

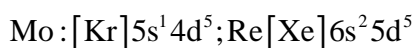
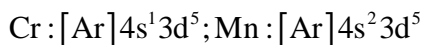
# d-BLOCK & CO-ORDINATION COMPOUNDS

## SYNOPSIS

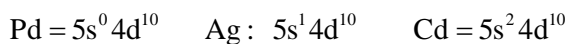
### d-BLOCK

1. Zn, Cd, Hg of group 12 (II B group) are not regarded as transition elements

2. Elements with  $d^5$  configuration:



3. Elements with  $d^{10}$  configuration:



4. Highest MP in 3d series : Cr  
4d series : Mo  
5d series : W

5. Enthalpy of atomisation is highest in 3d series : V  
Enthalpy of atomisation is lowest in 3d series : Zn

6. Mercury is a liquid metal because Hg has  $[\text{Xe}] 4f^{14} 5d^{10} 6s^2$  configuration. Due to poor shielding nature of 4f and 5d orbitals, the  $6s^2$  electrons are tightly held to the atom. This decreases the extent of delocalization of electrons and decrease the metal - metal bond strength.

### 7. SIZE OF ATOMS AND IONS

The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increase slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d electrons shield less efficiently than p electrons, which in turn shield less effectively than s electrons).

Because of this poor screening by d electrons, the nuclear charge attracts all of the electrons more strongly; hence a contraction in size occurs.

Atoms of the transition elements are smaller than those of the Group 1 or 2 elements in the same horizontal period.

This is partly because of the usual contraction in size across a horizontal period discussed above, and partly because the orbital electrons are added to the penultimate d shell rather than to the outer shell of the atom.

8. Elements with similar size : Fe, Co, Ni  
Zr, Hf  
Nb, Ta  
Mo, W

### 9. Oxidation states:

The transition metals exhibit a large number of oxidation states.

With the exception of a few elements, most of these show variable oxidation states.

These different oxidation states are related to the electronic configuration of their atoms.

The existence of the transition elements in different oxidation states mean that their atoms can lose different number of electrons.

This is due to the participation of inner  $(n-1)$  d-electrons in addition to outer ns-electrons because, the energies of the ns and  $(n-1)$  d-sub-shell are nearly same.

For example, scandium has the outer electronic configuration  $3d^1 4s^2$ .

It exhibits an oxidation state of +2 when it uses both of its 4s-electrons for bonding but it can also show oxidation state of +3 when it uses its two s-electrons and one d-electron.

Similarly, the other atoms can show oxidation states equal to ns- and  $(n-1)$  d-electrons.

It may be noted that the stability of a given oxidation state depends upon the nature of the elements with which the metal is combined.

The highest oxidation states are found in compounds of fluorides and oxides because fluorine and oxygen are most electronegative elements.

The examination of the common oxidation states exhibited by different transition metals reveals the following

(i) The variable oxidation states of transition metals are due to participation of inner (n-1) d and outer ns-electrons.

The lowest oxidation state corresponds to the number of ns-electrons.

For example, in the first transition series, the lowest oxidation states of Cr ( $3d^5 4s^1$ ) and

Cu ( $3d^{10} 4s^1$ ) are +1 while for other, it is +2 ( $3d^{1-10} 4s^2$ ).

(ii) Except scandium, the most common oxidation state of the first row transition elements is +2 which arises due to loss of two 4s-electrons. This means that after scandium 3d-orbitals become more stable and therefore, are lower in energy than the 4s-orbitals. As a result, electrons are first removed from 4s-orbitals.

(iii) The elements which show the greater number of oxidation states occur in or near the middle of the series.

For example, in the first transition series, manganese exhibits all the oxidation states from +2 to +7.

The lesser number oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti).

On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a few orbitals are available in which the electron can share with other for higher valence.

The highest oxidation state shown by any transition metal is +8.

(iv) In the +2 and +3 oxidation states, the bonds formed are mostly ionic.

In the compounds of higher oxidation states (generally formed with oxygen and fluorine), the bonds are essentially covalent.

Thus the bonds in +2 and +3 oxidation states are generally formed by the loss of two or three electrons respectively while the bonds in higher oxidation states are formed by sharing of d-electrons.

For example, in  $MnO_4^-$  (Mn in +7 state) all the bonds are covalent.

(v) Within a group, the maximum oxidation state increase with atomic number.

For example, iron (group 8) shows common oxidation states of +2 and +3 but ruthenium and osmium in the same group form compounds in the +4, +6 and +8 oxidation states.

(vi) transition metals also form compounds in low oxidation states such as +1 and 0 or negative. The common examples are

$[Ni(CO)_4]$ ,  $[Fe(CO)_5]$  in which nickel and iron are in zero oxidation state.

(vii) The variability of oxidation states in transition elements arises because of incomplete filling of the d-orbitals in such a way that their oxidation states differ by unity such as  $V^{II}$ ,  $V^{III}$ ,  $V^{IV}$  and  $V^V$ .

This behaviour is in contrast with the variability of oxidation states of non-transition elements (p-block elements), where oxidation states normally differ by a unit of two such as  $Sn^{2+}$ ,  $In^+$ ,  $In^{3+}$ , etc.

(viii) Unlike p-block elements where the lower oxidation states are favoured by heavier members (due to inert pair effect), the higher oxidation states are more stable in heavier transition elements.

For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). Therefore, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent whereas  $MoO_3$  and  $WO_3$  are not.

The magnitude of ionization enthalpy gives the amount of energy required to remove electrons to form a particular oxidation state of the metal in a compound. Thus, the value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states.

Smaller the ionisation enthalpy of the metal, the stable is its compound.

For example, the first four ionisation enthalpies of nickel and platinum are given below :

Ionisation enthalpies	Ni	Pt
$IE_1 + IE_2$	$2.49 \times 10^3 \text{ kJ mol}^{-1}$	$2.66 \times 10^3 \text{ kJ mol}^{-1}$
$IE_3 + IE_4$	$8.80 \times 10^3 \text{ kJ mol}^{-1}$	$6.70 \times 10^3 \text{ kJ mol}^{-1}$
Total	$11.29 \times 10^3 \text{ kJ mol}^{-1}$	$9.36 \times 10^3 \text{ kJ mol}^{-1}$

It is clear from the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.



Therefore, ionization of nickel to  $\text{Ni}^{2+}$  is energetically favourable as compared to that of platinum.

Thus, the nickel (II) compounds are thermodynamically more stable than platinum (II) compounds.

On the other hand, the sum of first four ionisation enthalpies is less for platinum than for nickel as :



Thus, the platinum (IV) compounds are relatively more stable than nickel (IV) compounds.

Therefore,  $\text{K}_2\text{PtCl}_6$  [having Pt (IV)] is a well-known compound whereas the corresponding nickel compound is not known.

However, in solutions the stability of the compounds depends upon electrode potentials.

#### 10. Electrode potentials

Metals with  $E_{SRP}^0 = -ve$  liberate  $\text{H}_2$  from dil.HCl and those with  $E_{SRP}^0 = +ve$  do not liberate. Zn,

Fe, Mn displace  $\text{H}_2$  from dil.HCl but Cu, Ag, Hg, Au do not displace.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^0_{(M^{2+}/M)}$ involts	-1.63	-1.18	-0.91	-0.44	-0.28	-0.25	-0.25	+0.34	-0.76
$E^0_{(M^{3+}/M^{2+})}$ (involts)	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97			

#### 11. Stability of the various oxidation states

Compounds are regarded as stable if they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures.

Within each of the transition Groups 3 - 12, there is a difference in stability of the various oxidation states that exist.

In general, the second and third row elements exhibit higher coordination numbers, and their higher oxidation states are more stable than the corresponding first row elements.

This gives the known oxides and halides of the first, second and third row transition elements. Stable oxidation states from oxides, fluorides, chlorides, bromides and iodides.

Strongly reducing states probably do not form fluorides and/or oxides, but may as well form the heavier halides.

Conversely, strongly oxidizing states form oxides and fluorides, but not iodides.

#### 12. In 3d series:

The element showing highest number of variable oxidation states: Mn

The elements which does not show variable oxidation states Sc, Zn (Sc: +3; Zn: +2)

#### 13. The stable highest oxidation state possible in 3d series elements in their fluorides is +6 (Cr) ( $\text{CrF}_6$ )

#### 14. The +7 state for Mn is not represented in simple halides but $\text{MnO}_3$ F is known,

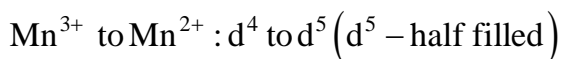
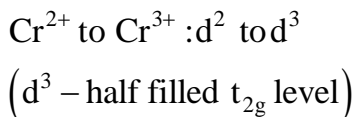
#### 15. The highest Mn fluoride is $\text{MnF}_4$ whereas the highest oxide is $\text{Mn}_2\text{O}_7$

#### 16. $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ : oxidising power

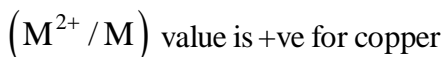
#### 17. In 3d series $\text{Mn}^{3+}$ and $\text{Co}^{3+}$ ions are the strongest oxidizing agents in aq. solution.

#### 18. $\text{Ti}^{2+}$ , $\text{V}^{2+}$ and $\text{Cr}^{2+}$ are strong reducing agents and will liberate hydrogen from dilute acids

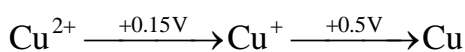
19. In 3d series, of the  $d^4$  species,  $\text{Cr}^{2+}$  is strongly reducing and  $\text{Mn}^{3+}$  is strongly reducing



20. In 3d series, standard electrode potential

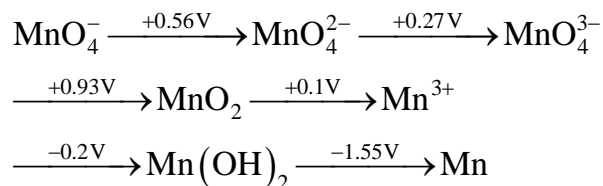


21. Many copper (I) compounds are unstable in aq solution and undergo disproportionation



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

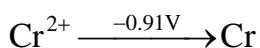
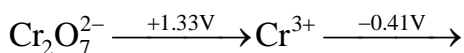
23. Acid solution



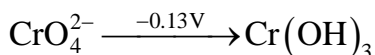
24.  $\text{MnO}_4^{2-}$  in acidic medium disproportionate to



25. Acid solution:



26. Basic solution



27. **DENSITY**

The atomic volumes of the transition elements are low compared to elements in neighbouring Groups 1 and 2.

This is because the nuclear charge is poorly screened and so attracts all the electrons more strongly.

In addition, the extra electrons added occupy inner orbitals.

Consequently the densities of the transition metals are high.

Practically all have a density greater than  $5 \text{ g cm}^{-3}$ . (The only exceptions are Sc  $3.0 \text{ g cm}^{-3}$  and Y and Ti  $4.5 \text{ g cm}^{-3}$ .)

The densities of the second row are high and third row values are even higher.

The two elements with the highest densities are osmium  $22.57 \text{ g cm}^{-3}$  and iridium  $22.61 \text{ g cm}^{-3}$ .

28. Lowest density in 3d series : Sc

highest density in 3d series : Ni, Cu

29. **High density of post lanthanide elements:**

It is because of unexpectedly smaller size due to lanthanide contraction.

	$r_0$	At.Wt	$d (\text{g/cc})$
Ag	1.44 Å	108	10.8
Au	1.44 Å	196	19.4

30. **REACTIVITY OF METALS**

Many of the metals are sufficiently electropositive to react with mineral acids, liberating  $\text{H}_2$ .

A few have low standard electrode potentials and remain unreactive or noble.

Noble character is favoured by high enthalpies of sublimation, high ionization energies and low enthalpies of solvation.

The high melting points indicate high heats of sublimation.

The smaller atoms have higher ionization energies, but this is offset by small ions having high solvation energies.

This tendency to favour noble character is most pronounced for the platinum metals (Ru, Rh, Pd, Os, Ir, Pt) and gold.

31. The metals of the second and third transition series have greater enthalpies of atomisation than the corresponding elements of the first transition series.

32. Lattice structures of transition metals : bcc/ccp/hcp (except Mn, Zn, Cd, Hg)

**33. COLOUR PROPERTY**

1. Most of the compounds of transition metals are coloured due to d - d transition.

Ex :  $\text{FeCl}_3$ ,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  etc

2. **Polarization** : NaCl, NaBr and NaI are all colourless; AgCl is also colourless. Thus the halide ions,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , and the metal ions

$\text{Na}^+$  and  $\text{Ag}^+$  are typically colourless.

However, AgBr is pale yellow and AgI is yellow.

The colour arises because the  $\text{Ag}^+$  ion polarizes the halide ions.

This means that it distorts the electron cloud, and implies a greater covalent contribution.

The polarizability of ions increases with size, thus  $\text{I}^-$  is the most polarized, and is the most

coloured. For the same reason,  $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_3\text{PO}_4$  are yellow, and  $\text{Ag}_2\text{O}$  and  $\text{Ag}_2\text{S}$  are black

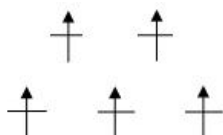
3. Some of the compounds of transition metals are coloured due to "Charge transfer"

Ex:  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{Cu}_2\text{O}$  etc

In  $\text{MnO}_4^-$  an electron is momentarily transferred from oxygen to the metal, thus momentarily changing  $\text{O}^{2-}$  to  $\text{O}^-$  and reducing the oxidation state of the metal from Mn(+7) to Mn(+6)

4. A dilute solutions of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  are colorless due to spin forbidden transition.



**34. COMMON COORDINATION NUMBERS SHOWN BY TRANSITION ELEMENTS OF FIRST ROW**

**i) Scandium** :  $\text{Sc}^{3+}$  forms complexes with coordination number of 6. examples of such complexes are  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{ScF}_6]^{3-}$  etc.

**ii) Titanium** :  $\text{Ti}^{4+}$  forms complexes with a coordination number of 6. For example,  $[\text{TiCl}_6]^{2-}$ ,  $[\text{Ti}(\text{SO}_4)_3]^{2-}$  etc.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has purple color.

**iii) Vanadium** :  $\text{V}^{2+}$  forms mostly octahedral complexes ( coordination number = 6), for example  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{K}_4[\text{V}(\text{CN})_6] \cdot 7\text{H}_2\text{O}$ . But  $\text{K}_4[\text{V}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  is also known with pentagonal bipyramidal structure ( coordination number = 7).

$\text{V}^{3+}$  Forms octahedral complexes such as  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$

$\text{V}^{4+}$  is known to form square pyramidal complexes with a coordination number of 5. Example of such complexes are  $[\text{VOX}_4]^{2-}$ ,  $[\text{VO}(\text{OX})_2]^{2-}$  (OX = oxalate),  $[\text{VO}(\text{bipyridyl})_2\text{Cl}]^+$  etc

**iv) Chromium**:  $\text{Cr}^{2+}$  forms octahedral complexes, such as  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{NH}_3)_6]^{2+}$  and coordination number 6.

$\text{Cr}^{3+}$  forms octahedral complexes, such as  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$  with coordination number 6.

**v) Manganese** :  $\text{Mn}^{2+}$  forms octahedral complexes, such as  $[\text{MnCl}_6]^{4-}$  and  $[\text{Mn}(\text{en})_3]^{2+}$  with coordination number 6.

$\text{Mn}^{3+}$  forms octahedral complexes, such as  $\text{K}_3[\text{Mn}(\text{CN})_6]$  with coordination number 6.

$\text{Mn}^{4+}$  forms octahedral complexes, such as  $\text{K}_2[\text{MnF}_6]$  and  $\text{K}_2[\text{Mn}(\text{CN})_6]$  with coordination number 6.

**vi) Iron :**

$\text{Fe}^{2+}$  forms mostly octahedral complexes like  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  but few tetrahedral halides with coordination number 4 like  $[\text{FeX}_4]^{2-}$  are also known.

$\text{Fe}^{3+}$  is known to form octahedral complexes such as  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Tetrahedral :  $[\text{FeCl}_4]^-$

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**vii) Cobalt :**

$\text{Co}^{2+}$  is known to form both tetrahedral like  $[\text{Co}(\text{Cl})_4]^{2-}$  and octahedral such as  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complexes.

$\text{Co}^{3+}$  forms octahedral complexes. For example,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{CN})_6]^{3-}$ .

**viii) Nickel Group :**

$\text{Ni}^{2+}$  forms octahedral

$[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and square planar  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{Ni}(\text{DMG})_2$  complexes.

Few tetrahedral:  $[\text{NiCl}_4]^{2-}$ , trigonal bipyramidal and square based pyramidal structures are also formed.

$\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  are all square planar.

$\text{Ni}^{3+}$  forms octahedral compounds. For example,  $\text{K}_3[\text{NiF}_6]$  and  $[\text{Ni}(\text{en})_2\text{Cl}_2]\text{Cl}$ .

$\text{Pd}^{4+}$  forms a few octahedral complexes like  $[\text{PdX}_6]^{2-}$ , where  $\text{X} = \text{F}, \text{Cl}$  or  $\text{Br}$ . These are generally reactive. Halide complexes are decomposed by hot water, giving  $[\text{PdX}_4]^{2-}$  and halogen. In contrast  $\text{Pt}^{4+}$  forms large number of very stable octahedral complexes like  $[\text{PtCl}_6]^{2-}$ .

**ix) Copper, silver and gold**

$\text{Cu}^+$  forms tetrahedral complexes with  $\text{Cl}$  (for example,  $[\text{Cu}(\text{Cl})_4]^{3-}$  and linear complexes like  $[\text{CuX}_2]^-$ ).

$\text{Cu}^{2+}$  forms complexes both of coordination number 4 (like  $[\text{CuX}_4]^{2-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and of coordination number 6

{like  $[\text{Cu}(\text{en})_3]^{2+}$ ,  $[\text{Cu}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+}$ }.

$\text{Ag}^+$ ,  $\text{Au}^+$  forms complexes with coordination number 2,  $[\text{M}(\text{CN})_2]^-$ ,  $[\text{M}(\text{NH}_2)]^+$   
( $\text{M} = \text{Cu}^+, \text{Ag}^+, \text{Au}^{2+}$ )

**x) Zinc and Cadmium**

$\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  forms both tetrahedral and octahedral complexes. For example,  $[\text{MCl}_4]^{2-}$ ,  $[\text{M}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{M}(\text{NH}_3)_4]^{2+}$ ,  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  etc.

$\text{Hg}$  forms  $[\text{Hg}(\text{NH}_3)_2]^+$ ,  $[\text{Hg}(\text{CN})_2]^{-1}$

**35. Catalytic Properties:**

$\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$  Used as the **Ziegler-Natta** catalyst in the production of polythene.

$\text{V}_2\text{O}_5$  Converts  $\text{SO}_2$  to  $\text{SO}_3$  in the **Contact process** for making  $\text{H}_2\text{SO}_4$

$\text{MnO}_2$  Used as a catalyst to decompose

$\text{KClO}_3$  has give  $\text{O}_2$

**Fe/Mo** Promoted iron is used in the **Haber-Bosch process** for making  $\text{NH}_3$

$\text{FeCl}_3$  Used in the production of  $\text{CCl}_4$  from  $\text{CS}_2$  and  $\text{Cl}_2$

**FeSO<sub>4</sub> & H<sub>2</sub>O<sub>2</sub>** : Used as **Fenton's reagent** for oxidizing alcohols to aldehydes.

$\text{PdCl}_2$  Wackers oxo process for converting  $\text{C}_2\text{H}_4 + \text{H}_2\text{O}$  to  $\text{CH}_3\text{CHO}$

**Pd** Used for hydrogenation (e.g. phenol to cyclohexanone).

**Pt/PtO<sub>2</sub>** **Adams catalyst**, used for reductions.

**Pt** Formerly used for  $\text{SO}_2 \rightarrow \text{SO}_3$  in the **contact process** for making  $\text{H}_2\text{SO}_4$

**Pt** is increasingly being used in three stage-converters for cleaning car exhaust fumes.

**Pt/Rh** Formerly used in the **Ostwald process** for making  $\text{HNO}_3$  to oxidize  $\text{NH}_3$  to  $\text{NO}$

**Cu** Is used in the direct process for manufacture of  $(\text{CH}_3)_2\text{SiCl}_2$  used to make silicones.

**Cu/V** Oxidation of cyclohexanol/cyclohexanone mixtures to adipic acid which is used to make nylon-66.

**CuCl<sub>2</sub>** Deacon process of making  $\text{Cl}_2$  from  $\text{HCl}$ .

**Ni Raney nickel**, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of  $\text{H}_2$  and

$\text{NH}_3$ , reducing anthraquinone to anthraquinol in the production of  $\text{H}_2\text{O}_2$ ).

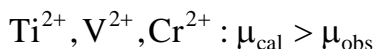
**Ni Reppe synthesis** (polymerization of alkynes) e.g. to give benzene or cyclooctatetraene. **complexes**

**Co<sub>2</sub>(CO)<sub>8</sub>** Hydroformylation catalyst

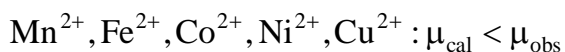
**RhCl(PPh<sub>3</sub>)<sub>3</sub>** Wilkinson catalyst. Stereo selective and Stereospecific hydrogenation of alkenes.

