

**COORDINATION COMPOUNDS**

- You are given the following two complexes X and Y which are isomers of each other X is  $\text{Hg}[\text{Co}(\text{SCN})_4]$ . It is further given that paramagnetic moment of X is found to be more than Y. Then which of the following is correct.

(A) Anion of X will be tetrahedral and that of Y will be square planar.  
 (B) Anion of X will be square planar but that of Y will be tetrahedral  
 (C) Both the anions will be tetrahedral  
 (D) Both the anions will be square planar
- In the reaction :  $[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow$  the complex formed will be :

(A) Tetrahedral                      (B) square planar                      (C) octahedral                      (D) triangular bipyramidal
- It is given that a complex formed by one  $\text{Ni}^{2+}$  ion and some  $\text{Cl}^-$  ions and some  $\text{PPh}_3$  molecules does not show geometrical isomerism and its solution does not show electrical conductance. Then which is correct about the complex :

(A) It is square planar      (B) It is tetrahedral                      (C) It is diamagnetic                      (D) none of the above is correct
- All the following complexes show a decrease in their weights when placed in a magnetic balance. Then which of these has square planar geometry :

(A)  $\text{Ni}(\text{Co})_4$                       (B)  $\text{K}[\text{AgF}_4]$                       (C)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$                       (D) None of these
- It is an experiment fact that  $\text{Cs}_2[\text{CuCl}_4]$  is orange coloured but  $(\text{NH}_4)_2[\text{CuCl}_4]$  is yellow. It is further known that total paramagnetic moment of a unpaired electron is due to spin as well as due to nature of orbital, 'd' orbital contributing more than 's' or 'p'. Thus the total paramagnetic moment of orange compound is found to be more than that of yellow compound. Then which of the following is correct :

(A) Anion of orange compound is tetrahedral and that of yellow is square planar  
 (B) Anion of orange compound is square planar and that of yellow is tetrahedral  
 (C) Both the anions are tetrahedral  
 (D) Both the anions are square planar
- It is an experiment fact that :

$\text{DMG} + \text{Ni(II)salt} + \text{NH}_4\text{OH} \longrightarrow \text{Red ppt.}$

Which of the following is wrong about this red ppt :

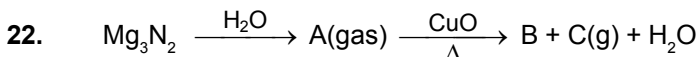
(A) It is a non-ionic complex                      (B) It involves intra molecular H-bonding  
 (C) Ni(II) is  $\text{sp}^3$  hybridised                      (D) It is a diamagnetic complex
- It is experimentally found that the compound  $\text{K}_3[\text{Ni}(\text{CN})_5]$  shows an increase in its weight when placed in a magnetic balance and four metal-ligand bond lengths are equal but the rest is different. Then which of the following set of informations is correct :

(i) The transition metal is  $\text{sp}^3\text{d}$  hybridised  
 (ii) The net dipole moment of complex is  $\neq$  zero  
 (iii) The transition metal is  $\text{dsp}^3$  hybridised  
 (iv) The net dipole moment of the complex is zero  
 (v) The complex ion is trigonal bipyramidal  
 (vi) The complex ion is square pyramidal

(A) (i),(ii),(v)                      (B) (i),(ii),(vi)                      (C) (iii),(iv),(v)                      (D) none of these

8. The green coloured complex  $K_2[Cr(CN)_4(NH_3)(NO)]$  is paramagnetic and its paramagnetic moment (spin only) is 1.73 B.M. Which of the following is correct about it :  
 (i) Its IUPAC name is Potassium amminetetrayanonitrosylchromate (II)  
 (ii) Its IUPAC name is Potassium amminetetrayanonitrosyliumchromate (I)  
 (iii) Hybridisation state of chromium is  $sp^3d^2$   
 (iv) It cannot show geometrical isomerism  
 (v) Hybridisation state of chromium is  $d^2sp^3$   
 (vi) It can show ligand isomerism  
 (A) (ii), (iii), (iv) (B) (i), (iii), (vi) (C) (i), (v) (D) (ii), (v), (vi)
9. Sodium nitroprusside is a diamagnetic substance and an important laboratory reagent for the testing of sulphide ions. The metal involved in the complexation in this is present in which of the following hybridisation state :  
 (A)  $sp^3$  (B)  $dsp^2$  (C)  $d^2sp^3$  (D)  $sp^3d^2$
10. All the following complex ions are found to be paramagnetic :  
 P :  $[FeF_6]^{3-}$  ; Q :  $[CoF_6]^{3-}$   
 R :  $[V(H_2O)_6]^{3+}$  ; S :  $[Ti(H_2O)_6]^{3+}$   
 The correct order of their paramagnetic moment (spin only) is :  
 (A)  $P > Q > R > S$  (B)  $P < Q < R < S$  (C)  $P = Q = R = S$  (D)  $P > R > Q > S$
11. When the complex  $K_6[(CN)_5Co-O-O-Co(CN)_5]$  is oxidised by bromine into  $K_5[(CN)_5Co-O-O-Co(CN)_5]$ . Then which of the following statements will be true about this change:  
 (A) Co(II) is oxidised to Co(III) (B) The O—O bond length will increase  
 (C) The O—O bond length will decrease (D) 'A' & 'B' both are correct
12. The octahedral complex  $[Rh(NO_2)(SCN)(en)_2]^+$  can exist in a total number of isomeric forms including stereoisomers :  
 (A) 2 (B) 4 (C) 8 (D) 12
13. Which of the following is true about the complex  $[PtCl_2(NH_3)(OH_2)]$  ; [Atomic no. of Pt = 78]  
 (i) It will have two geometrical isomeric forms, cis and trans  
 (ii) The hybridisation state of Pt(II) is  $sp^3$   
 (iii) It is a square planar complex  
 (iv) It is a diamagnetic complex  
 (v) It can show hydrate isomerism  
 (vi) It is a tetrahedral complex  
 (A) (i), (iii), (iv) (B) (ii), (iv), (v) (C) (ii), (v), (vi) (D) (i), (v), (vi)
14. For the reaction  $Ni^{2+} + 4NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$   
 at equilibrium, if the solution contains  $1.6 \times 10^{-4}\%$  of nickel in the free state, and the concentration of  $NH_3$  at equilibrium is 0.5 M. Then the instability constant of the complex will be approximately equal to :  
 (A)  $1.0 \times 10^{-5}$  (B)  $1.5 \times 10^{-16}$  (C)  $1.0 \times 10^{-7}$  (D)  $1.5 \times 10^{-17}$
15. Which of the following is true :  
 (A)  $[ZnCl_2(NH_3)_2]$  will not exhibit geometrical isomerism  
 (B)  $[Pt(Br)(Cl)(NH_3)(Py)]$  is an optically inactive compound  
 (C) The brown ring complex  $[Fe(H_2O)_5NO]^{2+}$  is paramagnetic  
 (D) All the above are true
16. In which of the following complex ions, the metal ion will have  $t_{2g}^6, e_g^0$  configuration according to CFT:  
 (A)  $[FeF_6]^{3-}$  (B)  $[Fe(CN)_6]^{3-}$  (C)  $[Fe(CN)_6]^{4-}$  (D) None of these
17. In which of the following complexes the effective atomic number is not equal to the atomic number of an inert gas :  
 (A)  $Ni(CO)_4$  (B)  $[Co(NH_3)_6]^{3+}$  (C)  $[Fe(CN)_6]^{4-}$  (D)  $[CuCl_2]^-$
18. A complex with the molecular formula  $CrCl_3 \cdot 6H_2O$  is such that  $1/3$  of the total chloride is precipitated by adding  $AgNO_3$  to its aqueous solution. Then which of the following is its best representation :  
 (A)  $CrCl_3 \cdot 6H_2O$  (B)  $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$   
 (C)  $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$  (D)  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

