  
 (C) Ln (III) hydroxides are mainly basic in character.  
 (D) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
- Q.36** The correct order of  $E_{M^{2+}/M}^{\circ}$  values with negative sign for the four successive elements Cr, Mn, Fe and Co is [AIEEE 2010]  
 (A) Mn > Cr > Fe > Co (B) Cr > Fe > Mn > Co  
 (C) Fe > Mn > Cr > Co (D) Cr > Mn > Fe > Co
- Q.37** Which one of the following has an optical isomer?  
 (A)  $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$  (B)  $[\text{Co}(\text{en})_3]^{3+}$   
 (C)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$  (D)  $[\text{Zn}(\text{en})_2]^{2+}$   
 (en = ethylenediamine) [AIEEE 2010]
- Q.38** Which of the following facts about the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is wrong? [AIEEE 2011]  
 (A) The complex involves  $d^2sp^3$  hybridisation and is octahedral in shape.  
 (B) The complex is paramagnetic.  
 (C) The complex is an outer orbital complex.  
 (D) The complex gives white precipitate with silver nitrate solution.
- Q.39** In context of the lanthanoids, which of the following statement is not correct? [AIEEE 2011]  
 (A) There is a gradual decrease in the radii of the members with increasing atomic number in the series.  
 (B) All the member exhibit +3 oxidation state.  
 (C) Because of similar properties the separation of lanthanoids is not easy.  
 (D) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.
- Q.40** The magnetic moment (spin only) of  $[\text{NiCl}_4]^{2-}$  is –  
 (A) 1.82 BM (B) 5.46 BM [AIEEE 2011]  
 (C) 2.82 BM (D) 1.41 BM
- Q.41** Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? [AIEEE 2012]  
 (A)  $[\text{Cr}(\text{en})_3]\text{Br}_3$  (B)  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$   
 (C)  $[\text{Cr}(\text{en})\text{Br}_4]^-$  (D)  $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$
- Q.42** Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [AIEEE 2012]  
 (A) Ferrous oxide is more basic in nature than the ferric oxide.  
 (B) Ferrous compounds are relatively more ionic than the corresponding ferric compounds  
 (C) Ferrous compounds are less volatile than the corresponding ferric compounds  
 (D) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
- Q.43** Which of the following complex species is not expected to exhibit optical isomerism? [AIEEE 2012]  
 (A)  $[\text{Co}(\text{en})_3]^{3+}$  (B)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (C)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (D)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
- Q.44** Which of the following arrangements does not represent the correct order of the property stated against it? [JEE MAIN 2013]  
 (A)  $V^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$ : paramagnetic behaviour  
 (B)  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$ : ionic size  
 (C)  $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$ : stability in aqueous solution  
 (D)  $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$ : number of oxidation states
- Q.45** Which series of reactions correctly represents chemical reactions related to iron and its compound? [JEE MAIN 2014]  
 (A)  $\text{Fe} \xrightarrow[\text{heat}]{\text{Cl}_2} \text{FeCl}_3 \xrightarrow[\text{Air}]{\text{Heat}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe}$   
 (B)  $\text{Fe} \xrightarrow[\text{heat}]{\text{O}_2} \text{Fe}_3\text{O}_4 \xrightarrow[600^\circ\text{C}]{\text{CO}} \text{FeO} \xrightarrow[700^\circ\text{C}]{\text{CO}} \text{Fe}$   
 (C)  $\text{Fe} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow[\text{O}_2]{\text{H}_2\text{SO}_4} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{Heat}} \text{Fe}$   
 (D)  $\text{Fe} \xrightarrow[\text{heat}]{\text{O}_2} \text{FeO} \xrightarrow[\text{H}_2\text{SO}_4]{\text{dil.}} \text{FeSO}_4 \xrightarrow{\text{heat}} \text{Fe}$
- Q.46** The octahedral complex of a metal ion  $M^{3+}$  with four monodentate ligands  $L_1, L_2, L_3$  and  $L_4$  absorb wavelengths in the region of red, green, yellow and blue, respectively.  
 The increasing order of ligand strength of the four ligands is – [JEE MAIN 2014]  
 (A)  $L_3 < L_2 < L_4 < L_1$  (B)  $L_1 < L_2 < L_4 < L_3$   
 (C)  $L_4 < L_3 < L_2 < L_1$  (D)  $L_1 < L_3 < L_2 < L_4$
- Q.47** The color of  $\text{KMnO}_4$  is due to – [JEE MAIN 2015]  
 (A) d - d transition  
 (B)  $L \rightarrow M$  charge transfer transition  
 (C)  $\sigma - \sigma^*$  transition  
 (D)  $M \rightarrow L$  charge transfer transition
- Q.48** Match the catalysts to the correct processes : [JEE MAIN 2015]
- | Catalyst                           | Process                            |
|------------------------------------|------------------------------------|
| a. $\text{TiCl}_3$                 | (i) Wacker process                 |
| b. $\text{PdCl}_2$                 | (ii) Ziegler-Natta polymerization  |
| c. $\text{CuCl}_2$                 | (iii) Contact process              |
| d. $\text{V}_2\text{O}_5$          | (iv) Deacon's process              |
| (A) a (ii), b (i), c (iv), d (iii) | (B) a-(ii), b-(iii), c-(iv), d-(i) |
| (C) a-(iii), b-(i), c-(ii), d-(iv) | (D) a-(iii), b-(ii), c-(iv), d-(i) |
- Q.49** The number of geometric isomers that can exist for square planar  $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$  is (py = pyridine)  
 (A) 3 (B) 4 [JEE MAIN 2015]  
 (C) 6 (D) 2
- Q.50** Which of the compounds is metallic and ferromagnetic?  
 (A)  $\text{CrO}_2$  (B)  $\text{VO}_2$  [JEE MAIN 2016]  
 (C)  $\text{MnO}_2$  (D)  $\text{TiO}_2$

- Q.51** The pair having the same magnetic moment is :  
[At.No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]  
(A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  [JEE MAIN 2016]  
(B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$   
(C)  $[\text{CoCl}_4]^{2-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
(D)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoCl}_4]^{2-}$
- Q.52** Which one of the following complexes shows optical isomerism ? [JEE MAIN 2016]  
(A) cis  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (B) trans  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
(C)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (D)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$   
(en = ethylenediamine)
- Q.53** On treatment of 100 mL of 0.1 M solution of  $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$  with excess  $\text{AgNO}_3$ ;  $1.2 \times 10^{22}$  ions are precipitated. The complex is: [JEE MAIN 2017]  
(A)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (B)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
(C)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$  (D)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
- Q.54** In the following reactions, ZnO is respectively acting as a/an: [JEE MAIN 2017]  
(a)  $\text{ZnO} + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{ZnO}_2$   
(b)  $\text{ZnO} + \text{CO}_2 \rightarrow \text{ZnCO}_3$   
(A) acid and base (B) base and acid  
(C) base and base (D) acid and acid
- Q.55** Consider the following reaction and statements :  
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{Co}(\text{NH}_3)_3\text{Br}_3] + \text{NH}_3$   
[JEE MAIN 2018]  
(a) Two isomers are produced if the reactant complex ion is a cis-isomer.  
(b) Two isomers are produced if the reactant complex ion is a trans-isomer.  
(c) Only one isomer is produced if the reactant complex ion is a trans-isomer.  
(d) Only one isomer is produced if the reactant complex ion is a cis-isomer.  
The correct statement are :  
(A) c and d (B) b and d  
(C) a and b (D) a and c
- Q.56** The oxidation state of Cr in  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ , and  $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$  respectively are: [JEE MAIN 2018]  
(A) +3, 0, and +6 (B) +3, 0 and +4  
(C) +3, +4 and +6 (D) +3, +2 and +4
- Q.57** Two complexes  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (a) and  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  (b) are violet and yellow coloured, respectively. The incorrect statement regarding them is [JEE MAIN 2019 (Jan)]  
(A)  $\Delta_0$  value of (a) is less than that of (b).  
(B)  $\Delta_0$  value of (a) & (b) are calculated from the energies of violet and yellow light, respectively  
(C) Both absorb energies corresponding to their complementary colours.  
(D) Both are paramagnetic with three unpaired electrons.
- Q.58** The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complex is [JEE MAIN 2019 (Jan)]  
(A) 5.92 (B) 3.87  
(C) 6.93 (D) 4.90
- Q.59** The following ligand is [JEE MAIN 2019 (April)]
- 
- (A) Bidentate (B) Hexadentate  
(C) Tetradentate (D) Tridentate
- Q.60** The correct order of the spin-only magnetic moment of metal ions in the following low spin complexes,  $[\text{V}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ , and  $[\text{Cr}(\text{NH}_3)_6]^{2+}$ , is: [JEE MAIN 2019 (April)]  
(A)  $\text{V}^{2+} > \text{Cr}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+}$   
(B)  $\text{V}^{2+} > \text{Ru}^{3+} > \text{Cr}^{2+} > \text{Fe}^{2+}$   
(C)  $\text{Cr}^{2+} > \text{V}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+}$   
(D)  $\text{Cr}^{2+} > \text{Ru}^{3+} > \text{Fe}^{2+} > \text{V}^{2+}$
- Q.61** The compound that inhibits the growth of tumors is [JEE MAIN 2019 (APRIL)]  
(A) cis- $[\text{Pd}(\text{Cl})_2(\text{NH}_3)_2]$  (B) cis- $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$   
(C) trans- $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_2]$  (D) trans- $[\text{Pd}(\text{Cl})_2(\text{NH}_3)_2]$
- Q.62** The statement that is INCORRECT about the interstitial compounds is: [JEE MAIN 2019 (APRIL)]  
(A) They have high melting points.  
(B) They are chemically reactive.  
(C) They have metallic conductivity.  
(D) They are very hard.
- Q.63** The calculated spin-only magnetic moments (BM) of the anionic and cationic species of  $[\text{Fe}(\text{H}_2\text{O})_6]_2$  and  $[\text{Fe}(\text{CN})_6]$ , respectively, are: [JEE MAIN 2019 (APRIL)]  
(A) 4.9 and 0 (B) 2.84 and 5.92  
(C) 0 and 4.9 (D) 0 and 5.92
- Q.64** The degenerate orbitals of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  are: [JEE MAIN 2019 (APRIL)]  
(A)  $d_{yz}$  and  $d_{z^2}$  (B)  $d_{z^2}$  and  $d_{xz}$   
(C)  $d_{xz}$  and  $d_{yz}$  (D)  $d_{x^2-y^2}$  and  $d_{xy}$
- Q.65** The one that will show optical activity is: (en = ethane-1,2-diamine) [JEE MAIN 2019 (APRIL)]
- 
- (A) (B) (C) (D)
- Q.66** Consider the hydrates ions of  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Ti}^{3+}$  and  $\text{Sc}^{3+}$ . The correct order of their spin-only magnetic moments is: [JEE MAIN 2019 (APRIL)]  
(A)  $\text{Sc}^{3+} < \text{Ti}^{3+} < \text{Ti}^{2+} < \text{V}^{2+}$   
(B)  $\text{Ti}^{3+} < \text{Ti}^{2+} < \text{Sc}^{3+} < \text{V}^{2+}$   
(C)  $\text{Sc}^{3+} < \text{Ti}^{3+} < \text{V}^{2+} < \text{Ti}^{2+}$   
(D)  $\text{V}^{2+} < \text{Ti}^{2+} < \text{Ti}^{3+} < \text{Sc}^{3+}$



- Q.67** Three complexes,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  (I),  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  (II) and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (III) absorb light in the visible region. The correct order of the wavelength of light absorbed by them is :  
[JEE MAIN 2019 (APRIL)]  
(A) (III) > (I) > (II) (B) (I) > (II) > (III)  
(C) (II) > (I) > (III) (D) (III) > (II) > (I)
- Q.68** The IUPAC name of the complex  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$  is : [JEE MAIN 2020 (JAN)]  
(A) Diammine (methanamine) chlorido platinum (II) chloride.  
(B) Bisammine (methanamine) chlorido platinum (II) chloride.  
(C) Diamminechlorido (aminomethane) platinum (II) chloride.  
(D) Diamminechlorido (methanamine) platinum (II) chloride.
- Q.69** For the complex  $[\text{MA}_2\text{B}_2]$  if M is  $sp^3$  or  $dsp^2$  hybridised respectively then total number of optical isomers are respectively :  
Note : A and B are unidentate neutral and unidentate monoanionic ligands, respectively  
[JEE MAIN 2020 (JAN)]  
(A) 1, 1 (B) 2, 1  
(C) 0, 0 (D) 1, 2
- Q.70** Among the statements(a)-(d), the incorrect ones are-  
[JEE MAIN 2020 (JAN)]  
(a) Octahedral Co(III) complexes with strong field ligands have very high magnetic moments.  
(b) When  $\Delta_0 < P$ , the d-electron configuration of Co(III) in an octahedral complex is  $t_{eg}^4 e_g^2$   
(c) Wavelength of light absorbed by  $[\text{Co}(\text{en})_3]^{3+}$  is lower than that of  $[\text{CoF}_6]^{3-}$ .  
(d) If the  $\Delta_0$  for an octahedral complex of Co(III) is  $18,000 \text{ cm}^{-1}$ , the  $\Delta_t$  for its tetrahedral complex with the same ligand will be  $16,000 \text{ cm}^{-1}$   
(A) (a) and (b) only (B) (c) and (d) only  
(C) (b) and (c) only (D) (a) and (d) only
- Q.71** Consider the following reactions :  
 $\text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4(\text{Conc.}) \rightarrow \text{(a)} + \text{Side products}$   
 $\text{(a)} + \text{NaOH} \rightarrow \text{(b)} + \text{Side product}$   
 $\text{(b)} + \text{H}_2\text{SO}_4(\text{dilute}) + \text{H}_2\text{O}_2 \rightarrow \text{(c)} + \text{Side product}$   
The sum of the total number of atoms in one molecule each of (a), (b) and (c) is [JEE MAIN 2020 (JAN)]
- Q.72** Which of the following complex exhibit facial meridional geometrical isomerism. [JEE MAIN 2020 (JAN)]  
(A)  $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$  (B)  $[\text{PtCl}_2(\text{NH}_3)_2]$   
(C)  $[\text{Ni}(\text{CO})_4]$  (D)  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$
- Q.73** The correct order of the calculated spin-only magnetic moments of complex (a) to (d) is:  
[JEE MAIN 2020 (JAN)]  
(a)  $\text{Ni}(\text{CO})_4$  (b)  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$   
(c)  $\text{Na}_2[\text{Ni}(\text{CN})_4]$  (d)  $\text{PdCl}_2(\text{PPh}_3)_2$   
(A) (a)  $\approx$  (c)  $\approx$  (d) < (b) (B) (a)  $\approx$  (c) < (b)  $\approx$  (d)  
(C) (c) < (d) < (b) < (a) (D) (c)  $\approx$  (d) < (b) < (a)
- Q.74** Among (a) – (d) the complexes that can display geometrical isomerism are : [JEE MAIN 2020 (JAN)]  
(a)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$  (b)  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$   
(c)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$  (d)  $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{2+}$   
(A) (d) and (a) (B) (a) and (b)  
(C) (b) and (c) (D) (c) and (d)
- Q.75** Complex  $[\text{ML}_5]$  can exhibit trigonal bipyramidal and square pyramidal geometry. Determine total number of  $180^\circ$ ,  $90^\circ$  &  $120^\circ$  L-M-L bond angles  
[JEE MAIN 2020 (JAN)]
- Q.76**  $[\text{Pd}(\text{F})(\text{Cl})(\text{Br})(\text{I})]^{2-}$  has n number of geometrical isomers. Then, the spin-only magnetic moment and crystal field stabilisation energy [CFSE] of  $[\text{Fe}(\text{CN})_6]^{n-6}$ , respectively, are: [Note : Ignore the pairing energy]  
[JEE MAIN 2020 (JAN)]  
(A) 2.84 BM and  $-1.6 \Delta_0$  (B) 1.73 BM and  $-2.0 \Delta_0$   
(C) 0 BM and  $-2.4 \Delta_0$  (D) 5.92 BM and 0
- Q.77** Complex X of composition  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_n$  has a spin only magnetic moment of 3.83 BM. It reacts with  $\text{AgNO}_3$  and shows geometrical isomerism. The IUPAC nomenclature of X is : [JEE MAIN 2020 (JAN)]  
(A) Tetraaquadichlorido chromium (III) chloride dihydrate.  
(B) Hexaaqua chromium (III) chloride  
(C) Dichloridotetraaqua chromium (IV) chloride dihydrate.  
(D) Tetraaquadichlorido chromium(IV) chloride dihydrate.
- Q.78** The isomer(s) of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  that has/have a Cl–Co–Cl angle of  $90^\circ$ , is/are :  
[JEE MAIN 2020 (JAN)]  
(A) meridional and trans (B) cis and trans  
(C) trans only (D) cis only

**EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]**
**PART A (d AND f BLOCK ELEMENTS)**

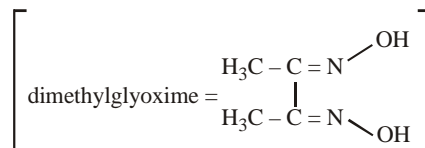
- Q.1** The aqueous solution containing which one of the following ions will be colourless ?  
(Atomic no. Sc = 21, Fe = 26, Ti = 22, Mn = 25)  
(A)  $\text{Sc}^{3+}$  (B)  $\text{Fe}^{2+}$  [AIPMT 2005]  
(C)  $\text{Ti}^{3+}$  (D)  $\text{Mn}^{2+}$
- Q.2** The main reason for larger number of oxidation states exhibited by the actinoids than the corresponding lanthanoids is – [AIPMT 2005 & 2006]  
(A) More energy difference between 5f and 6d orbitals than between 4f and 5d orbitals.  
(B) Lesser energy difference between 5f and 6d orbitals than between 4f and 5d orbitals.  
(C) Larger atomic size of actinoids than the lanthanoids.  
(D) Greater reactive nature of the actinoids than the lanthanoids.
- Q.3** In which of the following pairs are both the ions coloured in aqueous solutions – [AIPMT 2006]  
(A)  $\text{Sc}^{3+}$ ,  $\text{Ti}^{3+}$  (B)  $\text{Sc}^{3+}$ ,  $\text{Co}^{2+}$   
(C)  $\text{Ni}^{2+}$ ,  $\text{Cu}^{+}$  (D)  $\text{Ni}^{2+}$ ,  $\text{Ti}^{3+}$   
(At. No. Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
- Q.4** Copper sulphate dissolves in excess of KCN to give – [AIPMT 2006]  
(A)  $[\text{Cu}(\text{CN})_4]^{3-}$  (B)  $[\text{Cu}(\text{CN})_4]^{2-}$   
(C)  $\text{Cu}(\text{CN})_2$  (D)  $\text{CuCN}$
- Q.5** Which one of the following ions is the most stable in aqueous solution ? [AIPMT 2007]  
(A)  $\text{V}^{3+}$  (B)  $\text{Ti}^{3+}$   
(C)  $\text{Mn}^{3+}$  (D)  $\text{Cr}^{3+}$
- Q.6** Identify the incorrect statement among the following –  
(A) Lanthanoid contraction is the accumulation of successive shrinkages. [AIPMT 2007]  
(B) As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.  
(C) Shielding power of 4f electrons is quite weak.  
(D) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.
- Q.7** Which of the following ions will exhibit colour in aqueous solutions ? [AIPMT (PRE) 2010]  
(A)  $\text{La}^{3+}$  (Z = 57) (B)  $\text{Ti}^{3+}$  (Z = 22)  
(C)  $\text{Lu}^{3+}$  (Z = 71) (D)  $\text{Sc}^{3+}$  (Z = 21)
- Q.8** Which of the following ions has electronic configuration  $[\text{Ar}] 3d^6$  ? [AIPMT (PRE) 2010]  
(A)  $\text{Ni}^{3+}$  (B)  $\text{Mn}^{3+}$   
(C)  $\text{Fe}^{3+}$  (D)  $\text{Co}^{3+}$
- Q.9** Which of the following pairs has the same size ? [AIPMT (PRE) 2010]  
(A)  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  (B)  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$   
(C)  $\text{Zr}^{4+}$ ,  $\text{Hf}^{4+}$  (D)  $\text{Zn}^{4+}$ ,  $\text{Hf}^{4+}$
- Q.10** Which of the following oxidation states is the most common among the lanthanoids? [AIPMT (MAINS) 2010]  
(A) 4 (B) 2  
(C) 5 (D) 3
- Q.11** For the four successive transition elements (Cr, Mn, Fe and Co), the stability of + 2 oxidation state will be there in which of the following order? [AIPMT (PRE) 2011]  
(At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)  
(A)  $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$  (B)  $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$   
(C)  $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$  (D)  $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$
- Q.12** Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution turns green when  $\text{Na}_2\text{SO}_3$  is added to it. This is due to the formation of – [AIPMT (PRE) 2011]  
(A)  $\text{CrSO}_4$  (B)  $\text{Cr}_2(\text{SO}_4)_3$   
(C)  $\text{CrO}_4^{2-}$  (D)  $\text{Cr}_2(\text{SO}_3)_3$
- Q.13** Which one of the following does not correctly represent the correct order of the property indicated against it? [AIPMT (MAINS) 2012]  
(A) Increasing number of oxidation states:  $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$   
(B) Increasing magnetic moment:  $\text{Ti}^{3+} < \text{V}^{3+} < \text{Cr}^{3+} < \text{Mn}^{3+}$   
(C) Increasing melting points :  $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$   
(D) Increasing 2<sup>nd</sup> ionization enthalpy :  $\text{Ti} < \text{V} < \text{Mn} < \text{Cr}$
- Q.14** Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential ( $E_{\text{M}^{2+}/\text{M}}^0$ ) value has a positive sign [AIPMT (MAINS) 2012]  
(A) Co (Z = 27) (B) Ni (Z = 28)  
(C) Cu (Z = 29) (D) Fe (Z = 26)
- Q.15** The catalytic activity of transition metals and their compounds is ascribed mainly to [AIPMT (MAINS) 2012]  
(A) their magnetic behaviour  
(B) their unfilled d-orbitals  
(C) their ability to adopt variable oxidation state  
(D) their chemical reactivity
- Q.16** Which of the following exhibit only + 3 oxidation state ? [AIPMT (MAINS) 2012]  
(A) U (B) Th  
(C) Ac (D) Pa
- Q.17** Which of the following does not give oxygen on heating [NEET 2013]  
(A)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (B)  $\text{KClO}_3$   
(C)  $\text{Zn}(\text{ClO}_3)_2$  (D)  $\text{K}_2\text{Cr}_2\text{O}_7$
- Q.18** Which of the following lanthanoid ions is diamagnetic? (Atoms, Ce = 58, Sm = 62, Yb = 70) [NEET 2013]  
(A)  $\text{Yb}^{2+}$  (B)  $\text{Ce}^{2+}$   
(C)  $\text{Sm}^{2+}$  (D)  $\text{Eu}^{2+}$
- Q.19** Identify the correct order of solubility in aqueous medium: [NEET 2013]  
(A)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$  (B)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$   
(C)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$  (D)  $\text{Na}_2\text{S} < \text{CuS} > \text{ZnS}$
- Q.20** The reaction of aqueous  $\text{KMnO}_4$  with  $\text{H}_2\text{O}_2$  in acidic conditions gives : [AIPMT 2014]  
(A)  $\text{Mn}^{4+}$  and  $\text{O}_2$  (B)  $\text{Mn}^{2+}$  and  $\text{O}_2$   
(C)  $\text{Mn}^{2+}$  and  $\text{O}_3$  (D)  $\text{Mn}^{4+}$  and  $\text{MnO}_2$
- Q.21** Magnetic moment 2.83 BM is given by which of the following ions? [AIPMT 2014]  
(At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)  
(A)  $\text{Ti}^{3+}$  (B)  $\text{Ni}^{2+}$   
(C)  $\text{Cr}^{3+}$  (D)  $\text{Mn}^{2+}$

- Q.22** Reason of lanthanoid contraction is [AIPMT 2014]  
 (A) Negligible screening effect of f orbitals  
 (B) Increasing nuclear charge  
 (C) Decreasing nuclear charge  
 (D) Decreasing screening effect
- Q.23** Magnetic moment 2.84 BM is given by which of the following ions? [AIPMT 2015]  
 (At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)  
 (A)  $Ti^{3+}$  (B)  $Ni^{2+}$   
 (C)  $Cr^{3+}$  (D)  $Mn^{2+}$
- Q.24** Which of the following processes does not involve oxidation of iron? [AIPMT 2015]  
 (A) Decolourization of blue  $CuSO_4$  solution by iron.  
 (B) Formation of  $Fe(CO)_5$  from Fe.  
 (C) Liberation of  $H_2$  from steam by iron at high temperature.  
 (D) Rusting of iron sheets.
- Q.25** Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii (Numbers in the parenthesis are atomic numbers). [AIPMT 2015]  
 (A) Zr (40) and Nb (41) (B) Zr (40) and Hf (72)  
 (C) Zr (40) and Ta (73) (D) Ti (22) and Zr (40)
- Q.26** Gadolinium belongs to 4f series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? [RE-AIPMT 2015]  
 (A)  $[Xe] 4f^7 5d^1 6s^2$  (B)  $[Xe] 4f^6 5d^2 6s^2$   
 (C)  $[Xe] 4f^8 6d^2$  (D)  $[Xe] 4f^9 5s^1$
- Q.27** Assuming complete ionization, same moles of which of the following compounds will require the least amount of acidified  $KMnO_4$  for complete oxidation? [RE-AIPMT 2015]  
 (A)  $FeC_2O_4$  (B)  $Fe(NO_2)_2$   
 (C)  $FeSO_4$  (D)  $FeSO_3$
- Q.28** Which one of the following statements is corrected when  $SO_2$  is passed through acidified  $K_2Cr_2O_7$  [NEET 2016 PHASE 1]  
 (A) The solution turns blue  
 (B) The solution is decolourized  
 (C)  $SO_2$  is reduced  
 (D) Green  $Cr_2(SO_4)_3$  is formed
- Q.29** Which one of the following statements related to lanthanons is incorrect? [NEET 2016 PHASE 2]  
 (A) Europium shows +2 oxidation state.  
 (B) The basicity decreases as the ionic radius decreases from Pr to Lu.  
 (C) All the lanthanons are much more reactive than aluminium.  
 (D) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis.
- Q.30** The reason for greater range of oxidation states in actinoids is attributed to – [NEET 2017]  
 (A) actinoid contraction  
 (B) 5f, 6d and 7s levels having comparable energies  
 (C) 4f and 5d levels being close in energies  
 (D) the radioactive nature of actinoids.
- Q.31** Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code : [NEET 2018]
- | Column I     | Column II          |
|--------------|--------------------|
| a. $Co^{3+}$ | i. $\sqrt{8}$ BM   |
| b. $Cr^{3+}$ | ii. $\sqrt{35}$ BM |
| c. $Fe^{3+}$ | iii. $\sqrt{3}$ BM |
| d. $Ni^{2+}$ | iv. $\sqrt{24}$ BM |
|              | v. $\sqrt{15}$ BM  |
- (A) a-iv, b-i, c-ii, d-iii (B) a-i, b-ii, c-iii, d-iv  
 (C) a-iv, b-v, c-ii, d-i (D) a-iii, b-v, c-i, d-ii
- Q.32** Which one of the following ions exhibits d-d transition and paramagnetism as well? [NEET 2018]  
 (A)  $MnO_4^-$  (B)  $Cr_2O_7^{2-}$   
 (C)  $CrO_4^{2-}$  (D)  $MnO_4^{2-}$
- Q.33** The manganate and permanganate ions are tetrahedral, due to : [NEET 2019]  
 (A) The  $\pi$ -bonding involves overlap of p-orbitals of oxygen with d-orbitals of manganese.  
 (B) There is no  $\pi$ -bonding.  
 (C) The  $\pi$ -bonding involves overlap of p-orbitals of oxygen with p-orbitals of manganese.  
 (D) The  $\pi$ -bonding involves overlap of d-orbitals of oxygen with d-orbitals of manganese.

### **PART B (COORDINATION COMPOUNDS)**

- Q.1** Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? [AIPMT 2005]  
 Atomic no. Zn = 30, Cr = 24, Co = 27, Ni = 28  
 (A)  $[Zn(NH_3)_6]^{2+}$  (B)  $[Cr(NH_3)_6]^{3+}$   
 (C)  $[Co(NH_3)_6]^{3+}$  (D)  $[Ni(NH_3)_6]^{2+}$
- Q.2** Which one of the following is expected to exhibit optical isomerism – (en = ethylenediamine) [AIPMT 2005]  
 (A) cis- $[Pt(NH_3)_2Cl_2]$  (B) trans- $[Pt(NH_3)_2Cl_2]$   
 (C) cis- $[Co(en)_2Cl_2]$  (D) trans- $[Co(en)_2Cl_2]$
- Q.3**  $[Cr(H_2O)_6]Cl_3$  (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the Chromium of the complex is – [AIPMT 2006]  
 (A)  $3d\ xy^1, (3dx^2 - y^2), 3dyz^1$   
 (B)  $3d\ xy^1, 3dyz^1, 3dxz^1$   
 (C)  $3d\ xy^1, 3dyz^1, 3dz^2$   
 (D)  $(3dx^2 - y^2)^1, 3dz^2, 3dxz^1$
- Q.4**  $[Co(NH_3)_4(NO_2)_2]Cl$  exhibits [AIPMT 2006]  
 (A) linkage isomerism, ionization isomerism and geometrical isomerism.  
 (B) ionization isomerism, geometrical isomerism and optical isomerism.  
 (C) linkage isomerism, geometrical isomerism and optical isomerism.  
 (D) linkage isomerism, ionization isomerism and optical isomerism.
- Q.5** Which of the following will give a pair of enantiomorphs [AIPMT 2007]  
 (A)  $[Cr(NH_3)_6][Co(CN)_6]$  (B)  $[Co(en)_2Cl_2]Cl$   
 (C)  $[Pt(NH_3)_4][PtCl_6]$  (D)  $[Co(NH_3)_4Cl_2]NO_2$   
 (en =  $NH_2CH_2CH_2NH_2$ )

- Q.6** The d-electron configuration of  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  are  $3d^4$ ,  $3d^5$ ,  $3d^6$  and  $3d^8$  respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour – [AIPMT 2007]  
 (A)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (B)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$   
 (At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)
- Q.7** Which of the following complexes exhibits the highest paramagnetic behaviour? [AIPMT 2008]  
 (A)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$  (B)  $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^+$   
 (C)  $[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+}$  (D)  $[\text{Co}(\text{ox})_2(\text{OH})_2]^-$   
 Where gly = glycine, en = ethylenediamine and bpy = bipyridyl moieties  
 (at. nos. Ti = 22, V = 23, Fe = 26, Co = 27)
- Q.8** In which of the following coordination entities the magnitudes of  $\Delta_o$  (CFS E in octahedral field) will be maximum [AIPMT 2008]  
 (A)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (B)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (D)  $[\text{Co}(\text{CN})_6]^{3-}$   
 (At. no. Co = 27)
- Q.9** Out of  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$  (Z of Ti = 22, Co = 27, Cu = 29, Ni = 28) the colourless species are: [AIPMT 2009]  
 (A)  $\text{Cu}_2\text{Cl}_2$  &  $\text{NiCl}_4^{2-}$  (B)  $\text{TiF}_6^{2-}$  &  $\text{Cu}_2\text{Cl}_2$   
 (C)  $\text{CoF}_6^{3-}$  &  $\text{NiCl}_4^{2-}$  (D)  $\text{TiF}_6^{2-}$  &  $\text{CoF}_6^{3-}$
- Q.10** Which of the following does not show optical isomerism? [AIPMT 2009]  
 (A)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0$  (B)  $[\text{Co}(\text{en})\text{Cl}_2(\text{NH}_3)_2]^+$   
 (C)  $[\text{Co}(\text{en})_3]^{3+}$  (D)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (en = ethylenediamine)
- Q.11** Which of the following complex ions is expected to absorb visible light? [AIPMT 2009]  
 (A)  $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$  (B)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (C)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$  (D)  $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$   
 (At. no. Zn = 30, Sc = 21, Ti = 22, Cr = 24)
- Q.12** Which of the following complex ions is not expected to absorb visible light? [AIPMT (PRE) 2010]  
 (A)  $[\text{Ni}(\text{CN})_4]^{2-}$  (B)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (C)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
- Q.13** Crystal field stabilization energy for high spin  $d^4$  octahedral complex is: [AIPMT (PRE) 2010]  
 (A)  $-1.8 \Delta_o$  (B)  $-1.6 \Delta_o + P$   
 (C)  $-1.2 \Delta_o$  (D)  $-0.6 \Delta_o$
- Q.14** The existence of two different coloured complexes with the composition of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is due to – [AIPMT (PRE) 2010]  
 (A) linkage isomerism (B) geometrical isomerism  
 (C) coordination isomerism (D) ionization isomerism
- Q.15** Which of the following complexes is not expected to exhibit isomerism? [AIPMT (MAINS) 2010]  
 (A)  $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  (B)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   
 (C)  $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$  (D)  $[\text{Ni}(\text{en})_3]^{2+}$
- Q.16** Of the following complex ions, which is diamagnetic in nature? [AIPMT (PRE) 2011]  
 (A)  $[\text{CoF}_6]^{3-}$  (B)  $[\text{NiCl}_4]^{2-}$   
 (C)  $[\text{Ni}(\text{CN})_4]^{2-}$  (D)  $[\text{CuCl}_4]^{2-}$
- Q.17** The complexes  $[\text{Co}(\text{NH}_3)_6]$ ,  $[\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6]$   $[\text{Co}(\text{CN})_6]$  are the examples of which type of isomerism? [AIPMT (PRE) 2011]  
 (A) Geometrical isomerism (B) Linkage isomerism  
 (C) Ionization isomerism (D) Coordination isomerism
- Q.18** The complex,  $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$  will have how many geometrical isomers? [AIPMT (PRE) 2011]  
 (A) 2 (B) 3  
 (C) 4 (D) 0
- Q.19** The d-electron configurations of  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  are  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  respectively. Which one of the following will exhibit minimum paramagnetic behaviour? [AIPMT (PRE) 2011]  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  (B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$   
 (C)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$   
 (At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)
- Q.20** Which of the following carbonyls will have the strongest C – O bond? [AIPMT (MAINS) 2011]  
 (A)  $\text{Mn}(\text{CO})_6^+$  (B)  $\text{Cr}(\text{CO})_6$   
 (C)  $\text{V}(\text{CO})_6^-$  (D)  $\text{Fe}(\text{CO})_5$
- Q.21** Which of the following complex compounds will exhibit highest paramagnetic behaviour? [AIPMT (MAINS) 2011]  
 (A)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$  (B)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (D)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$   
 (At. No. : Ti = 22, Cr = 24, Co = 27, Zn = 30)
- Q.22** Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour? [AIPMT (PRE) 2012]  
 (A)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  (B)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$   
 (C)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  (D)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Q.23** Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammonical Ni (II). Which of the following statements is not true [AIPMT (MAINS) 2012]  
 (A) Red complex has a square planar geometry.  
 (B) Complex has symmetrical H-bonding  
 (C) Red complex has a tetrahedral geometry.  
 (D) Dimethylglyoxime functions as bidentate ligand.



- Q.24** Low spin complex of  $d^6$ -cation in an octahedral field will have the following energy: [AIPMT (MAINS) 2012]  
 (A)  $\frac{-12}{5} \Delta_o + P$  (B)  $\frac{-12}{5} \Delta_o + 3P$   
 (C)  $\frac{-2}{5} \Delta_o + 2P$  (D)  $\frac{-2}{5} \Delta_o + P$   
 ( $\Delta_o$  = Crystal field splitting energy in an octahedral field,  
 P = Electron pairing energy)

- Q.25** A magnetic moment of 1.73 BM will be shown by one among the following – [NEET 2013]  
 (A)  $[\text{CoCl}_6]^{4-}$  (B)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$   
 (C)  $[\text{Ni}(\text{CN})_4]^{2-}$  (D)  $\text{TiCl}_4$
- Q.26** An excess of  $\text{AgNO}_3$  is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium (III) chloride. The number of moles of  $\text{AgCl}$  precipitated would be – [NEET 2013]  
 (A) 0.01 (B) 0.001 (C) 0.002 (D) 0.003
- Q.27** Among the following complexes the one which shows zero crystal field stabilization energy (CFSE) is [AIPMT 2014]  
 (A)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- Q.28** Which of the following complexes is used to be as an anticancer agent? [AIPMT 2014]  
 (A)  $\text{mer-}[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (B)  $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$   
 (C)  $\text{cis-}[\text{PtCl}_2\text{Br}_2]$  (D)  $\text{Na}_2\text{CoCl}_4$
- Q.29** Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at  $25^\circ\text{C}$  [AIPMT 2015]  
 (A)  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (B)  $\text{CoCl}_3 \cdot 5\text{NH}_3$   
 (C)  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (D)  $\text{CoCl}_3 \cdot 3\text{NH}_3$
- Q.30** Which of these statements about  $[\text{Co}(\text{CN})_6]^{3-}$  is true? [AIPMT 2015]  
 (A)  $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a low-spin configuration.  
 (B)  $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a high-spin configuration.  
 (C)  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a high-spin configuration.  
 (D)  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a low-spin configuration.
- Q.31** The hybridization involved in complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is (At. No. Ni = 28) [RE-AIPMT 2015]  
 (A)  $d^2sp^2$  (B)  $d^2sp^3$   
 (C)  $dsp^2$  (D)  $sp^3$
- Q.32** The name of complex ion,  $[\text{Fe}(\text{CN})_6]^{3-}$  is – [RE-AIPMT 2015]  
 (A) Tricyanoferrate (III) ion  
 (B) Hexacyanidoferrate (III) ion  
 (C) Hexacyanoiron (III) ion  
 (D) Hexacyanitoferrate (III) ion
- Q.33** The sum of coordination number and oxidation number of the metal M in the complex  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$  (where en is ethylenediamine) is – [RE-AIPMT 2015]  
 (A) 7 (B) 8  
 (C) 9 (D) 6
- Q.34** Number of possible isomers for the complex  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  will be : (en = ethylenediamine) [RE-AIPMT 2015]  
 (A) 3 (B) 4  
 (C) 2 (D) 1
- Q.35** Which of the following has longest C – O bond length? (Free C – O bond length CO is  $1.128\text{\AA}$ ) [NEET 2016 PHASE 1]  
 (A)  $\text{Ni}(\text{CO})_4$  (B)  $[\text{Co}(\text{CO})_4]^-$   
 (C)  $[\text{Fe}(\text{CO})_4]^{2-}$  (D)  $[\text{Mn}(\text{CO})_6]^+$
- Q.36** Jahn-Teller effect not observed in high spin complexes of [NEET 2016 PHASE 2]  
 (A)  $d^4$  (B)  $d^9$   
 (C)  $d^7$  (D)  $d^8$
- Q.37** The correct order of the stoichiometries of  $\text{AgCl}$  formed when  $\text{AgNO}_3$  in excess is treated with the complex :  $\text{CoCl}_3 \cdot 6\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 5\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 4\text{NH}_3$  respectively is [NEET 2017]  
 (A) 3  $\text{AgCl}$ , 1  $\text{AgCl}$ , 2  $\text{AgCl}$  (B) 3  $\text{AgCl}$ , 2  $\text{AgCl}$ , 1  $\text{AgCl}$   
 (C) 2  $\text{AgCl}$ , 3  $\text{AgCl}$ , 1  $\text{AgCl}$  (D) 1  $\text{AgCl}$ , 3  $\text{AgCl}$ , 2  $\text{AgCl}$
- Q.38** Correct increasing order for the wavelengths of absorption in the visible region the complexes of  $\text{Co}^{3+}$  is [NEET 2017]  
 (A)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (B)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$   
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (D)  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- Q.39** Pick out the correct statement with respect to  $[\text{Mn}(\text{CN})_6]^{3-}$  [NEET 2017]  
 (A) It is  $sp^3d^2$  hybridised and tetrahedral.  
 (B) It is  $d^2sp^3$  hybridised and octahedral.  
 (C) It is  $dsp^2$  hybridised and square planar.  
 (D) It is  $sp^3d^2$  hybridised and octahedral.
- Q.40** Iron carbonyl,  $\text{Fe}(\text{CO})_5$  is [NEET 2018]  
 (A) Trinuclear (B) Mononuclear  
 (C) Tetranuclear (D) Dinuclear
- Q.41** The type of isomerism shown by the complex  $[\text{CoCl}_2(\text{en})_2]$  is [NEET 2018]  
 (A) Ionization isomerism (B) Coordination isomerism  
 (C) Geometrical isomerism (D) Linkage isomerism
- Q.42** The geometry and magnetic behaviour of the complex  $[\text{Ni}(\text{CO})_4]$  are [NEET 2018]  
 (A) Square planar geometry and paramagnetic.  
 (B) Tetrahedral geometry and diamagnetic.  
 (C) Square planar geometry and diamagnetic.  
 (D) Tetrahedral geometry and paramagnetic.
- Q.43** What is the correct electronic configuration of the central atom in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  based on crystal field theory? [NEET 2019]  
 (A)  $t_{2g}^4 e_g^2$  (B)  $t_{2g}^6 e_g^0$   
 (C)  $e^3 t_2^3$  (D)  $e^4 t_2^2$