36.  $Al_2O_3$  or  $BaO$  do not form nonstoichiometric oxides. But  $FeO$ ,  $VO$ ,  $MnO$  can form nonstoichiometric oxides as they can exhibit variable valency.

37.

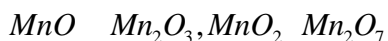
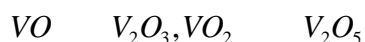
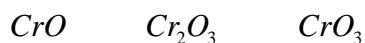


( $\mu$  – magnetic moment)

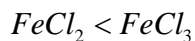
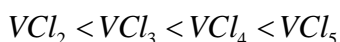


38. a)

*basic      amphoteric      acidic*



b) Covalent character increases in the order:



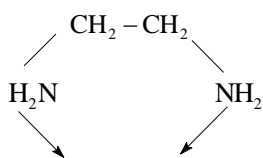
c)  $TiCl_4$  is a liquid at room temperature.

## CO-ORDINATION

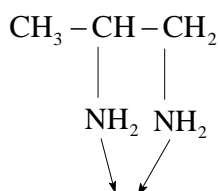
### 1. LIGANDS :

**Bidentate:** Two donations are accepted from the ligand. For example,

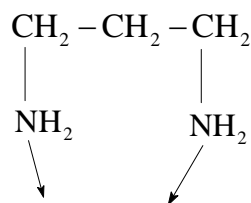
(i) en: ethylenediamine



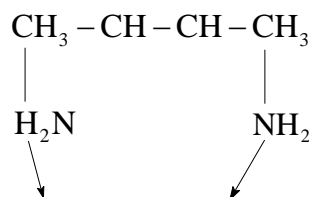
(ii) pn: propylenediamine



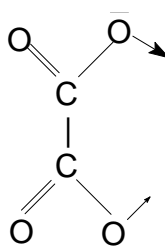
(iii) tn: trimethylenediamine



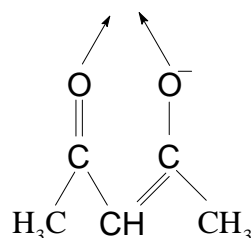
(iv) bn: butylenediamine



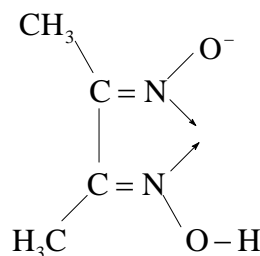
(v)  $OX^{2-}$ : oxalate



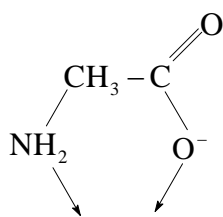
(vi)  $acac^-$ : acetylacetonate



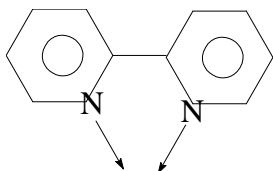
(vii)  $dmg^-$ : dimethylglyoximate



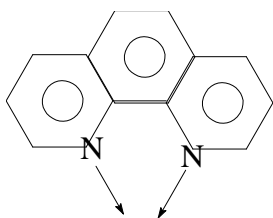
(viii)  $gly^-$ : glycinate



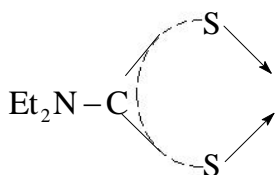
(ix) dipy: dipyridyl



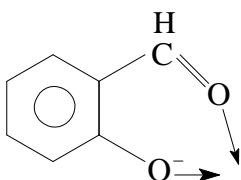
(x) o-phen: ortho-phenanthroline



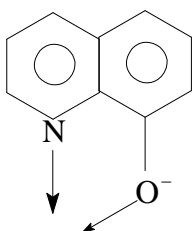
(xi) N, N'-Diethylthiocarbamate ion



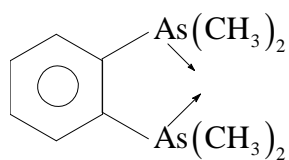
(xii) Salicylaldehyde anion



(xiii) 8-Hydroxyquinolinol ion (oxine)

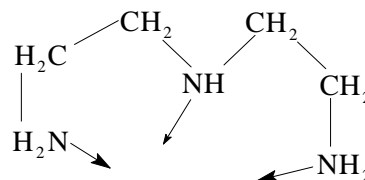


(xiv) o-Phenylenedimethylarsine (diarsine)

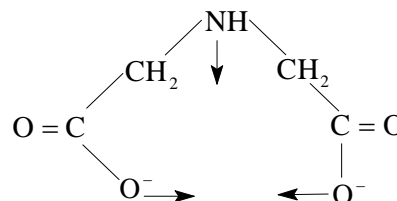


c. Tridentate: Three donations are accepted from the ligand. For example,

(i) dien: diethylenetriamine

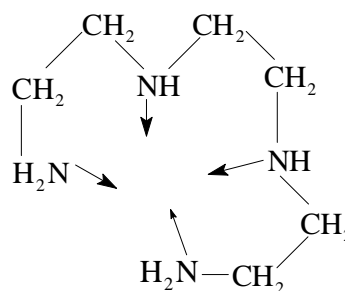


(ii) imda<sup>2-</sup>: iminodiacetate

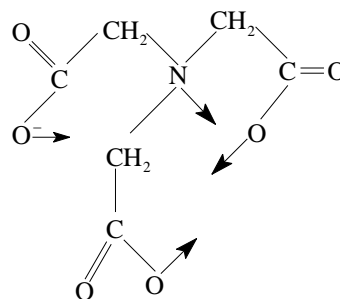


d) Tetradentate: Four donations are accepted from the ligand. For example

(i) trien: triethylenetetraamine

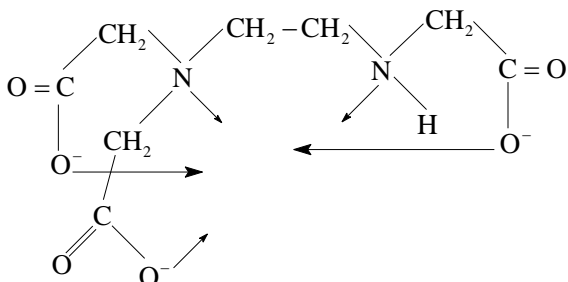


(ii) (NTA)<sup>3-</sup>: nitrilotriacetate

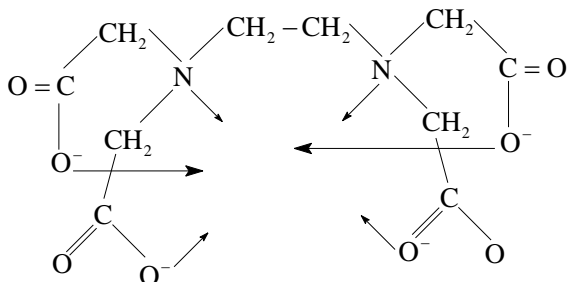




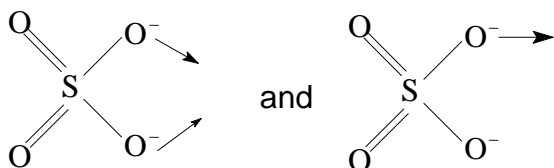
e. Pentadentate: Five donations are accepted from the ligand. For example,  $(EDTA)^{3-}$ : ethylenediamine triacetate



f. Hexadentate: Six donations are accepted from the ligand. For example,  $(EDTA)^{4-}$ : ethylenediamine tetracetate



g. Flexidentate: A ligand which shows variable denticity is called a flexidentate ligand. For example,

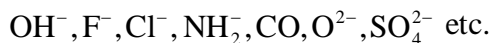


(ii)  $[Co(NH_3)_4CO_3]Br$  and  $[Co(NH_3)_5CO_3]Br$   
 $CO_3$  is bidentate                       $CO_3$  monodentate

2. **Bridging ligands:**

- \* It is also possible that a monodentate ligand may have more than one free electron pairs and thus may simultaneously coordinate with two or more atoms, i.e., the ligand forms two  $\sigma$ -bonds with two metal atoms and thus acts as a bridge between the metal atoms.

\* Examples of bridging ligands are:



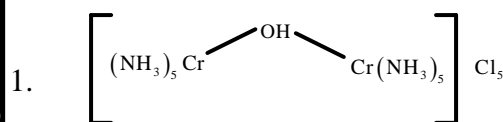
3. **Symmetrical and unsymmetrical bidentate ligands:**

- \* Bidentate ligands may be symmetrical or unsymmetrical ligands.
- \* In symmetrical bidentate ligands the two coordinating atoms (donor atoms) are the same. Ex: en (N,N - donor atoms)
- \* In unsymmetrical bidentate ligands the two coordinating atoms are different. Ex: gly (N, O - donor atoms)

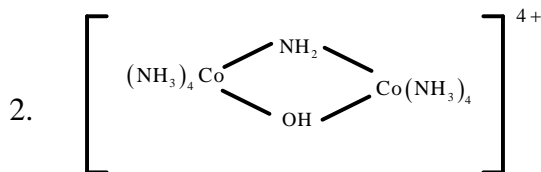
4. **Naming of the bridged ligands of the bridged polynuclear complexes:**

- \* The complexes having two or more metal atoms are called polynuclear complexes.
- \* In these complexes the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens and by adding the prefix  $\mu$  before its name.
- \* The greek letter  $\mu$  should be repeated before the name of each different bridging group
- \* Two or more bridging groups of the same kind are indicated by di-  $\mu$  -, tri-  $\mu$  - etc.

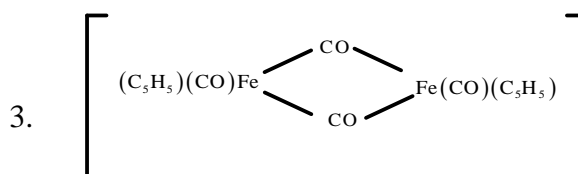
Ex:



$\mu$  - hydroxo-bis(pentaammine)chromium(III) chloride

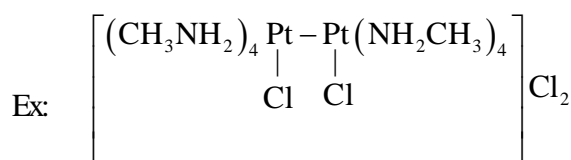


$\mu$  - amido- $\mu$  - hydroxo-octaammine dicobalt(III) ion



Di- $\mu$  - carbonyl-bis (carbonylcyclopentadienyliron)

4.  $[(CO)_3Fe(CO)_2Fe(CO)_3]$ :  
Tri- $\mu$  - carbonyl-bis(tricarbonyliron)
5. **Metal - to - metal bonding:**  
In complexes containing metal - to - metal bonds, the prefix bi - is used before the name of the metals forming a metal - to - metal bond.



dichlorooctakis(methylamine)bi-platinum(II) chloride

6.  $\pi$ -acid or  $\pi$ -acceptor ligands  
These ligands not only donate the lone pair of electrons to the central atom but also accept the electron from the central atom in their low-lying vacant orbitals. This type of back donation is known as "synergic effect" or synergic bonding
- Ex:  $CO, CN^-, NO^+, PF_3, PR_3, C_2H_4$  etc

(R = H, Et, Ph...)

### 7. ISOMERISM

- (a) **Hydrate Isomerism:** Three isomers of  $CrCl_3 \cdot 6H_2O$  are known. From conductivity measurements and quantitative precipitation of the ionized chlorine, they have been given the following formulae:

	% Loss of $H_2O$
1) $[Cr(H_2O)_6]Cl_3$ violet (three ionic chlorines)	-Nil-
2) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ green (two ionic chlorines)	6.75
3) $[Cr(H_2O)_4Cl_2] \cdot Cl \cdot 2H_2O$ dark green (one ionic chlorine)	13.50

$a$ : When the complex is placed along with conc.  $H_2SO_4$ , It does not show any weight loss.

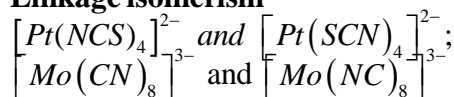
Lattice water is removed and not the coordinated water. Mol. Wt of the complex : 166.5

% Wt. Loss for one water molecule =

$$\frac{18 \times 100}{166.5} = 6.75\%$$

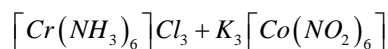
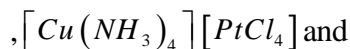
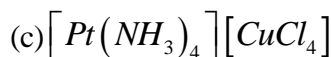
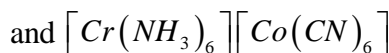
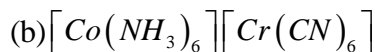
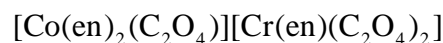
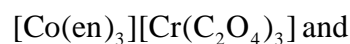
Experimental weight loss agrees with theoretical wt. loss.

- (b) **Linkage isomerism**

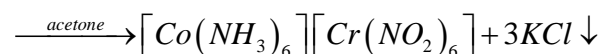
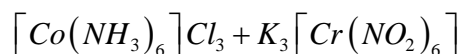
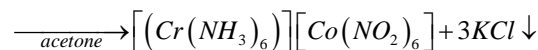


- (c) **Coordination Isomerism:**

(a)

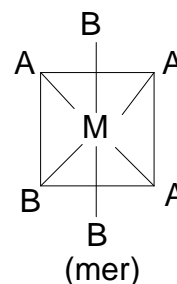
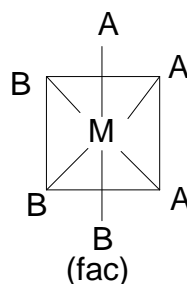
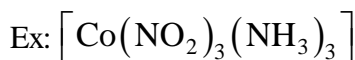


(d)



- (e) **GEOMETRICAL ISOMERISM**

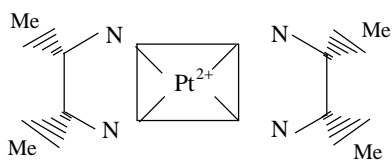
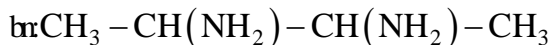
Complexes of type  $Ma_3b_3$  exists in two geometrical forms which are named as facial (fac) and meridional (mer) isomers



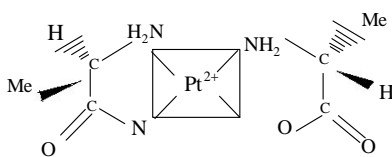
The complexes of the  $[M(AA)_2]^{n\pm}$  can show geometrical isomerism if the ligand AA has a chiral centre. For example, consider the

geometrical isomers of  $[Pt(bn)_2]^{2+}$ ,

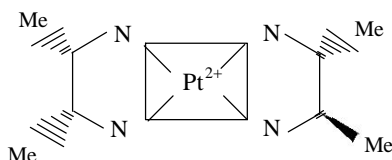
where



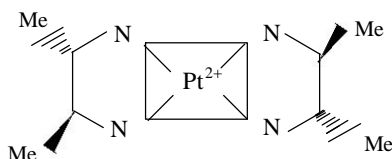
Optically inactive



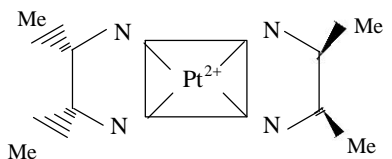
Optically inactive (cis)



Optically inactive

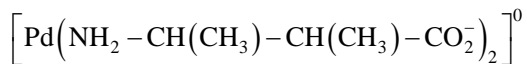


Optically inactive

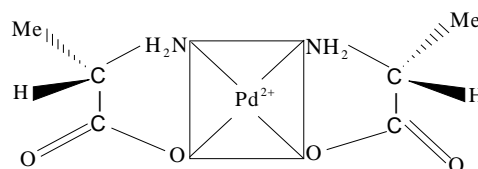


Optically inactive

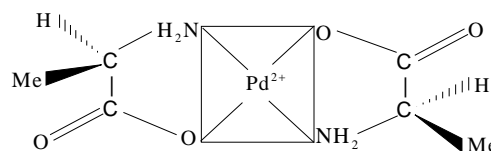
Vii) The complexes of the type  $[M(AB)_2]^{n\pm}$  can show geometric as well as, optical isomerism if the ligand AB has a chiral centre. For example, the compound



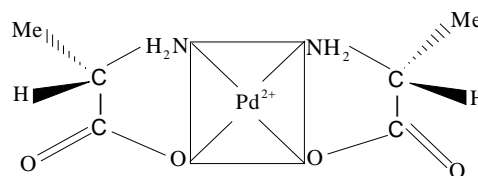
can have four geometrical isomers



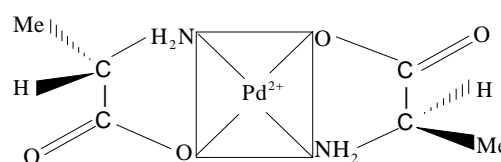
Optically inactive (Plane of symmetry) (cis)



Optically active (trans)

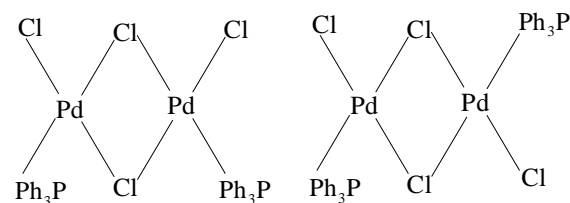
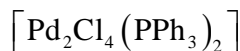


Optically inactive (Plane of symmetry) (cis)



Optically inactive (Centre of symmetry) (trans)

(viii) Geometrical isomers are possible for square planar binuclear complexes of the type



cis

trans

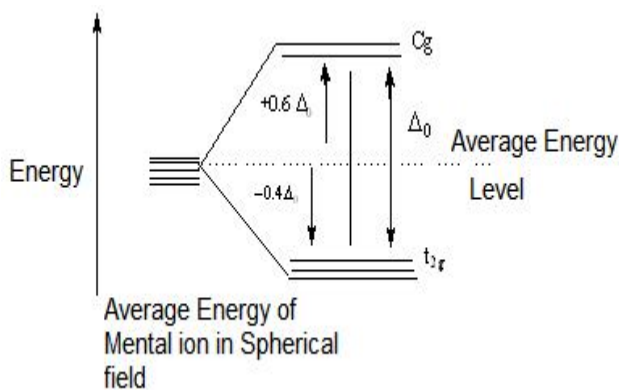
7. **Crystal field theory (CFT) :**

According to CFT, the bonding in complex ions is purely electrostatic. This theory regards the ligand atoms of ionic ligands such as  $F^-$ ,  $Cl^-$  or  $CN^-$  as negative point charges (also called point charges). If the ligand molecules are neutral, those are regarded as point dipoles or simply dipoles, the negative end pointing towards central metal ion.

The complex is regarded as a combination of a central metal ion surrounded by ligands which acts as point charges or point dipole. The arrangement of ligands around the central metal ion or atom is such that the repulsion between these negative points or dipoles is minimum.

In a free transition metal or ion, there are five d orbitals which are designated as

$d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The five d-orbitals are divided into different sets depending on the nature of their orientation in space.

8. **Ligand Field Splitting in Octahedral Complexes:**

In octahedral complexes, the filling of  $t_{2g}$  orbitals decreases the energy of a complex that makes it more stable by  $-0.4\Delta_0$  per electron. Filling  $e_g$  orbitals increases the energy by  $+0.6\Delta_0$  per electron.

The total crystal field stabilization energy is given by

$$CFSE_{(\text{Octahedral})} = -0.4x_{(t_{2g})} + 0.6x_{(e_g)}$$

Where  $x_{(t_{2g})}$  and  $x_{(e_g)}$  are the number of electron occupying the  $t_{2g}$  and  $e_g$  orbitals respectively.

The CFSE is zero for ions with  $d^0$  and  $d^{10}$  configuration in both strong and weak ligand fields.

The CFSE is also zero for  $d^5$  configurations in a weak field.

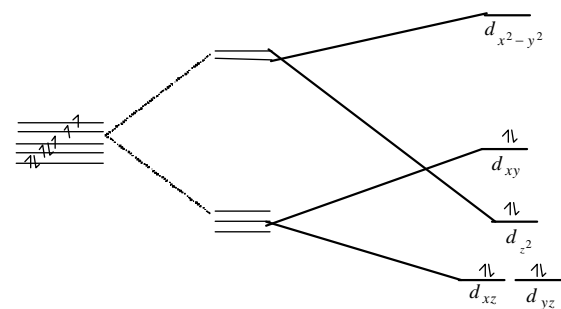
All the other arrangements have some CFSE, which increases the thermodynamic stability of the complexes.

9. In  $d^2sp^3$  or  $sp^3d^2$  the orbitals used in

hybridization are  $d_{x^2-y^2}$  and  $d_{z^2}$ .

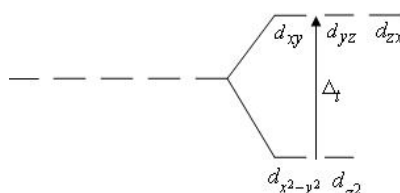
10. **Ligand Field Splitting in Square Planar Complex:**

$[PtCl_4]^{2-}$ ,  $Pt^{2+} : 5d^8$



The d-orbital used in  $dsp^2$  hybridisation is

$d_{x^2-y^2}$ .

11. **Ligand Field Splitting in Tetrahedral Complexes:**

12. **Factors influencing the magnitude of  $\Delta_o$  :**

I. Nature of the metal cation:

a) Among the cations from atoms of the same transition series cations with a higher oxidation states has a larger value of  $\Delta_o$  than that of lower oxidation states, because the central ion with higher oxidation state will polarise the ligands more effectively and thus the ligands would approach such cation more closely.