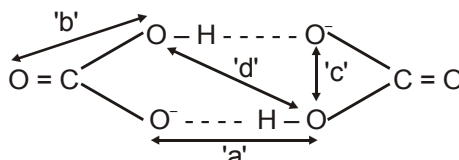
19. The correct order for the CFSE (numerical value) for the following complexes is
- | Complex             | P                     | Q                               | R                                 | S  |
|---------------------|-----------------------|---------------------------------|-----------------------------------|--|
| Formula             | $[\text{CoF}_6]^{3-}$ | $[\text{Co}(\text{CN})_6]^{3-}$ | $[\text{Co}(\text{NH}_3)_6]^{3+}$ | $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ |
| (A) $P > Q > R > S$ | (B*) $Q > R > S > P$  | (C) $S > R > P > Q$             | (D) $R > Q > P > S$               |  |
20. Spin only magnetic moment of a complex having  $\text{CFSE} = -0.6 \Delta_0$  and surrounded by weak field ligands can be
- (A) 1.73 BM                      (B) 4.9 BM                      (C) both (A) & (B)                      (D) None of these
21. Which of the following statements is not correct?
- (a)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  have same value of CFSE  
 (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  have same value of magnetic moment
- (A) Only a                      (B) Only b                      (C) Both a and b                      (D) None of these



C(g) can be obtained by heating

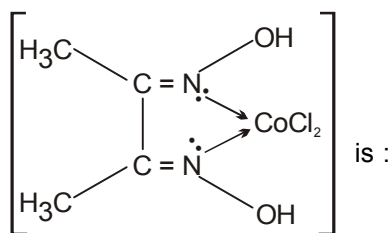
- (A)  $(\text{NH}_4)_2\text{SO}_4$                       (B)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$                       (C)  $\text{NH}_4\text{NO}_3$                       (D)  $\text{NH}_4\text{Cl}$
23. If  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in basic medium with oxidizing agent changes into the products –  $\text{KOH}$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  then the equivalent weight of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , will be approximately. [molecular weight of  $\text{K}_4\text{Fe}(\text{CN})_6 = 368$ ]
- (A) 61                      (B) 6                      (C) 50                      (D) 11
24. In which of the following configurations will there be the possibility of both para and diamagnetism, depending on the nature of the ligands?
- (A)  $d^7$                       (B)  $d^3$                       (C)  $d^6$                       (D)  $d^5$
25. Which of the following names is impossible :
- (A) Potassium tetrafluorooxochromate (VI)                      (B) Barium tetrafluorobromate (III)  
 (C) Dichlorobis (urea) copper (II)                      (D) All are impossible.

26. In  $\text{NaHCO}_3$  solid, two bicarbonate ions are bonded through strong H-bonds as shown below



The four O–O distances marked are 'a' 'b' 'c' & 'd'. The correct order of these distances is

- (A)  $a < c < b < d$                       (B)  $a < b < d < c$                       (C)  $a < d < c < b$                       (D)  $b < d < a < c$
27. A complex cation is formed by Pt (in some oxidation state) with ligands (in proper number so that coordination number of Pt becomes six). Which of the following can be its correct IUPAC name :
- (A) Diammineethylenediaminedithiocyanato-S-platinum (II) ion  
 (B) Diammineethylenediaminedithiocyanato-S-platinate (IV) ion  
 (C) Diammineethylenediaminedithiocyanato-S-platinum (IV) ion  
 (D) Diamminebis (ethylenediamine) dithiocyanate-S- platinum (IV) ion
28. The correct IUPAC name of the complex:



- (A) Dichlorodimethylglyoximatecobalt (II)                      (B) Bis(dimethylglyoxime)dichlorocobalt (II)  
 (C) Dimethylglyoximecobalt(II) chloride                      (D) Dichlorodimethylglyoxime-N, N-cobalt (II)