## ANSWER KEY

## EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	D	B	D	D	A	C	C	A	A	C	C	B	A	B	B	D	A	D	D	B	A	C	D	D
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	A	B	C	D	A	B	D	D	D	D	B	B	D	C	D	B	C	C	C	C	C	C	A	D	A
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	A	A	A	B	A	A	A	B	B	D	C	D	C	D	A	B	C	D	A	C	A	D	D	C	C
Q	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
A	A	C	D	A	D	B	D	B	B	D	C	B	D	D	B	D	C	A	C	B	A	C	B	A	D
Q	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125
A	A	A	A	A	C	C	B	B	B	B	A	A	C	A	A	C	C	C	A	C	D	A	C	B	A
Q	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
A	C	B	A	A	D	D	B	C	B	D	C	B	C	B	B	A	C	A	D	A	D	C	A	C	A
Q	151	152	153	154	155	156	157	158	159	160	161	162													
A	B	C	A	D	C	B	D	A	C	D	D	D													

## EXERCISE - 2 (PART-A)

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
A	C	A	A	D	A	C	A	C	C	C	C	B	C	B	C	C	B	A	C	A	B	B	D	A	B	D
Q	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52
A	D	A	B	C	C	B	A	B	A	D	B	B	A	A	A	B	B	C	A	B	A	A	B	C	D	D

## EXERCISE - 2 (PART-B)

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
A	C	B	A	D	B	B	A	A	C	C	C	A	A	A	C	D	C	D	A	B	A	A	D	A	B	B	A	B	B	B	D
Q	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62
A	A	D	D	A	B	C	B	A	A	D	A	D	D	B	A	B	A	A	C	B	B	C	B	B	C	B	A	A	D	C	C

## EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9	10
A	3	8	4	0	3	10	5	1	36	5

## EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	A	B	C	D	A	C	B	B	B	D	C	B	A	A	C	D	C	C	A	C	B	B	D	D	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	D	D	D	D	A	C	A	A	B	A	B	C	D	C	B	D	C	A	B	D	B	A	A	A
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	A	A	A	A	D	A	B	A	C	A	B	B	C	C	C	A	B	D	C	D	18	D	A	D	20
Q	76	77	78																						
A	B	A	D																						

**EXERCISE - 5 (SECTION-A)**

<b>Q</b>	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
<b>A</b>	A	B	D	A	D	B	B	D	C	D	B	B	C	C	C	C	A	A	A	B	B	A	B	B	B	A	C	D	C	B	C	D	A

**EXERCISE - 5 (SECTION-B)**

<b>Q</b>	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
<b>A</b>	C	C	B	A	B	B	C	D	B	A	B	A	D	B	C	C	D	B	D	A	B	A	C	B	B
<b>Q</b>	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43							
<b>A</b>	B	B	B	D	D	C	B	C	A	C	D	B	D	B	B	C	B	B							

## d, f-BLOCK ELEMENTS & COORDINATION COMPOUNDS

### TRY IT YOURSELF-1

- (1) (D)
- (2) (A)
- (3) (D)
- (4) (C). All atomic and molecular species which contains one or more unpaired electrons are paramagnetic. Most of the ions of transition elements have unpaired electrons. Hence, they are all paramagnetic. Some ions of d-block elements with no unpaired electrons are  $\text{Sc}^{+3}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zn}^{+2}$  and  $\text{Cu}^{+1}$ . These ions are not paramagnetic and they are also without colour.
- (5) (A). The order of stability of the complexes of some of the ions carrying the same charge but differing in ionic radii decreases as the ionic radii increase.
- |             |                  |                  |                  |                  |
|-------------|------------------|------------------|------------------|------------------|
| Ion         | $\text{Cu}^{+2}$ | $\text{Ni}^{+2}$ | $\text{Fe}^{+2}$ | $\text{Mn}^{+2}$ |
| Ionic radii | 0.69             | 0.78             | 0.83             | 0.91             |
- The complexes of  $\text{Cu}^{+2}$  are most stable while  $\text{Mn}^{+2}$  is least stable.
- (6) (D). It is a characteristic of transition elements. Vertical relationship is due to similar electronic configuration in a group and horizontal relationship due to shielding effect being more predominant in last five elements in a period.
- (7) (C). The correct statement is that iron belongs to first transition series of elements. It is called 3d series. The member of this series are :
- Sc Ti V Cr Mn Fe Co Ni Cu Zn
- The electronic configuration of  $\text{Fe}^{26}$  is  $3d^6, 4s^2$ .
- (8) (B). A metal ion from the first transition series has a magnetic moment (calculated) of 2.83 BM. The number of unpaired electrons are expected to be present in the ion are 2.
- $$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2\sqrt{2}$$
- $$= 2 \times 1.41 = 2.828 \text{ BM} = 2.83 \text{ BM}$$
- (9) (C). One of the most striking features of the transition elements, is that they exhibit variable valency. The variable valency occurs to some extent in the p-block element also. In this case the valency changes usually in units of two. Some examples are  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PCl}_3$ ,  $\text{PCl}_5$  etc. But in transition elements the valency changes in one unit e.g.,  $\text{Cu}^+$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ , etc.

- (10) (B). The soft test metal is Zn, while remaining all other metal are comparatively harder metals.
- (11) (D). The compound  $\text{Cu}_2\text{SO}_4$  is not stable because Cu is stabilized only in  $\text{Cu}^{+2}$  state in its compounds with  $\text{SO}_4^{-2}$  ions hence  $\text{Cu}_2\text{SO}_4$  is not stable while  $\text{CuSO}_4$  is stable.

(12) (A)

(13) (C)

### TRY IT YOURSELF-2

(1) (A)

(2) (D)

(3) (B)

(4) (C)

(5) (A)

(6) (BD)

(7) (BC)

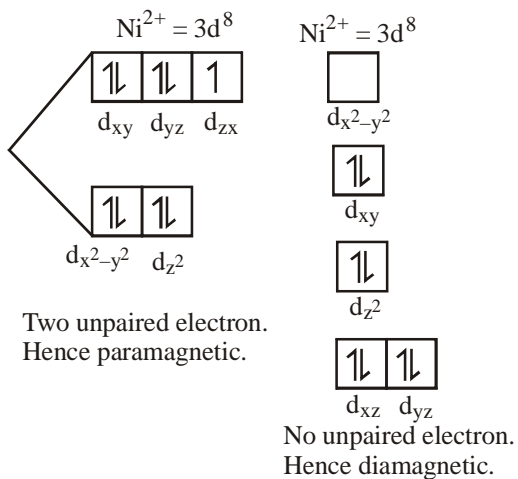
(8) (BC)

### TRY IT YOURSELF-3

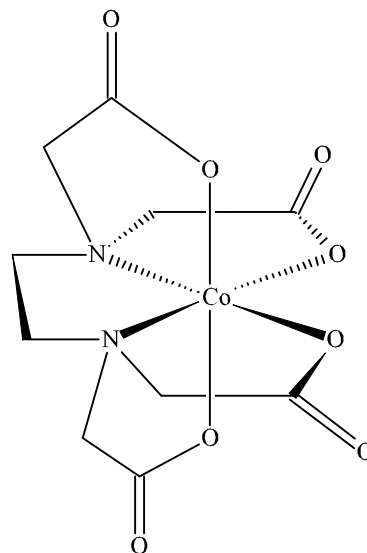
- (1) (a) Co-ordination (b) Double salt  
(c) Double salt (d) Co-ordination  
(e) Double salt
- (2) (i) tetraamminedichloridocobalt (III)  
(ii) triaamminetrichloridochromium (III)  
(iii) potassiumtrioxalatochromate(III)  
(iv) potassium hexaacyanoferrate (II)  
(v) pentaamminechloridoplatinum (IV) chloride
- (3) (A). Coordination number of Pt is 6, hence
- |     |  |   |            |
|-----|--|---|------------|
| I   | $\text{K}_2[\text{PtCl}_6]$                      | – | Three ions |
| II  | $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$          | – | Zero ions  |
| III | $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$ | – | Two ions   |
| IV  | $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ | – | Four ions  |
- (4) (C & D). Are coloured because  $\text{Cr}^{+3}$  in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $\text{V}^{3+}$  in  $[\text{VF}_6]^{3-}$  have  $3d^3$  and  $3d^2$  configuration respectively and thus show d-d transition.
- (5) Tetraamine cobalt (III) di- $\mu$ -hydroxo bis ethylenediamine cobalt (III) Chloride.
- (6) (D).  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$   
Diamminetetraaquacobalt(III) chloride



(7) (C). For tetrahedral compound



(9) 8.



Total no. of N – Co – O bond angles is 8.

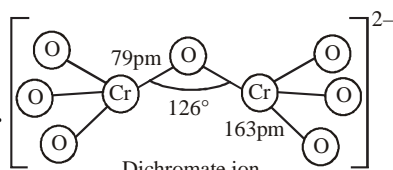
(8) (BD).  $[Co(NH_3)_4Cl_2]^+$  (an octahedral complex) and  $[Pt(NH_3)_2(H_2O)Cl]^+$  (a square planar complex) will show geometrical isomerism.  
 $[Pt(NH_3)_3(NO_3)]Cl$  and  $[Pt(NH_3)_3Cl]Br$  will show ionization isomerism.

(10) (C)

## CHAPTER-8 : d, f-BLOCK ELEMENTS & COORDINATION COMPOUNDS

### EXERCISE-1

- (1) (C). Cu; because last electron enters d-orbital ( $3d^{10} 4s^1$ ).
- (2) (D). Three series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg, omitting Ce to Lu).
- (3) (B). Ag belongs to second (4d) transition series remaining all are in first transition series.
- (4) (D). Zinc, cadmium and mercury of group 12 have full  $d^{10}$  configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.
- (5) (D). Transition metal as its last electron enters d-orbital.
- (6) (A). Their d-orbitals are completely filled.
- (7) (C).  $1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$ .
- (8) (C). Tantalum Ta(73)  $[Xe] 4f^{14} 5d^3 6s^2$
- (9) (A). Last electron in d-block elements goes to penultimate shell i.e.  $(n-1)d$ .
- (10) (A). In the case of Cr, configuration is  $3d^5 4s^1$  instead of  $3d^4 4s^2$ ; the energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d orbitals. Similarly in case of Cu, the configuration is  $3d^{10} 4s^1$  and not  $3d^9 4s^2$ .
- (11) (C). It show maximum oxidation state equal to +7 because the energy of  $(n-1)d$  and  $ns$  orbitals are nearly same and thus seven electrons can participate in bonding.
- (12) (C). Atomic radii of Fe, Co and Ni is almost same.
- |                   | Fe  | Co  | Ni  |
|-------------------|-----|-----|-----|
| Atomic radii (pm) | 126 | 125 | 125 |
- (13) (B). Hs ( $Z = 108$ ) belongs to 6d series with electronic configuration -  $[Rn]5f^{14} 6d^6 7s^2$ .
- (14) (A).  $(n-1)d^{1-10} ns^2$
- (15) (B). Electronic configuration ( $Z = 25$ )  
 $\rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$   
 'N' shell refers to 4th shell which has only two electrons.
- (16) (B). They show variable oxidation state due to participation of  $ns$  and  $(n-1)d$  electrons.
- (17) (D). Transitional elements form coloured salts due to the presence of unpaired electrons in d-orbital.
- (18) (A). Zn due to no unpaired electron in d-orbital.
- (19) (D). The first ionization energies of Ti, V, Cr, Mn are 656, 650, 652 and 717 kJ/mole respectively. I.E. increase in a period from L  $\rightarrow$  R hence, manganese has maximum first ionisation potential.
- (20) (D). Paramagnetic character is actually due to presence of unpaired electrons.
- (21) (B). In  $Cu^{+1}$  (cuprous ion) d orbitals are completely filled so it will form colourless complex.
- (22) (A).
- |           | $3d^5$ |   |   |   |   | $4s^2$ |
|-----------|--------|---|---|---|---|--------|
| Mn        | ↑      | ↑ | ↑ | ↑ | ↑ | ↑↓     |
| $Mn^{+2}$ | ↑      | ↑ | ↑ | ↑ | ↑ |        |
- As half filled orbitals are more stable than partial filled ones. Therefore, +2 is most stable oxidation state.
- (23) (C). Increased screening effect to nullify increased nuclear charge.
- (24) (D). In general, greater the number of unpaired electrons, greater is the number of bond and therefore, greater is the strength of these bonds, thus higher will be enthalpy of atomization.  
 Enthalpy of atomization first increases in a series (as unpaired electrons increases from 1 to 6), reaches to maxima and then decreases, and it is lowest for Zn, Cd, Hg (due to 0 unpaired electrons).
- (25) (D). In  $CrO_2Cl_2$ , O.S. of Cr = +6  
 $MnO_4^-$ , O.S. of Mn = +7  
 $Cr(CN)_6^{3-}$ , O.S. of Cr = +3  
 $NiF_6^{2-}$ , O.S. of Ni = +4.
- (26) (A).  $Tl^+$  is more stable than  $Tl^{3+}$  due to inert pair effect.  $Cu^{2+}$  is more stable than  $Cu^+$ .  $Cr^{3+}$  is more stable than  $Cr^{2+}$ .  $V^{4+}$  in aqueous solution is more stable than  $V^{2+}$ .
- (27) (B).  $Na_2[CuCl_4]$ , Cu = +2 or  $Cu^{2+} \rightarrow 3d^9$   
 $Na_2[CdCl_4]$ , Cd = +2 or  $Cd^{2+} \rightarrow 4d^{10}$   
 $K_4[Fe(CN)_6]$ , Fe = +2 or  $Fe^{2+} \rightarrow 3d^6$   
 $K_3[Fe(CN)_6]$ , Fe = +3 or  $Fe^{3+} \rightarrow 3d^5$   
 Since  $Cd^{2+}$  has completely filled d-subshell hence it is colourless.
- (28) (C). Density of transition metals increases from left to right in a transition series.
- (29) (D). The colour of transition metal ions is due to d-d transitions.
- (30) (A). First ionisation energy of the elements of first transition series (Ti  $\rightarrow$  Cu) increases as the atomic number increases due to increase of nuclear charge. The increase however is not regular.
- (31) (B). When the transition metals are in their highest oxidation state, they no longer have tendency to give away electrons, thus they are not basic but show acidic character and form anionic complexes.
- (32) (D). The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.  
 These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.
- (33) (D). All the four metals have nearly the same metallic radii and hence nearly the same atomic volume. On

- account of higher atomic mass of copper it has high density amongst given metals.
- (34) (D).  $\text{Sc}^{3+}$  ( $3d^0$ ),  $\text{Ti}^{4+}$  ( $3d^0$ ) are diamagnetic while  $\text{Pd}^{2+}$  ( $4d^8$ ) and  $\text{Cu}^{2+}$  ( $3d^9$ ) are paramagnetic.
- (35) (D). The common oxidation states of  $\text{Ti}(3d^2 4s^2)$  are +2, +3 and +4.
- (36) (B).  $3d^5$  configuration is more stable due to singly occupied half filled orbitals.
- (37) (B).  $\text{Ti}(22) \rightarrow 3d^2 4s^2$   
 $\text{Ti}^{2+} \rightarrow 3d^2 4s^0$   
 (d-d transition possible, so coloured)  
 $\text{Ti}^{4+} \rightarrow 3d^0 4s^0$   
 (no d-d transition, colourless)
- (38) (D).  ${}_{24}\text{Cr} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 \underbrace{4s^1 3d^5}_{\text{half-filled}}$
- (39) (C). Melting point of Zn, Cd and Hg follows the order :  $\text{Zn} > \text{Cd} > \text{Hg}$ .  
 Higher the melting point, higher will be the thermal stability. Hence order of thermal stability is  $\text{Zn} > \text{Cd} > \text{Hg}$ .
- (40) (D). Colourless compounds are those which have no unpaired electrons and paramagnetic substance do have unpaired electrons. Therefore paramagnetic substances possess colour.
- (41) (B). Reactivity of transition elements decreases almost regularly from Sc to Cu because of regular increase in ionisation enthalpy.
- (42) (C). Transition elements exhibit multiple oxidation state and their ions are usually coloured.
- (43) (C). During the reaction  $\text{K}_2\text{Cr}_2\text{O}_7$  is converted to  $\text{Cr}_2(\text{SO}_4)_3$   
 $\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{KI} \rightarrow 4\text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{I}_2$   
 In  $\text{Cr}_2(\text{SO}_4)_3$ , O.S. of Cr is +3.
- (44) (C). A greenish yellow gas is formed.  
 $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 10\text{HCl} \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{Cl}_2 \uparrow$   
 Greenish yellow
- (45) (C).  $\text{FeCr}_2\text{O}_4$  (Chromite) is used as the starting material for the preparation of potassium dichromate.
- (46) (C).  $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
- (47) (C).  $\text{K}_2\text{Cr}_2\text{O}_7$  contains  $\text{Cr}^{6+}(3d^0)$  which is diamagnetic but coloured due to charge transfer spectra.  $(\text{NH}_4)_2[\text{TiCl}_6]$  contains  $\text{Ti}^{4+}(3d^0)$ , which is diamagnetic and colourless.  $\text{VO}_4^{3-}$  contains  $\text{V}^{4+}(3d^1)$ , which is paramagnetic and coloured.  $\text{K}_3[\text{Cu}(\text{CN})_4]$  contains  $\text{Cu}^+(3d^{10})$ , which is diamagnetic and colourless.
- (48) (A).  $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$   
 Chromite ore  
 Sodium chromate (yellow)
- $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$
- $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$   
 Potassium dichromate
- (49) (D).  $\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{KI} \rightarrow 4\text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 3\text{I}_2 + 7\text{H}_2\text{O}$
- (50) (A). Sulphurous acid or sulphite is oxidised to sulphate or sulphuric acid.  
 $5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$
- (51) (A).  $2\text{KMnO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Mn}_2\text{O}_7 + 2\text{KHSO}_4 + \text{H}_2\text{O}$   
 (conc.) (green oily)
- (52) (A).  $\text{KMnO}_4$  in neutral medium.  
 $2\text{KMnO}_4 + \text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{MnO}_2 + 3(\text{O})$   
 $\text{KMnO}_4$  in basic medium.  
 $2\text{KMnO}_4 + 2\text{KOH} \rightarrow 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + (\text{O})$   
 Potassium permanganate is further reduced to manganese dioxide in presence of reducing agent.  
 $\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{KOH} + (\text{O})$   
 Potassium permanganate in acidic medium  
 $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5(\text{O})$
- (53) (A). It is one-third of its molecular weight in alkaline medium because it gives 3 nascent oxygen in alkaline medium.  
 $2\text{KMnO}_4 + \text{H}_2\text{O} \xrightarrow{+3e^-} 2\text{KOH} + 2\text{MnO}_2 + 3[\text{O}]$   
 $\rightarrow$  Equivalent weight =  $M/3$
- (54) (B). In acidic medium chromate ion converts to dichromate ion as  
 $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$   
 Yellow Orange
- (55) (A).  $\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Fe}^{3+} + 2\text{CO}_2 + 3e^-$   
 $\text{MnO}_4^- + 5e^- \rightarrow \text{Mn}^{2+}$   
 1 mole of  $\text{KMnO}_4$  accepts 5 electrons  
 1 mole of ferrous oxalate loses 3 electrons  
 $5e^- \equiv 1$  mole of  $\text{KMnO}_4$   
 $3e^-$  will be equivalent to  $3/5$  mole of  $\text{KMnO}_4$
- (56) (A).   
 Dichromate ion
- (57) (A). In  $\text{KMnO}_4$ , Mn is in +7 oxidation state.  
 $\text{Mn}^{7+}(Z = 25) \rightarrow [\text{Ar}]^{18} 3d^0 4s^0$ .  
 It has no unpaired electron but still  $\text{KMnO}_4$  is dark pink in colour.
- (58) (B). As we move down the lanthanoid series, the shielding effect of electrons is very little due to poor shielding of f-orbitals and hence the nuclear charge increases at each step increasing the pull of the electrons inwards which results in lanthanoid contraction.
- (59) (B). +3 oxidation state is common for all lanthanoids.
- (60) (D). The lanthanoids are silvery white soft metals.  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  ions are colourless.