Ex:

$$\Delta_o \text{ for } [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 10,400 \text{ cm}^{-1} (3d^6)$$

$$\Delta_o \text{ for } [\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 13,700 \text{ cm}^{-1} (3d^5)$$

b) Among the cations having same number of 'd' electrons and the same geometry of the complex, cations with higher oxidation state has large value of  $\Delta_o$ .

Ex:

$$\Delta_o \text{ for } [\text{V}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 12,400 \text{ cm}^{-1} (3d^3)$$

$$\Delta_o \text{ for } [\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 17,400 \text{ cm}^{-1} (3d^3)$$

c) In case of complexes having the cations with the same charges but with different number of 'd' electrons in the central metal cation, the magnitude of  $\Delta_o$  decreases with the increase of the number of 'd' electrons.

Ex:

$$\Delta_o \text{ for } [\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1} (3d^7)$$

$$\Delta_o \text{ for } [\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 8,500 \text{ cm}^{-1} (3d^8)$$

d) As the quantum number of the 'd' orbitals of the central atom increases  $\Delta_o$  value increases.

Ex:

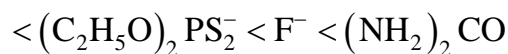
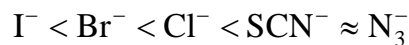
$$\Delta_o \text{ for } [\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+} = 23,000 \text{ cm}^{-1} (3d^6)$$

$$\Delta_o \text{ for } [\text{Rh}^{\text{III}}(\text{NH}_3)_6]^{3+} = 34,000 \text{ cm}^{-1} (4d^6)$$

II. Strong/weak ligands:

Strong ligands possess higher  $\Delta_o$  values.

Spectrochemical series:



This order independent of the nature of the central metal ion and the geometry of the complex.

III. Geometry of the complex:

As the geometry changes  $\Delta$  value changes.

$$\Delta_{\text{sp}} > \Delta_o > \Delta_t$$

$$\Delta_{\text{sp}} = \frac{4}{3} \Delta_o$$

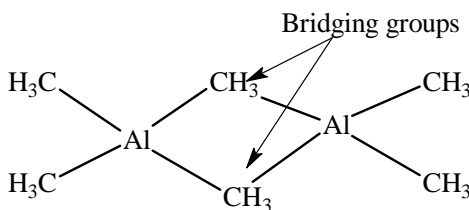
$$\Delta_t = \frac{4}{9} \Delta_o$$

13. **ORGANO METALLIC COMPOUNDS**

**EXAMPLES**

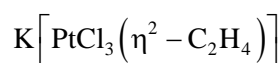
a) Grignard Reagent R-Mg-X where R is a alkyl or aryl group and X is halogen

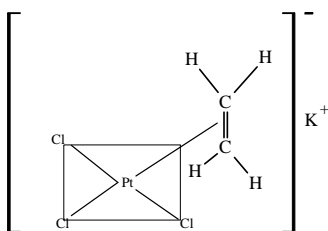
b)  $(\text{CH}_3)_4\text{Sn}, (\text{C}_2\text{H}_5)_4\text{Pb}, \text{Al}_2(\text{CH}_3)_6, \text{Al}_2(\text{C}_2\text{H}_5)_6$  etc



ii)  $\pi$  (p) bonded organometallic compounds : These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

e.g. Zeise's salt

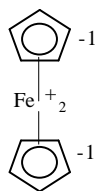




Potassium trichloro ( $\eta^2$ -ethylene)platinate(II)

Has both  $\sigma$  and  $\pi$  ligands.

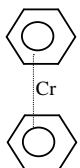
Ferrocene  $\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2$



bis ( $\eta^5$ -cyclopentadienyl)iron(II)

Sandwich complex

bis (benzene) chromium (0),  $\text{Cr}(\eta^6 - \text{C}_6\text{H}_6)_2$



sandwich complex

iii)  $\sigma$  &  $\pi$  bonded organometallic comp.

eg Metal carbonyls

#### 14. Metal carbonyls:

- \* The highest occupied molecular orbital of carbon monoxide, the  $\sigma_{2p_z}$  orbital, holds two electrons. This electron pair is loosely held and hence is available for donation to metal. The bonding takes place when the filled  $\sigma_{2p_z}$  molecular orbital of CO overlaps with an empty orbital of the metal. As a result, a normal ligand - to - metal  $\sigma$  bond is formed.
- \* CO also has two degenerate, empty, anti - bonding  $\pi$  orbitals. These are the lowest unoccupied molecular orbitals of CO, mutually perpendicular to each other. The overlap of one

of these vacant anti - bonding molecular orbitals with a filled metal orbital of  $\pi$  - symmetry results in the formation of a second bond called dative bond. The dative bond serves to pass the excessive negative charge (that accumulates on the metal due to the formation of  $\sigma$  - bond) to the ligand.

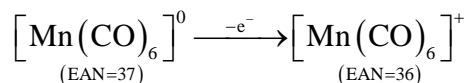
- \* Back donation of electrons from the metal to the ligands is possible only if the metal is in a low oxidation state. Hence, CO ligand stabilizes low oxidation states of metals in its complexes.
- \* The  $\sigma$  - and  $\pi$  - bonding mutually supplement each other. The donation of electrons to metal, during the formation of  $\sigma$  bond, increases the partial positive charge on the CO ligand, making it a better acceptor. The back donation of metal electrons to the ligands increases the partial negative charge on CO, making it, in effect, a better donor. This mutual reinforcement is called synergism. As a result of synergism,  $\sigma$  - bonding strengthens  $\pi$  - bonding vice versa.

A consequence of synergism is that CO ligand forms a large number of complexes with transition metals in low oxidation states, even though it is a poor Lewis base for the other species. Another consequence of synergism is that it increases the bond order of

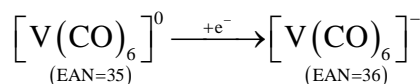
metal - carbon bond and decreases the bond order of carbon - oxygen bond. This results in  
a) shortening of metal - carbon bond as compared to the metal - carbon single bond.  
b) lengthening of carbon - oxygen bond as compared to carbon - oxygen bond.

- \* Metal carbonyls exhibit a strong tendency to achieve Sidgwick EAN values and as a result

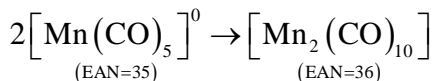
- 1)  $[\text{Mn}(\text{CO})_6]^0$  can act as a reducing agent. The complex loses an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



- 2)  $[\text{V}(\text{CO})_6]^0$  can act as oxidising agent. The complex gains an electron to attain the noble gas configuration and hence obey Sidgwick EAN rule.



- 3)  $[\text{Mn}(\text{CO})_5]^0$  undergoes dimerisation to attain the noble gas configuration and hence obey Sidgwick EAN rule.



\* Anionic carbonyl complexes are called carbonylate ions, these are also referred to as carbometallates.

Ex:

- 1)  $[\text{Ti}(\text{CO})_6]^{2-}$ ,  $[\text{V}(\text{CO})_6]^-$ : Isolelectronic, isostructural with  $[\text{Cr}(\text{CO})_6]$ .

- 2)  $[\text{V}(\text{CO})_5]^{3-}$ ,  $[\text{Cr}(\text{CO})_5]^{2-}$ ,

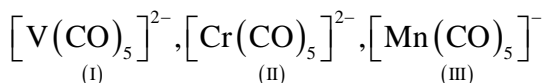
$[\text{Mn}(\text{CO})_5]^-$ : Isolelectronic, isostructural with  $[\text{Fe}(\text{CO})_5]$

- 3)  $[\text{Cr}(\text{CO})_4]^{4-}$ ,  $[\text{Mn}(\text{CO})_4]^{3-}$ ,

$[\text{Fe}(\text{CO})_4]^{2-}$ ,  $[\text{Co}(\text{CO})_4]^-$ : Isolelectronic, isostructural with  $[\text{Ni}(\text{CO})_4]$

\* As the negative charge on the coordination sphere of a carbonyl complex increases, the extent of back bonding also increases. This, in turn, leads to an increase in metal - carbon bond order and a decrease in carbon - oxygen bond order.

Ex: In

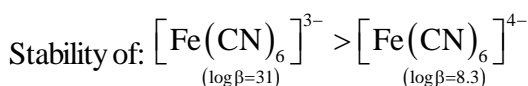


Carbon - oxygen bond order: I < II < III  
 Carbon - oxygen bond length: I > II > III  
 Carbon - oxygen bond strength: I < II < III  
 Metal - carbon bond strength: I > II > III

### 15. Factors affecting the stability of complexes:

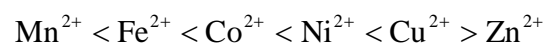
#### I. Charge and size of the metal ion:

In general the metal ion with larger charge and smaller size form more stable complexes.

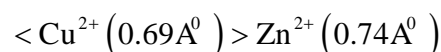
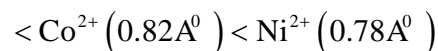
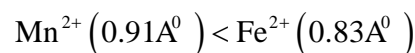


#### II. Irving - William order:

Stabilities of high spin complexes of the ions between  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  with a given ligand vary in the order:



Radii of these ions are in the order:



#### III. Electronegativity of the central metal ion:

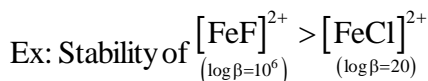
A central metal ion with higher electronegativity would give the most stable complexes.

#### IV. Size and charge of ligand:

For charged ligands, the higher the charge carried by them and the smaller their size, the more stable are the complexes formed

(for class a metals)

(Class a metals: Sc, Ti, V, Cr etc)

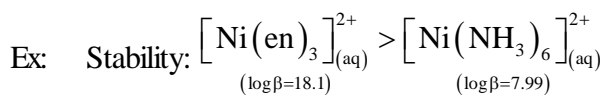


#### V. Basic character of the ligands:

The more basic is the ligand, more easily it can donate electron pairs to the central ion and hence more easily it can form complexes of greater stability.

#### VI. Chelating effect:

\* Complexes containing chelate rings are usually more stable than similar complexes containing no rings, i.e., multidentate ligands in general form more stable complexes than the monodentate ligands.



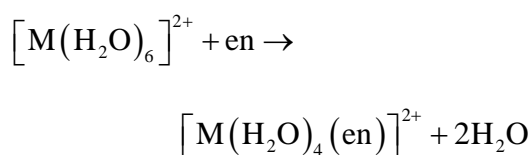
\* The greater the amount of disorder produced in the products during the reaction relative to the reactants, the greater the increase in entropy during the reaction and hence the greater the stability of the products.

LEVEL - V**SINGLE ANSWER QUESTIONS**

Ex: When ethylene diamine(en) is allowed to react with hydrated complex ion,  $[M(H_2O)_6]^{2+}$ , it replaces two  $H_2O$  molecules from it, since it is a bidentate ligand.

This process increases the number of particles in the system and hence its disorder and entropy.

Thus the complex  $[M(H_2O)_4(en)]^{2+}$  is more stable than  $[M(H_2O)_6]^{2+}$



VII. Chelate ring size:

- \* The large the number of the chelate rings in a complex, the greater is its stability.
- \* The stability of the complexes also depends on the number of the atoms present in the ring.
- \* The chelates containing 3 - membered ring including the metal are very unstable.
- \* 4- membered chelate rings are rare and occur in carbonate, nitrate and sulphate chelates.
- \* 5-membered chelates are frequently more stable than the 6-membered chelates when the atoms in the ring are joined by single bonds only.
- \* 6-membered chelates are more stable than 5-membered chelates of heterocyclic ligands or of ligands involving conjugation in the chelate ring.

VIII. Steric effects:

When a bulky group is either attached to or present near the donor atoms of a ligand, mutual repulsion among the ligand occurs and consequently the metal - ligand bond is weakened. Thus large bulky ligands form less stable complexes than do the analogous smaller ligands.

1. Which of the following statements is incorrect?
  - (A) Mercurous ion exist as  $Hg^+$
  - (B) Mercurous ion is diamagnetic and exist as dimer  $Hg_2^{2+}$
  - (C) Mercurous ion is colourless
  - (D) There is a covalent bond between two  $Hg^+$  ions
2. The metal that has the highest melting point and used in making hard steel is
  - (A) Cu      (B) Mn      (C) Zn      (D) W
3. The property, which is not characteristics of transition metals
  - (A) variable oxidation states
  - (B) tendency to form complexes
  - (C) formation of coloured compounds
  - (D) They are usually diamagnetic
4. The pair that has the greatest malleability and ductility property is
  - (A) Na, K                      (B) Pb, Sn
  - (C) Zn, Mn                    (D) Cu, Au
5. The metal that has the lowest boiling point among the following is
  - (A) Ti      (B) Zn      (C) Cu      (D) Fe
6. In a transition series, as the atomic number increases, paramagnetism
  - (A) increases gradually
  - (B) decreases gradually
  - (C) first increases to a maximum and then decreases
  - (D) first decreases to a minimum and then increases
7. Oxide of metal cation which is not amphoteric
  - (A)  $Al^{3+}$       (B)  $Cr^{3+}$       (C)  $Fe^{3+}$       (D)  $Zn^{2+}$
8. The most abundant transition metal in earth crust is:
  - A) Zn      B) Fe      C) Hg      D) Au



9. The electron which take part in order to exhibit variable oxidation states by transition metals are

- A) ns only
- B)  $(n-1)d$  only
- C) ns and  $(n-1)d$  only but not np
- D)  $(n-1)d$  and np only but not ns

10. Zn and Cd metals do not show variable valency because:

- A) They have only two electrons in the outermost subshells
- B) their d-subshells are completely filled
- C) their d-subshells are partially filled
- D) they are relative soft metals

11. Each of the following ion contains vanadium the +5 oxidation state except

- A)  $VO_2^+$
- B)  $V(OH)_4^+$
- C)  $VO^{2+}$
- D)  $[VO_3 OH]^{2-}$

12. Paramagnetism is not exhibited by :

- A)  $CuSO_4 \cdot 5H_2O$
- B)  $CuCl_2 \cdot 5H_2O$
- C) CuI
- D)  $NiSO_4 \cdot 6H_2O$

13. The wrongly statement regarding transition metals among the following is

- A) 4s electrons penetrates towards the nucleus more than 3d electrons
- B) Atomic radii of transition metals increase rapidly with increase in atomic number because of poor shielding of nuclear attraction by  $(n-1)d$  electrons
- C) second and third transition series elements have nearly the same size
- D) their densities are higher and densities of the 5d series elements are higher than those of 4d series elements

14. Ionisation energies of Ni and Pt in  $kJ\ mol^{-1}$  are given below

	$(IE)_1 + (IE)_2$	$(IE)_3 + (IE)_4$
	⏟	⏟
Ni →	2.49	8.80
Pt →	2.60	6.70

So, (select the correct statement )

- A) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)
- B) Platinum (IV) compounds tend to be more stable than nickel (IV)
- C) (A) & (B) Both
- D) none of these

15.  $MnO_4^-$  is intense pink colour, though Mn is (+7) oxidation state , It is due to

- A) oxygen gives colour to it
- B) charge transfer when oxygen gives its electron to oxygen
- C) Charge transfer when oxygen gives its electron to Mn making it  $Mn(+VI)$  hence coloured
- D) None of these

16. Cementite is:

- A) Interstitial compound of iron and carbon
- B) An alloy of Fe and Cr
- C) A compound resembling cement
- D) An ore of iron

17. The radii (metallic) of Fe,Co and Ni are nearly same

This is due to

- (A)lanthanide contraction
- (B) increase in radii due to increase in 'n' is compensated by decrease in radii due to increase in effective nuclear charge(Z)
- (C) Decrease in radii due to increasing screening effect is compensated by increase in size due to increasing effective nuclear charge
- (D) Atomic radii do not remain constant but decrease in a normal gradation

18.  $VO_4^-$ ,  $CrO_4^{2-}$  and  $MnO_4^-$  are pale yellow , strong yellow and intense purple respectively in aqueous solution. The darkening of colour is due to

- (A) charge transfer
- (B) d – d transition
- (C) half-filled d-sub -shells
- (D) increasing number of unpaired electrons

19. Metals which do not form amalgam are

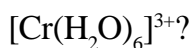
- (A) Fe
- (B) Zn
- (C) Ni
- (D) Au

20. The hybridization of the metal in  $[CoF_6]^{3-}$  is

- (A)  $sp^3d^2$
- (B)  $d^2sp^3$
- (C)  $dsp^3$
- (D)  $sp^3d$

21. The hybridization of Cr in  $[Cr(en)_3]^{3+}$  is  
 (A)  $d^2sp^3$  (B)  $sp^3d$  (C)  $sp^3d^2$  (D)  $dsp^3$
22. The magnetic moment of the complex  $[Ti(H_2O)_6]^{3+}$  is  
 (A) 3.87 BM (B) 1.73 BM  
 (C) 2.84 BM (D) 5.87 BM
23. Which one of the following coordination numbers can show a square pyramidal geometry?  
 (A) 4 (B) 3 (C) 7 (D) 5
24. If the formation constant of  $[Cu(NH_3)_4]^{2+}$  is  $2 \times 10^3$ , then its dissociation constant is  
 (A)  $5 \times 10^{-4}$  (B)  $2 \times 10^3$   
 (C)  $5 \times 10^{-2}$  (D)  $0.2 \times 10^3$
25. The IUPAC name of  $[Fe(H_2O)_6]Cl_3$  is  
 (A) Hexaaquairon(III) chloride  
 (B) Hex aquoiron(III) trichloride  
 (C) Hexaaquairon(III) chloride  
 (D) Hexa aquairon(III) trichloride
26. IUPAC name of  $[Co(en)_2Cl_2]Cl$  is  
 (A) dichloridobis (ethylene diammine) cobalt (III) Chloride.  
 (B) dichloridobis (ethylenediammine) cobalt(III) Chloride  
 (C) dichlorobis (ethylene diamine) cobalt(II) Chloride.  
 (D) dichloridobis (ethylene diamine) cobalt(III) chloride
27. Which is not true statement?  
 (A) Ions of d-block elements are coloured due to d—d transition.  
 (B) Ions of f-block elements are coloured due to f—f transition.  
 (C)  $[Sc(H_2O)_6]^{3+}$  and  $[Ti(H_2O)_6]^{4+}$  are colourless complexes  
 (D)  $Cu^+$  is colourless ion.
28. Among the following ions, which one has the highest paramagnetism?  
 (A)  $[Cr(H_2O)_6]^{3+}$  (B)  $[Fe(H_2O)_6]^{2+}$   
 (C)  $[Cu(H_2O)_6]^{2+}$  (D)  $[Zn(H_2O)_6]^{2+}$
29. Which of the following statements is correct?  
 (A)  $[CoF_6]^{3-}$  and  $[Co(NH_3)_6]^{3+}$  both are paramagnetic complexes  
 (B)  $[CoF_6]^{3-}$  and  $[Co(NH_3)_6]^{3+}$  both are high spin complexes  
 (C)  $[CoF_6]^{3-}$  is octahedral while  $[Co(NH_3)_6]^{3+}$  has a pentagonal pyramid shape  
 (D)  $[CoF_6]^{3-}$  is outer orbital complex while  $[Co(NH_3)_6]^{3+}$  is inner orbital complex
30. What is wrong about the compound  $K[Pt(\eta^2-C_2H_4)Cl_3]$ ?  
 (A) It is called Zeise's salt  
 (B) It is only  $\pi$  - bonded complex  
 (C) Oxidation number of Pt is +2  
 (D) Four ligands surrounds the Platinum atom.
31. Which species is not available in Fenton's reagent.  
 a)  $Fe^{+2}$  b)  $HO\cdot$   
 c)  $HO^-$  d)  $HO^+$
32. Zinc gives  $H_2$  gas with  $H_2SO_4$  and conc HCl but not with conc.  $HNO_3$  because.  
 a)  $NO_3^-$  ion is reduced in preference to hydronium ion  
 b) Conc.  $HNO_3$  is a weaker acid than conc.  $H_2SO_4$  and conc HCl  
 c) Conc.  $HNO_3$  acts as a reducing agent  
 d) Zinc is more reactive than  $H_2$
33. Which complex is likely to show optical activity  
 A) Trans -  $[Co(NH_3)_4Cl_2]^+$   
 B)  $[Cr(H_2O)_6]^{3+}$   
 C) Cis -  $[Co(NH_3)_2(en)_2]^{3+}$   
 D) Trans -  $[Co(NH_3)_2(en)_2]^{3+}$

34. Which of the following complex ion has a magnetic moment same as that of



- A)  $[\text{Mn}(\text{H}_2\text{O})_6]^{4+}$       B)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$   
 C)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$       D)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

35. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is

- a)  $\text{CrO}_3$                                   b)  $\text{Cr}_2\text{O}_3$   
 c) Cr    d)  $\text{CrO}(\text{O}_2)$

36. Identify the incorrect statement among the following :

- a) misch metal is a pure lanthanide metal  
 b) Magnetic moment increases from Ce( $4f^1 5d^1 6s^2$ ) to Pr( $4f^3 6s^2$ ) in their +3 oxidation state.  
 c) In lanthanides from Ce<sup>+3</sup> to Lu<sup>+3</sup> there is a regular decrease in size  
 d) Ce<sup>+4</sup> is a powerful oxidizing agent

37. For which one of the following ions, the colour is not due to a d-d transition ?

- a)  $\text{CrO}_4^{2-}$                                   b)  $\text{Cu}(\text{NH}_3)_4^{2-}$   
 c)  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$                           d)  $\text{CoF}_6^{3-}$

38. Gold and platinum dissolves in aquaregia to produce respectively

- a)  $\text{H}[\text{AuCl}_4]$  and  $\text{H}[\text{PtCl}_3]$   
 b)  $\text{H}[\text{AuCl}_4]$  and  $\text{H}_2[\text{PtCl}_6]$   
 c)  $\text{H}_2[\text{AuCl}_6]$  and  $\text{H}[\text{PtCl}_4]$   
 d)  $\text{H}_2[\text{AuCl}_6]$  and  $\text{H}[\text{PtCl}_6]$

39. AgCl on fusion with  $\text{Na}_2\text{CO}_3$  forms:

- a)  $\text{Ag}_2\text{CO}_3$                                   b)  $\text{Ag}_2\text{O}$   
 c) Ag    d)  $\text{Ag}_2\text{C}_2$

40.  $\text{CrO}_3$  dissolves in aqueous NaOH to give :

- a)  $\text{Cr}_2\text{O}_7^{2-}$                                   b)  $\text{CrO}_4^{2-}$   
 c)  $\text{Cr}(\text{OH})_3$                                   d)  $\text{Cr}(\text{OH})_2$

41. In acidic medium (conc.  $\text{H}_2\text{SO}_4$ ) Hydrogen peroxide reacts with  $\text{K}_2\text{Cr}_2\text{O}_7$  in the presence of ether forms a deep violet coloured chromium peroxide. The oxidation state of chromium in chromium peroxide is .