29. Which of the following pair of complexes have the same EAN of the central metal atoms/ions?  
 (A)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (B)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
 (C)  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Ni}(\text{CO})_4]$  (D) all of the above
30. In the reaction  $[\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^- \longrightarrow [\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$  only one isomer of product is obtained. Hence the initial complex must be  
 (A) cis isomer (B) trans isomer (C) both (D) mixture of both
31. Match List A and List B
- | LIST A                  | LIST B                                     |
|-------------------------|--|
| 1. Tetrahedral          | 1. $[\text{Ni}(\text{CN})_4]^{2-}$         |
| 2. Octahedral           | 2. $[\text{Ag}(\text{NH}_3)_2]^+$          |
| 3. Square planar        | 3. $[\text{Fe}(\text{CO})_5]$              |
| 4. Trigonal bipyramidal | 4. $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ |
| 5. Linear               | 5. $[\text{NiCl}_4]^{2-}$                  |
- (A) 1 – 5 ; 2 – 4 ; 3 – 3 ; 4 – 2 ; 5 – 1 (B) 1 – 4 ; 2 – 3 ; 3 – 2 ; 4 – 5 ; 5 – 1  
 (C) 1 – 5 ; 2 – 4 ; 3 – 1 ; 4 – 3 ; 5 – 2 (D) 1 – 5 ; 2 – 4 ; 3 – 2 ; 4 – 3 ; 5 – 1
32. The magnetic moment of  $[\text{Mn}(\text{CN})_6]^{3-}$  is 2.8 BM and that of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. The hybridization and geometries of these complex ions  
 (A)  $\text{sp}^3\text{d}^2$  octahedral and  $\text{dsp}^2$  tetrahedral (B)  $\text{d}^2\text{sp}^3$  octahedral and  $\text{dsp}^2$  square planar  
 (C)  $\text{d}^2\text{sp}^3$  octahedral and  $\text{sp}^3$  tetrahedral (D)  $\text{sp}^3\text{d}^2$  octahedral and  $\text{sp}^3$  square planar
33. In which of the following pairs hybridisation of the central atom is same  
 (A)  $\text{ClF}_3$ ,  $\text{ClF}_3\text{O}$  (B)  $\text{ClF}_3\text{O}$ ,  $\text{ClF}_3\text{O}_2$   
 (C)  $[\text{ClF}_2\text{O}]^+$ ,  $[\text{ClF}_4\text{O}]^-$  (D)  $[\text{ClF}_4\text{O}]^-$ ,  $[\text{XeOF}_4]$
34. Wilkinson's catalyst reacts with  $\text{H}_2$  to form an octahedral complex in which Rh (Z = 45) has the following electronic configuration in the ligand field  $t_{2g}^{2,2,2}$ ,  $e_g^{0,0}$ .  
 Then which of the following is/are correct about this new complex  
 (A) It is diamagnetic  
 (B) Its IUPAC name is chlorodihydridotris(triphenylphosphine) rhodium (III)  
 (C) Hybridisation of Rh(I) is  $\text{d}^2\text{sp}^3$   
 (D) It is a paramagnetic complex
35. The complex  $\text{K}_4[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$  is oxidised into  $\text{K}_2[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$ , then which of the following is/are correct -  
 (A) Zn(II) is oxidised into Zn(IV) (B) Paramagnetic moment decreases  
 (C) O–O bond length decreases (D) Paramagnetic moment increases
36. Which of the following compounds are expected to be ionic in their solid state  
 (A)  $\text{HBF}_4$  (B)  $\text{B}(\text{OH})_3$  (C)  $\text{Cl}(\text{OH})\text{O}_3$  (D)  $\text{HPF}_6$
37. Which of the following is/are correct statement/s (assuming oxidation number of metal does not affect crystal field energy much)  
 (A) Considering  $\text{H}_2\text{O}$  to be a weak ligand then on the basis of CFSE only, we can say that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is more stable than  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (B) On the basis of CFSE only  $[\text{Fe}(\text{NH}_3)_6]^{2+}$  is more stable than  $[\text{Fe}(\text{NH}_3)_6]^{3+}$   
 (C) All octahedral complexes of Ni(II) are bound to be outer-d-complexes  
 (D) The type of 'd' orbital involved in the hybridisation for a square planar complex (CN = 4) is  $d_z^2$
38. **Assertion** :  $\text{Mg}(\text{OH})_2$  ppt is soluble in  $\text{NH}_4\text{Cl}(\text{aq})$  but not in  $\text{NaCl}(\text{aq})$   
**Reason** : Because  $\text{Mg}^{++}$  form ammine complex which is soluble in water  
 (A) Both A and R are true and R is the correct explanation of A.  
 (B) Both A and R are true but R is not correct explanation of A  
 (C) A is true but R is false  
 (D) A is false but R is true

39. (a) What is the geometry of each of the following and the hybridization of the central atom ?  
 (i)  $\text{CO}_2$                     (ii)  $\text{CO}_3^{2-}$                     (iii)  $\text{Sn}(\text{OH})_6^{2-}$
- (b) A green complex  $\text{K}_2[\text{Cr}(\text{NO})(\text{CN})_4(\text{NH}_3)]$  is paramagnetic and has paramagnetic moment ( $\mu_{\text{eff}} = 1.73 \text{ BM}$ ). Write its IUPAC name and draw the structure of the anion.
40. Explain :  
 (a)  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic, why?  
 (b) All the octahedral complexes of  $\text{Ni}^{2+}$  are outer orbital complex.
41. For the complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ , it is found that electron pairing energy (P) is equivalent to  $23000 \text{ cm}^{-1}$  and  $\Delta_0$  is equivalent to  $15000 \text{ cm}^{-1}$ . Then predict for this complex.  
 (i) electronic configuration of metal in the ligands field as  $t_{2g}^{n_1}, e_g^{n_2}$  (fill the answers in the sequence  $n_1$  then  $n_2$  in the boxes given in the answer sheet, this answer will be followed (without any gap) by answer to (ii) part. Fill the corresponding bubbles also).  
 (ii) Calculate CFSE (including pairing energy, if any) for the above complex in  $\text{kJ mol}^{-1}$  using Avogadro's number as  $6 \times 10^{23}$ , Plank's constant,  $h = 6 \times 10^{-34} \text{ J sec}$ ,  $c = \text{speed of light} = 3 \times 10^8 \text{ m sec}^{-1}$
42. A symmetrical bridged complex cation made of  $\text{Co}(\text{III})$ ,  $\text{NH}_3$  molecules and oxygen (in the proper ligand form) is found to contain the following composition [Atomic mass of  $\text{Co} = 59$ ]  
 $\text{Co} = 36.875\%$  ;  $\text{NH}_3 = 53.125\%$  ;  $\text{O} = 10\%$   
 The complex cation exists in three ionic forms with cationic charges A :  $(n^+)$  ; B :  $(n-1)^+$  and C :  $(n-2)^+$  such that O – O in all of them is found to be more than that in  $\text{O}_2[\text{PtF}_6]$ . Calculate the value of n,  $(n-1)$  and  $(n-2)$ . [Fill your answer in the order n,  $(n-1)$  and then  $(n-2)$  e.g. if your answer is such that  $n = 3$  then fill 321 as your answer].
43. In the crystal field of the complex  $[\text{Fe}(\text{Cl})(\text{CN})_4(\text{O}_2)]^{4-}$  the electronic configuration of metal is found to be  $t_{2g}^6, e_g^0$  then which of the following is true about this complex ion :  
 (A) It is a diamagnetic complex  
 (B) O–O bond length will be less than found in  $\text{O}_2$  molecule  
 (C) Its IUPAC name will be chlorotetracyanosuperoxidoferrate (II) ion  
 (D) All the above are true
44. **S<sub>1</sub>** : The brown ring complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  has  $sp^3d^2$  hybridisation and is paramagnetic with one unpaired electron  
**S<sub>2</sub>** : The total number of Stereo isomers of  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (including) are four.  
**S<sub>3</sub>** : Hybridisation of  $[\text{Zn}(\text{CN})_4]^{2-}$  and  $[\text{RhCl}(\text{PPh}_3)_3]$  are  $sp^3$  and  $dsp^2$  but both are diamagnetic in nature.  
**S<sub>4</sub>** : Complex  $\text{K}_2[\text{Cr}(\text{CN})_4(\text{NH}_3)\text{NO}]$  has 'spin only' magnetic moment equal to 1.73 B.M in which chromium is in +1 oxidation state.  
 (A) T T T T                    (B) T T F F                    (C) F F T T                    (D) F T T F
45.                    **Column – I**                    **Column – II**  
 (A)  $[\text{Ni}(\text{CO})_4]$                     (p)  $sp^3$  hybridisation  
 (B)  $[\text{AgF}_4]^-$                     (q) Diamagnetic  
 (C)  $[\text{Zn}(\text{CN})_4]^{2-}$                     (r)  $dsp^2$   
 (D)  $[\text{RhCl}(\text{PPh}_3)_3]$                     (s) Unidentate ligand.
46.                    **Column – I**                    **Column – II**  
 (A)  $[\text{Ni}(\text{CO})_4]$                     (p)  $sp^3$  hybridisation  
 (B)  $[\text{AgF}_4]^-$                     (q) Diamagnetic  
 (C)  $[\text{Zn}(\text{CN})_4]^{2-}$                     (r)  $dsp^2$  hybridisation  
 (D)  $[\text{RhCl}(\text{PPh}_3)_3]$                     (s) Colourless
47. Calculate the difference in net stabilisation energies (in  $\text{kJ mol}^{-1}$ ) of  $\text{Fe}^{2+}$  complexes with  $\text{CN}^-$  ligands ( $\Delta_0 = 25000 \text{ cm}^{-1}$ ) and with  $\text{H}_2\text{O}$  ligands ( $\Delta_0 = 10000 \text{ cm}^{-1}$ ). Given that the pairing energy,  $P = 15000 \text{ cm}^{-1}$  for  $\text{Fe}^{2+}$  ion for both the complexes. (Given that  $1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$ ). (Give your answer in whole number e.g. If your answer is 80.6 then your correct answer is 81.)