The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

- (61) (C). Due to Lanthanoid contraction  
Zr = Hf = same radius
- (62) (D). Ce is most commonly used lanthanide, nobelium (No) & Th (thorium) are actinides.
- (63) (C). Due to lanthanoid contraction Zr and Hf have nearly equal size.
- (64) (D).  $Ce \rightarrow [Xe] 4f^1 5d^1 6s^2$ ;  $Ce^{4+} \rightarrow [Xe]$   
 $Yb \rightarrow [Xe] 4f^{14} 6s^2$ ;  $Yb^{2+} \rightarrow [Xe] 4f^{14}$   
 $Lu \rightarrow [Xe] 4f^{15} 5d^1 6s^2$ ;  $Lu^{3+} \rightarrow [Xe] 4f^{14}$   
 $Eu \rightarrow [Xe] 4f^7 6s^2$ ;  $Eu^{2+} \rightarrow [Xe] 4f^7$
- (65) (A). Lanthanum is a d-block element which resembles lanthanides.
- (66) (B). Across lanthanoid series basicity of lanthanoid hydroxide decreases.
- (67) (C). 95% of a lanthanoid metal, 5% of iron and traces of S, C, Ca and Al.
- (68) (D). Total number of inner transition elements in periodic table is 28, 14 each in lanthanoid and actinoid series.
- (69) (A). For the first four actinide elements, Th, Pa, U and Np, the difference in energy between 5f and 6d-orbitals is small. Thus, in these elements (and their ions) electrons may occupy the 5f or the 6d levels or sometimes both. Later in the actinide series the 5f-orbitals do become appreciably lower in energy. Thus, from Pu onwards the 5f-shell fills in a regular way and the elements become very similar.
- (70) (C). Actinoid series has elements from atomic no. 90 to 103. Thulium (Tm) has atomic no. 69.
- (71) (A). Terbium is lanthanide as it belongs to 4f-series having configuration  $[Xe] 4f^9 s^2$ . However the remaining members belong to 5f-series (actinides).
- (72) (D). Cobalt is used in cancer therapy.
- (73) (D). Ta because it is non-corrosive.
- (74) (C). Undecomposed AgBr forms a soluble complex with hypo.  
 $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$   
It is washed with water and the image is fixed.
- (75) (C). Primary valence are also known as oxidation state.  
 $K_2[Ni(CN)_4]$   
 $2 + x - 4 = 0 \Rightarrow x = +2$
- (76) (A).  $[Co(NH_3)_6]Cl_3$  gives 3 moles of AgCl.  
 $[Co(NH_3)_5Cl]Cl_2$  gives 2 moles of AgCl.  
 $[Co(NH_3)_4Cl_2]Cl$  gives 1 mole of AgCl.  
 $[Co(NH_3)_3Cl_3]$  will not give AgCl.
- (77) (C). According to Werner's theory, only those ions are precipitated which are attached to the metal atoms with ionic bonds and are present outside the coordination sphere.
- (78) (D).  $4KCN \cdot Fe(CN)_2$  or  $K_4[Fe(CN)_6]$  is a complex salt.
- (79) (A). According to Werner's theory primary valence is ionisable.
- (80) (D). Primary valence of binary compounds  $CrCl_3$ ,  $CoCl_2$

and  $PdCl_2$  are 3, 2 and 2 respectively.

- (81) (B).  $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$
- (82) (D). The primary valences are normally ionisable and are satisfied by negative ions.  
The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions.  
The secondary valence is equal to the coordination number and is fixed for a metal.  
Werner's theory does not explain the magnetic spectral properties.
- (83) (B).  $K_3[Fe(CN)_6]$  because in it  $CN^-$  donates a lone pair of electron.
- (84) (B). Al has 6 co-ordination number.
- (85) (D).  $x + 6 \times (0) + 3 \times (-1) = 0$   
 $x - 3 = 0$ ,  $x = +3$ ,  
Oxidation number of Cr is  $= +3$
- (86) (C). Number of donor atoms in  $N(CH_2CH_2NH_2)_3$  is four hence it is a tetradentate ligand.
- (87) (B).  $C_2H_4$  is neutral and Cl is uninegative ligand thus in  $[Pt(C_2H_4)Cl_3]^-$ ,  $x + 3(-1) = -1 \Rightarrow x = +2$ .
- (88) (D).  $[EDTA^{4-}]$  is ethylenediamine tetracetate ion and a hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. Its structure is
- $$\begin{array}{c} H_2C - N \begin{cases} CH_2COO^- \\ CH_2COO^- \end{cases} \\ | \\ H_2C - N \begin{cases} CH_2COO^- \\ CH_2COO^- \end{cases} \end{array}$$
- (89) (D).  $SCN^-$  is a monodentate ligand hence cannot show chelation.
- (90) (B). Coordination number is the number of ligands that are directly bound to the central metal atom by coordination bonds. Oxidation state is the residual charge on the central metal atom left after removing all ions.
- (91) (D). Ligands are ions or molecules linked by coordinate bonds to a central atom or ion.
- (92) (C). Lithium tetrahydridoaluminate:  $Li[AlH_4]$   
Here ligand is hydride ion ( $H^-$ ).
- (93) (A). In 4-coordinate complexes Pt, the four ligands are arranged about the central bivalent platinum ion in a square planar configuration.
- (94) (C).  $BF_3$  is an electron deficient compound and act as Lewis acid hence it cannot donate a pair of electrons and does not act as ligand.
- (95) (B).  $NH_4^+$  ion has no lone pair of electrons thus, cannot act as a ligand.
- (96) (A). Let oxidation state of Fe is x.  
 $H_2O$  is neutral and  $NO$  has +1 charge.  
Thus in  $[Fe(H_2O)_5NO]^{2+}$   
 $x + 1 = +2 \therefore x = +1$
- (97) (C).  $ONO$  is an anionic ligand ( $ONO^-$ ).
- (98) (B). A ligand donates its lone pair to metal atom ion.
- (99) (A).  $SCN^-$  and  $NO_2^-$  are ambidentate ligands since they

- have more than one donor atoms to attach to the central metal atom.
- (100) (D).  $K_3[Fe(CN)_6]$ :  
Potassium hexacyanoferrate (III)
- (101) (A). It is potassium ammine dicyano dioxo peroxy-chromate (VI)
- (102) (A).  $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ :  
Diamminechlorido(methylamine) platinum(II) chloride
- (103) (A). Pentaammineisothiocyanatochromium (III) tetrachlorozincate (II).
- (104) (A). Potassium trichloroethyleneplatinate(II) :  $K[PtCl_3(C_2H_4)]$
- (105) (C). Given compound is  $[Pt(NH_3)_2(en)(SCN)_2]^{2+}$  ion.
- (106) (C). Positively charged ligands have suffix 'ilum'.
- (107) (B).  $K_3[Ir(C_2O_4)_3]$ :  
potassium trioxalatoiridate(III)
- (108) (B).  $K[SbCl_5(C_6H_5)]$ :  
Potassiumpentachlorophenylantimonate (IV).
- (109) (B).  $[Co(NH_3)_5CO_3]Cl$   
Pentaamminecarbonatocobalt(III) chloride.
- (110) (B). Hexaamminecobalt(III) hexacyano-chromate (III).
- (111) (A). The correct IUPAC name of  $[Pt(NH_3)_2Cl_2]$  is diamminedichloridoplatinum (II)
- (112) (A). Chlorodiaquatrimminecobalt(III) chloride  $[CoCl(NH_3)_3(H_2O)_2]Cl_2$ .
- (113) (C). Tetraamminechloronitroplatinum (IV) sulphate can be written as  $[Pt(NH_3)_4(NO_2)Cl]SO_4$ .
- (114) (A). Octahedral complexes of the type  $[Ma_4b_2]$ ,  $[Ma_2b_4]$ ,  $[Ma_3b_3]$  exhibit geometrical isomerism.
- (115) (A). Co-ordination isomerism is caused by the interchange of ligands between cis and trans structure.
- (116) (C).  $[Co(en)_2NO_2Cl]Br$   
 $[Co(en)_2ONOC]Br$
- (117) (C). Geometrical isomers (cis and trans) and linkage isomers ( $-SCN$  and  $-NCS$ ).
- (118) (C). Optical isomerism : Cis- $[Co(en)_2Cl_2]$
- (119) (A).   
cis-isomer                      trans-isomer
- (120) (C). Both optical and geometrical isomerism are included in stereoisomerism.
- (121) (D). Sulphatopentaamminecobalt (III) bromide :  $[Co(SO_4)(NH_3)_5]Br$   
Sulphatopentaamminecobalt(III) chloride :  $[Co(SO_4)(NH_3)_5]Cl$   
Two compounds have different molecular formula hence there is no isomerism between two.
- (122) (A). When different number of water molecules are present inside and outside the coordination sphere, the isomers are known as hydrate isomers or solvate isomers.
- (123) (C). cis-isomers : (a), (b)  
trans-isomers : (c), (d)
- (124) (B). Linkage isomerism is exhibited by compounds containing ambidentate ligands.  
In  $[Pd(PPh_3)_2(NCS)_2]$ , the linkage of NCS and Pd is through N.  
In  $[Pd(PPh_3)_2(SCN)_2]$ , the linkage of SCN and Pd is through S.
- (125) (A).  $[Co(en)(NH_3)_2Cl_2]Cl$  exists in three geometrical isomeric forms and one of the geometrical isomers exhibit enantiomers.
- (126) (C). Linkage isomer of  $[Co(NH_3)_5NO_2]Cl_2$  will be  $[Co(NH_3)_5ONO]Cl_2$ .  
The name of the linkage isomer of  $[Co(NH_3)_5NO_2]Cl_2$  is pentaamminenitritocobalt(III) chloride.
- (127) (B). Geometrical isomerism arises when didentate ligands (L-L) are present in complexes of formula  $[MX_2(L-L)_2]$ .
- (128) (A). (i) Ionisation (ii) Hydrate
- (129) (A). Linkage isomerism is shown by ambidentate ligands.
- (130) (D). Solvate isomerism is also called 'hydrate isomerism' where water is involved as a solvent. It is also similar to ionisation isomerism. Aqua complex  $[Cr(H_2O)_6]Cl_3$  (violet) is an example of solvate isomerism.
- (131) (D).  $[Co(NH_3)_4Cl_2]NO_2$  and  $[Co(NH_3)_4Cl(NO_2)]Cl$  are ionization isomers.
- (132) (B). It is an example of solvate isomerism as different number of water molecules are present inside and outside the coordination sphere.
- (133) (C). Octahedral complex of type  $[Ma_5b]$  cannot show geometrical isomerism.
- (134) (B). The ligands are interchanged in both the cationic and anionic entities of different metal ions present in a complex to form coordination isomers.
- (135) (D).  $CrCl_3 \cdot 6H_2O$  shows hydrate isomerism.  
 $[Cr(H_2O)_6]Cl_3$  - Violet  
 $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$  - Green
- (136) (C). In general, the ligands can be arranged in a series in the order of increasing field strength:  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$ .
- (137) (B).  $CN^-$  is strongest field ligand in the given option.
- (138) (C). In octahedral complexes,  $t_{2g}$  orbitals possess low energy as compared to  $e_g$  orbitals while in tetrahedral complexes  $t_{2g}$  orbitals possess high energy as compared to  $e_g$  orbitals.
- (139) (B). Octahedral complex is formed by  $sp^3d^2$  hybridisation.
- (140) (B). The ligands with small value of  $\Delta_0$  are called weak field ligands whereas those with large value of  $\Delta_0$  are called strong field ligands, hence  $CN^-$  causes more splitting than  $H_2O$  and  $NH_3$ .
- (141) (A). If CFSE ( $\Delta_0$ ) < P (Energy required for pairing), the electrons do not pair up and fourth electrons goes to  $e_g$  of higher energy. Hence, high spin complex is formed. Pairing of electrons does not take place in case of weak field ligands.

(142) (C).  $\Delta_t = 4/9\Delta_0 = (4/9)(18,000 \text{ cm}^{-1}) = 8000 \text{ cm}^{-1}$

(143) (A). Limitations of VBT –

- \* It does not give quantitative interpretation of magnetic data.
- \* It does not distinguish between weak and strong ligands.
- \* It does not explain the colour exhibited by coordination compounds.
- \* It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- \* It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.

(144) (D). Hexafluorocobaltate(III) ion:  $[\text{CoF}_6]^{3-}$

It is an octahedral compound. Since the compound is high spin complex it must be  $sp^3d^2$  hybridised.

(145) (A). An experimental fact depending upon the ability of the ligand to cause crystal field splitting (i.e., strength of ligand).

(146) (D). In  $\text{Fe}(\text{CO})_5$ , Fe is  $sp^3d$  hybridised and thus trigonal bipyramidal in shape.

(147) (C). Ambident ligands show linkage isomerism e.g.  $-\text{NO}_2$ ,  $-\text{ONO}$ .

(148) (A). **Crystal Field theory** : The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. If a spherically symmetrical field of negative charges surrounds the metal atom/ion, the degeneracy is maintained. When this negative field is due to ligands in a complex, it becomes asymmetrical and the degeneracy of the d-orbitals is lifted. It results in splitting of d-orbitals. This pattern of splitting depends upon the nature of the crystal field.

(149) (C). Tetrahedral complexes generally involve  $sp^3$  hybridisation.

(150) (A). All the statements are correct with respect to the geometry of complex ions.

(151) (B). In an octahedral crystal field,  $t_{2g}$  orbitals are lowered in energy by  $0.4 \Delta_0$ .

(152) (C). In  $d^6$  (low spin), electrons get paired up to make two d-orbitals empty. Hybridisation is  $d^2sp^3$  (octahedral) and the complex is low spin.

(153) (A). Crystal field stabilisation energy for tetrahedral complexes is less than pairing energy hence they do not pair up to form low spin complexes.

(154) (D).  $[\text{CuCl}_4]^{2-}$  : Tetrahedral  
 $[\text{Fe}(\text{NH}_3)_6]^{2+}$  : Octahedral

(155) (C). Homoleptic carbonyls formed by most of the transition metals, have simple, well-defined structures and only carbonyl ligands.

(156) (B). In metal carbonyls, metal is in zero oxidation state.

(157) (D).  $V^-$  can have better back bonding with vacant p-orbital of carbon in carbonyl, thus carbon and oxygen interaction (donation of electron) will be the least, thus bond order will be the lowest.

(158) (A). The  $M-C\pi$  bond is formed by the donation of a pair

of electrons.

(159) (C). The reciprocal of the formation constant is called instability constant or dissociation constant.

(160) (D). Chelating ligands form more stable complexes as compared to monodentate ligands.

(161) (D). Chlorophyll contains magnesium.

(162) (D). In  $\text{K}_3[\text{Cu}(\text{CN})_2]$  copper is in +1 oxidation state while in  $\text{K}_2[\text{Cd}(\text{CN})_2]$  cadmium in +2 oxidation state. The more the oxidation state of the central metal atom, the more is the stability of the complex.

## EXERCISE-2

### PART A (d AND f BLOCK ELEMENTS)

(1) (C).  $\text{Fe}(\text{OH})\text{SO}_4$  ;  $\text{FeSO}_4 \xrightarrow{\text{H}_2\text{O}} \text{Fe}(\text{OH})\text{SO}_4$

(2) (A). Greater the oxidation number of the metal stronger oxidising agent, hence  $\text{Ag}_2\text{O}$  is mild oxidising agent.

(3) (A).

(i) Transition metals and many of their compounds show paramagnetic behaviour- It is due to the presence of unpaired electrons due to which they are attracted by magnetic field and show paramagnetism.

(ii) The enthalpies of atomisation of the transition metals are high - It is due to strong metallic bonding and additional covalent bonding due to the presence of unpaired electrons in d-orbitals due to which they have high lattice energy and consequently high enthalpy of atomisation.

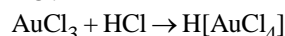
(4) (D). Iron;  $\text{Fe} + \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

(5) (A). In photography as it is sensitive towards light.

(6) (C). Iron is oxidised to ferrous nitrate and nitric acid is changed to ammonium nitrate



(7) (A). Except Au all other metals, i.e., Ag, Hg and Cu are dissolved in conc.  $\text{H}_2\text{SO}_4$  or conc.  $\text{HNO}_3$ . The compound X is  $\text{AuCl}_3$  which forms a complex with HCl.



It is used for toning in photography.

(8) (C). We get a yellow filtrate (due to the presence of  $\text{CrO}_4^{2-}$  ion in it) and a brown residue of  $\text{Fe}(\text{OH})_3$ .

(9) (C). In case of copper d-electrons are involved in metallic bonding that's why melting point of Cu is higher than that of Zn.

(10) (C).  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Sn}^{2+} \rightarrow 2\text{Cr}^{3+} + 3\text{Sn}^{4+} + 7\text{H}_2\text{O}$

(11) (C).  $\text{Mn}^{2+}$  ( $d^5$ ) is more stable than  $\text{Mn}^{3+}$  ( $d^4$ ) because  $\text{Mn}^{2+}$  has half-filled configuration.

(12) (B).  $\text{La}(\text{OH})_3$  is most basic. Hence, (I) is wrong. (II) is correct due to lanthanoid contraction. (III) is correct because  $\text{Ce}^{4+}$  tends to change to stable  $\text{Ce}^{3+}$ .

(13) (C). Hg, when comes in contact with  $\text{O}_3$  it forms  $\text{Hg}_2\text{O}$  which dissolves in mercury and mercury loses its meniscus. Finally it sticks to the surface of glass. The phenomenon is known as tailing of mercury.  
 $2\text{Hg} + \text{O}_3 \rightarrow \text{Hg}_2\text{O} + \text{O}_2$ .