- a) +2    b) +3  
 c) +5    d) +6

42. The ratio of magnetic moments of Fe (III) and Co(II) is :

- a)  $\sqrt{5} : \sqrt{7}$                                   b)  $\sqrt{35} : \sqrt{15}$   
 c) 7 : 3    d)  $\sqrt{24} : \sqrt{15}$

43. Which of the following statement is incorrect ?

- a) The electronic configuration of Cr is  $[\text{Ar}]3d^5, 4s^1$   
 b) The magnetic quantum no. may have negative value  
 c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type  
 d) The oxidation state of nitrogen in  $\text{HN}_3$  is -3.

44. Pick out the correct option. Where T stands for true. F stands for false.

- I) The energy of the 3d orbital is high when compared to 4s orbital in hydrogen atom  
 II) The electron density in xy plane in  $d_{x^2-y^2}$  orbital is zero  
 III) 24th electron in Cr goes to 3d orbital  
 IV) The three quantum numbers were clearly explained in terms of schrodinger wave equation  
 a) TTFB    b) TFFT  
 c) TFTF    d) FFTT

### MULTIPLE ANSWER QUESTIONS

45. The unstable compounds are

- (A)  $\text{MnI}_7$     (B)  $\text{CrO}_3$     (C)  $\text{Mn}_2\text{O}_7$     (D)  $\text{CrI}_6$

46. Which one of the following reactions cannot occur ?

- (A)  $\text{Cu} + \text{ZnSO}_4 \rightarrow \text{CuSO}_4 + \text{Zn} \downarrow$   
 (B)  $\text{Cu} + 2\text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag} \downarrow$   
 (C)  $\text{Cu} + \text{FeSO}_4 \rightarrow \text{CuSO}_4 + \text{Fe} \downarrow$   
 (D)  $3\text{Ag} + \text{AuCl}_3 \rightarrow 3\text{AgCl} + \text{Au} \downarrow$

47. Which of these are liquids at room temperature ?

- (A)  $\text{TiCl}_4$     (B) Zn    (C) Hg    (D)  $\text{CuCl}_2$

48. The typical acidic oxides are  
(A) MnO (B)  $Mn_2O_7$  (C) CrO (D)  $CrO_3$
49. The compounds that undergo hydrolysis readily is/are  
(A)  $TiCl_4$  (B)  $VCl_5$  (C)  $FeCl_3$  (D)  $CaCl_2$
50. Which are the best suitable as coinage metals?  
(A) Mg (B) Cu (C) Ag (D) Au
51. Order of paramagnetic character among following elements is/are  
(A)  $Mn > Fe > Cr$  (B)  $Fe > Zn > Cr$   
(C)  $Cr > Fe > Zn$  (D)  $Cr > Mn > Fe$
52. Which of the following statements are correct?  
(A) Transition elements exhibit higher enthalpies of atomization as they have stronger interatomic interaction  
 $IE_2$  of  ${}_{23}V < {}_{24}Cr > {}_{25}Mn$   
(B) and  ${}_{28}Ni < {}_{29}Cu > {}_{30}Zn$   
(C) Ni(II) compounds are more stable than Pt(II) where as Pt (IV) compounds are more stable than nickel (IV)  
(D) The elements which gives the greatest number of oxidation states does not occur near the middle of the series
53. The diamagnetic compounds is/are  
(A)  $HgCl_2$  (B)  $Hg_2Cl_2$   
(C)  $Cu_2Cl_2$  (D)  $K_2Cr_2O_7$
54. The colour of the transition metal ions/are due to  
A) d-d transition of electrons in presence of ligands  
B) charge transfer from ligands to metal ion  
C) change in the geometry  
D) polarisation of anion by cation
55. Select the correct statement(s) with respect to oxides and oxoanions of transition metals  
(A) Among oxides of chromium CrO is basic,  $Cr_2O_3$  amphoteric and  $CrO_3$  is acidic  
(B) No higher oxides of iron above  $Fe_2O_3$  are found  
(C) Ti, V, Cr and Mn form oxides MO and their correct increasing order of acidic character is  $MnO < CrO < VO < TiO$   
(D) Vanadium (V) oxide does not react with acids but reacts with alkalis only
56. In which of the following compounds (s), the colour is due to the charge transfer spectra  
(A)  $KMnO_4$  (B)  $CrO_3$   
(C)  $CuCl_2$  (D)  $Cu_2O$
57. Transition elements act as good catalysts because  
(A) Presence of partially filled 'd' orbitals  
(B) Form H-bonding easily  
(C) Transition elements show variable oxidation state  
(D) Easy interconvertibility of oxidation states due to low oxidation and reduction potential
58. The true statements among the following are:  
(A)  $Cu^{2+}$  undergoes disproportionation in aq solutions  
(B) All Cu(II) salts are known except the iodide  
(C) The only transition metal in 3d series with a positive  $E^0(M^{2+}/M)$  value is copper  
(D) Copper has the highest second ionization enthalpy among all the 3d elements
59. Which of the following statements is/are true?  
(A) In metal carbonyl complexes  $d_{C-O}$  increases compared to that in CO molecule  
(B) The pair of compounds  $[Cr(H_2O)_6]Cl_3$  and  $[CrCl_3(H_2O)_3] \cdot 3H_2O$  show hydrate isomerism  
(C)  $d_{z^2}$  orbital of central metal atom/ion is used in  $dsp^2$  hybridisation  
(D) Facial and meridional isomers associated with  $[Ma_3b_3]^{n+}$  type complex compound, both are optically inactive
60. A d-block element forms octahedral complex but its magnetic moment remains same either in strong field or weak field ligand. Which of the following is/are correct?  
(A) d-block element always forms colourless compound  
(B) Number of electrons in  $t_{2g}$  orbitals are higher than in  $e_g$  orbitals  
(C) It can have either  $d^3$  or  $d^8$  configuration  
(D) It can have either  $d^7$  or  $d^8$  configuration

61. The complexes that have a magnetic moment of 1.73 BM is

- (A)  $[Ti(H_2O)_6]^{3+}$  (B)  $[V(H_2O)_6]^{4+}$   
 (C)  $[Mn(H_2O)_6]^{2+}$  (D)  $[Mn(H_2O)_6]^{3+}$

62. The square planar complexes are

- (A)  $[Pt(NH_3)_2Cl_2]$  (B)  $[Ni(CN)_4]^{2-}$   
 (C)  $[NiCl_4]^{2-}$  (D)  $[PtCl_4]^{2-}$

63. The tetrahedral complexes are

- (A)  $Ni(CO)_4$  (B)  $[FeCl_4]^{-1}$   
 (C)  $[MnCl_4]^{2-}$  (D)  $[CoCl_4]^{2-}$

64. The diamagnetic complexes are

- (A)  $[Cr(CO)_6]$  (B)  $[Co(NH_3)_6]^{3+}$   
 (C)  $[Fe(CN)_6]^{4-}$  (D)  $[Ni(NH_3)_6]^{2+}$

65. The strong field ligands or moderate ligand are

- (A)  $NH_3$  (B)  $en$   
 (C)  $CO$  (D)  $CN^-$

66.  $d \rightarrow d$  transition is possible in

- (A)  $[Cu(NH_3)_4]^{2+}$  (B)  $KMnO_4$   
 (C)  $K_2Cr_2O_7$  (D)  $[Co(NH_3)_6]^{3+}$

67. Which of the following can act as bridging ligands ?

- (A)  $OH^-$  (B)  $H_2O$   
 (C)  $CO$  (D)  $Cl^-$

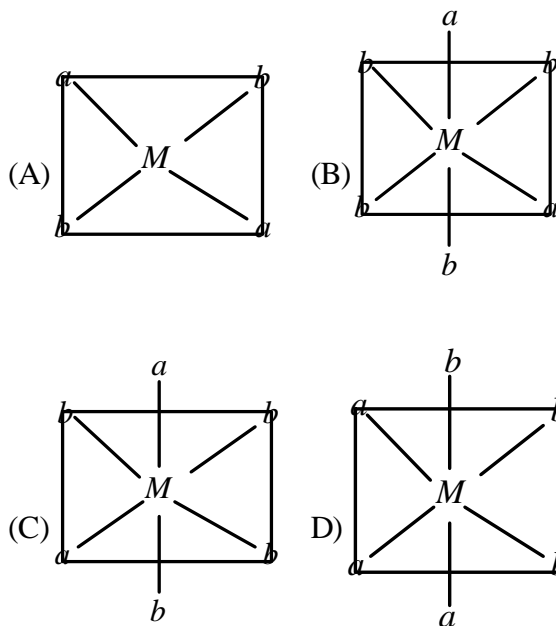
68. Which of the following can give rise to linkage isomerism ?

- (A)  $en$  (B)  $NO_2^-$   
 (C)  $CN^-$  (D)  $SCN^-$

69. Which of the following can show geometrical isomers (M = metal, a, b, c - monodentate ligands ?

- (A)  $Ma_3b$  (B)  $Ma_4b_2$   
 (C)  $Ma_2bc$  (square planar) (D)  $Ma_2b_2c_2$

70. Which of the following are cis isomers ?



71. The following complexes are given

- 1) trans -  $[Co(NH_3)_2Cl_2]^+$
- 2) cis-  $[Co(NH_3)_2(en)_2]^{3+}$
- 3) trans -  $[Co(NH_3)_2(en)_2]^{3+}$
- 4)  $NiCl_4^{2-}$
- 5)  $TiF_6^{2-}$
- 6)  $CoF_6^{3-}$

Choose the correct code

- (A) (1), (2) are optically active,  
 (B) (2) is optically active, (1),(3) are optically inactive  
 (C) (4), (6) are colourless and (5) is coloured  
 (D) (4) is coloured and (5) is colourless

72. Among the following which is most stable ?

- (1)  $[Fe(CN)_6]^{3-}$  and  $[FeF_6]^{3-}$   
 (X) (Y)  
 (2)  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$   
 (S) (T)  
 (3)  $[Cr(CN)_6]^{3-}$  and  $[Cr(CN)_6]^{4-}$   
 (P) (Q)

Choose the correct code

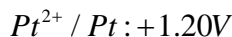
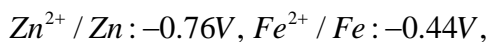
- (A) 1-X, 2-T, 3-Q (B) 1-X, 2-S, 3-Q  
 (C) 1-X, 2-S, 3-P (D) 1-Y, 2-T, 3-Q

73. Which of the following is/are correct?  
 (A) Ligands with filled  $\pi$  orbitals are called  $\pi$  donors  
 (B)  $\pi$  donor ligand forms sigma bond with metal  $t_{2g}$  orbital  
 (C) Ligand to metal charge transfer favoured when the central metal has a high oxidation state  
 (D) Delocalization of  $\pi$  electrons from the ligand to the metal reduces the value of  $\Delta_0$
74. The magnitude of crystal field stabilization energy depends on  
 (A) The nature of ligands  
 (B) The charge on the metals atom  
 (C) The charge on the ligand  
 (D) Position of metal in periodic table

### COMPREHENSION QUESTIONS

#### Passage-I

The  $E^0$  values are



75. The most unreactive metal is  
 (A) Zn (B) Fe (C) Ni (D) Pt
76. The element that does not displace hydrogen from dilute acids is  
 (A) Zn (B) Mn (C) Cu (D) Fe
77. The metal that does not displace Cu from the  $CuSO_4$  solution is  
 (A) Zn (B) Fe (C) Mg (D) Ag

#### Passage-II

The transition metals and their compounds have paramagnetic properties.. This is due to the reason that ions of transition metals have unpaired electrons in  $(n-1)d$  orbitals. As the number of unpaired electrons increases from one to five in moving from Sc to Mn, the paramagnetic character increases accordingly. From Mn

onwards, this character decreases as electrons get paired up. The paramagnetic behavior is expressed in terms of magnetic moment which is because of the spin of unpaired electrons ( $n$ ). It is given as Magnetic moment =  $\sqrt{n(n+2)}$  B.M  
 Majority of transition metal compounds are coloured both in solid state as well as in aqueous solution. due to d-d transition in which unpaired electrons from the lower energy d-orbitals are transferred to higher energy d-orbitals. The energy of this transition correspond to the radiation in visible region. Thus, when white light falls on such a transition metal compound, some light energy corresponding to a particular colour is absorbed and one or more electrons are raised from lower energy set of orbitals to those of higher energy. With the absorption of radiations corresponding to specific colour from the white light, a colour known as the complementary colour is observed or transmitted.

78. The compound which have the same magnetic moment like that of  $FeCl_2$ .  
 A)  $CrCl_3$  (B)  $MnCl_2$   
 C)  $CoCl_3$  (D)  $NiCl_2$
79. A compound of metal ion  $M^{x+}$  ( $z = 24$ ) has a spin only magnetic moment of  $\sqrt{15}$  B.M. The number of unpaired electrons in the metal ion of the compound are  
 A) 2 (B) 3  
 C) 4 (D) 5
80. For which one of the following ions, the colour is not due to a d-d transition:  
 A)  $CrO_4^{2-}$  (B)  $Cu(NH_3)_4^{2+}$   
 C)  $Ti(H_2O)_6^{3+}$  (D)  $CoF_6^{3-}$

#### Passage-III

A metal complex having composition  $[Cr(NH_3)_4Br_2I]$  was isolated in two forms(X) and (Y). Form (X) reacts with  $AgNO_3$  to give a pale yellow precipitate which is partially soluble in excess of  $NH_4OH$  whereas (Y) gives a greenish yellow precipitate which is insoluble in  $NH_4OH$ .

81. (A) The formula of (X) and (Y) are  $[\text{Cr}(\text{NH}_3)_4 \text{Br I}] \text{Br}$  and  $[\text{Cr}(\text{NH}_3)_3 \text{Br}_2 \text{I}] \text{NH}_3$  respectively  
 (B) The formula of (X) and (Y) are  $[\text{Cr}(\text{NH}_3)_4 \text{Br I}] \text{Br}$  &  $[\text{Cr}(\text{NH}_3)_4 \text{Br}_2 \text{I}]$  respectively  
 (C) The formula of (X) and (Y) are both  $[\text{Cr}(\text{NH}_3)_4 \text{I}] \text{Br}_2$   
 (D) The formula of (X) and (Y) are  $[\text{Cr}(\text{NH}_3)_2 \text{I Br}_2] (\text{NH}_3)_2$
82. Both the (X) form and (Y) form show  
 (A) linkage isomerism  
 (B) Coordination isomerism  
 (C) Ionization isomerism  
 (D) None of these
83. Which of the following statement is true?  
 (A) (X) - cis form optically inactive (Y) - cis form optically active  
 (B) (X) - cis form optically inactive (Y) - trans form optically active  
 (C) The cis and trans forms of both X and Y are optically active  
 (D) The cis and trans form of both X and Y are optically inactive.

**MATRIX MATCHING QUESTIONS**

84. Match the pair of substances having similar properties
- Column - I**
- a)  $\text{NiSO}_4$  and  $\text{VO}^+$   
 b)  $\text{TiCl}_4$  and  $\text{ZnSO}_4$   
 c)  $\text{MnCl}_{3(\text{aq})}$  and  $\text{CoCl}_{3(\text{aq})}$   
 d)  $\text{FeCl}_3$  and  $\text{MnSO}_4$
- Column - II**
- p) Same magnetic moment  
 q) Nearly similar colour  
 r) Same oxidation state  
 s) Same outer electronic configuration
85. Match the following:
- |               |                            |
|---------------|----------------------------|
| <b>List-I</b> | <b>List-II</b>             |
| <b>Metals</b> | <b>Characteristic</b>      |
| (A) Cd        | (p) d-block metal          |
| (B) Rh        | (q) Transition metal       |
| (C) Fm        | (r) Inner transition metal |
| (D) Gd        | (s) Lanthanide             |
|               | (t) Actinide               |

86. Match the following:
- |  |                              |
|--|------------------------------|
| <b>List-I</b>                                | <b>List-II</b>               |
| <b>(Property)</b>                            | <b>(Transition elements)</b> |
| (A) Highest oxidation state                  | p) Cr                        |
| (B) Highest density                          | q) Os                        |
| (C) Elements with maximum unpaired electrons | r) Tc                        |
| (D) Radioactive transition element           | s) Ru                        |
87. Match the following
- |                            |   |
|----------------------------|---|
| <b>Column - I</b>          | <b>Column - II</b>                                      |
| <b>(molar conductance)</b> |   |
| a) 229                     | p) $[\text{Pt}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_3$   |
| b) 0                       | q) $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_4]$             |
| c) 404                     | r) $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}_2$ |
| d) 523                     | s) $[\text{Pt}(\text{NH}_3)_6] \text{Cl}_4$             |
|                            | t) $[\text{Co}(\text{NH}_3)_3 \text{Cl}_3]$             |
88. Match the following
- |                                      |                             |
|--------------------------------------|-----------------------------|
| <b>Column - I</b>                    | <b>Column - II</b>          |
| a) $\text{K}_2 [\text{NiCl}_4]$      | p) $\text{sp}^3$ hybridized |
| b) $[\text{Ni}(\text{CO})_4]$        | q) para magnetic            |
| c) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ | r) outer orbital complex    |
| d) $[\text{FeF}_6]^{3-}$             | s) digmagnetic              |
89. Match the following
- |   |   |
|---|---|
| <b>Column - I</b>                               | <b>Column - II</b>                        |
| a) $[\text{Fe}(\text{CN})_6]^{4-}$              | p) Paramagnetic, $\text{sp}^3 \text{d}^2$ |
| b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$     | q) Diamagnetic, $\text{d}^2 \text{sp}^3$  |
| c) $[\text{CrCl}_2(\text{NH}_3)_4] \text{NO}_3$ | r) Diamagnetic $\text{sp}^3 \text{d}^2$   |
| d) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$     | s) Ionization isomerism                   |
90. Match the following
- |   |                             |
|---|-----------------------------|
| <b>Column - I</b>                           | <b>Column - II</b>          |
| a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$        | p) Diagonal magnetic        |
| b) $[\text{Ni}(\text{CO})_4]$               | q) $\text{sp}^3 \text{d}^2$ |
| c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | r) $\text{d}^2 \text{sp}^3$ |
| d) $[\text{Ni}(\text{CN})_4]^{2-}$          | s) Inner orbital complex    |

91. Match the following

Column - I

Column - II

- a)  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$  p) Geometrical isomers  
 b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  q) Diamagnetic  
 c)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$  r) Paramagnetic  
 d)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  s) optical isomers

92. Match the following:

List-I

List-II

- (A)  $[\text{CoF}_6]^{3-}$  (p) High spin complex  
 (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (q) Low spin complex  
 (C)  $[\text{Co}(\text{en})_3]^{3+}$  (r) Outer orbital complex  
 (D)  $[\text{Cr}(\text{CO})_6]$  (s) Inner orbital complex  
 (t) Paramagnetic

93. Match the following

List-I

List-II

- (A)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (p) Dipole Moment  
 (B)  $\text{K}_3[\text{Cr}(\text{OX})_3]$  (q) Polarimeter  
 (C)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (r) Precipitation with  $\text{AgNO}_3$   
 (D)  $[\text{Co}(\text{en})_2\text{Cl}_2]$  (s) Cation exchange Resin  
 (t) Anion exchange Resin

94. Match the following

List-I

List-II

- (A) Wilkinson catalyst (p) +1 O.S.  
 (B) deoxy haemoglobin (q) +2 O.S.  
 (C) Brown Ring complex (r) Coordination number 4  
 (D) Vaska's complex (s) Coordination number 6  
 (t) Neutral complex

95. Match the following

Column-I

Column-II

- A)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  p) Optical isomerism  
 B)  $[\text{Co}(\text{en})_3]\text{Cl}_2$  q) Ionization isomerism  
 C)  $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$  r) Coordination isomerism  
 D)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  s) Geometrical isomerism

## STATEMENT QUESTIONS

(A) Statement - 1 is True, Statement - 2 is True; Statement - 2 is a correct explanation for Statement - 1.