Ans. 311

48. Calculate the difference in net stabilisation energies (in  $\text{kJ mol}^{-1}$ ) of  $\text{Fe}^{2+}$  complexes with  $\text{CN}^-$  ligands ( $\Delta_0 = 25000 \text{ cm}^{-1}$ ) and with  $\text{H}_2\text{O}$  ligands ( $\Delta_0 = 10000 \text{ cm}^{-1}$ ). Given that the pairing energy,  $P = 15000 \text{ cm}^{-1}$  for  $\text{Fe}^{2+}$  ion for both the complexes.  
(Given that  $h = 6 \times 10^{-34} \text{ J sec.}$ , Avogadro Number =  $6 \times 10^{23}$ , Speed of light in vacuum =  $3 \times 10^8 \text{ m sec}^{-1}$ ).
49. **STATEMENT-1:** The 'spin only' magnetic moment of a green complex, potassium amminetetrayano nitrosonium chromate (I) is 1.73 BM.  
**STATEMENT-2:** To have two d-orbitals empty, the pairing of electrons take place leaving behind one unpaired electron as  $\text{CN}^-$  is a stronger ligand.  
(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
50. Match the following :
- | Column I                                     | Column II                 |
|--|---------------------------|
| (A) $[\text{Fe}(\text{CN})_6]^{4-}$          | (p) Paramagnetic          |
| (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | (q) Diamagnetic           |
| (C) $[\text{Cu}(\text{NH}_3)_4]^{2+}$        | (r) Inner orbital complex |
| (D) $[\text{Ni}(\text{CN})_4]^{2-}$          | (s) Outer orbital complex |
- 51.
- | Column - I                                   | Column - II                 |
|--|-----------------------------|
| (A) $[\text{Co}(\text{en})_3]^{3+}$          | (p) Chelation               |
| (B) $[\text{Co}(\text{OX})_3]^{3-}$          | (q) Diamagnetic             |
| (C) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | (r) $d^2sp^3$ hybridisation |
| (D) $[\text{Co}(\text{NO}_2)_6]^{4-}$        | (s) Paramagnetic            |
52. Which of the following is/are characteristic of a tetrahedral complex ?  
(A) the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are the low energy orbitals  
(B) most tetrahedral complex are high spin  
(C) crystal field splitting is about thrice found in octahedral complexes  
(D) the splitting pattern is just opposite of that in octahedral complexes
- 53.
- | Column - I                                   | Column - II                 |
|--|-----------------------------|
| (A) $[\text{MnCl}_6]^{2-}$                   | (p) One unpaired electron   |
| (B) $[\text{Fe}(\text{CN})_6]^{3-}$          | (q) $d^2sp^3$               |
| (C) $[\text{CoF}_6]^{3-}$                    | (r) $sp^3d^2$               |
| (D) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | (s) Four unpaired electrons |
54. The green coloured complex  $\text{K}_2[\text{Cr}(\text{CN})_4(\text{NH}_3)(\text{NO})]$  is paramagnetic and its paramagnetic moment (spin only) is found to be 1.73 B.M. Which of the following is /are correct about it.  
(A) Hybridisation state of chromium is  $sp^3d^2$  and it cannot show geometrical isomerism  
(B) Its IUPAC name is Potassium amminetetrayanonitrosylchromate(II)  
(C) In the complex chromium is in (+III) oxidation number.  
(D) None of the above is correct
55. Which of the following pairs show co-ordination isomerism ?  
(A)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Mn}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  (B)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Br}_2$  and  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})\text{ClBr}]\text{Br} \cdot \text{H}_2\text{O}$   
(C)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_3\text{Br}_2]\text{Cl}_2$  (D)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$
56. An aqueous solution of titanium chloride, when subjected to magnetic measurement, measured zero magnetic moment. Assuming the complex, octahedral in aqueous solution, the formulae of the complex is :  
(A)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_2$  (B)  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_4$  (C)  $[\text{TiCl}_6]$  (D)  $[\text{Ti}(\text{H}_2\text{O})_4\text{Cl}_2]$
57. A complex cation is formed by Pt (in same oxidation state) with ligands (in proper number so that coordination number of Pt becomes six). Which of the following can be its correct IUPAC name :  
(A) Diaquaethylenediaminedithiocyanato-S-platinum(IV) ion  
(B) Diaquaethylenediaminedithiocyanato-S-platinate(IV) ion  
(C) Diaquaethylenediaminedithiocyanato-S-platinum(II) ion  
(D) Diaquabis (ethylenediamine) dithiocyanate-S-platinum(IV) ion

58. A co-ordination complex has the formula  $\text{PtCl}_4 \cdot 2\text{KCl}$ . The electrical conductance of this complex is found to be 256.8 (in same units as given in table below). Using the table given below for electrical conductance measurements and using the fact that treatment with  $\text{AgNO}_3$  produces no ppt. of  $\text{AgCl}$ . What is the co-ordination number of Pt in this complex :

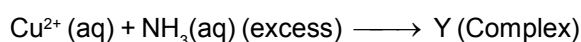
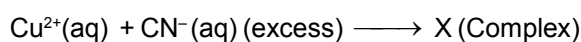
| Type of complex        | Electrical Conductivity    |
|------------------------|----------------------------|
| Nonelectrolyte         | 0 – 10 (due to impurities) |
| 1:1 Electrolyte        | 90 – 130                   |
| 1:2 or 2:1 Electrolyte | 230 – 290                  |
| 1:3 or 3:1 Electrolyte | 390 – 450                  |
| 1:4 Electrolyte        | 500 – 550                  |