- (14) (B). The third ionisation energy of Mn required to change  $\text{Mn}^{2+}(\text{d}^5)$  to  $\text{Mn}^{3+}(\text{d}^4)$  is much larger due to stable half-filled  $\text{d}^5$  electronic configuration.
- (15) (C).  $\text{Cu}^+$  salts are unstable in aqueous solution since they disproportionate easily to Cu and  $\text{Cu}^{2+}$  state.
- (16) (C).  $\text{Zn}^{2+} \rightarrow 3\text{d}^{10}$  has no unpaired electrons for excitation.
- (17) (B).  $\text{Ti}^{3+} \rightarrow 3\text{d}^1 4\text{s}^0$ ;  $\text{Sc}^{3+} \rightarrow 3\text{d}^0$   
 $\text{Mn}^{2+} \rightarrow 3\text{d}^5 4\text{s}^0$ ;  $\text{Zn}^{2+} \rightarrow 3\text{d}^{10} 4\text{s}^0$   
 In  $\text{Mn}^{2+}$  number of unpaired electron = 5.  
 So it has maximum magnetic moment according to the formula  $\mu = \sqrt{n(n+1)}$
- (18) (A). Cr forms  $\text{CrF}_3$ . Cu and Ni do not form  $\text{CuF}_3$  and  $\text{NiF}_3$ .
- (19) (C).  $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
- (20) (A). Zn, Cd and Hg have smaller ionic radii than group-2 elements because former involve 10 d-electrons which have poor shielding effect so that electrons are more strongly attracted towards nucleus.
- (21) (B). Tb (Z = 65) have  $[\text{Xe}] 4\text{f}^9 5\text{d}^0 6\text{s}^2$  configuration. Tb<sup>4+</sup> have half-filled 4f subshell, i.e.  $4\text{f}^7$ .
- (22) (B).  $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI}_2$   
 The  $\text{CuI}_2$  immediately decomposes to liberate  $\text{I}_2$  and insoluble copper (I) iodide.  
 $2\text{CuI}_2 \rightarrow 2\text{CuI} + \text{I}_2$
- (23) (D).  $2\text{CuSO}_4 + 10\text{KCN} \rightarrow 2\text{K}_3[\text{Cu}(\text{CN})_4] + 2\text{K}_2\text{SO}_4 + (\text{CN})_2$
- (24) (A). All the d-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. All the f-block elements are also metals but they are not good conductors of heat and electricity. However, the colour and magnetic properties of d- and f-block elements depend on the number of unpaired electrons.
- (25) (B). Melting point of Cu, Ag and Au follows the order  $\text{Cu} > \text{Au} > \text{Ag}$ .
- (26) (D). Elements or ions containing unpaired electrons are paramagnetic.  
 ${}_{28}\text{Ni} = [\text{Ar}] 3\text{d}^8 4\text{s}^2$   
 $\text{Ni}^{2+} = [\text{Ar}] 3\text{d}^8 4\text{s}^0$   
 $\text{Ni}^{2+}$  stage
- |  |    |    |    |   |   |   |   |
|--|----|----|----|---|---|---|---|
| 3d   | 4s |    |    |   |   |   |   |
| <table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="padding: 2px 5px;">↑↓</td> <td style="padding: 2px 5px;">↑↓</td> <td style="padding: 2px 5px;">↑↓</td> <td style="padding: 2px 5px;">↑</td> <td style="padding: 2px 5px;">↑</td> </tr> </table> | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | <table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="padding: 2px 5px;">□</td> </tr> </table> | □ |
| ↑↓   | ↑↓ | ↑↓ | ↑  | ↑ |   |   |   |
| □  |    |    |    |   |   |   |   |
- Because  $\text{Ni}^{2+}$  have 2 unpaired electrons in 3d subshell therefore it is paramagnetic.
- (27) (D). Ion  $\text{Ti}^{4+}$   $\text{Cu}^+$   $\text{Zn}^{2+}$   $\text{Cr}^{3+}$   
 Outer  $3\text{d}^0$   $3\text{d}^{10}$   $3\text{d}^{10}$   $3\text{d}^3$   
 electronic configuration  
 No. of 0 0 0 3  
 unpaired d-electrons
- (28) (A).  $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$   

Yellow coloured solution	Orange coloured solution
--------------------------------	--------------------------------
- (29) (B). Configuration  $3\text{d}^5$  has 5 unpaired electrons which shows highest magnetic moment.
- (30) (C). Greater the number of unpaired electrons more will be the magnetic moment.
- |                                |                 |                  |                  |                  |
|--------------------------------|-----------------|------------------|------------------|------------------|
| Ion                            | $\text{V}^{3+}$ | $\text{Cr}^{3+}$ | $\text{Fe}^{3+}$ | $\text{Co}^{3+}$ |
| Outer electronic configuration | $3\text{d}^2$   | $3\text{d}^3$    | $3\text{d}^5$    | $3\text{d}^6$    |
| No. of unpaired d-electrons    | 2               | 3                | 5                | 4                |
- Thus  $\text{Fe}^{3+}$  has highest value of magnetic moment.
- (31) (C). Potassium dichromate, on heating gives oxygen and chromic oxide ( $\text{Cr}_2\text{O}_3$ ).  
 $4\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}} 4\text{K}_2\text{Cr}_2\text{O}_4 + 3\text{O}_2 + 2\text{Cr}_2\text{O}_3$
- (32) (B).  $2\text{KI} + \text{HgCl}_2 \rightarrow \text{HgI}_2$  (scarlet red) +  $2\text{KCl}$
- (33) (A). The transition metals and their compounds are known for their catalytic activity because of their ability to adopt multiple oxidation states and to form complexes.
- (34) (B).  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + 2\text{CrO}_5 + 5\text{H}_2\text{O}$
- (35) (A). Acidic strength of oxides of transition metals increases with increase in oxidation number.
- |              |                         |                         |                |                         |
|--------------|-------------------------|-------------------------|----------------|-------------------------|
| +2           | +8/3                    | +3                      | +4             | +7                      |
| $\text{MnO}$ | $\text{Mn}_3\text{O}_4$ | $\text{Mn}_2\text{O}_3$ | $\text{MnO}_2$ | $\text{Mn}_2\text{O}_7$ |
- Hence acidic strength is of the order of
- |              |     |                         |     |                         |     |                |     |                         |
|--------------|-----|-------------------------|-----|-------------------------|-----|----------------|-----|-------------------------|
| $\text{MnO}$ | $<$ | $\text{Mn}_3\text{O}_4$ | $<$ | $\text{Mn}_2\text{O}_3$ | $<$ | $\text{MnO}_2$ | $<$ | $\text{Mn}_2\text{O}_7$ |
| Basic        |     |                         |     | Amphoteric              |     |                |     | Acidic                  |
- (36) (D).  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
- (37) (B). The typical oxidation state of the lanthanides is +3. The other oxidation state +2 and +4 are also exhibited by few of lanthanides. (These are shown by those elements which acquire stable configuration by losing 2 and 4 electrons).
- (38) (B).  $\text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
- (39) (A). In (I),  $\text{Cu}^+$  is oxidised as well as reduced. In (II),  $\text{MnO}_4^-$  ions are oxidised as well as reduced.
- (40) (A).  $\text{H}_2\text{O}_2$  reduces acidified  $\text{KMnO}_4$  solution. As a result, the pink colour of  $\text{KMnO}_4$  is changed.
- (41) (A). In  $\text{K}_2\text{Cr}_2\text{O}_7$ , the oxidation number of Cr = +6. The electronic configuration of  $\text{Cr}^{6+}$  is  ${}_{24}\text{Cr}^{6+} \rightarrow [\text{Ar}] 3\text{d}^0 4\text{s}^0$   
 So it has no unpaired electron, but is orange coloured.
- (42) (B). The ionic radii of lanthanide elements decreases steadily with increase in atomic number due to lanthanoid contraction.
- (43) (B).  $\text{Fe}^{3+} (\text{Z} = 26) \rightarrow 3\text{d}^5$   
 $\text{Mn}^{2+} (\text{Z} = 25) \rightarrow 3\text{d}^5$
- (44) (C).  
 (a) The transition metals generally form coloured compounds - It is due to the presence of unpaired electrons, they undergo d-d transitions by absorbing light from visible region and radiate complementary colour.  
 (b) Transition metals and their many compounds act as good catalyst - It is due to variable oxidation states. They have large surface area and can form

- intermediate with reactants which readily changed into products.
- (45) (A).  $\text{Mn}^{7+} + 3e \rightarrow \text{Mn}^{4+}$   
 $\text{Mn}^{7+} + 5e \rightarrow \text{Mn}^{2+}$   
 $\text{Mn}^{7+} + 4e \rightarrow \text{Mn}^{3+}$   
 $\text{Mn}^{7+} + e \rightarrow \text{Mn}^{6+}$
- (46) (B). The overall decrease in atomic and ionic radii from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$  is called lanthanoid contraction. Hence, the correct order is  $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$
- (47) (A).  $\text{Gd} (Z = 64) \rightarrow [\text{Xe}]4f^7 5d^1 6s^2$   
 $\therefore \text{Gd}^{3+} \rightarrow [\text{Xe}]4f^7$   
 $\text{Gd}^{3+}$  is highly stable due to stable half filled configuration.
- (48) (A). Zn does not show variable valency because of completely filled 'd' subshell.
- (49) (B). Oxidation number of I in  $\text{KIO}_4 = +7$   
 Oxidation number of Mn in potassium manganate  $\text{K}_2\text{MnO}_4 = +6$   
 Oxidation number of Mn in potassium permanganate  $\text{KMnO}_4 = +7$   
 Thus oxidation number of Mn in  $\text{KMnO}_4$  is equal to oxidation number of I in  $\text{KIO}_4$ .
- (50) (C). Potassium dichromate is prepared from chromite,  $\text{FeCr}_2\text{O}_4$ .
- (51) (D). Ion  $\text{Ti}^{3+}$   $\text{V}^{3+}$   $\text{Cu}^{3+}$   $\text{Sc}^{3+}$   
 Outer  $3d^1$   $3d^2$   $3d^8$   $3d^0$   
 electronic configuration  
 No. of l 2 2 0  
 unpaired d-electrons
- (52) (D). Hg is the last element of third transition series.

### PART B (COORDINATION COMPOUNDS)

- (1) (C). In Cuprammonium sulphate  
 $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
 co-ordination no. of Cu is 4.
- (2) (B). As it makes use of its two atoms to form two coordinate covalent bonds with the central metal ion.
- (3) (A). The co-ordination no. = no. of ligands attached.
- (4) (D).  $\text{CH}_3\text{Li}$  is the organometallic compound in which lithium bonded with carbon and organometallic are those in which metal-carbon bond found.
- (5) (B). The oxidation state of metal in metal carbonyl is zero.
- (6) (B).  $3 \times (+1) + x + 6 \times (-1) = 0$   
 or  $x = 6 - 3 = +3$   
 Oxidation state of Fe = +3.
- (7) (A). Complex with  $sp^3d$  hybridisation show square pyramidal geometry.
- (8) (A). Since hybridisation is  $dsp^2$  so it is square planar.
- (9) (C). Ammine ( $\text{NH}_3$ ) is neutral ligand.
- (10) (C). A strong field ligand produces low spin complexes.
- (11) (C). A person suffering from lead poisoning should be fed with  $[\text{Ca}(\text{EDTA})]^{2-}$
- (12) (A). An outer orbital complex is  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- (13) (A). Spin only magnetic moment =  $\sqrt{n(n+2)}$  B.M.  
 Where, n = no. of unpaired electrons.  
 Given,  $\sqrt{n(n+2)} = 2.84$   
 or,  $n(n+2) = 8.0656$  or  $n = 2$   
 In an octahedral complex, for a  $d^4$  configuration in a strong field ligand, number of unpaired electrons = 2.
- (14) (A). If the solution is blue, then absorbed wavelength of light will be of orange to transfer electron from  $t_{2g}$  to  $e_g$ .  
 If the solution is green, then absorbed wavelength of light will be of red to transfer electron from  $t_{2g}$  to  $e_g$ . As  $\lambda_{\text{orange}} < \lambda_{\text{red}}$ ,  
 $\therefore$  CFSE for blue solution will be maximum.
- (15) (C). The two forms dextro and laevo depend upon the direction they rotate the plane of polarised light in a polarimeter.  $l$ -rotates to the left and  $d$ -rotates to the right.
- (16) (D). In  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  primary valence is 2 and secondary valence is 4.
- (17) (C).  $\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$   
 Soluble complex
- (18) (D).  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is square planar involving  $dsp^2$  hybridisation.
- (19) (A). One mole of  $\text{AgCl}$  is precipitated, when excess of  $\text{AgNO}_3$  is added to the one mole of  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (green) mixed with  $\text{NH}_3$ .
- (20) (B). More the number of unpaired electrons, higher is its paramagnetism.  
 $\text{Cr}^{3+} : 3d^3$ ,  $\text{Fe}^{2+} : 3d^6$ ,  $\text{Cu}^{2+} : 3d^9$ ,  
 $\text{Zn}^{2+} : 3d^{10}$   
 $\text{Fe}^{2+}$  has four unpaired electrons hence it shows highest paramagnetism.
- (21) (A). In metal carbonyls, metal is in zero oxidation state.
- (22) (A). Overall dissociation constant  
 $= \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}$
- (23) (D). Optical isomers are mirror images and cannot be superimposed on one another. These are also called as enantiomers.
- (24) (A).  $\text{F}^-$  being weak field ligand results in high spin complex.
- (25) (B).  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4 \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{SO}_4^{2-}$   
 $\text{SO}_4^{2-} + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{Cl}^-$   
 white ppt.
- (26) (B).  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  is a coordination compound containing cationic complex ion.
- (27) (A). Higher the number of ions in the solution, higher is the conductivity.  
 No. of ions :  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] = 0$   
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} = 2$   
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 = 3$   
 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = 4$
- (28) (B). Sodium nitroprusside :  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$

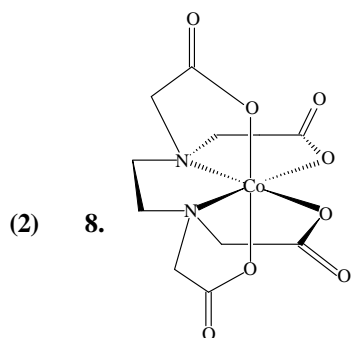
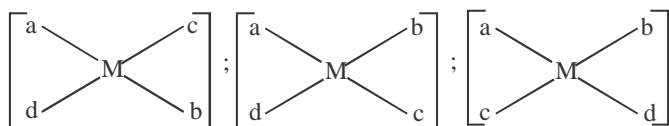


- (29) (B).  $\text{Fe}^{3+} + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{KFe}[\text{Fe}(\text{CN})_6] + 3\text{K}^+$   
Prussian blue
- (30) (B).  $3d^5$  has maximum number of unpaired electrons.
- (31) (D). In the complex linkage, geometrical and optical isomerism are possible.
- (32) (A). Co has six coordination number hence formulae for compounds A, B and C should be  
(a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
(b)  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$   
(c)  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$   
Primary valence is equal to the oxidation state of the central metal ion.
- (33) (D).  $\text{NH}_2\cdot\text{NH}_2$  is a monodentate ligand.
- (34) (D).  $\text{NH}_3$  can act as both weak field and strong field ligand hence forms both high spin and low spin complex.
- (35) (A).  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  shows geometrical isomerism..
- (36) (B). In  $[\text{Co}(\text{SO}_4)]$ , the oxidation state of Co is +2. Configuration of  $\text{Co}^{2+} = 3d^7$ , it has unpaired electrons in 3d-orbitals so it is paramagnetic. Because of incompletely filled d-orbitals it is coloured.
- (37) (C).  $\text{NH}_4^+$  ion does not possess any lone pair of electrons which it can donate to central metal ion hence it does not form complexes.
- (38) (B). Organometallic compounds contain metal carbon bond.
- (39) (A). I and II are geometrical isomers.
- (40) (A).  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{en})\text{NO}_2]\text{Cl}_2$   
Diamminechloro (Ethylenediamine) nitroplatinum(IV) chloride.
- (41) (D).  $\text{Fe}^{3+} + \text{SCN}(\text{excess}) \rightarrow \text{Fe}(\text{SCN})_3$   
$$\xrightarrow{\text{F}^-(\text{excess})} [\text{FeF}_6]^{3-}$$
  
 $\text{F}^-$  being weak ligand does not cause pairing, thus total no. of unpaired electron = 5. Magnetic moment,  
 $\mu = \sqrt{n(n+2)}$ , Where n=number of unpaired electrons.
- (42) (A). Change in composition of coordination sphere yields ionization isomers. e.g.  $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ .
- (43) (D). CO and  $\text{CN}^-$  are strong field ligands which force the electrons to pair up and thus complex is generally diamagnetic.  
 $\text{NH}_3$  is weak field ligand so that electrons remain unpaired and complex is generally paramagnetic.
- (44) (D). Oxidation state of Fe in  $[\text{Fe}(\text{CN})_6]^{3-} = +3$   
EAN of iron = electrons on  $\text{Fe}^{3+}$  + electron from six  $\text{CN}^- = 23 + 12 = 35$ .
- (45) (B).  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  ionizes to  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and  $2\text{Cl}^-$   
These  $2\text{Cl}^-$  reacts with  $\text{Ag}^+$  to form white ppt. of  $\text{AgCl}$ .
- (46) (A). In the given complex  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)]^+\text{NO}_2^-$  ethylene diamine is a bidentate ligand and  $(\text{C}_2\text{O}_4^{2-})$  oxalate ion is also bidentate ligand. Therefore co-ordination number of the complex is 6 i.e., it is an octahedral complex. Oxidation number of E in the given complex is
- $x + 2 \times 0 + 1 \times (-2) = +1 \therefore x = 3$
- (47) (B).  $\text{CuSO}_4 + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
- (48) (A).  $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$  : tetrakis(pyridine)platinum(II) tetrachloroplatinate (II).
- (49) (A). A substance absorbs light at specific wavelength in the visible part of the spectrum and reflects the rest of the wavelengths. Each wavelength represents a different colour hence corresponding colour is observed.
- (50) (C).  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}_3 \rightleftharpoons [\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+} + 3\text{Cl}^-$
- (51) (B). If  $\Delta_0 < P$ , the fourth electron will go to higher energy  $e_g$  orbital, giving the configuration  $t_{2g}^3 e_g^1$ .
- (52) (B). 0.2 moles of  $\text{AgCl}$  are obtained when 0.1 mol  $\text{CoCl}_3(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$  which shows that one molecule of the complex gives two  $\text{Cl}^-$  ions in solution. thus, the formula of the complex is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  i.e., 1 : 2 electrolyte.
- (53) (C).  $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{Br}$  and  $[\text{Co}(\text{en})_2(\text{ONO})\text{Cl}]\text{Br}$  are linkage isomers.
- (54) (B). For the reaction of the type  $\text{M} + 4\text{L} \rightleftharpoons \text{ML}_4$  larger the stability constant, higher the proportion of  $\text{ML}_4$  that exists in solution.
- (55) (B). A simple salt is a compound which has been prepared by the combination of two simple ions like  $\text{Na}^+$  and  $\text{Cl}^-$  ions to form  $\text{NaCl}$ . Similarly  $\text{KBr}$ ,  $\text{K}_2\text{S}$ ,  $\text{MgCl}_2$ ,  $\text{CaC}_2$  etc., simple ionic salts. Another set of simple salts can be  $\text{Zn}_3\text{P}_2$ ,  $\text{V}_2\text{O}_5$  etc., which are bonded covalently. Salts like  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{CO}_3)_3$ ,  $\text{NH}_4\text{Br}$  etc., are ionic, but formed by the combination of a simple ion and a compound ion such as  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NH}_4^+$  etc.
- (56) (C). Fe is present in the form of complex ion, i.e.,  $[\text{Fe}(\text{CN})_6]^{3-}$  which is not ionized to give  $\text{Fe}^{3+}$  and  $\text{CN}^-$ .
- (57) (B). Metal ions with  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  configuration can form high spin and low spin complexes. For transition metal ions with configuration  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  or  $d^{10}$  all the octahedral complexes of a given metal ion have approximately the same magnetic moment and there is no high spin versus low spin complexes.
- (58) (A). Weak field ligands produce small degree of splitting of 'd' orbitals and strong field ligands cause large splitting.  $\text{I}^-$  is the weakest ligand,  $\text{CN}^-$  is the strongest.
- (59) (A). The IUPAC name of the coordination compound  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$  is Potassium pentacyanonitrosylferrate(II)
- (60) (D). Mol. of  $\text{AgCl} = \frac{4.305}{143.5} = 0.03$   
= mol of  $\text{Cl}^-$  given by the complex.  
Mol of the complex =  $100 \times 10^{-3} \times 0.1 = 0.01$   
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \rightarrow [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$   
0.01 mol                      0.01 mol                      0.03 mol
- (61) (C). Dien (Diethylenetriamine) has the following structure  
 $\text{H}_2\ddot{\text{N}} - \text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H} - \text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$

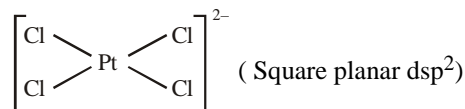
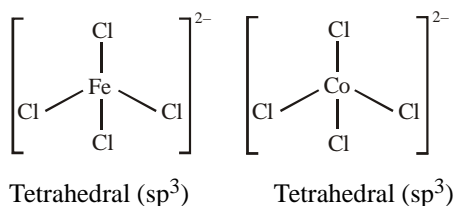
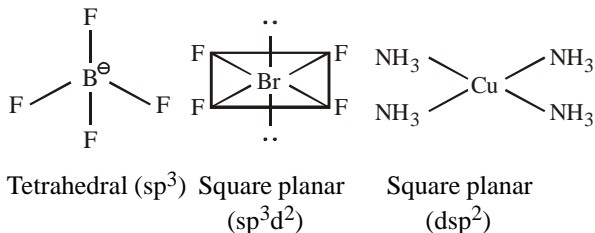
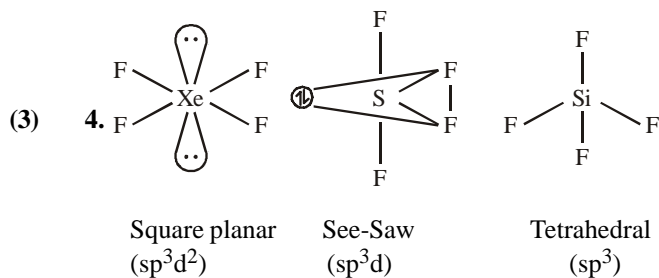
- (62) (C). In  $\text{Hg}[\text{Co}(\text{SCN})_4]$ , Co exists as  $\text{Co}^{2+}$   
 $_{27}\text{Co} : 3d^7 4s^2; _{27}\text{Co}^{2+} : 3d^7$   
 $\therefore$  Magnetic moment =  $\sqrt{n(n+2)}$   
 $\sqrt{3(3+2)} = \sqrt{15} \text{ BM}$ .