(B) Statement - 1 is True, Statement - 2 is True; Statement - 2 is NOT a correct explanation for Statement - 1.

(C) Statement - 1 is True, Statement - 2 is False.

(D) Statement - 1 is False, Statement - 2 is True.

96. Statement-1:  $\text{Co}(\text{CO})_4$  is not stable but  $[\text{Co}(\text{CO})_4]^-$  is stable.

Statement-2:  $[\text{Co}(\text{CO})_4]^-$  obeys EAN rule

97. Statement-1:  $[\text{W}(\text{CO})_6]$  obeys EAN rule as it attains  $x_e$  configuration.

Statement-2: It is stable because it attains  $Rn$  configuration.

98. Statement-1: The  $[\text{Ni}(\text{en})_3]\text{Cl}_2$  has lower stability than  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  because  
 Statement-2: In  $[\text{Ni}(\text{en})_3]\text{Cl}_2$ , the geometry of Ni is octahedral.

## INTEGER TYPE QUESTIONS

99. The oxide formed in the maximum oxidation state is  $\text{ZrO}_x$ .  $x$  is
100. How many of the following cannot displace  $\text{H}_2$  from dil. HCl?  
 Cu, Zn, Ni, Fe, Ag, Au, Pt, Hg, Cd



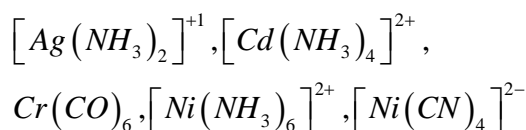
101. How many of the following reactions cannot occur ?

- (1)  $Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow$
- (2)  $Cu + 2HCl \rightarrow CuCl_2 + H_2 \uparrow$
- (3)  $Cu + ZnSO_4 \rightarrow CuSO_4 + Zn \downarrow$
- (4)  $Zn + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2Ag \downarrow$
- (5)  $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag \downarrow$
- (6)  $Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow$

102. The number of transition metals in the alloy Alnico is

103. The secondary valency in  $[Co(EDTA)]^{2-}$  is

104. How many of the following are diamagnetic ?



105. The number of isomers possible for  $[Pt(Cl)(Br)(NH_3)(py)]$  is

106. The number of oxygen atoms involved in bonding in the coordination sphere of



107. How many number of unpaired electrons present in  $[Cr(en)_3]^{+2}$  ?

108. How many geometrical isomers are possible for  $[Pt(NO_2)(NH_3)(NH_2OH)(Py)]^{+2}$  ?

109. How many stereoisomers are possible for  $[Pt(Br)(Cl)(NH_3)_2]$  ?

110. Dimethyl glyoxime forms a square planar complex with  $Ni^{+2}$ . This complex contain how many number of unpaired electrons?

111. How many number of d-electrons are present in  $[Co(NH_3)_5CO_3]ClO_4$  ?

112. A compound of metal ion  $M^{x+}$  ( $Z = 24$ ) has a spin only magnetic moment of  $\sqrt{15}$  B.M. The number of unpaired electrons in the compound are

113. A compound of vanadium has a magnetic moment ( $\mu$ ) of 1.73BM. If the vanadium ion in the compound is present as  $V^{x+}$ , then, the value of x is ? \_\_\_

114. Number of outer most 'd' electrons in Rhodium are

115. The sum of ns and (n-1)d electrons in Tc are

116. How many statements given below are correct ?

i) Pyrolusite on fusion with  $KNO_2$  in  $NaOH$  gives  $K_2MnO_4$

ii) Potassium manganate ( $K_2MnO_4$ ) on electrolytic oxidation gives  $KMnO_4$

iii) Potassium manganate ( $K_2MnO_4$ ) is formed, when formaldehyde reacts with potassium permanganate in acidic medium

iv) Potassium manganate ( $K_2MnO_4$ ) is formed, when potassium permanganate is moderately heated with potassium hydroxide.

117. Number of correct statements among the following are

i) Ferrous sulphate is used for making blue black ink.

ii) Ferrous sulphate is a strong reducing agent

iii) Hydrated ferrous sulphate is a green crystalline compound

iv) The aqueous ferrous sulphate is slightly acidic due to hydrolysis

118. How many of the following are correct about the stability of oxidation states of manganese?

i)  $Mn(II) > Mn(VII)$  – (acidic solution)

ii)  $Mn(II) < Mn(IV)$  – (alkaline solution)

iii)  $Mn(VI) > Mn(IV)$  – (acidic solution)

iv)  $Mn(VI) > Mn(VII)$  – (strong alkaline solution)

## LEVEL-V

## KEY

## SINGLE ANSWER

- 01) A 02) D 03) D 04) D 05) B  
 06) C 07) C 08) B 09) C 10) B  
 11) C 12) C 13) B 14) C 15) C  
 16) A 17) B 18) A 19) A 20) A  
 21) A 22) B 23) D 24) A 25) C  
 26) D 27) C 28) B 29) D 30) B  
 31) D 32) A 33) C 34) A 35) B  
 36) A 37) A 38) B 39) C 40) B  
 41) D 42) B 43) D 44) D

## MULTIPLE ANSWER

- 45) A,D 46) A,C 47) A,C 48) B,D  
 49) A,B,C 50) B,C,D 51) C,D  
 52) A,B,C 53) A,B,C,D 54) A,B,D  
 55) A,B 56) A,B,D 57) A,C,D 58) B,C,D  
 59) A,D 60) B,C 61) A,B 62) A,B,D  
 63) A,B,C,D 64) A,B,C 65) A,B,C,D  
 66) A,D 67) A,B,C,D 68) B,C,D  
 69) B,C,D 70) B,C,D 71) B, D  
 72) C 73) A,D 74) A,B,D

## COMPREHENSION TYPE

## Passage-I

- 75) D 76) C 77) D

## Passage-II

- 78) C 79) B 80) A

## Passage-III

- 81) B 82) C 83) D

## MATRIX MATCHING TYPE

- 84) a - p, q; b - p, q; c - p, q, r; d - p, s  
 85) A: p; B: p, q; C: r, t; D: r, s  
 86) A-q, s B-q, C-p D-r  
 87) A-r B-q, t C-p, D-s  
 88) A-p, q B-p, s C-q, D-q, r  
 89) A-q, B-p, C-s, D-r  
 90) A-q, B-p, C-r, s, D-p  
 91) A-p, r, B-p, q, C-r, D-r  
 92) A-p, r, t, B-p, r, t C-q, s, D-q, s  
 93) A-p; B-q, t; C-p, r, s; D-p, q

- 94) A - p, r, t; B - q, s, t; C - p, s; D - p, r, t  
 95) A - s; B - p; C - p, q, s; D - r

## STATEMENT TYPE

- 96) A 97) D 98) D

## INTEGER TYPE

- 99) 2 100) 5 101) 2 102) 2  
 103) 6 104) 4 105) 3 106) 4 107) 2  
 108) 3 109) 2 110) 0 111) 6 112) 3  
 113) 4 114) 8 115) 7 116) 3 117) 4  
 118) 3

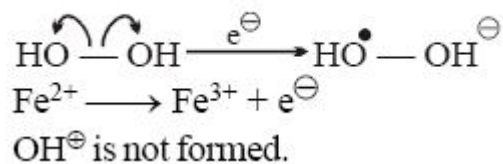
## LEVEL - V

## HINTS

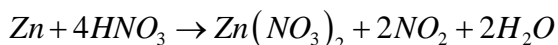
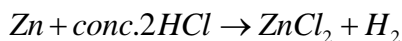
2. W belongs to VI B group. It has high MP. It has greater metal - metal bond strength.
- 3.
4. FCC lattice. One plane slides over another. effective M - M bond strength
5.  $Zn, 3d^{10}, 4s^2$ . Weak metal-metal bond. Purified by distillation.
20.  $F^-$  is a weak field ligand.
21.  $en$  is a strong field ligand.
22.  $Ti^{3+} : 3d^1$
23.  $dsp^3$ , coordination number : 5
24.  $K_D = \frac{1}{K_F} = \frac{1}{2 \times 10^3} = 5 \times 10^{-2}$
25.  $H_2O$  is 'aqua' and not 'aquo'
26. Organic amine and for  $NH_3$  - ammine. Note the spelling
27. They have  $d^0$  configuration.
28.  $d^6$ , 4 unpaired electrons, high spin complex.
29.  $F^-$  is a weak field ligand,  $NH_3$  is strong field ligand.
30. It has both  $\sigma$  and  $\pi$  bonding

31.

$\text{FeSO}_4 + \text{HO}-\text{OH}$  is Fenton's reagents



32. SOL :  $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$



33 :  $[\text{M}(\text{aa})_2\text{b}_2]$  Type. Cis isomer occurs in two enantiomeric forms.

34:  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   $\text{Cr}^{3+} - 4s^03d^3$   
 $[\text{Mn}(\text{H}_2\text{O})_6]^{4+}$   $\text{Mn}^{4+} - 4s^03d^3$   
 Same no. of unpaired electrons.

35.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$

Hence green coloured powder blown in the air is  $\text{Cr}_2\text{O}_3$

36. Misch metal is 40.5% Ce, 44% La and Nd, 5% Fe and others.

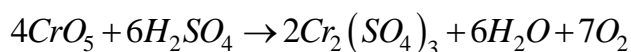
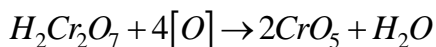
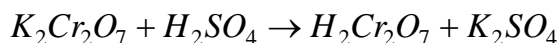
37.  $\text{CrO}_4^{2-}$  is colour due to charge transfer.

38.  $\text{Au}^{3+}$  C.N. 4,  $\text{Pt}^{4+}$  C.N. 6

39.  $\Delta G$  of AgO is very close to positive value, therefore thermally less stable.

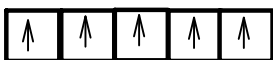
40.  $\text{Cr}^{6+}$  in basic medium exist as  $\text{CrO}_4^{2-}$ , colour yellow.

41.  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + [\text{O}]$

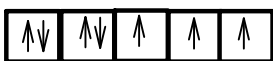
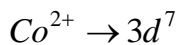


$\text{CrO}_5$  is blue in colour.

42.  $\text{Fe}^{3+} \rightarrow 3d^5$



5 unpaired electrons



3 unpaired electrons

43. In  $\text{HN}_3$  the O.S. of nitrogen is  $-\frac{1}{3}$ , and hydrogen +1.

44. 1) In hydrogen atom  $3s, 3p, 3d$  has same energy

2)  $dx^2 - y^2$  the electron density is along  $xy$  plane

3) Cr is a d-block element, the differentiating electron enters  $(n-1)$  d orbital.

4) the three Quantum Numbers n, l, m are given by schrodinger wave equation.

**MULTIPLE ANSWER**

45.  $\text{Mn}^{+7}$  and  $\text{Cr}^{+6}$  can oxidize  $\text{I}^-$  to  $\text{I}_2$ .

46. Cu cannot displace as it has higher  $E_{SRP}^0$  (+ve) value.

47.  $\text{TiCl}_4$  is covalent. Metallic bond strength is weak in Hg.

48. Highest oxidation state. Oxides are acidic

49. Transition metal compounds that are covalent undergo hydrolysis.  $\text{CaCl}_2$  is ionic and no hydrolysis.

50. Resistant to oxidation.

53. All are diamagnetic.

59. Water of hydration exists in ionic compounds.  $d_{x^2-y^2}$  orbitals is used in  $dsp^2$  hybridization.

60.  $\text{Ni}^{2+}(d^8)$  or  $\text{Cr}^{3+}(d^3)$  form octahedral complexes whether the ligand is strong or weak field ligand, they have same magnetic moment. They are all colored.

61. A & B :  $3d^1$  configuration.

62.  $[\text{NiCl}_4]^{2-}$  is tetrahedral

63. (A):  $\text{Ni}(\text{O}) : 3d^{10}$ ; (B):  $\text{Fe}^{3+} : 3d^5$

(C)  $\text{Mn}^{2+} : 3d^5$ ; (D)  $\text{Co}^{2+} : 3d^7$ . All have  $sp^3$  hybridization.

64. D is paramagnetic (2 unpaired  $e^-$ ).
65. All are strong field ligands.
66. B and D are colored due to charge transfer transition.
67. small ligands, can act as bridging ligands.
68. They are ambidentate ligands.
69. In 'A', for any position of b gives identical isomer.
70. A is a trans isomer. Others are cis isomers.
71. (1) and (3) are symmetrical not optically active. (5) has  $Ti^{4+} (d^0)$  configuration.
72.  $CN^- > F^-$  (Field higher the charge on the metal greater the stability. 6 coordinate complexes are more stable than four coordinated one.
73. (A) is correct answer  
(B) is incorrect because  $\pi$  donor ligand forms  $\pi$  bond and C is incorrect.  
(D) is correct answer.
74. (A) is correct because strong field ligand cause more splitting  
(B) is correct because  $\Delta_0$  increases with increasing oxidation number of metal.  
(C) is incorrect because  $\Delta_0$  is independent of charge on ligand.  
(D) is correct because  $\Delta_0$  increases down the group.

### COMPREHENSION TYPE

#### Passage-I

75. High positive  $E_{SRP}^0$  value.
76. Positive  $E_{SRP}^0$  value.
77. More positive  $E_{SRP}^0$  value.

#### Passage-II

78. Since 'X' gives pale yellow ppt and 'Y' gives yellow ppt. Hence, in 'X' Br is ionisable while in 'Y' I is ionisable.  
 $X = [Cr(NH_3)_4Br]Br$   
 $Y = [Cr(NH_3)_4Br_2]I$   
 Hence choice (B) is correct while a, c, and d are ruled out.

79. X and Y are actually ionisation isomers  
Hence, Choice (C) is correct, while (A) and (B) are incorrect.
80.  $[Cr(NH_3)_4IBr]^+$  and  $[Cr(NH_3)_4Br_2]^+$  are  $Ma_4bc$  type and  $Ma_4b_2$  type respectively.  
Both show geometrical isomerism but each isomer is optically inactive.  
Hence a, b and c are incorrect.

### MATRIX MATCHING TYPE

94. Vaska's complex is Trans-  
 $[IrCl(CO)(PPh_3)_2]$

### STATEMENT TYPE

96.  $[Co(CO)_4]^- : 27 + 4 \times 2 + 1 = 36e^-$
97.  $[W(CO)_6] : 74 + 6 \times 2 = 86 (Rn)$
98. The chelates are more stable. Statement-1 is false.

### INTEGER TYPE

99.  $ZrO_2$
100. They have  $E_{SRP}^0 = +ve$ ,  $Cu, Ag, Au, Pt, Hg$
101. 2 and 3. Refer the electro chemical series.
102. Ni and Co. is two
103. EDTA: Tetravalent hexadentate ligand is 6
104.  $[Ni(NH_3)_6]^{2+}$  is paramagnetic.
105. Square planar complex
106. The four tetraacetate oxygen atoms are involved in coordination.
107.  $G^{2+} : 3d^4 : \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\times} \boxed{\times} \boxed{\times} \boxed{\times} \boxed{\times}$
110.  $Ni^{2+} : 3d^8, dsp^2, \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\times} \boxed{\times} \boxed{\times} \boxed{\times}$
111.  $x + 0 - 2 - 1 = 0, x = +3, Co^{3+} : 3d^6$

112.  $\mu = \sqrt{n(n+2)}$ , where  $n$  = no. of unpaired electrons.
113. Vanadium.E.C =  $3d^3 4s^2$   
and +4 O.S.  $V^{4+} = 3d^1$
114. Rh E.C =  $4d^8 5s^1$
115. Tc E.C =  $4d^6 5s^1$
116. Conceptual
117. Conceptual
118. Mn in acid media changes from +7 to +2, in neutral media +7 to +4, in strong alkaline media +7 to +6.

LEVEL - VI

SINGLE ANSWER QUESTIONS

- Which one of the forms a metallide ( $M^-$ ) easily ?  
(A) Na (B) Au (C) Ti (D) Zn
- The pair that can exhibit more stable +4 oxidation state is  
(A) Fe, Ni (B) Ag, Au  
(C) Pt, Pd (D) Cd, Hg
- Which of the following electronic configurations is associated with the highest stable oxidation state  
A)  $[Ar]3d^1 4s^2$  B)  $[Ar]3d^5 4s^1$   
C)  $[Ar]3d^5 4s^2$  D)  $[Ar]3d^6 4s^2$
- The alloy that is used for making permanent magnet is  
(A) Al, Ni, Co (B) Pb, Sn, Bi  
(C) Fe, Mn, Cu (D) Cu, Au, Hg
- Which one of the following pairs is colored ?  
(A)  $TiCl_3, VCl_2$  (B)  $TiCl_4, Cu_2Cl_2$   
(C)  $Hg_2Cl_2, anhydrous CuSO_4$   
(D)  $AgNO_3, Cd(NO_3)_2$

- The metal that has the least melting point among the following is  
(A) Mn (B) Fe (C) Cr (D) W
- The metal that forms interstitial nitride is  
(A) Mg (B) Ca (C) Cr (D) Li
- Which of the following is paramagnetic  
A)  $[V(Co)_6]$  B)  $Ir_4(Co)_{12}$   
C)  $[Cr(Co)_6]$  D)  $Fe_2(Co)_9$
- The correct statement about iron includes  
I)  $Fe_3O_4$  is a mixed oxide of iron  
II) that the iron shows +2 oxidation state with six electrons in the unfilled 3d orbitals  
III) the common oxidation state iron is +3 with five unpaired electrons in the 3d orbitals  
A) I, II, III B) I, II  
C) II, III D) I only
- Which is highly colored due to inter valence electron transfer transition ?  
(A) FeO (B)  $Cr_2O_3$   
(C)  $Fe_3O_4$  (D) CuO
- The transition metals exhibit higher enthalpies of atomisation due to  
A) their ability to show variable oxidation states  
B) the presence of incompletely filled d-subshell  
C) their ability to exist in the solid state with unpaired electrons  
D) Strongly interatomic interaction arises because of having large number of unpaired electrons in their atoms
- Which of the following statement are correct about Zn, Cd and Hg ?  
I) they exhibit high enthalpies of atomisation as the d-subshell is full  
II) Zn and Cd do not show variable oxidation states while Hg shows +1 and +II  
III) Compound of Zn, Cd and Hg are paramagnetic in nature  
IV) Zn, Cd and Hg are called soft metals  
A) I, II, III B) I, II  
C) II, IV D) IV only

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- 13 In the calculation of magnetic moment, the orbital magnetic moment contribution is negligible for the following ion  
 A)  $Pt^{+2}$                       B)  $Mo^{+2}$   
 C)  $Pd^{+2}$                       (D)  $Ti^{+3}$
- 14 The acidic character of manganese is correct  
 A)  $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$   
 B)  $MnO < MnO_2 < Mn_2O_3 > Mn_2O_7$   
 C)  $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$   
 D)  $Mn_2O_7 < Mn_2O_3 < MnO_2 < MnO$
- 15 Among the following series of transition metal ions, the one where all metal ions have  $3d^2$  electronic configuration is  
 A)  $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$   
 B)  $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{5+}$   
 C)  $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$   
 D)  $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$
- 16 Which of the following is not responsible for the catalytic activity of transition metals and their compounds?  
 A) Transition metals have large surface area  
 B) Transition metals show variable oxidation states  
 C) Transition metals form intermediate complexes  
 D) Transition metals are coloured
- 17 The melting points and the boiling points of the transition elements are higher than the corresponding s-block elements. This is because  
 A) Transition metals have smaller size  
 B) Of the presence of one or more unpaired electrons contribution to higher inter atomic forces on account of covalent bond  
 C) of strong metallic bond due to small size and higher ionization energy  
 D) of the presence of vacant d-orbitals
- 18 A compound of metal ion  $M^{x+}$  ( $z = 25$ ) has a spin only magnetic moment of  $\sqrt{15}$  B.M. The positive O.S. of the metal is  
 A) 2                                      B) 3  
 C) 4                                      D) 5
- 19 Amongst  
 $TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2$  and  $NiCl_4^{2-}$ , the colourless species are  
 A)  $CoF_6^{3-}$  and  $NiCl_4^{2-}$   
 B)  $TiF_6^{2-}$  and  $CoF_6^{3-}$   
 C)  $TiF_6^{2-}$  and  $Cu_2Cl_2$   
 D)  $NiCl_4^{2-}$  and  $Cu_2Cl_2$
- 20 The magnetic moment of two ions  $M^{x+}$  and  $M^{y+}$  of the element  $M$  ( $Z=26$ ) is found to be 5.916 B.M. If  $x > y$ , then which of the following statement is correct?  
 A)  $M^{y+}$  is more stable than  $M^{x+}$   
 B)  $M^{y+}$  is less stable than  $M^{x+}$   
 C) Both are equally stable  
 D) Can not be predicated
- 21 The magnetic moment of ion is close to  $36 \times 10^{-24}$  joule/Tesla. The number of unpaired electrons of the ion are  
 A) 4                      B) 2                      C) 1                      D) 3
- 22 Which of the following compounds are coloured substances?  
 I –  $Ag_2CO_3$                       II –  $Ag_3PO_4$   
 III –  $AgI$                               IV –  $Ag_2S$   
 A) Only III  
 B) only III and IV  
 C) only I, III and IV  
 D) all the four
23. In Zieses salt, the C = C bond length is  
 Note:  $\left\{ \begin{array}{l} C-C \text{ bond length in ethane is } 1.54 \text{ \AA} \\ C=C \text{ bond length in ethene is } 1.34 \text{ \AA} \\ C\equiv C \text{ bond length in ethyne is } 1.20 \text{ \AA} \end{array} \right\}$   
 (A)  $1.37 \text{ \AA}$                       (B)  $1.19 \text{ \AA}$   
 (C)  $1.87 \text{ \AA}$                       (D)  $1.34 \text{ \AA}$

24. Which one of the following can get oxidized easily ?

- (A)  $[Co(NH_3)_6]^{3+}$  (B)  $[Co(NH_3)_6]^{2+}$   
 (C)  $Fe(CO)_5$  (D)  $Cr(CO)_6$

25. The magnetic moments (BM) of the complexes  $[Ni(H_2O)_6]^{2+}$  and  $[Ni(NH_3)_6]^{2+}$  are respectively

- (A) 1.73, 2.84 (B) 0, 2.84  
 (C) 2.84, 0 (D) 2.84, 2.84

26. The number of electrons in  $t_{2g}$  orbitals in

$K_4[Fe(CN)_6]$  is

- (A) 2 (B) 3 (C) 6 (D) 5

27. The CFSE of  $[Mn(H_2O)_6]^{2+}$  is

- (A)  $-1.2\Delta_\theta$  (B)  $-1.9\Delta_\theta$   
 (C) 0 (D)  $-2.4\Delta_\theta$

28. The theoretical percentage weight loss when  $[Cr(H_2O)_4Cl_2] \cdot 2H_2O$  is kept over conc.  $H_2SO_4$  in a closed desicator is

- (A) 13.50% (B) 6.75% (C) 18% (D) 36%

29. 0.2435g of a complex gave 0.2870g of AgCl when treated with a excess  $AgNO_3$  solution.