- (A) 5 (B) 6 (C) 4 (D) 3
59. Which of the following is correct -  
 (A)  $\text{N}_2\text{H}_4$  can exhibit geometrical isomerism  
 (B) In  $\text{C}_2\text{H}_4$  the bond angle  $\angle\text{HCC} < \text{bond angle } \angle\text{HCH}$   
 (C)  $\text{Ag}_2\text{S}$  is much less soluble than  $\text{Ag}_2\text{O}$ , this fact can **not** be explained on the basis of Fajan's rule.  
 (D) The correct order of C – O bond length is  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$
60. Which of the following is (are) correct statement(s) (assuming oxidation number of metal does not affect crystal field energy)  
 (A) Considering  $\text{H}_2\text{O}$  to be a weak ligand then on the basis of CFSE only, we can say that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is more stable than  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (B) On the basis of CFSE only  $[\text{Fe}(\text{NH}_3)_6]^{2+}$  is more stable than  $[\text{Fe}(\text{NH}_3)_6]^{+3}$   
 (C) All octahedral complexes of Ni(II) are bound to be outer d-complex  
 (D) The type of d-orbital involved in the hybridisation for a square planar complex (CN = 4) is  $dz^2$ .
61. 2665 mg of an octahedral complex  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  needs 3.4 g of  $\text{AgNO}_3$  for complete precipitation of its all the free chloride ions. If the given complex is subjected to dehydration then the weight (in mg) of anhydrous complex obtained will be [Cr = 52, Cl = 35.5, Ag = 108, N = 14, O = 16, H = 1]
62. The equivalent weight of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in the following reaction is :  

$$3\text{Zn}^{2+} + 2\text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2 + 6\text{K}^+$$
- (A)  $\frac{\text{M.W.}}{4}$  (B)  $\frac{\text{M.W.}}{3}$  (C)  $\frac{\text{M.W.}}{6}$  (D)  $\frac{\text{M.W.}}{2}$
63. The compound which show paramagnetism is :  
 (A)  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$  (B)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  (C) NO (D)  $\text{NO}_2$
64. Which of the following is **incorrect** about Wilkinson's catalyst  
 (A) It is non-ionic complex  
 (B) It is diamagnetic complex  
 (C) It is tetrahedral complex  
 (D) It is very effective for selective hydrogenation of organic molecule at room temp. and pressure
65. Among the following metal carbonyls, the C – O bond order is lowest in :  
 (A)  $[\text{Mn}(\text{CO})_6]^+$  (B)  $[\text{Fe}(\text{CO})_5]$  (C)  $[\text{Cr}(\text{CO})_6]$  (D)  $[\text{V}(\text{CO})_6]^-$
66. The IUPAC name for  $\text{K}_2[\text{Cr}^{\text{VI}}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$  is  
 (A) potassium amminedicyanodioxoperoxochromate (VI)  
 (B) potassium amminedicyanatotetraoxochromium(III)  
 (C) potassium amminedicyanochromate (IV)  
 (D) potassium aminocyanodiperioxochromate (VI)
67. **STATEMENT-1** : Acetylaceton complexes of the metal ions are more stable than the corresponding ethylene-diamine complexes.  
**STATEMENT-2** : Acetylaceton complexes of the metal ions contain a six membered conjugate chelate rings and the resonance in its chelate ion is an additional factor contributing to the stability.  
 (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

68. The pair of molecules that exhibit geometrical isomerism are  
 (A)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{CO}(\text{NH}_3)_4\text{Cl}_2]^+$  (B)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$  and  $[\text{CO}(\text{NH}_3)_5\text{Cl}]^{2+}$   
 (C)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{CO}(\text{NH}_3)_6]^{3+}$  (D) All of the above show geometric isomerism
69. The correct IUPAC name of complex 'A' is  
 (A) cis-dichlorodiammineplatinate (II) (B) cis-diamminedichloridoplatinum (II)  
 (C) trans-diamminedichlorodoplatinum (II) (D) trans-diamminedichloridoplatinate (II).
70. Which of the following statements is true ?  
 (A) Both 'A' and 'B' forms are diamagnetic involving square planar geometry.  
 (B) Both 'A' and 'B' forms are paramagnetic involving square planar geometry.  
 (C) Both 'A' and 'B' forms are diamagnetic involving tetrahedral geometry.  
 (D) Both 'A' and 'B' forms are paramagnetic involving tetrahedral geometry.
71. Select the correct statement from the following statements.  
 (A) 'A' form is used as anti-cancer. (B) 'A' form has some dipole moment.  
 (C) (A) and (B) both. (D) None.

### Paragraph for Question Nos. 72 to 74



72. The IUPAC name of complexes (X) and (Y) are respectively :  
 (A) tetracyanocuprate (II) and tetraamminecuprate (II)  
 (B) tetracyanocuprate (I) and tetraamminecopper (II)  
 (C) tetracyanocopper (I) and tetraamminecuprate (II)  
 (D) tetracyanocopper (II) and tetraamminecopper (II)
73. The hybridisation of (X) and (Y) complexes are respectively :  
 (A) Both  $sp^3$  (B) Both  $dsp^2$  (C)  $dsp^2$  and  $sp^3$  (D)  $sp^3$  and  $dsp^2$
74. Which of the following statement is **incorrect** with respect to the complexes (X) and (Y) ?  
 (A) The complex (X) does not give black precipitate with  $\text{H}_2\text{S}$  in slightly acidic medium.  
 (B) The complex (Y) is deep blue in colour in aqueous solution.  
 (C) The copper is in +1 and +2 oxidation states in complex (X) and complex (Y) respectively.  
 (D) None

### Paragraph for Question Nos. 75 to 77

Splitting energy ( $\Delta_0$ ) can usually be measured from the absorption spectra of the complex ions. In simple cases when light is absorbed by a complex ion, an electron in one of the lower energy orbitals is excited to one of the higher energy orbital. The energy corresponding to the frequency of absorbed light is equal to  $\Delta_0$ . If value of  $\Delta_0$  for the complex is in visible region, the complex is coloured and the value of  $\Delta_0$  lies in ultraviolet or infrared region, the complex is colourless. For octahedral complexes the crystal field stabilisation energy is given by  $\text{CFSE} = [-0.4 t_{2g} N + 0.6 e_g N'] \Delta_0$  where N and N' are number of electrons in  $t_{2g}$  and  $e_g$  orbitals respectively.

The values of CFSE can be used for the correction of the experimental values of heats of hydration of divalent ions of first row transition metals. The correction is done by subtracting the calculated CFSE values from the experimental values.