### EXERCISE-3

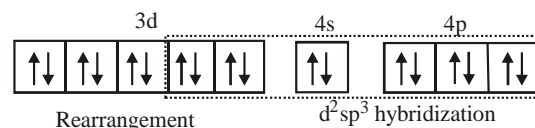
- (1) 3.  $[\text{M}(\text{abcd})]$  complex is square planar, so will have 3 geometrical isomers.  
 (i) (a T b) (c T d) ; (ii) (a T c) (b T d) ; (iii) (a T d) (b T c)



Total no. of N – Co – O bond angles is 8.

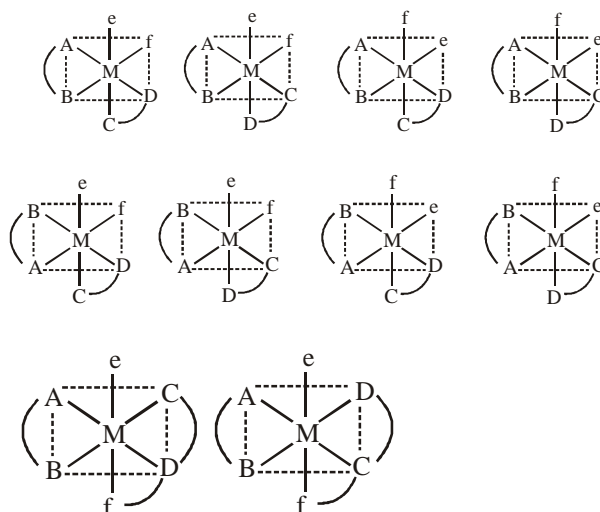


- (4) 0. The chromium is in zero oxidation state having configuration  $[\text{Ar}]^{18} 3d^5 4s^1$ . The CO is a strong field ligand so compels for the pairing of electrons. Thus the complex has  $d^2 sp^3$  hybridisation and is diamagnetic.  
 $[\text{Cr}(\text{CO})_6]$



$$\mu_{\text{BM}} = \sqrt{n(n+2)} = 0 \text{ as there is no unpaired electrons.}$$

- (5) 3. The algebraic sum of oxidation no. of all atoms in a complex ion is equal to charge on that ion,  
 i.e.,  $a + 6 \times (-1) = -3 \therefore a = +3$ .
- (6) 10.

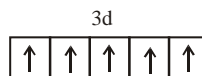


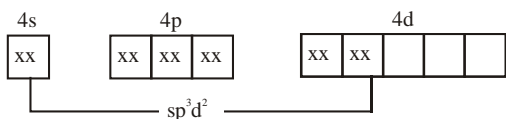
- (7) 5. Hexafluoroferrate (III) is  $[\text{FeF}_6]^{3-}$ . The O.N. of Fe in it is  $x + (-6) = -3$  or  $x - 6 = -3$  or  $x = +3$ .  
 Thus in it Fe is present as  $\text{Fe}^{3+}$ , which contains 5 unpaired electrons.

- (8) 1. The configuration of Mn is  $[\text{Ar}]d^5$ . Thus it is expected to have 5 unpaired electrons. But the strong ligand  $\text{CN}^-$  causes the pairing of electrons as  $\uparrow\downarrow \uparrow\downarrow \uparrow$   
 Thus there is only one unpaired electron left.

- (9) 36. Effective atomic no. (EAN) = at. no. of central atom - oxidation state +  $2 \times$  (no. of ligands) =  $28 - 0 + 2 \times 4 = 36$ .

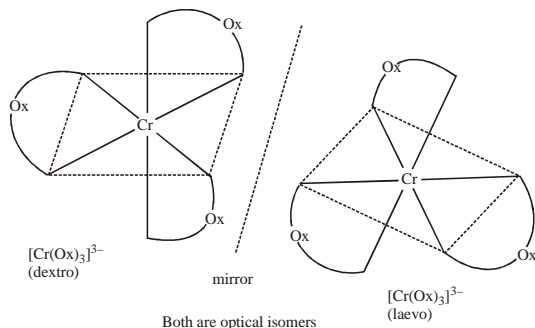
- (10) 5. Electronic configuration of  $[\text{FeF}_6]^{3-}$  is :





**EXERCISE-4**

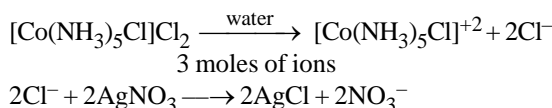
(1) (A).



(2) (B).

(3) (C).

(4) (D). The structure of complex is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
On dissolve in  $\text{H}_2\text{O}$



(5) (A).

(6) (C).

(7) (B). Ammonia does not form complex in with copper in acidic solution because protons co-ordinates with  $\text{NH}_3$  molecule forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecule are not available.

(8) (B).

(9) (B).

(10) (D). In a period : Atomic number ( $Z$ )  $\propto \frac{1}{\text{Atomic radius}}$

$$\text{So, } \frac{Z_1}{Z_2} = \frac{r_2}{r_1} \Rightarrow r_2 = \frac{Z_1 \times r_1}{Z_2} = \frac{57 \times 1.06}{71} = 0.85 \text{ \AA}$$

(11) (C). In solution phase, cerium show +4 oxidation state.

(12) (B).

(13) (A).  $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Hg} + \text{Hg}(\text{NH}_2)\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$

(14) (A).

(15) (C). Co-ordination number of complex compound = No. of ligands around a metal in bonded by sigma bond.

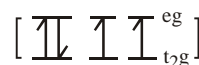
(16) (D). From the option  $[\text{Ni}(\text{NH}_3)_6]^{+2}$  is an outer orbital complex. In Ni hybridization is  $\text{sp}^3\text{d}^2$ .

(17) (C).

(18) (C).  $[\text{MnCl}_4]^{-2}$  has 5-unpaired electron,  $[\text{CoCl}_4]^{2-}$  has three unpaired electrons and  $[\text{Fe}(\text{CN})_6]^{4-}$  does not has any unpaired electron. So, the order of magnetic moment (spin only moment) is  $[\text{MnCl}_4]^{-2} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$

(19) (A). We know that, spin only moment =  $\sqrt{n(n+2)}$  BM.

The value of 2.84 correspond to the presence of 2 unpaired  $e^-$ . So,  $\text{d}^4$  system in strong field will adopt this arrangement as :

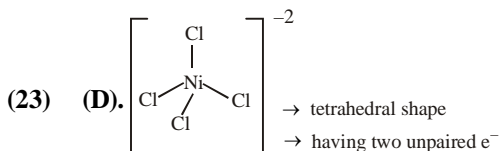


(20) (C). Due to Lanthanoid contraction

$\text{Zr} = \text{Hf} = \text{same radius}$

(21) (B). Lanthanoid contraction is caused due to the imperfect shielding on outer electron by 4f from the nuclear charge.

(22) (B).  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$   
pentaammine nitrito-N-cobalt (III) chloride



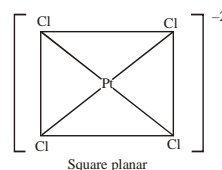
(24) (D). In  $\text{Fe}(\text{CO})_5$ , the Fe - C bond has  $\sigma$ -character as well as  $\pi$ -character due to back  $\pi$ -donation.

(25) (A). EDTA an hexadentate ligand, so only one EDTA molecule is required for forming octahedral complex entity.

(26) (C).  $\text{Ni}^{+2} = [\text{Ar}] 3\text{d}^8$   
There is two unpaired electron presence

$$\text{spin only moment} = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.84$$

We know that Cl is weak field ligand, so it does not able to pair up the orbital  $e^-$  of  $\text{Co}^{+2}$ ,  $\text{Fe}^{+2}$  &  $\text{Ni}^{+2}$  and they show tetrahedral shape it is found that  $\text{Pt}^{+2}$  having mostly square planar complex with field ligand as halogen.

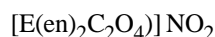
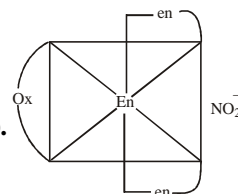


(27) (D).

(28) (D).

(29) (D). Actinoids exhibit more number of oxidation states in general than Lanthanoids because the 5f orbitals extend further from the nucleus than the 4f-orbitals.

(30) (D).



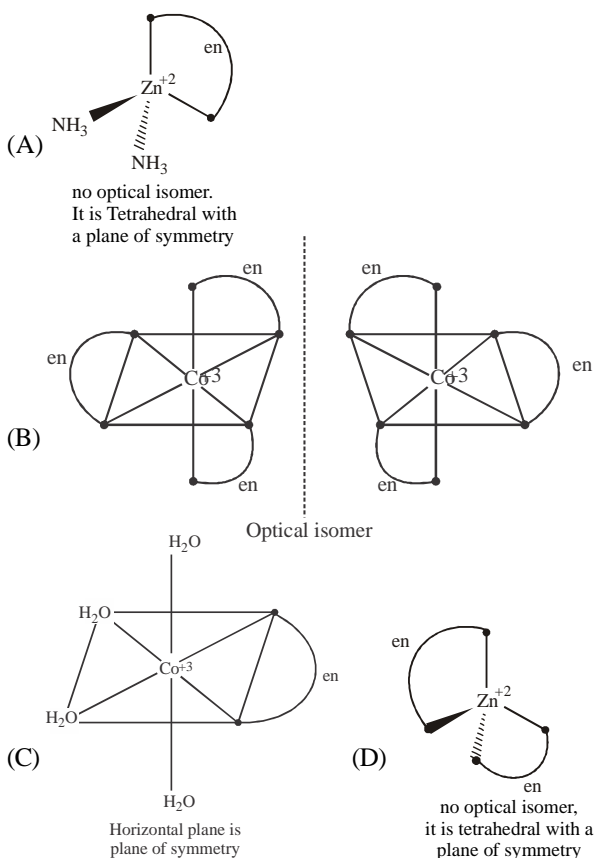
Co-ordination number =  $x + 2 \times 2 + 2 = 6$

Oxidation number =  $x + 2 \times 0 - 2 = +1$ ;  $x = +3$

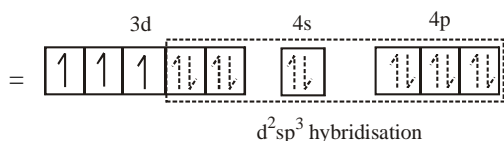
en  $\rightarrow$  neutral bidentate ligand

$\text{C}_2\text{O}_4^{-2} \rightarrow$  negative bidentate ligand

- (31) In  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $\text{CN}^-$  is strong field ligand, so  $\Delta_0$  is highest for  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $(\text{C}_2\text{O}_4)^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  are weak field ligand.
- (32) (C). Square planar complexes can not show optical isomerism. So, option (B) and (C) are ruled out. Compound in option (D) i.e.  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$  has a plane of symmetry, so it is also optically inactive.
- (33) (A). Linkage isomerism is shown by ambidentate ligands. ( $\text{SCN}^-$  and  $\text{NCS}^-$  are ambidentate groups).
- (34) (A). In highest oxidation state, the transition metal will form complexes which will have large degree of covalent character, which shows acidic behaviour.
- (35) (B).
- (36) (A).  $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$
- (37) (B). Only option (B) is having non-super imposable mirror image & hence one optical isomer.

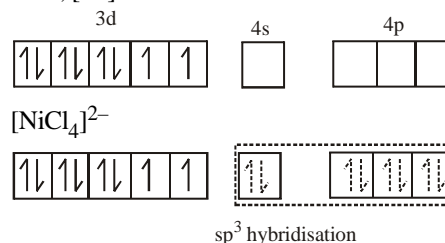


- (38) (C). In case of  $d^3$  configuration, the number of unpaired electrons remains 3 whether the ligand is strong field or weak field. The hybridisation scheme can be shown as follow:  $[\text{Cr}(\text{NH}_3)_3]^{3+}$



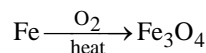
Hence the complex is inner orbital complex as it involves  $(n-1)$  d orbitals for hybridisation,  
 $3.93 = \sqrt{n(n+2)}$ , so  $n = 3$  (here  $n$  is number of unpaired electron(s)).

- (39) (D). Availability of 4f electrons donot results in the formation of compounds in +4 state for all themembers of the seires.
- (40) (C). In the paramagnetic and tetrahedral complex  $[\text{NiCl}_4]^{2-}$  the nickel is in +2 oxidation state and the ion has the electronic configuration  $3d^8$ . The hybridisation scheme is as shown in figure.

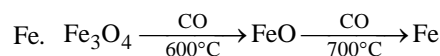


$$\mu_{\text{B.M.}} = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.82 \text{ BM}$$

- (41) (B).  $[\text{Cr}(\text{en})_2\text{Br}_2] \text{Br}$   
dibromidobis(ethylenediamine)chromium(III) Bromide.
- (42) (D).  $\text{Fe}^{3+}$  is easily hydrolysed than  $\text{Fe}^{2+}$  due to more positive charge.
- (43) (C).  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  show facial as well as meridional isomerism. But both contain plane of symmetry.
- (44) (A).  $\text{V}^{2+} = 3$  unpaired electrons  
 $\text{Cr}^{2+} = 4$  unpaired electrons  
 $\text{Mn}^{2+} = 5$  unpaired electrons  
 $\text{Fe}^{2+} = 4$  unpaired electrons  
 Hence the order of paramagnetic behaviour should be:  $\text{V}^{2+} < \text{Cr}^{2+} = \text{Fe}^{2+} < \text{Mn}^{2+}$
- (2) Ionic size decrease from left to right in same period
- (3) As per data from NCERT.  
 $\text{Co}^{3+}/\text{Co}^{2+} = 1.97$ ;  $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77$  ;  
 $\text{Cr}^{3+}/\text{Cr}^{2+} = -0.41$   
 $\text{Sc}^{3+}$  is highly stable (It does not show +2)
- (4) The oxidation states increases as we go from group 3 to group 7 in same period.
- (45) (B). In Eq. (1)  $\text{FeCl}_3$  cannot be reduced when heated in air. In Eq. (3)  $\text{Fe}_2(\text{SO}_4)_3$  cannot convert to Fe on heating; instead oxide(s) will be formed. In Eq. (4)  $\text{FeSO}_4$  cannot be converted to Fe on heating; instead oxide(s) will be formed.

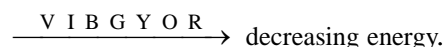


This reaction is corresponding to the combustion of



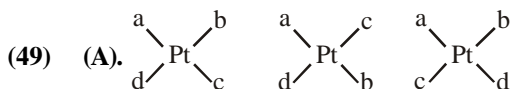
These reactions correspond to the production of Fe by reduction of  $\text{Fe}_3\text{O}_4$  in blast furnace.

- (46) (D). Strong field ligands cause higher magnitude of crystal field splitting which is accompanied by the absorption of higher energy radiation.



- (47) (B). Charge transfer spectra from ligand (L) to metal (M) is responsible for color of  $\text{KMnO}_4$ .

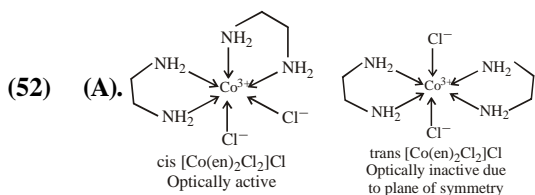
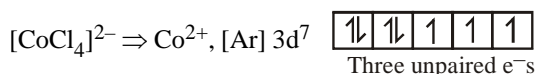
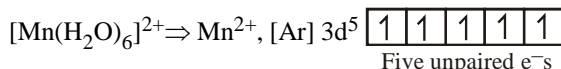
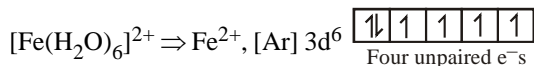
- (48) (A).  $\text{TiCl}_3$  - Ziegler Natta polymerisation  
 $\text{V}_2\text{O}_5$  - Contact process ;  $\text{PdCl}_2$  - Wacker process  
 $\text{CuCl}_2$  - Deacon's process



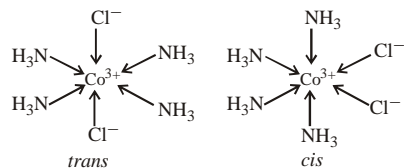
As per question  $a = \text{Cl}$ ,  $b = \text{py}$ ,  $c = \text{NH}_3$  and  $d = \text{NH}_2\text{OH}$  are assumed.

- (50) (A).  $\text{CrO}_2$  is metallic and ferromagnetic substance.

- (51) (A).  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} \Rightarrow \text{Cr}^{2+}$ ,  $[\text{Ar}] 3d^4$    
Four unpaired  $e^-$ s



$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  can exist in both *cis* and *trans* form and both are optically inactive.



$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  exist in *fac* and *Mer* forms and both are optically inactive.

- (53) (A). Moles of complex

$$= \frac{\text{Molarity} \times \text{volume (ml)}}{1000} = \frac{100 \times 0.1}{1000} = 0.01 \text{ mole}$$



Moles of ions precipitated with excess of  $\text{AgNO}_3$

$$= \frac{1.2 \times 10^{22}}{6.0 \times 10^{23}} = 2 \times 10^{-2} \text{ moles} = 0.02$$

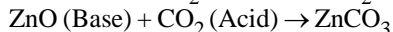
Number of  $\text{Cl}^-$  present in ionization sphere

$$= \frac{\text{Mole of ion precipitated with excess } \text{AgNO}_3}{\text{mole of complex}} = \frac{0.02}{0.01} = 2$$

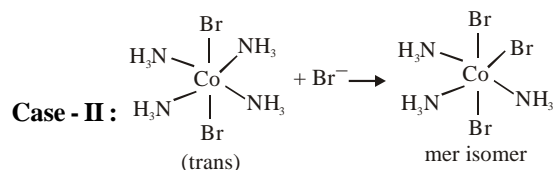
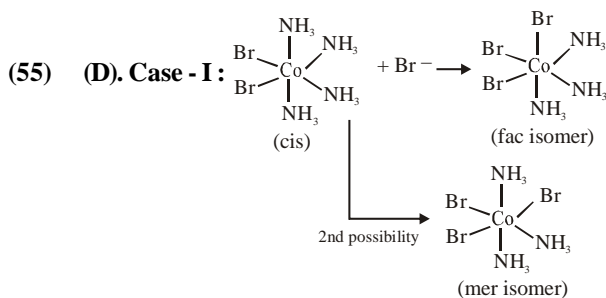
It means  $2\text{Cl}^-$  ions present in ionization sphere

$\therefore$  Complex is  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

- (54) (A).  $\text{ZnO}$  (Acid) +  $\text{Na}_2\text{O}$  (Base)  $\rightarrow \text{Na}_2\text{ZnO}_2$

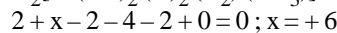
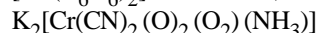
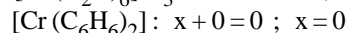


Non-metal oxides are generally acidic while alkali metal oxides are basic.



$\therefore$  Two isomers (*fac* and *mer*) are produced if reactant complex ion is a *cis* isomer. Only one isomer (*fac*) is formed if reactant complex ion is a *trans* isomer.