The complex is

- (A)  $[Cr(NH_3)_4Cl_2]Cl$   
 (B)  $[Cr(NH_3)_5Cl]Cl_2$   
 (C)  $[Cr(NH_3)_3Cl_3]$   
 (D)  $[Cr(NH_3)_6]Cl_3$

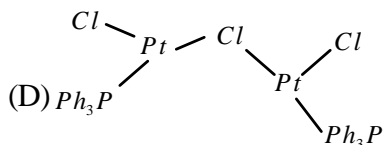
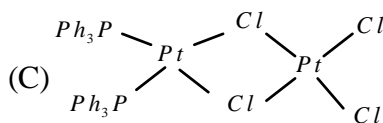
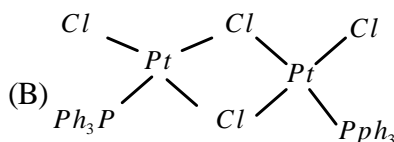
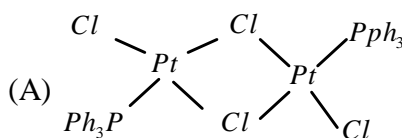
30.  $[Fe(CN)_5(CO)]^{3-}$  IUPAC name is

- (A) pentacyanocarbonylferrate (II)  
 (B) carbonylpentacyanidoferrate (II)  
 (C) pentacyanocarbonyliron(III)  
 (D) carbonylpentacyanoiron (III)

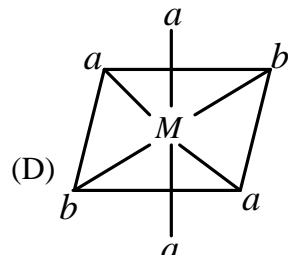
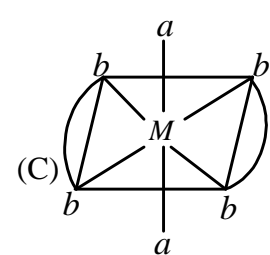
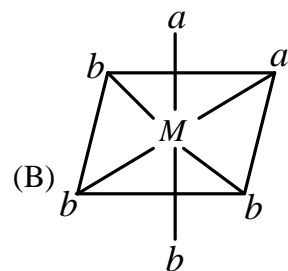
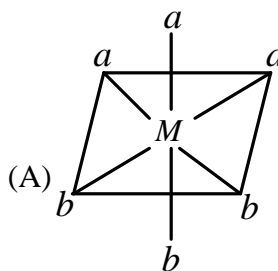
31. The IUPAC name of ferrocene is

- (A) bis ( $\mu^5$  - cyclopentadienyl) iron (O)  
 (B) bis ( $\eta^{10}$  -cyclopentadienyl)iron (O)  
 (C) bis ( $\eta^5$  - cyclopentadienyl)iron (II)  
 (D) bis ( $\mu^{10}$  - cyclopentadienyl)iron (II)

32. Cis di -  $\mu$  - chloro bis [chloro(triphenyl phosphine) platinum (II)] is



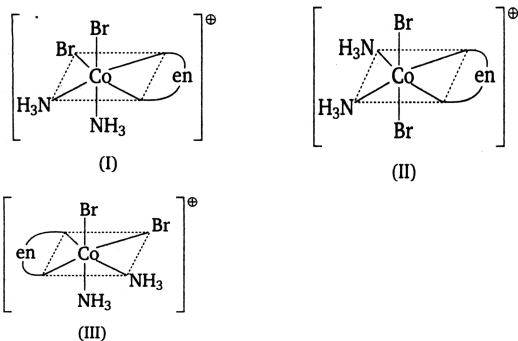
33. Which one of the following represents a Cis isomer ?



34. The total number of possible geometrical isomers in  $Mabcdef$  where a to f are different monodentate ligands is given by  
(A)  $4C_2$  (B)  $5C_1$  (C)  $3C_2$  (D)  $6C_2$
35. The complex formed by  $Pt^{2+}$  with diethylenetriamine (dien) and chlorido ligand is given by  
(A)  $[Pt(dien)]^{2+}$   
(B)  $[Pt(dien)Cl_2]^{2+}$   
(C)  $[Pt(dien)Cl]^{1+}$   
(D)  $[Pt(dien)Cl]^{2+}$
36. Which one of the following give an acid when passed through cation exchange resin ( $RSO_3H$ )?  
(A)  $K_4[Fe(CN)_6]$   
(B)  $K_3[Al(C_2O_4)_3]$   
(C)  $[Co(NH_3)_6]Cl_3$   
(D)  $[Cr(CO)_6]$
37. Which one of the following give a base when passed through anion exchange resin  $[R_4N^+]OH^-$ ?  
(A)  $K_4[Fe(CN)_6]$  (B)  $[Co(en)_3]Cl_3$   
(C)  $[Co(NH_3)_6]Cl_3$  (D)  $[Fe(H_2O)_6]SO_4$
38. Which one of the following does not form a chelate with oxalate ion by reacting in aqueous solution?  
(A)  $cis-[Co(NH_3)_4Br_2]^{+1}$   
(B)  $cis-[Co(NH_3)_4Cl_2]^+$   
(C)  $cis-[Co(en)_2Cl_2]^{+1}$   
(D)  $trans-[Co(en)_2Cl_2]^{+1}$
39. The neutral and positive charged species that can coordinate to a metal atom is  
(A)  $Cl^-$  (B)  $NH_3$  (C)  $CO$  (D)  $NO$
40. Which of the following pair of compounds is expected to exhibit same colour in aqueous solution?  
(A)  $FeCl_2, CuCl_2$  (B)  $VOCl_2, CuCl_2$   
(C)  $VOCl_2, FeCl_2$  (D)  $FeCl_2, MnCl_2$
41. The oxidation state of Mo in its oxido-complex species  $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$  is  
(A) +2 (B) +3 (C) +4 (D) +5
42. The donor sites of  $(EDTA)^{4-}$  are  
(A) O atoms only  
(B) N atoms only  
(C) Two N atoms and four O atoms  
(D) Three N atoms and three O atoms
43. In nitroprusside ion, the iron and NO exist as  $Fe^{2+}$  and  $NO^+$  rather than  $Fe^{3+}$  and  $NO$ . These forms can be differentiated by  
(A) Estimating the concentration of iron  
(B) Measuring the concentration of  $CN^-$   
(C) Measuring the solid state magnetic moment  
(D) Thermally decomposing the compound
44. In the isoelectronic series of metal carbonyl, the CO bond strength is expected to increase in the order  
(A)  $[Mn(CO)_6]^+ < [Cr(CO)_6] < [V(CO)_6]^-$   
(B)  $[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$   
(C)  $[V(CO)_6]^- < [Mn(CO)_6]^+ < [Cr(CO)_6]$   
(D)  $[Cr(CO)_6] < [Mn(CO)_6]^+ < [V(CO)_6]^-$
45. The magnetic moments of complexes given below are in the order  
I)  $[Ni(CO)_4]$  II)  $[Mn(CN)_6]^{4-}$   
III)  $[Cr(NH_3)_6]^{3+}$  IV)  $[CoF_6]^{3-}$   
(A) I > II > III > IV (B) I < II < III < IV  
(C) IV > II > I > III (D) IV < II < I < III

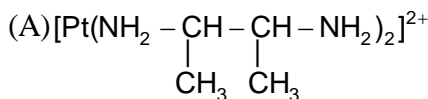


46. Three arrangements are shown for the complex  $[\text{CoBr}_2(\text{NH}_3)_2(\text{en})]^+$ . Which one is wrong statement?



- (A) I and II are geometrical isomer  
 (B) II and III are optical isomers  
 (C) I and III are optical isomers  
 (D) II and III are geometrical isomers
47. Among the following, which is not the  $\pi$ -bonded organometallic compound?
- (A)  $(\text{CH}_3)_4\text{Sn}$   
 (B)  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$   
 (C)  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$   
 (D)  $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$
48. Complex compound(s) of which optical activity does not depend upon the orientation of the ligands around metal cation
- i)  $[\text{CoCl}_3(\text{NH}_3)_3]$   
 ii)  $[\text{Co}(\text{en})_3]\text{Cl}_3$   
 iii)  $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]^-$   
 iv)  $[\text{CrCl}_2(\text{NH}_3)_2(\text{en})]^+$
- (A) II, III and IV (B) I, II and IV  
 (C) II and IV (D) Only II
49. The total possible coordination isomers for the following compounds respectively are  $[\text{Co}(\text{en})_3][\text{Cr}(\text{C}_2\text{O}_4)_3]$ ,  $[\text{Cu}(\text{NH}_3)_4][\text{CuCl}_4]$ ,  $[\text{Ni}(\text{en})_3][\text{Co}(\text{NO}_2)_6]$
- (A) 4,4,4 (B) 2,2,2 (C) 2,2,4 (D) 4,2,4

50. Which of the following can show geometrical isomerism?



- (B)  $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$   
 (C) Both a and b  
 (D) None of these

51. The complex which does not obey EAN rule is

- (A)  $[\text{Fe}(\text{CO})_5]^0$   
 (B)  $[\text{Cr}(\text{CO})_3(\text{NO})_2]^0$   
 (C)  $[\text{Fe}(\text{CO})_3(\text{NO})_2]^0$   
 (D)  $[\text{Fe}(\text{CO})_2(\text{NO})_2]^0$

MULTIPLE ANSWER QUESTIONS

52. The correct stability order of the oxidation states is

- (A)  $\text{Mn}^{2+} > \text{Fe}^{2+}$  (B)  $\text{Ni}^{3+} > \text{Fe}^{3+}$   
 (C)  $\text{Fe}^{3+} > \text{Ni}^{3+}$  (D)  $\text{Co}^{2+} > \text{Ni}^{2+}$

53. The compounds that cannot exist

- (A)  $\text{WO}_4^-$  (B)  $\text{NbCl}_6$   
 (C)  $\text{HfCl}_4$  (D)  $\text{ZrO}_2$

54. Which of the following oxides are amphoteric?

- (A)  $\text{V}^{5+}$  (B)  $\text{Zn}^{2+}$  (C)  $\text{Fe}^{2+}$  (D)  $\text{Fe}^{3+}$

55. Which of the following are nonferrous alloys?

- (A) Brass (B) Bronze  
 (C) Chromium Steel (D) German Silver

56. In the formation of interstitial compounds by transition metals, identify the correct statements

- (A) Melting points of interstitial carbides are more than those of respective pure metals  
 (B) Densities of interstitial hydrides are less than those respective pure metals  
 (C) Electrical conductivity is lost in the formation of interstitial compound from a metal  
 (D) Interstitial borides are very hard in nature and less reactive than the parent metals

57. Complex ions  $[\text{NiCl}_6]^{4-}$ ,  $[\text{Ni}(\text{CN})_6]^{4-}$  similar in their given properties :
- (A) oxidation state, geometry  
 (B) co-ordination number, EAN  
 (C) Magnetic moment, geometry  
 (D) stability, colour
58. Select correct statement(s) regarding given complexes
- (A)  $[\text{Fe}(\text{CO})_5]$ , the orbitals used for hybridization in Fe atom are s,  $p_x, p_y, p_z, d_{z^2}$
- (B)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , the orbitals used for hybridization on Pt atom are s,  $p_x, p_y, d_{x^2-y^2}$  and it is low spin complex
- (C)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , the orbitals used for hybridization in Cr atom are s,  $p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$  and it is high spin complex
- (D)  $[\text{Ni}(\text{CO})_4]$ , the orbitals used for hybridization in Ni atom are s,  $p_x, p_y, p_z$  and it is low spin complex
59. Complex compound  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4]\text{Cl}$  exhibit
- (A) ionization isomerism  
 (B) Geometrical isomerism  
 (C) optical isomerism  
 (D) linkage isomerism
60. Which of the following compound has/have effective atomic number equal to the atomic number of a noble gas
- A)  $\text{K}[\text{Co}(\text{CO})_4]$  (B)  $\text{K}_2[\text{Fe}(\text{CO})_4]$   
 C)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  (D)  $[\text{CoCl}_3(\text{H}_2\text{O})_3]$
61.  $\text{K}_2[\text{Ni}(\text{CN})_4] \xrightarrow[\text{NH}_3]{\text{K in liq}} \text{'X'}$  regarding this reaction correct statement is/are
- (A) 'X' is  $\text{K}_4[\text{Ni}(\text{CN})_4]$   
 (B) The oxidation state of Ni changed +2 to zero  
 (C) The structure of 'X' is tetrahedral  
 (D)  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar complex
62. Which one of the following statement(s) is/ are false
- (A) Weak ligands like  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{OH}^-$  usually form low spin complexes  
 (B) Strong ligand like  $\text{CN}^-$  and  $\text{NO}_2^-$ , generally form high spin complexes  
 (C)  $[\text{FeF}_6]^{3-}$  is high spin complex  
 (D)  $[\text{Ni}(\text{CO})_4]$  is high spin complex
63. Which of the following is correct about tetraammine dithiocyanato-s cobalt (III) tris (oxalato) cobaltate(III)
- A) Formula of the complex is  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4][\text{Co}(\text{ox})_3]$   
 B) It is a chelating complex and show linkage isomerism  
 C) It shows optical isomerism  
 D) It shows geometrical isomerism
64. Select the correct statement :
- A) Chelation effect is maximum for five and six membered rings  
 B) Greater the charge on the central metal cation, greater, the value of  $\Delta$  (CFSE)  
 C) In complex ion  $[\text{CoF}_6]^{3-}$ ,  $\text{F}^-$  is a weak field ligand so that  $\Delta_{\text{oct}} < p$  (Pairing energy) and it is low spin complex  
 D)  $[\text{CoCl}_2(\text{NH}_3)_2(\text{en})]^\oplus$  complex ion will have four different isomers

65. Which of the following obey  $18e^-$  rule ?

- (A)  $Cr(CO)_6$  (B)  $Ni(CO)_4$   
 (C)  $Cr(C_6H_6)_2$  (D)  $Fe(C_5H_5)_2$

66. Which of the following obey EAN rule ?

- (A)  $[Co(NH_3)_6]^{3+}$  (B)  $Cr(CO)_6$   
 (C)  $[V(CO)_6]^-$  (D)  $[Co(CO)_4]^-$

67. Which of the following are four coordinated complexes?

- (A)  $Be(acac)_2$   
 (B)  $[Zn(EDTA)]^{2-}$   
 (C)  $[Pt(dien)Cl]^+$  (dien = diethylene triamine)  
 (D)  $[Pt(trien)]^{2+}$  (trien = triethylene tetraamine)

68. In  $Ni^{2+}$  octahedral complexes, which of the following ligands do not pair up the electrons ?

- (A)  $NH_3$  (B)  $H_2O$  (C)  $en$  (D)  $dien$

69. The  $\pi$  - complexes are

- (A) Ferrocene  
 (B) Zeises salt  
 (C) dibenzenechromium(0)  
 (D) Grignard Reagent

70. Which of the following exhibits optical activity ?

- (A) Cis -  $[Co(en)_2Cl_2]^+$   
 (B) trans -  $[Co(en)_2Cl_2]^+$   
 (C)  $K_3[Al(C_2O_4)_3]$   
 (D)  $[Co(NH_3)_4Cl_2]^+$

71. The optically active complexes are

- (A)  $[As(CH_3)(Cl)(Br)(I)]^+$   
 (B)  $[Pt(NH_3)(Py)(Cl)(Br)]$   
 (C)  $[Pt(gly)_2]$  (D)  $[Cr(en)_3]Cl_3$

72. Which is/are correct statement (s)?

- (A)  $[Ag(NH_3)_2]^+$  is linear with sp hybridised  $Ag^+$  ions  
 (B)  $NiCl_4^{2-}$ ,  $CrO_4^{2-}$  and  $MnO_4^-$  have tetrahedral geometry  
 (C)  $[Cu(NH_3)_4]^{2+}$ ,  $[Pt(NH_3)_4]^{2+}$  and  $[Ni(CN)_4]^{2-}$  have  $dsp^2$  hybridisation of the metal ion  
 (D)  $Fe(CO)_5$  has trigonal bipyramidal structure with  $d_{z^2} sp^3$  hybridised ion

73. Which of the following is/are correct relations(s)?

- (A)  $\Delta_o = \frac{4}{9}\Delta_t$  (B)  $\Delta_t = \frac{4}{9}\Delta_o$   
 (C)  $\Delta_s = 1.3\Delta_o$  (D)  $\Delta_t = \frac{3}{7}\Delta_o$

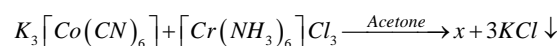
74. Which of the following is /are correct about Wilkinson's catalyst?

- (A) It is used as homogeneous catalyst for selective hydrogenation of organic molecule at room temperature and pressure  
 (B) It is tetrahedral complex  
 (C) It does not have unpaired electrons  
 (D) Its formula is  $TiCl_4 + Al(C_2H_5)_3$

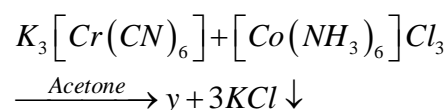
### COMPREHENSION QUESTIONS

#### Passage-I

I. (i)



(ii)



The solution was filtered.

$x$  and  $y$  are obtained after evaporation of the solvent from the filtrate.

75.  $x$  and  $y$  are

- (A) Linkage isomers  
 (B) Geometrical Isomers  
 (C) Coordinate Isomers  
 (D) Positional Isomers.

76. When  $x$  is sent through cation exchange resin, the complex coming out in solution is

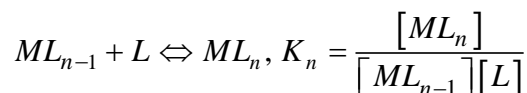
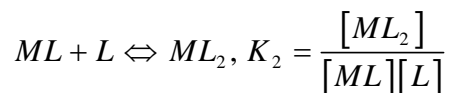
- (A)  $[Co(NH_3)_6]^{3+}$  (B)  $[Cr(NH_3)_6]^{3+}$   
 (C)  $[Co(CN)_6]^{3-}$  (D)  $[Cr(CN)_6]^{3-}$

77. When  $y$  is sent through anion exchange resin, then the complex eluted is

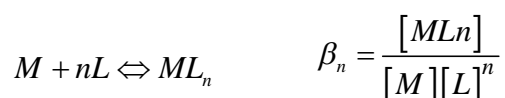
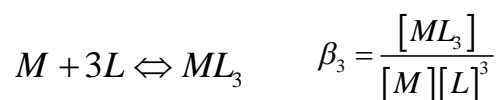
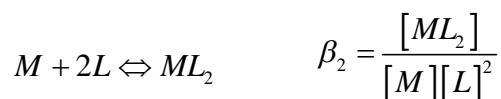
- (A)  $[Co(NH_3)_6]^{3+}$   
 (B)  $[Cr(NH_3)_6]^{3+}$   
 (C)  $[Co(CN)_6]^{3-}$   
 (D)  $[Cr(CN)_6]^{3-}$

### Passage-II

Consider the following complex equilibrium



$K_1, K_2, K_3$  are step wise stability constant



$\beta_1, \beta_2, \beta_3, \beta_n$  are called overall formation constants.