75. The value of crystal field energy ( $\Delta_0$ ) for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is  $243 \text{ kJ mol}^{-1}$ . The crystal field stabilization energy (CFSE) in this complex is : (in  $\text{kJ mol}^{-1}$ ).  
 (A)  $\frac{3}{5} \times 243$  (B)  $\frac{2}{5} \times 243$  (C)  $3 \times \frac{2}{5} \times 243$  (D) 243
76. The heat of hydration of  $\text{Cr}^{2+}$  ion is  $460 \text{ k cal/mole}$ . For  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $\Delta_0 = 13,900 \text{ cm}^{-1}$ . What heat of hydration would be, if there were no crystal field stabilisation energy ?  
 (A)  $-436 \text{ k cal/mole}$  (B)  $-245 \text{ k cal/mole}$  (C)  $-4.84 \text{ k cal/mole}$  (D) i.e. none



77. An ion  $M^{II}$  forms the complexes of the types  $[M(H_2O)_6]^{2+}$ ,  $[MBr_6]^{4-}$  and  $[M(en)_3]^{2+}$ . The expected colours of the complexes, not necessarily in order, are green, red and blue. ( $\Delta_0 \propto$  Strength of ligand and the colour observed is the complimentary colour of the light absorbed)

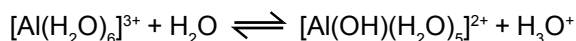
Select the correct matching :

| Column – I<br>(complex) |                    |     | Column – II<br>(colour of complex) |     |     |     |
|-------------------------|--------------------|-----|------------------------------------|-----|-----|-----|
| (a)                     | $[M(H_2O)_6]^{2+}$ | (P) | Green                              |     |     |     |
| (b)                     | $[M(Br)_6]^{4-}$   | (Q) | Red                                |     |     |     |
| (c)                     | $[M(en)_3]^{2+}$   | (R) | Blue.                              |     |     |     |
|                         | (a)                | (b) | (c)                                | (a) | (b) | (c) |
| (A)                     | (P)                | (R) | (Q)                                | (B) | (R) | (P) |
| (C)                     | (Q)                | (R) | (P)                                | (D) | (R) | (Q) |

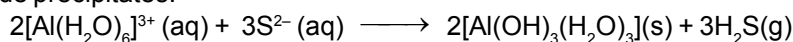
### Paragraph for Question Nos. 78 to 82

(Read the following passage and answer the questions numbered 1 to 5. They have only one correct option)

When aluminium salts are added to water,  $Al^{3+}$  ions are immediately attracted to the negative end of polar water molecules. They form hexaaquaaluminum(III) ions,  $[Al(H_2O)_6]^{3+}$ . This is often written simply as  $Al^{3+}(aq)$ . However the electric field associated with small, highly charged  $Al^{3+}$  ion is so intense that it draws electrons in the O – H bonds of water towards itself. This enables the water molecules to become donors. In aqueous solution, free water molecules act as bases and the following equilibrium is established ;



Thus, solutions of  $Al^{3+}$  salts are acidic, in fact as acidic as vinegar. When a base stronger than  $H_2O$ , e.g.  $S^{2-}$  is added to aqueous aluminium salts further  $H^+$  ions are removed from  $[Al(H_2O)_6]^{3+}$  and insoluble aluminium hydroxide precipitates.



More stronger base can remove  $4H^+$  ions as follows :



78. Which of  $[Al(H_2O)_6]^{3+}$ ,  $H_2S$  or  $H_2O$  is the strongest acid ?  
 (A)  $[Al(H_2O)_6]^{3+}$  (B)  $H_2S$  (C)  $H_2O$  (D) all same
79. A base which will behave just like  $S^{2-}$   
 (A)  $CO_3^{2-}$  (B)  $CH_3OH$  (C)  $NH_4^+$  (D)  $NH_2^-$
80. Another ion that would behave similar to  $Al^{3+}(aq)$  in forming an acidic solution is  
 (A)  $Ga^{+3}(aq)$  (B)  $Ba^{+2}(aq)$  (C)  $Cu^{+2}$  (D)  $Tl^+$
81.  $[Al(OH)_3(H_2O)_3](s)$  more simply written as  $Al(OH)_3(s)$  is
82. Which gas would get absorbed when passed into a solution of  $Al^{3+}(aq)$  ?  
 (A)  $NH_3$  (B)  $NO$  (C)  $CO$  (D)  $O_2$

### Paragraph for Question Nos. 83 to 84

Read the following passage carefully and answer the questions. (Q.24 to Q.26)

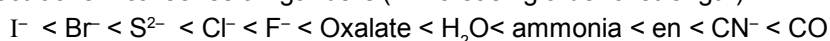
The colour of a complex is dependent on crystal field splitting and it can be decided by knowing the energy or wavelength of photon which it absorbs to get excited from lower energy level to higher energy level which corresponds to the splitting created by the ligands, hence crystal field splitting will be generally equal to energy of photon absorbed. The colour exhibited by the complex is generally complimentary to colour absorbed by it. If photon of higher energy is absorbed then color shown by it will be generally of photon of low energy. Hence the electronic spectra can be used to predict the nature of the ligands, the crystal field stabilization energy of complexes and many other similar properties. By knowing the complementray colour to a colour the colour of the complexes can be predicted if energy or wavelength of photons absorbed by the

complex is known to us. (Energy of photon =  $\frac{hc}{\lambda}$  where  $h = 6 \times 10^{-34}$  J sec,  $c = 3 \times 10^8$  m sec $^{-1}$  ,

$\lambda$  = wavelength of the photon, Avogadro number =  $6 \times 10^{23}$ )

Given that :

The spectrochemical series of ligands is (in increasing order of strength)



83. The value of  $\Delta_0$  for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is found to be  $240 \text{ kJ mol}^{-1}$  then predict the colour of the complex using the following table.

| Absorbed light | $\lambda$ (nm) (absorbed) | Colour exhibited |
|----------------|---------------------------|------------------|
| Blue           | 435 – 480                 | Yellow           |
| green-blue     | 480 – 490                 | orange           |
| blue – green   | 490 – 500                 | red              |
| green          | 500 – 560                 | purple           |
| yellow – green | 560 – 580                 | violet           |
| Yellow         | 580 – 595                 | blue             |
| Red            | 605 – 700                 | blue green       |

- (A) blue green      (B) orange      (C) yellow      (D) Purple

84. Given that the energy of the photons of different colours decreases in the order of VIBGYOR (Violet > Indigo > Blue > Green > Yellow > Orange > Red) and that if complex absorbs a photon of low energy then it shows colour of high energy photon then if an ion,  $M^{2+}$ , forms the complexes  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{MBr}_6]^{4-}$ , and  $[\text{M}(\text{en})_3]^{2+}$ . The colours of the complexes, though not necessarily in order, are green, red, and blue. Match the complexes with the appropriate colour. (**do not use the table of complementary colours as given in question number 24, for this question**)

- (A)  $[\text{MBr}_6]^{4-}$  blue,  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  green,  $[\text{M}(\text{en})_3]^{2+}$  red  
 (B)  $[\text{MBr}_6]^{4-}$  green,  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  blue,  $[\text{M}(\text{en})_3]^{2+}$  red  
 (C)  $[\text{MBr}_6]^{4-}$  green,  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  red,  $[\text{M}(\text{en})_3]^{2+}$  blue  
 (D)  $[\text{MBr}_6]^{4-}$  red,  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  green,  $[\text{M}(\text{en})_3]^{2+}$  blue

#### Paragraph for Question Nos. 85 to 89

Read the following passage carefully and answer the questions.