- (56) (A).  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ :  $x + 0 - 3 = 0$ ;  $x = +3$



- (57) (B).  $\Delta_0$  order will be compared by spectro chemical series not by energies of violet & yellow light so  $\Delta_0$  order is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 < [\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$

- (58) (A).  $\mu = \sqrt{n(n+2)}$  B.M.  $n$  = Number of unpaired electrons,  $n$  = Maximum number of unpaired electron = 5  
Ex:  $\text{Mn}^{2+}$  complex.

- (59) (C). Donating atoms are both nitrogen & oxygen.

- (60) (A). According to question all the complexes are low spin.

Complex	Configuration	No. of unpaired electrons
$[\text{V}(\text{CN})_6]^{4-}$	$t_{2g}^2 e_g^0$	3
$[\text{Cr}(\text{NH}_3)_6]^{2+}$	$t_{2g}^4 e_g^0$	2
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	$t_{2g}^5 e_g^0$	1
$[\text{Fe}(\text{CN})_6]^{4-}$	$t_{2g}^6 e_g^0$	0

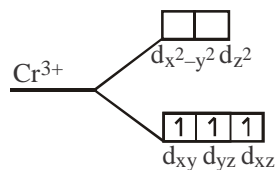
- (61) (B). *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$  is used in chemotherapy to inhibits the growth of tumors.

- (62) (B). Generally interstitial compounds are chemically inert.

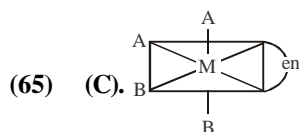
- (63) (C). Complex is  $[\text{Fe}(\text{H}_2\text{O})_6]_2 [\text{Fe}(\text{CN})_6]$

Complex ion	Configuration	No. of unpaired electrons	Magnetic moment
$\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$t_{2g}^4 e_g^2$	4	4.9 BM
$\text{Fe}(\text{CN})_6]^{4-}$	$t_{2g}^6 e_g^0$	0	0

(64) (C). Degenerate orbitals of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$



Hence according to the options given, degenerate orbitals are  $d_{xz}$  &  $d_{yz}$ .



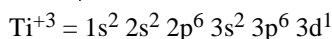
This structure does not contain plane of symmetry hence it is optically active, rest of all options has plane of symmetry and they are optically inactive.

(66) (A).  $\text{Ti}^{+2} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

Unpaired electrons = 2.

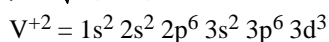
Spin only magnetic moment

$$(\mu) = \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.}$$

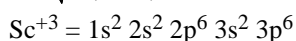


Unpaired electrons = 1

$$\mu = \sqrt{1(1+2)} = \sqrt{3} \text{ B.M.}$$



$$\mu = \sqrt{3(3+2)} = \sqrt{15} \text{ B.M.}$$



$\mu = 0$

(67) (B). A complex having strong field ligand has tendency to absorb light of highest energy. Among the three complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$  will absorb radiation of highest energy and least wavelength.

$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  has field weaker than the above compound and therefore absorb radiation of lesser energy and more wavelength.

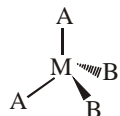
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$  has the weakest field and therefore will absorb light of least energy and highest wavelength.

Strength of ligand  $\text{NH}_3 > \text{H}_2\text{O} > \text{Cl}$ .

(68) (D).

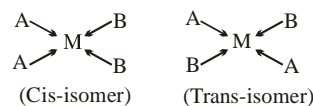
(69) (C).

(a) If the complex  $\text{MA}_2\text{B}_2$  is  $sp^3$  hybridised then the shape of this complex is tetrahedral this structure is optically inactive due to the presence of plane of symmetry.



Optical isomers = 0

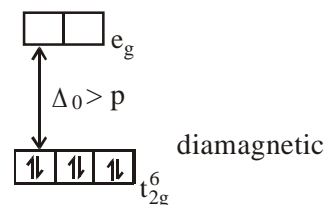
(b) If the complex  $\text{MA}_2\text{B}_2$  is  $dsp^2$  hybridised then the shape of this complex is square planar.



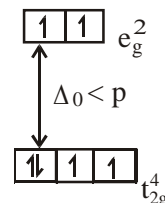
Both isomers are optically inactive due to the presence of plane of symmetry.

Optical isomers = 0

(70) (D).  $\text{Co}^{+3}$  (with strong field ligands)



(b) If  $\Delta_0 < p$



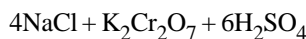
(c) Splitting power of ethylenediamine (en) is greater than fluoride ( $\text{F}^-$ ) ligand therefore more energy absorbed by  $[\text{Co}(\text{en})_3]^{3+}$  as compared to  $[\text{CoF}_6]^{3-}$ . So wave length of light absorbed by  $[\text{Co}(\text{en})_3]^{3+}$  is lower than that of  $[\text{CoF}_6]^{3-}$

(d)  $\Delta_t = \frac{4}{9}\Delta_0$ , so if  $\Delta_0 = 18,000 \text{ cm}^{-1}$

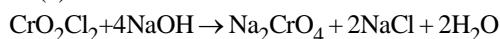
$$\Delta_t = \frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$$

Statement (a) and (d) are incorrect.

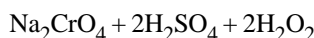
(71) 18.00



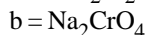
(a)



(b)

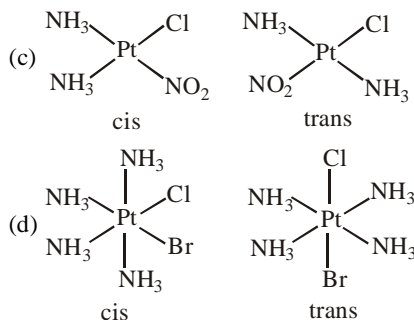


(c)

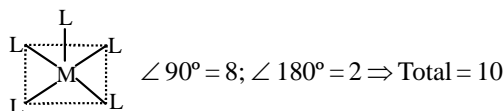
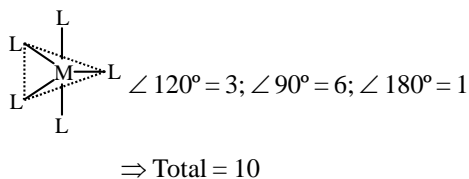


Total number of atom in  $a + b + c = 18$ .

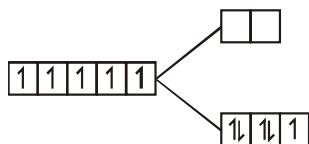
- (72) (D).  $[Ma_3b_3]$  type complex shows facial and meridional isomerism.
- (73) (A).  $Ni(CO)_4$   $\mu_m = 0$  B.M.  
 $[Ni(H_2O)_6]Cl_2$   $\mu_m = 2.8$  B.M.  
 $Na_2[Ni(CN)_4]$   $\mu_m = 0$  B.M.  
 $PdCl_2(PPh_3)_2$   $\mu_m = 0$  B.M.  
 $\therefore (a) \approx (c) \approx (d) < (b)$
- (74) (D).  $[Pt(NH_3)_3Cl]^+$  &  $[Pt(NH_3)Cl_5]^-$  does not show geometrical isomerism.



- (75) 20.00



- (76) (B).  $[Pb(F)(Cl)(Br)(I)]^{2-}$  have three geometrical isomer so formula for  $[Fe(CN)_6]^{n-6}$  is  $[Fe(CN)_6]^{3-}$  and CFSE for this complex is  $Fe^{3+} \Rightarrow 3d^5 4s^0$

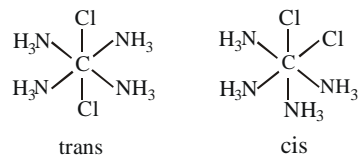


Magnetic Moment =  $\sqrt{3} = 1.73$  B.M

CFSE =  $[(-0.4 \times 5) + (0.6 \times 0)] \Delta_0 = -2.0 \Delta_0$

- (77) (A).  $Cr(H_2O)_6 Cl_n$   
 If magnetic moment is 3.83 BM then it contain three unpaired electrons. It means chromium in +3 oxidation state so molecular formula is  $Cr(H_2O)_6 Cl_3$ .  
 $\therefore$  This formula have following isomers.
- (a)  $[Cr(H_2O)_6]Cl_3$  : react with  $AgNO_3$  but does not show geometrical isomerism.
- (b)  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$  react with  $AgNO_3$  but does not show geometrical isomerism.

- (c)  $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$  react with  $AgNO_3$  & show geometrical isomerism.
- (d)  $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$  does not react with  $AgNO_3$  & show geometrical isomerism.  
 $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$  react with  $AgNO_3$  & show geometrical isomerism and it's IUPAC nomenclature is Tetraaquadichlorido chromium (III) Chloride dihydrate.
- (78) (D).  $[Co(NH_3)_4Cl_2]$  has 2 geometrical isomers



cis isomer has  $Cl-Co-Cl$  angle of  $90^\circ$ .

### EXERCISE-5

#### PART A (d AND f BLOCK ELEMENTS)

- (1) (A).  $Sc^{3+} \rightarrow 3d^0 4s^0$   
 $Fe^{2+} \rightarrow 3d^6 4s^0$
- 
- $Ti^{3+} \rightarrow 3d^1 4s^0$
- 
- $Mn^{2+} \rightarrow 3d^5 4s^0$
- 
- In  $Sc^{3+}$  there as no unpaired electron. So the aqueous solution of  $Sc^{3+}$  will be colourless.
- (2) (B). The cause of showing different oxidation is due to the fact that there is only a small difference between the energies of electron in the ns orbitals and (n - 1) d orbitals with the result both ns as well (n - 1) d electrons can be used for compound formation. Lesser energy difference between 5f and 6d orbitals than between 4f and 5d orbitals result in larger no. of oxidation state.
- (3) (D).  $Sc^{3+} : 1s^2, 2s^2p^6, 3s^2p^6d^0, 4s^0$ ; no unpaired electron  
 $Cu^+ : 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^0$ ; no unpaired electron  
 $Ni^{2+} : 1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^0$ ;  
 unpaired electron present  
 $Ti^{3+} : 1s^2, 2s^2p^6, 2s^2p^6d^1, 4s^0$ ;  
 unpaired electron present  
 $Co^{2+} : 1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^0$ ;  
 unpaired electron present
- So, from the given option the only correct combination is  $Ni^{2+}$  and  $Ti^{3+}$ .
- (4) (A). Copper sulphate on treatment with excess of KCN forms complex  $K_3[Cu(CN)_4]$  or  $Cu(CN)_4]^{3-}$   
 $CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$   
 $2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$   
 $Cu_2(CN)_2 + 3KCN \rightarrow K_3[Cu(CN)_4] + CuCN$

- (5) (D). For chromium ion +3 oxidation state is most stable.
- (6) (B). There is steady decrease in the radii as the atomic number of the lanthanide elements increases. For every additional proton added in nucleus the corresponding electron goes to 4f subshell. The shape of f-orbitals is very much diffused and they have poor shielding effect. The effective nuclear charge increases which causes the contraction in the size of electron charge cloud. This contraction in size is quite regular and known as Lanthanoid contraction. Since the change in the ionic radii in the lanthanide series is very small, thus their chemical properties are similar.
- (7) (B).  $Ti^{3+}$  (Z = 22)  
Ions which have unpaired electrons exhibit colour in solution.  
 $Ti^{3+}$  has an outer electronic configuration of  $4s^0 3d^1$ , i.e., 1 unpaired electron.  
Thus its solution will be coloured.  
 $Sc^{3+} \rightarrow d^0$   
In case of  $La^{3+}$ ,  $4f^0$  configuration is present and in  $Lu^{3+}$ ,  $4f^{14}$  is present. So, there is no possibility of f-f transition, hence these ions do not appear coloured.
- (8) (D). Electronic configurations of given ions :  
 $NH^{3+}$  (28) = [Ar]  $3d^7$      $Mn^{3+}$  (25) = [Ar]  $3d^4$   
 $Fe^{3+}$  (26) = [Ar]  $3d^5$      $Co^{3+}$  (27) = [Ar]  $3d^6$
- (9) (C). In general, the atomic and ionic radii increases on moving down a group. But the elements of second series (eg, Zr, Nb, Mo etc.) have the almost same radii as the elements of third transition series (eg, Hf, Ta, W etc). This is because of lanthanide contraction ie, imperfect shielding of one 4f-electron by another.
- (10) (D). The common stable oxidation state of all the lanthanoids is + 3. The oxidation state of + 2 and + 4 are also exhibited by some of the elements. These oxidation states are only stable in those cases where stable  $4f^0$ ,  $4f^7$  or  $4f^{14}$  configuration are achieved.
- (11) (B). This can be understood on the basis of  $E^\circ$  values for  $M^{2+}/M$ .
- | $E^\circ/V$ | Cr    | Mn    | Fe    | Co    |
|-------------|-------|-------|-------|-------|
| $M^{2+}/M$  | -0.90 | -1.18 | -0.44 | -0.28 |
- $E^\circ$  value for Mn is more negative than expected from general trend due to extra stability of half-filled  $Mn^{2+}$  ion. Thus, the correct order should be  
 $Mn > Cr > Fe > Co$   
An examination of  $E^\circ$  values for redox couple  $M^{3+}/M^{2+}$  shows that  $Cr^{2+}$  is strong reducing agent ( $E_{Mn^{3+}/Mn^{2+}} = 0.41V$ ) and liberates  $H_2$  from dilute acids.  $2Cr^{2+}(aq) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + H_2 \uparrow(g)$   
 $\therefore$  The correct order is  $Mn > Fe > Cr > Co$ .
- (12) (B).  $K_2Cr_2O_7 + 3 Na_2SO_3 + 4H_2SO_4 \rightarrow 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3$
- (13) (C). Melting point of Mn and Zn has low M.P. than their adjacent element due to stable configuration.
- (14) (C).  $E^\circ_{Cu^{2+}/Cu} = 0.34$  volt, other has -ve  $E^\circ_{RP}$
- (15) (C). Has variable oxidation state  
e.g.  $V_2O_5$  catalyst in contact process.
- (16) (C). Only Ac form  $Ac^{+3}$
- (17) (A).  $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4 H_2O$   
do not produce  $O_2$ .
- (18) (A).  $Sm^{2+}$  (Z = 62) : [Xe]  $4f^6$   
 $Eu^{2+}$  (Z = 63) : [Xe]  $4f^7$   
 $Yb^{2+}$  (Z = 70) : [Xe]  $4f^{14}$   
 $Ce^{2+}$  (Z = 58) : [Xe]  $4f^1 5d^1$   
Only  $Yb^{2+}$  is diamagnetic.
- (19) (A). Correct order of solubility in aqueous medium:  
 $Na_2S > ZnS > CuS$
- (20) (B).  $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$
- (21) (B).  $\mu = 2.83$  BM, unpaired electrons = 2  
 $28Ni^{+2} = 3d^8 = \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$
- (22) (A). Lanthanoid contraction is due to negligible shielding effect of f-orbitals.  
Order of shielding effect =  $s > p > d > f$
- (23) (B).  $\mu = 2.83$  BM, unpaired electrons = 2  
 $28Ni^{+2} = 3d^8 = \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$
- (24) (B). There is no change in O.N. of Iron in  
 $Fe + 5CO \rightarrow Fe(CO)_5$   
O.N. = 0    O.N. = 0
- (25) (B). Zr and Hf has nearly same radius due to lanthanide contraction.
- (26) (A).  ${}_{64}Gd = {}_{54}[Xe] 6s^2 4f^7 5d^1$
- (27) (C).  $KMnO_4$  ( $Mn^{7+}$ ) changes to  $Mn^{2+}$  i.e., number of electrons involved per mole of  $KMnO_4$  is 5.  
(a) For  $FeSO_3$ ,  $Fe^{2+} \rightarrow Fe^{3+}$   
(No. of electron involved = 1)  
 $SO_3^{2-} \rightarrow SO_4^{2-}$  (No. of electrons = 2)  
Total number of electrons = 1 + 2 = 3  
(b) For  $FeC_2O_4$ ,  $Fe^{2+} \rightarrow Fe^{3+}$  (No. of electron = 1)  
 $C_2O_4^{2-} \rightarrow 2CO_2$  (No. of electron = 2)  
Total number of electrons = 1 + 2 = 3  
(c) For  $Fe(NO_2)_2$ ,  $Fe^{2+} \rightarrow Fe^{3+}$  (No. of electron = 1)  
 $2NO_2^- \rightarrow 2NO_3^-$  (No. of electron = 4)  
Total number of electrons = 1 + 4 = 5  
(d) For  $FeSO_4$ ,  $Fe^{2+} \rightarrow Fe^{3+}$   
(No. of electron involved = 1)  
Total number of electrons involved = 1  
As  $FeSO_4$  requires least number of electrons thus, it will require least amount of  $KMnO_4$ .
- (28) (D).  $K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3$  green solution obtain where as  $SO_2$  oxidise into sulphate  $SO_4^{2-}$   
( $K_2Cr_2O_7 + SO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + K_2SO_4$ )
- (29) (C).  
(i) Lanthanoid's are less reactive than aluminium due to high IP (Lanthanoid contraction)  
(ii)  $Ce^{+4}$  is good oxidising agent and easily converted into  $Ce^{+3}$ .



- (iii)  $\text{Eu} (63) = 4f^7 5d^0 6s^2, \text{Eu}^{+2} = 4f^7$   
 (iv) In lanthenoids series 'Ce' to Lu ionic radius regular decreases and covalent character increase, basic character of hydroxide decrease.

(30) (B). Minimum energy gap between 5f, 6d & 7s subshell. That's why  $e^-$  excitation will be easier.

(31) (C).  $\text{Co}^{3+} = [\text{Ar}] 3d^6$ , Unpaired  $e^- (n) = 4$

$$\text{Spin magnetic moment} = \sqrt{4(4+2)} = \sqrt{24} \text{ BM}$$

$$\text{Cr}^{3+} = [\text{Ar}] 3d^3, \text{Unpaired } e^- (n) = 3$$

$$\text{Spin magnetic moment} = \sqrt{3(3+2)} = \sqrt{15} \text{ BM}$$

$$\text{Fe}^{3+} = [\text{Ar}] 3d^5, \text{Unpaired } e^- (n) = 5$$

$$\text{Spin magnetic moment} = \sqrt{5(5+2)} = \sqrt{35} \text{ BM}$$

$$\text{Ni}^{2+} = [\text{Ar}] 3d^8, \text{Unpaired } e^- (n) = 2$$

$$\text{Spin magnetic moment} = \sqrt{2(2+2)} = \sqrt{8} \text{ BM}$$

(32) (D).  $\text{CrO}_4^{2-} \Rightarrow \text{Cr}^{6+} = [\text{Ar}]$

Unpaired electron (n) = 0; Diamagnetic

$\text{Cr}_2\text{O}_7^{2-} \Rightarrow \text{Cr}^{6+} = [\text{Ar}]$

Unpaired electron (n) = 0; Diamagnetic

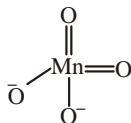
$\text{MnO}_4^{2-} = \text{Mn}^{6+} = [\text{Ar}] 3d^1$

Unpaired electron (n) = 1; Paramagnetic

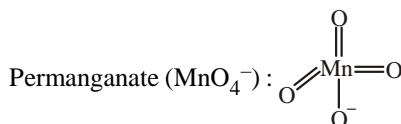
$\text{MnO}_4^- = \text{Mn}^{7+} = [\text{Ar}]$

Unpaired electron (n) = 0; Diamagnetic

(33) (A). Manganate ( $\text{MnO}_4^{2-}$ ):



$\Rightarrow \pi$ -bonds are of  $d\pi-p\pi$  type



$\Rightarrow \pi$ -bonds are of  $d\pi-p\pi$  type

### PART B (COORDINATION COMPOUNDS)

(1) (C).  $[\text{Co}(\text{NH}_3)_6]^{3+} \text{ Co}^{3+} (27-3=24)$



$d^2sp^3$ : (inner octahedral complex & diamagnetic)

$[\text{Cr}(\text{NH}_3)_6]^{3+} \text{ Cr}^{3+} (24-3=21)$



$d^2sp^3 \rightarrow$  (inner octahedral complex & paramagnetic)

$[\text{Ni}(\text{NH}_3)_6]^{2+} \text{ Ni}^{2+} (28-2=26)$

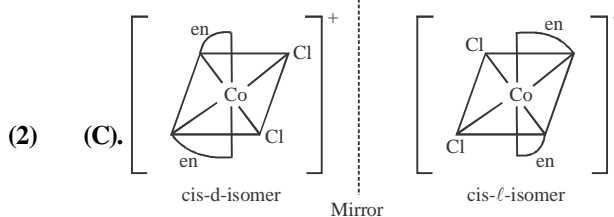


$sp^3d^2 \rightarrow$  (outer octahedral complex & paramagnetic)

$[\text{Zn}(\text{NH}_3)_6]^{2+} \text{ Zn}^{2+} (30-2=28)$



$sp^3d^2 \rightarrow$  (outer octahedral complex & diamagnetic)



(3) (B).  $\mu = \sqrt{n(n+2)}$ ;  $3.83 = \sqrt{n(n+2)}$ .