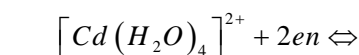
78.  $\prod_{i=1}^{i=n} K_i$  and  $\sum_{i=1}^{i=n} \log K_i$  are respectively

- (A)  $\beta_n$  and  $\log \beta_n$   
 (B)  $K_n$  and  $\log K_n$   
 (C)  $\beta_{n-1}$  and  $\log \beta_{n-1}$   
 (D)  $K_{n-1}$  and  $\log K_{n-1}$

79. Choose the correct order

- (A)  $K_3 > K_2 > K_1$  (B)  $K_3 = K_2 = K_1$   
 (C)  $K_1 > K_2 > K_3$  (D)  $K_1 = K_2 \neq K_3$

80. (1)  $[Cd(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+} + 4H_2O, \log \beta_1$



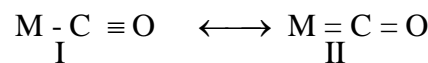
(2)  $[Cd(en)_2]^{2+} + 4H_2O, \log \beta_2$

$\log \beta_2 > \log \beta_1$ , is due to

- (A) Enthalpy change  
 (B) Entropy change  
 (C) Ring strain in the chelate  
 (D) Large change in  $\Delta_0$

### Passage-III

Bonding in metal carbonyls is represented by the end structures.



The contribution of I and II to the real structure depends upon the extent of  $\pi$  - back bonding. Both  $\sigma$  donation and  $\pi$  - back bonding are synergistic. The filled orbitals CO overlap with vacant metal d orbitals, which is called  $\sigma$  donation. The filled metal d orbitals overlap with  $\pi$  antibonding molecular orbital of CO, which is called  $\pi$  - back bonding.

81. Which one of the following has the highest C - O bond length ?

- (A)  $[Cr(CO)_6]$  (B)  $[Ti(CO)_6]^{2-}$   
 (C)  $[Mn(CO)_5]^+$  (D)  $[Fe(CO)_5]$

82. In which one of the following M - C bond length is the longest ?

- (A)  $Ti(C_2H_5)_4$  (B)  $Ni(CO)_4$   
 (C)  $Cr(CO)_6$  (D)  $[Fe(CN)_6]^{4-}$

83. The C - O bond order is maximum in

- (A)  $[Ti(CO)_6]^{2-}$  (B)  $[V(CO)_6]^-$   
 (C)  $[Mn(CO)_5]^+$  (D)  $Cr(CO)_6$

**Passage-IV**

According to crystal field theory d-orbitals split up in octahedral field into two sets.  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  have lower energy and  $d_{x^2-y^2}$  and  $d_{z^2}$  have higher energy. The difference in energy of these two sets of d-orbitals is called crystal field splitting energy denoted by  $\Delta_0$ .

In tetrahedral field  $d_{x^2-y^2}$  and  $d_{z^2}$  have lower energy whereas  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  have higher energy. The difference in energy is denoted  $\Delta_t$ .

$\Delta_0$  can be determined by measuring  $\lambda_{max}$  for absorption and converting into energy units.

$\Delta_0$  depends upon nature of metal ions as well as nature of ligands. The magnitude of  $\Delta_0$  also decides low energy levels are filled.

84. Which of the following is low spin due to strong field ligands?

- (A)  $d_{xy}^2 d_{yz}^2 d_{zx}^1$  (B)  $d_{xy}^1 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1 d_{z^2}^1$   
 (C)  $d_{xy}^2 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^1$  (D)  $d_{xy}^2 d_{yz}^1 d_{zx}^1 d_{x^2-y^2}^2$

85. Given the following data about absorption maxima of several complex ions, the correct order of  $\Delta_0$  for these ions is

Complexes	$\lambda_{max}$
$[Cr(H_2O)_6]^{3+}$	694 nm
$[Cr(NH_3)_6]^{3+}$	465 nm
$[CrCl_6]^{3-}$	758 nm

- (A)  $\Delta_0 [Cr(NH_3)_6]^{3+} > \Delta_0 [Cr(H_2O)_6]^{3+} > \Delta_0 [CrCl_6]^{3-}$   
 (B)  $\Delta_0 [Cr(NH_3)_6]^{3+} = \Delta_0 [Cr(H_2O)_6]^{3+} > \Delta_0 [CrCl_6]^{3-}$   
 (C)  $\Delta_0 [Cr(NH_3)_6]^{3+} < \Delta_0 [Cr(H_2O)_6]^{3+} < \Delta_0 [CrCl_6]^{3-}$   
 (D)  $\Delta_0 [Cr(H_2O)_6]^{3+} > \Delta_0 [CrCl_6]^{3-} > \Delta_0 [Cr(NH_3)_6]^{3+}$

86. Which one of the following has the highest magnetic moment ?

- (A)  $[CoF_6]^{3-}$  (B)  $[Ni(H_2O)_6]^{2+}$   
 (C)  $[Fe(CN)_6]^{3-}$  (D)  $[Cu(NH_3)_4]^{2+}$

**MATRIX MATCHING QUESTIONS**

87. Match the following:

Column - I Metals	Column - II Properties
(A) $Hf > Zr$	(p) density
(B) $Au > Ag$	(q) IE
(C) $Fe > Mn$	(r) MP
(D) $Cu > K$	(s) Higher nuclear charge
	(t) More positive $E_{SRP}^0$ value.

88. Match the following:

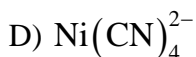
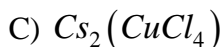
Column - I Compound	Column - II Characteristic
(A) $TiCl_4$	(p) Liquid at room temperature
(B) $CaCl_2$	(q) Has the highest MP among the compounds given
(C) $FeCl_3$	(r) Aqueous solution is acidic
(D) $ZnCl_2$	(s) Undergoes hydrolysis
	(t) Solid at room temperature

89. Match the following

Column - I [Pair of complex]	Column - II [Property which compounds is different in given(Pair)]
A) $[Ni(CO)_4]$ & $K_2[Ni(CN)_4]$	p) Magnetic moment
B) $[Cu(NH_3)_4]SO_4$ & $K_3[Cu(CN)_4]$	q) Oxidation no of central metal
C) $K_2[NiCl_4]$ & $K_2[Ni(CN)_4]$	r) Geometry
D) $K_2[NiCl_4]$ & $K_2[PtCl_4]$	s) EAN of central atom

90. Match the following

## Column - I



## Column - II

p) Square planar

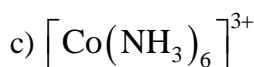
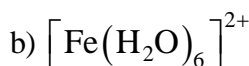
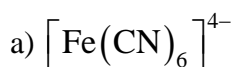
q) Tetrahedral

r) Diamagnetic

s) Paramagnetic

91. Match the following

## Column - I



## Column - II

p) Paramagnetic

q) Diamagnetic

r) Inner orbital

complex

s) Outer orbital

complex

t) octahedral

92. Match the following:

Complex	Characteristic
(A) $[Pt(gly)_2]$	(p) exhibits geometric isomerism
(B) $[Co(gly)_3]$	(q) exhibits optical isomerism
(C) $[Pt(en)_2]^{2+}$	(r) $dsp^2$
(D) $[Co(en)_3]^{3+}$	(s) $d^2sp^3$ (t) 3.87 BM

93. Match the following:

List-I	List-II
(A) $Be(acac)_2$	(p) Octahedral
(B) $[Zn(EDTA)]^{2-}$	(q) Square planar
(C) $K_3[Al(C_2O_4)_3]$	(r) Tetrahedral
(D) $Ni(DMG)_2$	(s) Diamagnetic (t) Exhibits optical activity

94. Match the following:

List-I	List-II
(A) deoxyhaemoglobin	(p) Oxidation state of the metal is +2
(B) Wilkinson catalyst	(q) Oxidation state of the metal is +1
(C) Sodium nitroprusside	(r) Oxidation state of the metal is +3
(D) Reineck salt	(s) Coordination number : 4 (t) Coordination number : 6

95. Match the following

Complex	I	II	III
(1) $[Co(NH_3)_6]^{3+}$	(A) 5.87 BM	(P) $sp^3d^2$	(U) Outer orbital complex
(2) $[Fe(CN)_6]^{3-}$	(B) diamagnetic	(Q) $d^2sp^3$	(V) Inner orbital complex
(3) $[Mn(H_2O)_6]^{2+}$	(C) 1.73 BM	(R) $dsp^3$	(W) Having only $\sigma$ donation from the ligand

Choose the correct choice

(A) 1: B, Q, V, W	2: C, Q, V	3: A, P, U, W
(B) 1: A, Q, V, W	2: B, P, V, W	3: B, Q, U, W
(C) 1: B, Q, U, W	2: A, P, U, W	3: C, R, V
(D) 1: A, P, U	2: C, R, U, W	3: A, Q, V

96. Match the following:

Complex	I
(1) $[Pt(CN)_4]^{2-}$	(A) 2.83 BM
(2) $[NiCl_4]^{2-}$	(B) 5.87 BM
(3) $[MnBr_4]^{2-}$	(C) 3.87 BM
(4) $[CoCl_4]^{2-}$	(D) Diamagnetic

II

III

- 1) (P)  $sp^3$  (U)  $d^8$  (Low spin)  
 2) (Q)  $dsp^2$  (V)  $d^5$   
 3) (R) Tetrahedral (W)  $d^7$   
 (4) (S) Square planar (X)  $d^8$  (high spin)

Choose the correct choice

- (A) 1 : A,P,R,W 2 : D,Q,S,U 3 : D,Q,S,W 4 : A,Q,S,X  
 (B) 1 : C,Q,S,W 2 : B,P,R,W 3 : A,P,R,V 4 : B,Q,S,W  
 (C) 1 : B,P,R,V 2 : C,Q,S,V 3 : C,Q,S,X 4 : D,P,R,V  
 (D) 1 : D,Q,S,U 2 : A,P,R,X 3 : B,P,R,V 4 : C,P,R,W

97. Match the following

List-I

List-II

- (A)  $[Co(en)_2 Cl_2]Cl$  (p) Geometrical Isomerism  
 (B)  $[Co(en)_3]Cl_3$  (q) Optical isomerism  
 (C)  $[Cr(NH_3)_4 Cl_2]Cl$  (r) Paramagnetic  
 (D)  $K_3[Cr(C_2O_4)_3]$  (s) Diamagnetic  
 (t) Cationic complex

98. Match the following:

Column - I

Column - II

- A)  $[Cr(gly)_3]$  p) Low spin complex  
 B)  $[Co(Br)_2(Cl)_2(SCN)_2]^{3-}$  q) High spin complex  
 C)  $[Co(NH_3)_6]^{3+}$  r) Optical isomerism  
 D)  $Na[Pt(Br)(Cl)(NO_2)(NH_3)]$  s) Geometrical isomerism  
 t) Linkage isomerism

STATEMENT TYPE QUESTIONS

- (A) Statement – 1 is True, Statement – 2 is True; Statement – 2 is a correct explanation for Statement – 1.  
 (B) Statement – 1 is True, Statement – 2 is True; Statement – 2 is NOT a correct explanation for Statement – 1.  
 (C) Statement – 1 is True, Statement – 2 is False.  
 (D) Statement – 1 is False, Statement – 2 is True.

99. **Statement-1:** All octahedral  $Ni^{2+}$  complexes are paramagnetic and outer orbital complexes whether strong or weak field ligand is present.

**Statement-2:** In octahedral  $Ni^{2+}$  complexes, the strong field ligands give, inner orbital complexes and weak field ligands give outer orbital complexes.

100. **Statement-1:**  $[NiCl_4]^{2-}$  is square planar and paramagnetic whereas  $[PtCl_4]^{2-}$  is tetrahedral and diamagnetic.

**Statement-2:**  $[NiCl_4]^{2-}$  is tetrahedral and paramagnetic but  $[PtCl_4]^{2-}$  is square planar and diamagnetic.

101. **Statement-1:**  $[FeF_6]^{3-}$  is more stable than  $[FeI_6]^{3-}$

**Statement-2:**  $Fe^{3+}$  cannot oxidize  $F^-$  but  $Fe^{3+}$  can oxidize  $I^-$  to  $I_2$ .

102. **Statement-1:**  $[Co(NH_3)_6]^{2+}$  is easily oxidized to  $[Co(NH_3)_6]^{3+}$

**Statement-2:** By losing one electron from  $[Co(NH_3)_6]^{2+}$ ,  $[Co(NH_3)_6]^{3+}$  obeys  $18e^-$  rule.

103. **Statement-1:**  $Ca^{2+}$  and  $Mg^{2+}$  in water can be determined by EDTA titration.

**Statement-2:** EDTA precipitates  $Ca^{2+}$  and  $Mg^{2+}$ .

104. **Statement-1:** Square planar complexes are formed by  $d^8$  ions with strong field ligands. because

**Statement-2:** The crystal field splitting is larger for the square planar complexes.

<b>INTEGER TYPE QUESTIONS</b>
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105. In how many of the following, the second element has a higher density than the first one ?

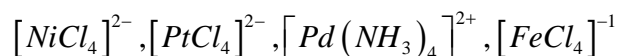
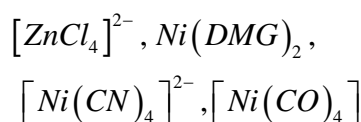
- (1) *Ag, Au*    (2) *Hf, Zr*    (3) *Zn, Hg*  
 (4) *Na, Cu*    (5) *Ca, Co*    (6) *Ta, Nb*

106. The number of transition metal in bronze is  $x$ , in brass is  $y$  and in German silver is  $z$ . Then  $(x + y + z)$  is

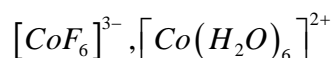
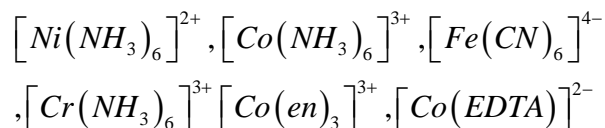
107. The number of  $t_{2g}$  electrons in  $[Fe(H_2O)_6]^{3+}$  is

108. In the complex  $[Al(EDTA)_x]^{-y}$ ,  $(x + y)$  is

109. How many of the following are  $sp^3$  hybridized ?



110. How many of the following have  $d^2sp^3$  hybridization ?



111. The coordination number of the metal in sodium nitroprusside is

112. The number of unpaired electrons in the brown ring complex is

113. The number of five membered chelate rings in  $[Zn(EDTA)]^{2-}$  is

114. DMG is  $x$ -valent and  $y$ -dentate ligand. Taking  $x$  and  $y$  as numbers, find  $(x + y)$

115. The number of isomers possible for  $[Ir(Cl)(Br)(NH_3)(py)]$  is

116.  $Cr(C_6H_6)_2$  is named as bis ( $\eta^x$  - benzene) chromium ( $y$ )  $x + y$  is

117. The oxidation number of the metal in Zeises salt is

118. The oxidation state of the metal in Reinecks salt is  $+x$ ,  $x$  is

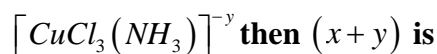
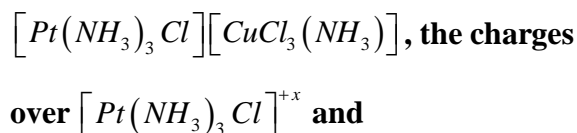
119. The coordination number of the metal in the Vaska's complex is

120. The oxidation number of the metal in the Wilkinson catalyst is

121. In the complex  $[Co(NH_3)_6][Cr(CN)_6]$  charges over  $[Co(NH_3)_6]^{x+}$  and



122. In the complex



123. The number of stereoisomers possible in  $Ma_2b_2c_2$  are

124. The number of nitrogen atoms coordinated in  $[Zn(EDTA)]^{2-}$  is

125. The number of five membered rings in  $[Pt(trien)]^{2+}$  (trien = triethylenetetraamine) is

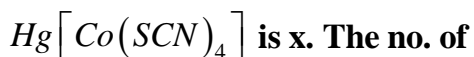
126. The oxidation state of metal is  $(+x)$ , number of nitrogen atoms coordinated to iron ( $y$ ).  $x + y$  in deoxy haemoglobin is

127. The oxidation state and coordination number of the metal in Wilkinson catalyst are  $+x$  and  $y$  respectively.  $(x + y)$  is



128. The oxidation state of the metal atom in sodium nitroprusside is  $+x$ ,  $x$  is
129. The number of intramolecular hydrogen bondings in  $Ni(DMG)_2$  is
130. What are the possible number of geometrical isomers exhibit by  $[CrCl_2(NO_2)_2(NH_3)_2]^-$  ?
131. How many possible coordination isomers are observed in following compound (excluding the given compound)  
 $[Cr(en)_3][Co(NO_2)_6]$
132. A metal complex of coordination number six having three different types of ligands a, b & c of composition  $Ma_2b_2c_2$  can exist in several stereo isomeric forms. What is the total number of such isomer?
133. The crystal field stabilisation energy of  $[Mn(H_2O)_6]^{+2}$  is
134. If  $\Delta_0 < P$  then electronic arrangement of metal atom/ion in an octahedral complex with  $d^4$  configuration is  $t_{2g}^x e_g^y$ . What is the value of  $x$
135. The no. of complexes showing fac and mer isomerism  
 A)  $[Co(NH_3)_3Cl_3]$     B)  $[Co(en)_3]^{+3}$   
 C)  $[Co(gly)_3]$   
 D)  $[Co(NH_3)_2(H_2O)_2Cl_2]$   
 E)  $[Fe(dipy)_3]^{+2}$   
 F)  $[Fe(O-phen)_3]^{+2}$
136. The no. of complexes showing hepticity 5  
 1) ferrocene                      2) zeise's salt  
 3) ruthenocene                4) chromocene
137. The no. of flexible ligands are  
 a) Sulphato                      b) Edta  
 c) nitrate                         d) thiosulphato
138. In complex  $[Cr(NH_3)_6][Co(C_2O_4)_3]$  the total No. of ions formed are
139. In complex  $[Fe(CO)_2(NO)_2]$  the oxidation state of Fe is  $(+/-)$
140. In the coordination compound  $K_4[Ni(CN)_4]$ , the oxidation state of nickel is :
141. The no. of statement(s) is /are correct ?  
 a) Primary valency of the central metal of a complex is always satisfied by anions.  
 b) Secondary valency of the central metal of a complex may be satisfied by either negative ions or neutral molecules.  
 c) Species which show primary valencies in complex compound and are present outside, can be precipitated out.  
 d) Species which show secondary valencies in a complex are Lewis acids
142. Consider the following complex :  
 $[Co(NH_3)_5CO_3]ClO_4$   
 the coordination number is  $X$  and oxidation number is  $Y$ , number of d-electrons is  $Z$ , and number of unpaired d-electrons of the metal is  $A$  are respectively.  $(X + Y) - (Z + A)$ .
143. The CFSE for  $[CoCl_6]^{4-}$  is  $18000cm^{-1}$ . The  $\Delta$  for  $[CoCl_4]^{2-}$  will be  $Y \times 1000 cm^{-1}$  the value of  $y$  is
144. Amongst  $[Co(OX)_3]^{3-}$ ,  $[CoF_6]^{3-}$ ,  
 $[Co(NH_3)_6]^{3+}$  and  
 $[Co(NH_3)_6]^{+2}$  the no. of coloured complexes

145. This spin magnetic moment of cobalt in



unpaired electrons are

146. From  $Ma_3b_3$ , when 1b is replaced by c, the total no. of geometrical possible are

### LEVEL-VI

#### KEY

##### SINGLE ANSWER

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

##### MULTIPLE ANSWER

- 52) A,C                    53) A,B                    54) A,B  
 55) A,B,D                56) A,B,D                57) A,B,C  
 58) A,B,C,D             59) A,B,D                60) A,B,D  
 61) A,B,C,D             62) A,B,D                63) B,C,D  
 64) A,B,D                65) A,B,C,D             66) A,B,C,D  
 67) A,C,D                68) A,B,C,D             69) A,B,C  
 70) A,C                    71) A,D                    72) A,B,C,D  
 73) B,C                    74) A,C

##### COMPREHENSION TYPE

###### Passage-I

- 75) C    76) C    77) A

###### Passage-II

- 78) A    79) C    80) B

###### Passage-III

- 81) B    82) A    83) C

###### Passage-IV

- 84) A    85) A    86) A

### MATRIX MATCHING TYPE

- 87) A: p, q, r, s, t ; B: p,q,r,s,t  
       C: p,q,r,s,t ; D: p,q,r,s,t  
 88) A: p,r,s ; B: q,t ; C: r,s,t ; D: r,s,t  
 89) A-q,r,s B- p,q,r,s; C-p, r    D- p,r,s  
 90) A-q,s B- q,s C-q,s    D- p,r  
 91) A-q,r,t B- p,s,t ; C-q,r,t ; D- p,s,t  
 92) A: p,r ; B: p,q,s ; C: r ; D: q,s  
 93) A - q,s,t B - p,s,t C- p,s,t ; D- q,s  
 94) A - p,t ; B - q,s ; C - p,t ; D - r,t  
 95) A    96) D  
 97) A - p, q, s,t B - q,s,t C-p, r, t D-q, r  
 98) A - r,s B - q,r,s,t C - p D - s,t

### ASSERTION AND REASON TYPE

- 99) C    100) D    101) A  
 102) A    103) C    104) A

### INTEGER TYPE

- 105) 4    106) 4    107) 3    108) 2    109) 4  
 110) 5    111) 6    112) 3    113) 5    114) 3  
 115) 3    116) 6    117) 2    118) 3    119) 4  
 120) 1    121) 6    122) 2    123) 6    124) 2  
 125) 3    126) 7    127) 5    128) 2    129) 2  
 130) 5    131) 3    132) 6    133) 0    134) 3  
 135) 2    136) 2    137) 3    138) 4    139) 2  
 140) 0    141) 3    142) 3    143) 8    144) 4  
 145) 3    146) 3

### LEVEL - VI

#### HINTS

#### SINGLE ANSWER QUESTION

- Au has higher electron affinity and so can form  $Au^-$  readily.
- Pd and Pt in VIII B group.  $IE_4 < IE_4(Ni)$
- Famous alloy for permanent magnets
- $Ti^{3+} 3d^1, V^{2+}, 3d^3$ . Others have  $d^0$  or  $d^{10}$  configuration.  $CuSO_4$  has no splitting of d orbitals. No  $d \rightarrow d$  transition is possible chelate.