In coordination chemistry there are a variety of methods applied to find out the structure of complexes. One method involves treating the complex with known reagents and from the nature of reaction, the formula of the complex can be predicted. An isomer of the complex  $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}_2\text{Br}$ , on reaction with concentrated  $\text{H}_2\text{SO}_4$  (dehydrating agent) it suffers loss in weight and on reaction with  $\text{AgNO}_3$  solution it gives a white precipitate which is soluble in  $\text{NH}_3$  (aq).

85. The **correct** formula of the complex is :  
 (A)  $[\text{CoClBr}(\text{en})_2] \text{H}_2\text{O}$       (B)  $[\text{CoCl}(\text{en})_2 (\text{H}_2\text{O})] \text{BrCl}$   
 (C)  $[\text{CoBr}(\text{en})_2(\text{H}_2\text{O})]\text{Cl}_2$       (D)  $[\text{CoBrCl}(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$
86. If all the ligands in the coordination sphere of the above complex be replaced by  $\text{SCN}^-$ , then the paramagnetic moment of the complex ion (due to spin only) will be :  
 (A) 2.8 BM      (B) 5.9 BM      (C) 4.9 BM      (D) 1.73 BM
87. Similarly if all the ligands in the coordination sphere be replaced by  $\text{NCS}^-$  then the paramagnetic moment of the complex ion (due to spin only) will be :  
 (A) 1.73 BM      (B) 0.0 BM      (C) 4.9 BM      (D) 5.9 BM
88. If one mole of original complex is treated with excess  $\text{Pb}(\text{NO}_3)_2$  solution, then the number of moles of white precipitate (of  $\text{PbCl}_2$ ) formed will be :  
 (A) 0.5      (B) 1.0      (C) 0.0      (D) 3.0
89. The number of geometrical isomers of the formula of the above complex are (including the complex)  
 (A) 2      (B) 3      (C) 4      (D) 1

### Paragraph for Question Nos. 90 to 92

With the help of CFT number of unpaired electron in a compound can be calculated and we can calculate its paramagnetic moment(due to spin only), by the formula :

$\mu = \sqrt{n(n+2)}$  Bohr magneton (BM). where n is the number of unpaired electron in the complex.

For spectral analysis the separation between  $t_{2g}$  and  $e_g$  orbitals, called ligand field splitting. Parameter  $\Delta_0$  (for octahedral complexes) should be known to us, which can be easily calculated by observing the absorption spectrum of one electron complex. Figure shows the optical absorption spectrum of the  $d^1$  hexaaquatitanium(III) ion  $[\text{Ti}(\text{H}_2\text{O})]^{3+}$ . The CFT assigns the first absorption maximum at  $20,300 \text{ cm}^{-1}$  to the transition  $e_g \leftarrow t_{2g}$ . For multielectronic( $d^2$  to  $d^{10}$ ) system, the calculation of  $\Delta_0$  by absorption spectrum is not that easy as the absorption spectrum will also be affected by electron-electron repulsions.

90. The crystal field stabilization energy (CFSE) for complex given in the passage,  $[\text{Ti}(\text{H}_2\text{O})]^{3+}$  will be (in kJ/mol)  
(A) 243 kJ/mole (B) 97 kJ/mole (C) 194 kJ/mole (D) 143 kJ/mole
91. The complex for which the calculation of crystal field splitting can be most easily done, by knowing its absorption spectrum, will be  
(A)  $[\text{TiCl}_6]^{2-}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (C)  $[\text{Ti}(\text{CN})_6]^{3-}$  (D)  $[\text{CoF}_6]^{3-}$
92. The magnetic moments of following, arranged in increasing order will be (atomic number of Co = 27)  
(1)  $\text{Co}^{3+}$  (octahedral complex with a strong field ligand)  
(2)  $\text{Co}^{3+}$  (octahedral complex with a weak field ligand)  
(3)  $\text{Co}^{2+}$  (tetrahedral complex)  
(4)  $\text{Co}^{2+}$  (square planar complex)

### Paragraph for Question Nos. 93 to 95

Formula of complex is determined by many experimental methods. One of which is measurement of depression in freezing point, which gives the number of ions present in the complex. In one of the experiment..... Compound  $(\text{PdCl}_4 \cdot 6\text{H}_2\text{O})$  is a hydrated complex ; 1 molal aqueous solution of it has freezing point of 269.28 K. Assuming 100% ionization of the complex, calculate the magnetic moment of the complex (given :  $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$  ; and atomic number of Pd = 46) then answer the following question :

93. The correct formula of complex is :  
(A)  $[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  (B)  $[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$   
(C)  $[\text{Pd}(\text{H}_2\text{O})_6]\text{Cl}_4$  (D)  $[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$
94. Magnetic moment of the complex is :  
(A) 1.3 B.M. (B) 4.89 B.M. (C) 5.9 B.M. (D) 3.89 B.M.
95. The maximum number of moles of AgCl can be formed by the reaction of  $\text{AgNO}_3$  with one of its hydrated isomers :  
(A) 1 mole (B) 2 mole (C) 3 mole (D) 4 mole

## ANSWER KEY AND SOLUTION

1. (A)

**Sol.** X :  $\text{Hg} [\text{Co}(\text{SCN})_4]$       Y :  $[\text{Co}(\text{NCS})_4]$   
 Co(II) is  $sp^3$                       Co(II) is  $dsp^2$   
 paramagnetic = (3e)      paramagnetic = (1e)

2. (A)

**Sol.**  $2 [\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2 \text{Ag}$   
 Tetrahedral

3. (B)

**Sol.**  $[\text{NiCl}_2(\text{PPh}_3)_2]$  is non-ionic and tetrahedral

4. (B)

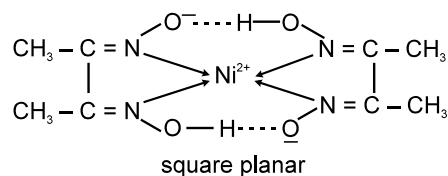
**Sol.**  $\text{K} [\text{AgF}_4]$  is square planar because  $\text{Ag}(\text{III})$  is  $4d^8$  and complex is diamagnetic.