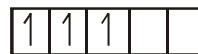
On solving,  $n = 3$

As per magnetic moment, it has three unpaired electron.

$\text{Cr}^{3+}$  will have configuration as

$\text{Cr} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$

$\text{Cr}^{3+} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$



$dxy \quad dyz \quad dzx$

So,  $3dxy^1 3dyz^1 3dxz^1$

(4) (A). The given compound may have linkage isomerism due to presence of  $\text{NO}_2$  group which may be in the form  $-\text{NO}_2$  or  $-\text{ONO}$ .

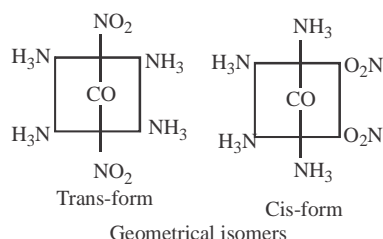
It may have ionisation isomerism due to presence of two ionisable group  $-\text{NO}_2$  &  $-\text{Cl}$ . It may have geometrical isomerism in the form of cis-trans form as follows:

$[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{NO}_2$  &

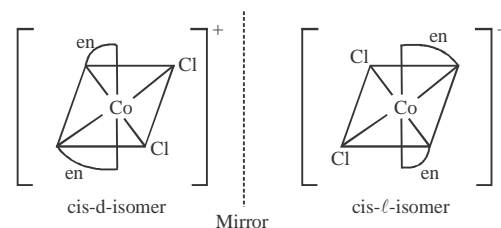
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$  - Ionisation isomers

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)_2]\text{Cl}$

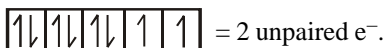
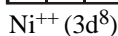
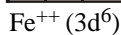
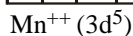
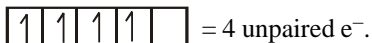
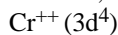
&  $[\text{Co}(\text{NH}_3)_5(\text{ONO})_2]\text{Cl}$  - Linkage isomers



(5) (B). Either a pair of crystals, molecules or compounds that are mirror images of each other but are not identical, and that rotate the plane of polarised light equally, but in opposite directions are called as enantiomorphs.



- (6) (B). Lesser is the number of unpaired electrons smaller will be the paramagnetic behaviour.  
As  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  contains.



As  $\text{Ni}^{2+}$  has minimum no. of unpaired  $e^-$  thus this is least paramagnetic.

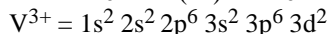
- (7) (C). Oxidation state of Ti in the complex  $[\text{Ti}(\text{NH}_3)_6]^{3+}$   
 $\text{Ti}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

Number of unpaired electron in d orbital is one.

O.S. of V in complex



$$= x + 2 \times 0 + 2 \times (-1) + 2 \times 0 = +1 \quad \therefore x = +3$$



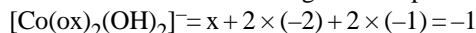
Number of unpaired electron in d orbital is two.

Oxidation state of Fe in the given complex is +2

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

No. of unpaired electron in d orbital is four.

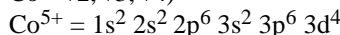
Oxidation state of Co in the given complex



$$= x - 4 - 2 = -1 \quad \therefore x = +5$$

(not possible, common oxidation number of

$\text{Co} = +2, +3, +4$ )



It should be an inner orbital complex ( $d^2sp^3$  hybridisation) containing only one unpaired electron.

So the complex of iron highest paramagnetism would be the complex of iron containing four unpaired electrons.

- (8) (D).  $\text{CN}^-$  is the strongest ligand & thus CFSE is maximum.

- (9) (B). A species is coloured when it contains unpaired d-electrons which are capable of undergoing d-d transition on adsorption of light of a particular wavelength.

In  $\text{TiF}_6^{2-}$ ,  $\text{Ti}^{4+} : 3d^0$ , colourless

In  $\text{CoF}_6^{3-}$ ,  $\text{Co}^{3+} : 3d^6$ , coloured

In  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}^+ : 3d^{10}$ , colourless

In  $\text{NiCl}_4^{2-}$ ,  $\text{Ni}^{2+} : 3d^8$ , coloured.

Thus,  $\text{TiF}_6^{2-}$  ( $3d^0$ ) and  $\text{Cu}_2\text{Cl}_2$  ( $3d^{10}$ ) with empty and fully filled d-orbitals appear colourless as they are not capable of undergoing d-d transition.

- (10) (A). Optical isomerism is exhibited by only those complexes in which element by symmetry are absent. Octahedral complexes of the types  $[\text{M}(\text{aa})_3]$ ,  $[\text{M}(\text{aa})_2(\text{x}_2, \text{y}_2)]$  and  $[\text{M}(\text{aa})_2(\text{x}_2)]$  have absence of elements of symmetry, thus exhibit optical isomerism.

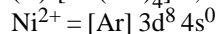
Here, aa represents bidentate ligand, x or y represents monodentate ligand and M represents central metal ion. Hence,  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0$  due to presence of symmetry elements does not exhibit optical isomerism.

- (11) (B).  $\text{Ti}^{4+} \rightarrow 3d^0$ ,  $\text{Cr}^{3+} \rightarrow 3d^3$   
 $\text{Zn}^{2+} \rightarrow 3d^{10}$ ,  $\text{Sc}^{3+} \rightarrow 3d^0$

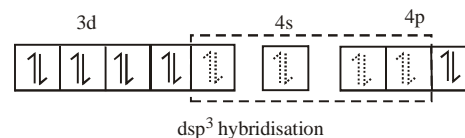
Transition metal ions containing completely filled d-orbitals or empty d-orbitals are colourless species.

- (12) (A). For the absorption of visible light, presence of unpaired d-electrons is the necessity.

(A)  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni is present as  $\text{Ni}^{2+}$ .



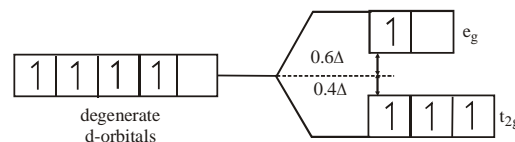
$$\therefore [\text{Ni}(\text{CN})_4]^{2-} =$$



(Pairing occurs because  $\text{CN}^-$  is a strong field ligand).

Since, in  $[\text{Ni}(\text{CN})_4]^{2-}$ , no unpaired electron is present in d-orbitals, it does not absorb visible lights.

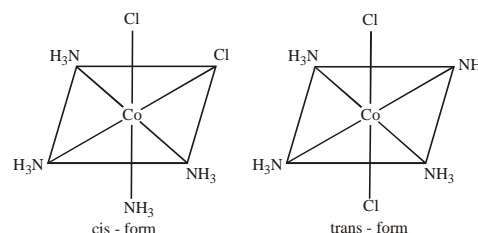
- (B) In  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ , Cr is present as  $\text{Cr}^{3+}$ .  
 $\text{Cr}^{3+} = [\text{Ar}] 3d^3 4s^0$  (Three unpaired electrons)
- (C) In  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , Fe is present as  $\text{Fe}^{3+}$ .  
 $\text{Fe}^{2+} = [\text{Ar}] 3d^6 4s^0$  (Four unpaired electrons)
- (D) In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is present as  $\text{Ni}^{2+}$ .  
 $\text{Ni}^{2+} = [\text{Ar}] 3d^8 4s^0$  (Two unpaired electrons)
- (13) (D). In case of high spin complex,  $\Delta_0$  is small. Thus, the energy required to pair up the fourth electron with the electrons of lower energy d-orbitals would be higher than that required to place the electrons in the higher d orbital. Thus, pairing does not occur. For high spin  $d^4$  octahedral complex,



$\therefore$  Crystal field stabilisation energy

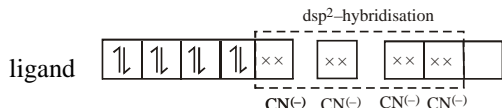
$$= (-3 \times 0.4 + 1 \times 0.6) \Delta_0 = (-1.2 + 0.6) \Delta_0 = -0.6 \Delta_0$$

- (14) (B). Complexes of  $[\text{MA}_4\text{B}_2]$  type exhibit geometrical isomerism. The complex  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is a  $[\text{MA}_4\text{B}_2]$  type complex and thus, fulfills the conditions that are necessary to exhibit geometrical isomerism. It has two geometrical isomers of different colours. The structure of the geometrical isomers :

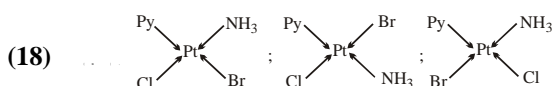


For linkage isomerism, presence of ambidentate ligand is necessary. For coordination isomerism, both the cation and anion of the complex must be complex ions. For ionisation isomerism, an anion different to the ligands must be present outside the coordination sphere. All these conditions are not satisfied by this complex. Hence, it does not exhibit other given isomerisms.

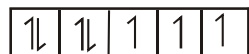
- (15) (C).  $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$  has tetrahedral geometry and thus, does not exhibit isomerism due to presence of symmetry elements.
- (16) (C). Ni has  $dsp^2$  hybridisation where  $\text{CN}^-$  is a strong



- (17) (D). The complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  are the examples of Co-ordination isomerism. This isomers occurs only in those complexes in which both cation and anion are complex. It occurs due to exchange of ligands between cation and anion.

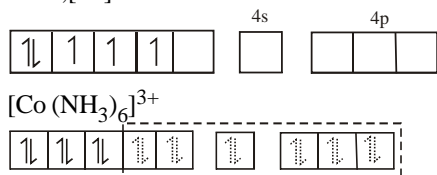


- (19) (D).  $\text{Co}^{2+} \rightarrow 3d^7 4s^0$



having minimum no. of unpaired electrons

- (20) (A). As +ve charge on the central metal atom increases, the less readily the metal can donate electron density into the  $\pi^*$  orbitals of CO ligand to weaken the C – O bond. Hence the C – O bond would be strongest in  $\text{Mn}(\text{CO})_6^+$ .
- (21) (B).  
 (A)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$ :  $3d^1$  configuration and thus has one unpaired electron.  
 (B)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ : The complex is inner orbital complex but  $3d^3$  configuration has three unpaired electrons.  
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ : The cobalt ion is in +3 oxidation state with  $3d^6$  configuration and thus is diamagnetic octahedral complex,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , and has the electronic configuration represented as shown below.  $\text{Co}^{3+}, [\text{Ar}] 3d^6$



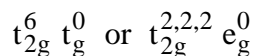
(inner orbital or  $d^2sp^3$  hybrid orbital low spin complex) Six pairs of electrons from six  $\text{NH}_3$  molecules.

(D)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$ : Because of  $3d^{10}$  configuration no  $(n - 1)$  d orbital is available for  $d^2sp^3$  hybridisation and thus forms outer orbital complex. The complex is diamagnetic.

- (22) (A).  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   $sp^3d^2$  (outer), octahedral, paramagnetic  
 $[\text{Zn}(\text{NH}_3)_6]^{2+}$   $sp^3d^2$  (outer), octahedral, diamagnetic  
 $[\text{Cr}(\text{NH}_3)_6]^{3+}$   $d^2sp^3$  (inner), octahedral, paramagnetic  
 $[\text{Co}(\text{NH}_3)_6]^{3+}$   $d^2sp^3$  (inner), octahedral, diamagnetic
- (23) (C).  $\text{NiCl}_2 + \text{DMG} \longrightarrow [\text{Ni}(\text{DMG})_2]$   
 Square planar

It is not tetrahedral

- (24) (B). C.F.S.E. =  $(-0.4x + 0.6y)\Delta_0 + zP$   
 where x = number of electrons occupying  $t_{2g}$  orbital  
 y = number of electrons occupying  $e_g$  orbital  
 z = number of paired of electrons  
 For low spin  $d^6$  complex electronic configuration



$$\therefore x = 6, y = 0, z = 3$$

$$\text{C.F.S.E.} = (-0.4 \times 6 + 0 \times 0.6)\Delta_0 + 3P$$

$$= \frac{-12}{5}\Delta_0 + 3P$$

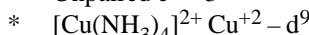
- (25) (B). Magnetic moment 1.73 BM

$$\mu = \sqrt{n(n+2)} \text{ B.M.}, n = \text{no. of unpaired } e^-$$

$$1.73 = \sqrt{n(n+2)} \text{ B.M.}; n = 1$$



Unpaired  $e^- = 3$



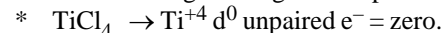
$\text{NH}_3$  Strong field ligand, hybridisation  $dsp^2$

One  $e^-$  of 3d jumps into 4p subshell.

unpaired  $e^- = 1$



$\text{CN}^-$  - Strong field ligand  $dsp^2$

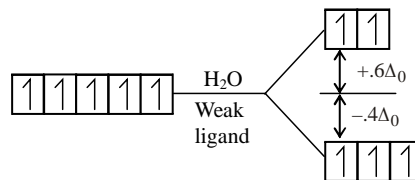


- (26) (B).  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} + \text{AgNO}_3 \rightarrow [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3 + \text{AgCl} \downarrow$

$$\text{No. of mole} = 0.01 \times \frac{100}{1000} = 10^{-3}$$

So, mole of  $\text{AgCl} = 0.001$

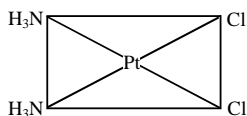
- (27) (B).  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 $\text{Fe}^{3+} = [\text{Ar}] 3d^5$



Configuration  $\Rightarrow t_{2g}^3 e_g^2$

$$\text{C.F.S.E.} = (-.4\Delta_0 \times 3) + (.6\Delta_0 \times 2) = -1.2\Delta_0 + 1.2\Delta_0$$

$$\text{C.F.S.E.} = 0 \Delta_0$$

(28) (B). Cis -  $[\text{PtCl}_2(\text{NH}_3)_2]$ 

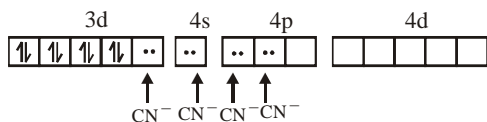
cis-platin used as anticancer agent.

(29) (D).  $\text{CoCl}_3 \cdot 3\text{NH}_3$  is  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  so it will not ionize .....  $^-$  ion test.(30) (D).  $[\text{Co}(\text{CN})_6]^{3-}$  O.N. of Co = +3  
 $\text{Co}^{+3} = 4s^0 3d^6$ As  $\text{CN}^-$  is strong field ligand so all electrons will be paired up and complex will be low spin complex.(31) (C).  $[\text{Ni}(\text{CN})_4]^{2-}$ : Oxidation state of Ni is +2

$$x - 4 = 2; x = +2$$



Due to presence of strong field ligand all unpaired electrons are paired up.

Hybridisation of  $[\text{Ni}(\text{CN})_4]^{2-}$  is  $dsp^2$ .(32) (B).  $[\text{Fe}(\text{CN})_6]^{3-}$ : Hexacyanidoferrate (III) ion.(33) (C).  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$ ; Oxidation state of M = +3

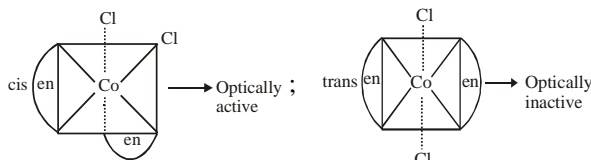
Coordination number of M = 6

Sum of oxidation state + coordination number

$$= 3 + 6 = 9$$

(34) (A).  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ ; Possible isomers

(i) Geometrical isomers:



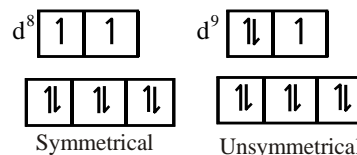
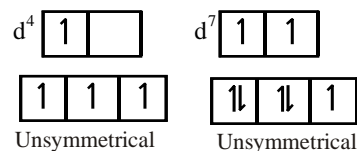
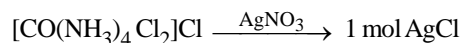
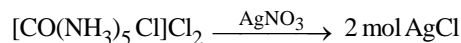
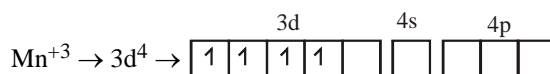
(ii) In trans form plane of symmetry present, so trans form is optically inactive but cis is optically active.

Total number of stereoisomer = 2 + 1 = 3.

(35) (C). The greater the negative charge on the carbonyl complex, the more easy it would be for the metal to permit its electrons to participate in the back bonding, the higher would be the M - C bond order and

simultaneously there would be larger reduction in the C-O bond order. Thus,  $[\text{Fe}(\text{CO})_4]^{2-}$  has the lowest C-O bond order means the longest bond length.

(36) (D). Jahn teller effect: This is geometric distortion occur in unsymmetrical octahedral complexes for example high spin complexes of (high spin)

(37) (B).  $[\text{CO}(\text{NH}_3)_6]\text{Cl}_3 \xrightarrow{\text{AgNO}_3} 3 \text{ mol AgCl}$ (38) (D).  $\left[ \epsilon_a \propto \frac{1}{\lambda_a} \right]$ ,where  $\epsilon_a \Rightarrow$  absorbed energy (splitting energy) $\lambda_a \Rightarrow$  absorbed wavelengthPresence of SFL  $\Rightarrow \epsilon_a (\uparrow) \lambda_a (\downarrow)$  $\text{H}_2\text{O} < \text{NH}_3 < \text{en}$  ligand strength  $\uparrow$  splitting energy  $\uparrow$  so absorbed  $\lambda \downarrow$ .(39) (B).  $[\text{Mn}(\text{CN})_6]^{3-} \rightarrow$  O.S. of Mn is (+3); C.N. = 6

Presence of SFL (Pairing is possible)

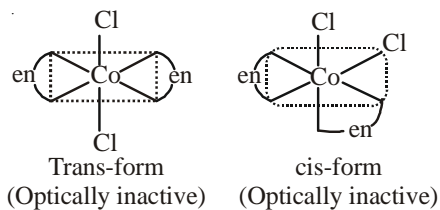
 $[d^2sp^3, \text{octahedral}]$ 

(40) (B). Based on the number of metal atoms present in a complex, they are classified into mononuclear, dinuclear, trinuclear and so on.

eg:  $\text{Fe}(\text{CO})_5$ : mononuclear $\text{Co}_2(\text{CO})_8$ : dinuclear $\text{Fe}_3(\text{CO})_{12}$ : trinuclear

Hence, option (B) should be the right answer.

- (41) (C). In  $[\text{CoCl}_2(\text{en})_2]$ , Coordination number of Co is 6 and this compound has octahedral geometry.

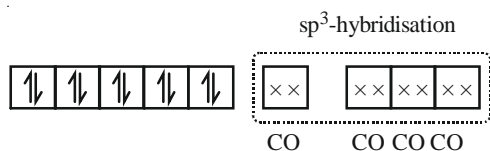


- As per given option, type of isomerism is geometrical isomerism.

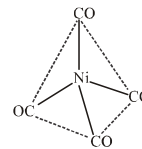
- (42) (B). Ni (28) :  $[\text{Ar}] 3d^8 4s^2$

CO is a strong field ligand

Configuration would be :



For, four 'CO'-ligands hybridisation would be  $sp^3$  and thus the complex would be diamagnetic and of tetrahedral geometry.



- (43) (B).  $\text{K}_4[\text{Fe}(\text{CN})_6]$

Fe ground state:  $[\text{Ar}] 3d^6 4s^2$

$\text{Fe}^{2+} : 3d^6 4s^0$