8.  $[V(CO)_6]$  is paramagnetic with 1 unpaired electron, all others are diamagnetic.
39.  $NO, NO^+, NO^-$  can act as ligands.
40.  $V^{4+} : 3d^1, Cu^{2+}, 3d^9$ . So they have same color.
41.  $2x - 8 + 0 + 0 = -2, x = +3$
42. See the structure
43. 3.87 BM, it has 3 unpaired electrons.
44. The more negative charge will give more electrons into  $\pi^*$  MO of CO. So the bond order decreases.
45. Use Pauling VB theory.
46. (II) has symmetry.
47. It is a  $\sigma$  complex.
48. In other complexes the orientation decides whether the complex is optically active or not.
49. Coordination isomerism
50. In A all the coordinating atoms are identical, no geometrical isomerism.
51. Note that  $2NO \equiv 3CO$ . NO is  $3e^-$  donor and CO is  $2e^-$  donor.

**MULTIPLE ANSWER QUESTIONS**

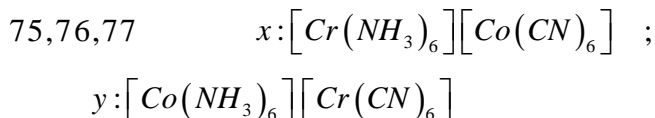
53. Have oxidation number greater than the group number.
54.  $V^{+5}, Zn^{+2}$  react with both acids and basis, are amphoteric.
55. Do not contain Iron.
65. Consider outer electronic configuration.  
E g :
- $[Cr(CO)_6]: Cr(O): d^4 s^2, 6 + 6 \times 2 = 18e^-$
- $C_6H_6$  and  $C_5H_5^-$  are  $6\pi e^-$  systems.
66. All obey EAN rule.
67. B is a 6 coordinated complex.
68.  $Ni^{2+} : 3d^8$ , All octahedral  $Ni^{2+}$  complexes are  $sp^3 d^2$  and paramagnetic.
69.  $RMgX$  is a  $\sigma$  complex. No  $\pi$  - bond.
70. B and D have symmetry

71. A is tetrahedral, D is unsymmetrical, B and C are square planar and not optically active.
72. Apply Pauling VB theory. See the structures.
73.  $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \Delta_0$
74. (A) and (C) are correct about Wilkinson's catalyst whereas (D) is Ziegler-Natta catalyst.

Wilkinson's catalyst is  $[(Ph_3P)_3 RhCl]$

**COMPREHENSION TYPE**

**Passage-I**



**Passage-II**

78.  $K_1 K_2 K_3 = \beta_3, \beta_n = K_1 K_2 \dots K_n$   
 $\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \dots + \log K_n$
79.  $[Cd(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cd(H_2O)_3(NH_3)]^{2+} + H_2O$   
Any of the four water molecules can be replaced by one  $NH_3$  molecule. Statistical or probability factor favours.
80. Both the reactions involve Cd - N bonds and so no much change in enthalpy. In (1) four water molecules are replaced by four  $NH_3$  molecules. But in (2) four water molecules are replaced by two en molecules. This increases the entropy and is called as Entropy effect.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G^0 = -2.303 RT \log \beta$$

In (2),  $\Delta G^0$  varies due to  $\Delta S^0$  and so the  $\log \beta_2$  has a higher value. For (1),  $\Delta S^0 = -ve$  and (2)  $\Delta S^0 = +ve$

**Passage-III**

81. More negative charge on Ti atom, which pumps more electrons into  $\pi$  MO of CO, So Bond order decreases, bond length increases.
82. Metal - alkyl. No  $\pi$  - back donation. Only  $\sigma$  donor.

83. Note positive charge on the complex. Due to less electron density over the metal, less electrons are given into the  $\pi$  MO of CO.

**Passage-IV**

84. Electrons are filled in  $t_{2g}$  orbitals

$$85. \Delta_0 = \frac{hc}{\lambda}$$

86. Cobalt (III),  $d^6$ , Highspin complex, 4 unpaired electrons

**MATRIX MATCHING TYPE**

87. II and III row transition elements have similar atomic radii but with increase in atomic weight, so density is more for III row elements.

94. Reineck salt  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$

It is a dark red crystalline compound

It is used to precipitate primary and secondary amines as their ammonium salts

**ASSERTION AND REASON TYPE**

99.  $\text{Ni}^{2+} : 3d^8$ 

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
----------------------	----------------------	----------------------	------------	------------

x	x	x	x
---	---	---	---

x	x		
---	---	--	--

Note that by pairing up  $d^2sp^3$  cannot be obtained in the case of strong field ligands.

100.  $\Delta_0 \text{Pt}^{2+} > \Delta_0 \text{Ni}^{2+}$ , The  $\text{Cl}^-$  ligand could pair up  $e^-$  in 5d orbitals but could not pair up  $e^-$  in 3d orbitals.

101.  $\text{Fe}^{3+}$  is hard acid and  $\text{F}^-$  is a hard base (Pearson concept).

Stable complex is formed. Further  $\text{Fe}^{3+}$  can oxidize  $\text{I}^-$  to  $\text{I}_2$ .

102.  $[\text{Co}(\text{NH}_3)_6]^{2+}$ , has  $7 + 6 \times 2 = 19e^-$

$[\text{Co}(\text{NH}_3)_6]^{3+}$  has  $6 + 6 \times 2 = 18e^-$

$18e^-$  is more stable.

103. EDTA forms complex with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

**INTEGER TYPE QUESTIONS**

105. Three row transition elements have higher density than second row elements. d-block elements have higher density than group IA and IIA elements. Note that atomic size decreases or remains almost same and atomic weight increases and so show higher density.

106. Bronze:

$\text{Cu, Sn; Brass : Cu, Zn; German silver : Cu, Zn, Ni}$

$$1 + 1 + 2 = 4$$

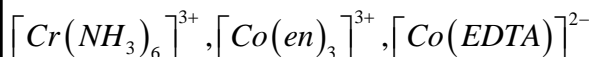
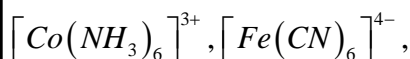
107.  $(t_{2g})^3 (e_g)^2$

108.  $[\text{Al}(\text{EDTA})]^{-1}$

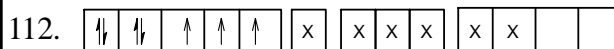
109.  $[\text{ZnCl}_4]^{2-}, \text{Ni}(\text{CO})_4, [\text{NiCl}_4]^{2-}, [\text{FeCl}_4]^{-1}$

are tetrahedral and  $sp^3$  hybridized.

110. They are



111.  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$



113. See the structure of the complex.

114. univalent bidentate ligand.

115. Square planar complex

$\text{bis}(\eta^6\text{-benzene})\text{chromium}$

116. (O),  $6 + 0 = 6$

117.  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$

118.  $(\text{NH}_4)[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$

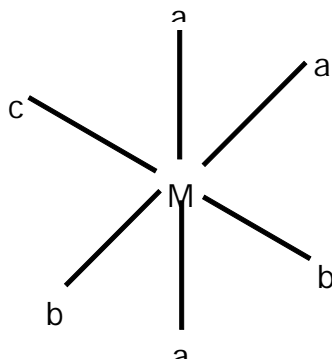
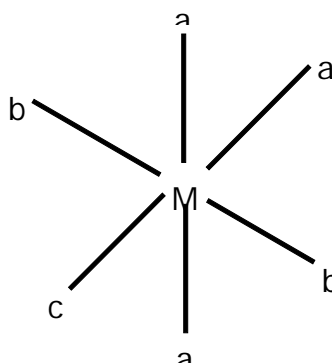
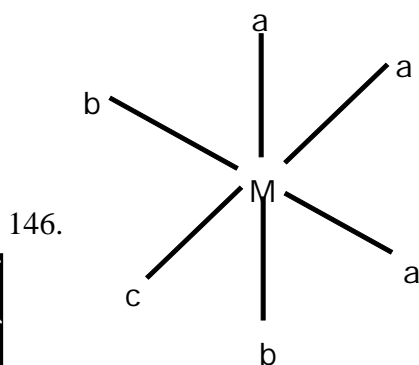
119.  $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$

120.  $[\text{RhCl}(\text{PPh}_3)_3]$

121.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Cr}(\text{CN})_6]^{3-}$

122.  $[Pt(NH_3)_3Cl]^{+1}$  and  $[CuCl_3(NH_3)]^{-1}$   
 $1+1=2$
123. Give both geometrical and optical isomers (3 + 1).
124. See the structure of the complex.
125.  $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
126. Iron is in +2, 4 pyrrole nitrogens and one histidine nitrogen  $2+4+1=7$ .
127.  $[RhCl(PPh_3)_3]$ ,  $1+4=5$
128.  $Na_2[Fe(CN)_5(NO)]$ , +  
 $2+x-5+1=0$ ,  $x=+2$
129. See the structure.
131. 1)  $[Cr(en)_3]^{3+}$ ,  $[Co(NO_2)_6]^{3-}$   
 2)  $[Cr(en)_2(NO_2)_2]^+$ ,  $[Co(en)(NO_2)_4]^-$   
 3)  $[Co(en)_2(NO_2)_2]^+$ ,  $[Cr(en)(NO_2)_4]^-$   
 4)  $[Co(en)_3]$ ,  $[Cr(NO_2)_6]$
133.  $CFSE = [-0.6p + 0.4q]\Delta_0$ ,  $t_{2g}^3 e_g^2$ ,  $CFSE = 0$   
 p and q are the number of electrons in  $t_{2g}$  and  $e_g$  orbitals.
134.  $(t_{2g}^3)(e_g^1)$
135.  $[Ma_3b_3]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$  show fac and mer isomerism.
136. Ferrocene and osmocene are linked to cyclopentadienyl ion, which contains 5 carbon atoms in a ring.
137. Conceptual
138.  $[Cr(NH_3)_6]^{+3}$  is 1 ion and  
 $[Co(C_2O_4)_3]^{-3}$  is other
139. NO is a positive ligand
140. Cyanide is a negative ligand

141. Werner's theory
142. C.N. 6, O.S. 3, No. of d-electrons 6  
 $[Co^{+3} \rightarrow 3d^6]$ , unpaired electrons 0.
143.  $\Delta_t = \frac{4}{9}\Delta_0$
144.  $d^1$  to  $d^9$  coloured
145. Co is in +2 O.S.  $3d^7$  configuration.



## PREVIOUS IIT QUESTIONS

- 1  $\text{NiCl}_2 \{ \text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5) \}$  exhibits temperature dependent magnetic behaviour (para magnetic and dia magnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively (IIT2012)

- A) Tetrahedral and tetrahedral  
 B) Square planar and square planar  
 C) tetrahedral and square planar  
 D) Square planar and tetrahedral

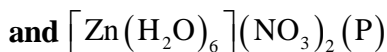
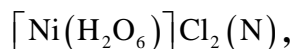
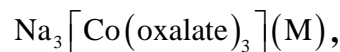
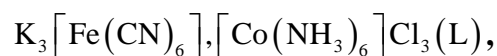
- 2 As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_2$  (IIT-2012)

- A) Tetra aqua diamine cobalt (III) chloride  
 B) Tetra aqua diammine cobalt (III) chloride  
 C) Diamine tetra aqua cobalt (III) chloride  
 D) Diammine tetraaqua cobalt (III) chloride

- 3 Geometrical shapes of the complexes formed by the reaction of  $\text{Ni}^{2+}$  with  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{H}_2\text{O}$ , respectively, are (IIT2011)

- A) Octahedral, tetrahedral and square planar  
 B) tetrahedral, square planar and octahedral  
 C) square planar, tetrahedral and octahedral  
 D) octahedral, square planar and octahedral

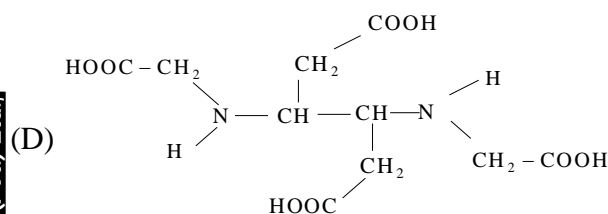
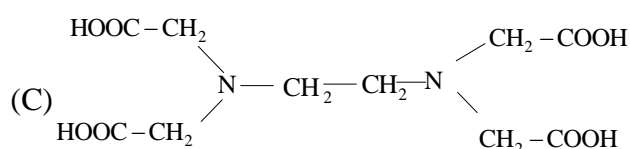
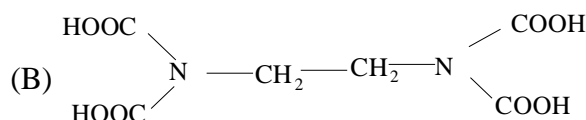
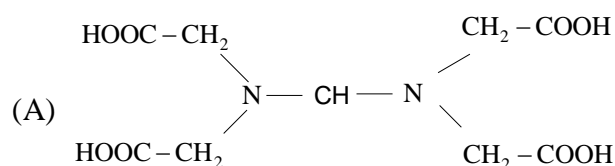
- 4 Among the following complexes (K - P)



the diamagnetic complexes are

- A) K, L, M, N                      B) K, M, O, P  
 C) L, M, O, P                      D) L, M, N, O

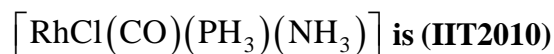
- 5 The correct structure of ethylenediaminetetraacetic acid (EDTA) is (IIT2010)



- 6 The ionization isomer of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$  is (IIT2010)

- (A)  $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$   
 (B)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$   
 (D)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)]\text{H}_2\text{O}$

- 7 Total number of geometrical isomers for the complex



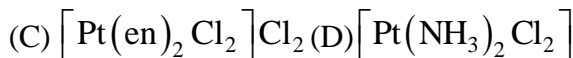
- 8 The complex showing a spin-only magnetic moment of 2.82 B.M is (IIT2010)

- (A)  $\text{Ni}(\text{CO})_4$                       (B)  $[\text{NiCl}_4]^{2-}$   
 (C)  $\text{Ni}(\text{PPh}_3)_4$                       (D)  $[\text{Ni}(\text{CN})_4]^{2-}$

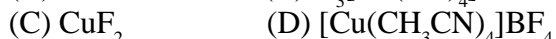
- 9 The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is (IIT-2009)

- (A) 0                      (B) 2.84                      (C) 4.90                      (D) 5.92

10 The compound (s) that exhibit(s) geometrical isomerism is (are) (IIT-2009)



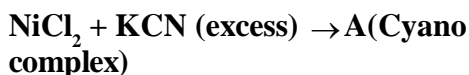
11 Among the following, the coloured compound is [IIT -2008]



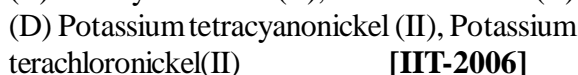
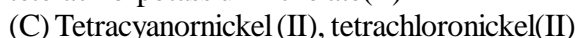
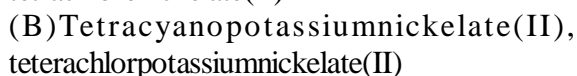
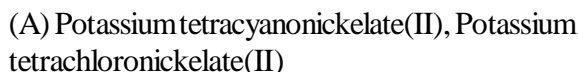
12. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [IIT-2008]



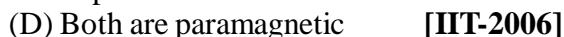
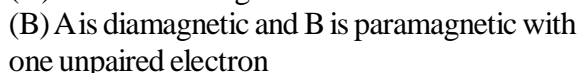
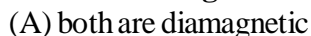
13 The coordination number of  $\text{Ni}^{2+}$  is 4



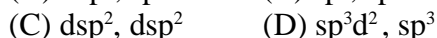
The IUPAC name of A and B are



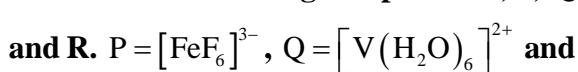
14. Predict the magnetic nature of A and B



15. The hybridization of A and B are [IIT-2006]

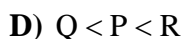
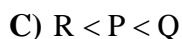
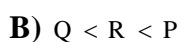
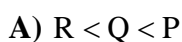


16. Consider the following complex ions, P, Q

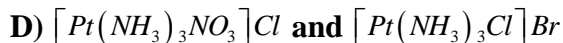
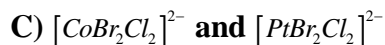
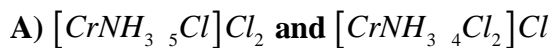


complex ions, according to their spin - only magnetic moment values ( in BM ) is

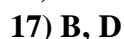
[ IIT - 2013 ]



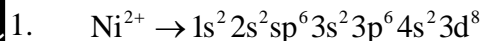
17. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is ( are )



PREVIOUS IIT KEY

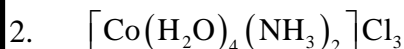


SOLUTIONS



low spin complex :  $dsp^2$  – square planar ( diamagnetic )

high spin complex :  $sp^3$  – tetrahedral ( paramagnetic )



According IUPAC nomenclature rule it is Diamminetetraaquacobalt (III) chloride i.e.,

$\text{NH}_3$  is neutral ligand and it is named as ammine and  $\text{H}_2\text{O}$  (aqua)

3.  $\text{Cl}^-$  is weak field ligand and  $\text{CN}^-$  is a strong field ligand,  $\text{Ni}^{+2}$  with chloride and Cyanide has C.N. 4.

With water has C.N. 6.

4. Complexes L, M, O form inner orbital complexes due to high charge density metal, or high Q. N of metal.

$\text{Zn}^{+2}$  with C.N. 6  $3d^{10}$  configuration has no unpaired electrons.

7.  $[\text{RhCl}(\text{CO})(\text{PH}_3)(\text{NH}_3)]$  is an example of

$[\text{Mabcd}]^{n\pm}$  type, squareplanar geometry having three geometrical isomers.

8. Complex  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPh}_3)_4$  are tetrahedral complexes with Ni in 0 O.S., complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is a squareplanar, and all these three are diamagnetic.

complex  $[\text{NiCl}_4]^{2-}$  is tetrahedral complex with Ni in +2 O.S., paramagnetic with 2 unpaired electrons.

9.  $\text{Cr}(\text{CO})_6$  is octahedral geometry with Cr in 0 O.S.

10.  $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$  this complex is octahedral with Pt in +4 O.S. and C.N. 6.

$[\text{M}(\text{AA})_2\text{a}_2]^{n\pm}$  type.

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  this complex is squareplanar geometry with Pt in +2 O.S. and C.N. 4.

$[\text{Ma}_2\text{b}_2]^{n\pm}$  type.

11. Cu in +2 has  $3d^9$  configuration can have d-d transition, coloured

12. In complex  $[\text{Ni}(\text{CO})_4]$  Ni is in 0 O.S., tetrahedral.

In complex  $[\text{Ni}(\text{CN})_4]^{2-}$  Ni is in +2 O.S., squareplanar.

13. Conceptual

14 & 15. Complex is  $\text{K}_2[\text{Ni}(\text{CN})_4]$ , squareplanar complex b is  $\text{K}_2[\text{Ni}(\text{Cl})_4]$  tetrahedral.

16.  $[\text{FeF}_6]^{3-}$ ,  $\text{Fe}^{3+}$  has 5 unpaired electron

$$\therefore \mu = \sqrt{35}\text{BM}$$

$\Rightarrow [\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{V}^{2+}$  has 3 unpaired electrons

$$\therefore \mu = \sqrt{15}\text{BM}$$

$\Rightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Fe}^{2+}$  has 4 unpaired electrons

$$\therefore \mu = \sqrt{25}\text{BM}$$

$$\Rightarrow \text{P} > \text{R} > \text{Q}$$

17. A)  $[\text{CrNH}_3_5\text{Cl}]\text{Cl}_2$  does not exhibit isomerism,  $[\text{CrNH}_3_4\text{Cl}_2]\text{Cl}$  exhibits geometrical isomerism

B)  $[\text{CoNH}_3_4\text{Cl}_2]^+$  and

$[\text{PtNH}_3_2\text{H}_2\text{OCl}]^+$  both can show geometrical isomerism

C)  $\text{CoBr}_2\text{Cl}_2^{2-}$  tetrahedral so it does not exhibit isomerism

$\text{PtBr}_2\text{Cl}_2^{2-}$  - squareplanar so it exhibits geometrical isomerism

D)  $[\text{PtNH}_3_3\text{NO}_3]\text{Cl}$  and  $[\text{PtNH}_3_3\text{Cl}]\text{Br}$  both can show ionisation isomerism