5. (A)

**Sol.**  $\text{Cs}_2 [\text{CuCl}_4]$  (orange) is tetrahedral because in  $\text{Cu}(\text{II})$  the unpaired electron is in 3d. But  $(\text{NH}_4)_2 [\text{CuCl}_4]$  yellow is square planar because the unpaired electron is not in 3d rather in some promoted state 's' or 'p'.

6. (C)

**Sol.** The complex is

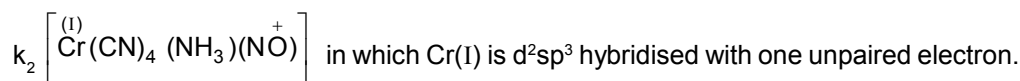


7. (B)

**Sol.** According to the question  $k_3 [\text{Ni}(\text{CN})_5]$  is paramagnetic and square pyramidal with non-zero dipole moment.

8. (D)

**Sol.** The complex is actually



9. (C)

**Sol.** Sodium nitroprusside is  $\text{Na}_2 [\text{Fe}(\text{CN})_5 (\text{NO})^+]$ ; a diamagnetic complex.

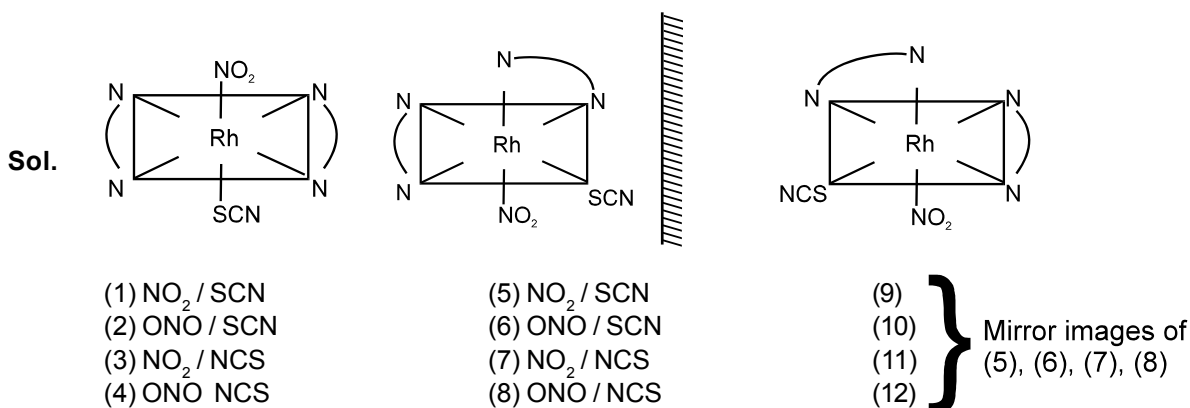
10. (A)

**Sol.** On the basis of number of electrons the correct order is  $P > Q > R > S$ .

11. (C)

**Sol.** In the first complex ligand is  $\text{O}_2^{2-}$  which is oxidised into  $\text{O}_2^{1-}$ .  
 hence  
 O – O bond length decreases.

12. (D)



13. (A)

Sol. Pt(II) is  $5d^8$ , forms square planar complex which is diamagnetic.  $[\text{PtCl}_2(\text{NH}_3)(\text{OH}_2)]$  will show geometrical isomerism.

14. (C)

Sol.  $\text{Ni}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_4]^{2+}$

$$\therefore k = \frac{[\text{Ni}(\text{NH}_3)_4]^{2+}}{[\text{Ni}^{2+}][\text{NH}_3]^4}$$

$$\text{But } \frac{[\text{Ni}^{2+}]}{[\text{Ni}^{2+}] + [\text{Ni}(\text{NH}_3)_4]^{2+}} = 1.6 \times 10^{-6}$$

$$\text{or } \frac{\text{Ni}^{2+}}{[\text{Ni}(\text{NH}_3)_4]^{2+}} \approx 1.6 \times 10^{-6}$$

$$\therefore k = \frac{10^6}{1.6 \times (0.5)^4} = 10^7$$

Hence instability constant =  $10^{-7}$

15. (D)

Sol. (A) is tetrahedral

(B) is square planar [Pt(II) complex]

(C) is Fe(I) complex, contains one unpaired  $e^-$

16. (C)

Sol. In  $[\text{Fe}(\text{CN})_6]^{4-}$ ; Fe(II) is  $t_{2g}^6$ ,  $e_g^0$  due to strong ligands.

17. (D)

Sol. In  $[\text{CuCl}_2]^-$  EAN =  $28 + 4 = 32$

18. (C)

Sol.  $[\text{CrCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  will liberate  $\frac{1}{3}$  of the total chloride ions for precipitation.

19. (B)

Sol. On the basis of nature of ligands the correct order is  $Q > R > S > P$ .

20. (C)

Sol. The options can give CFSE =  $-0.6 \Delta_0$  with weak field ligands  $\Rightarrow d^4$  and  $d^9$ .

21. (A)

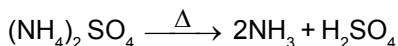
Sol. Ammonia is a stronger field ligand than water.

22. (B)

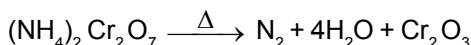
Sol.  $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$  (A)

$3\text{CuO} + 2\text{NH}_3 \longrightarrow 3\text{Cu} + \text{N}_2$  (C)  $\uparrow$  +  $3\text{H}_2\text{O}$

Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidizing (e.g.  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ ) then ammonia is evolved.



If the anion is more oxidising (e.g.  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) then  $\text{NH}_4^+$  is oxidised to  $\text{N}_2$  or  $\text{N}_2\text{O}$ .



23. (B)

Sol. When  $\text{K}_4[\text{Fe}(\text{CN})_6]$  changes into products -  $\text{KOH}$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ , then the n-factor of the compound is 61 and its equivalent weight =  $M/61$ .

24. (C)

Sol. SFL  $d^6 = t_{2g}^{2,2,2} e_g^{0,0}$  - diamagnetic

WFL  $d^6 = t_{2g}^{2,1,1} e_g^{1,1}$  - Paramagnetic

25. (A)

Sol. (A) compound is a neutral molecule so there should not be potassium cation.

26. (A)

Sol. From the given figure it is clear a – being strong H-bond (minimum distance)

27. (C)

Sol. (A)  $[\text{Pt}(\text{en})_2(\text{SCN})_2]^0$  – it is not an ion

(B)  $[\text{Pt}(\text{en})_2(\text{SCN})_2]^{2+}$  – it should not be planitnate

(C) Correct

(D)  $[\text{Pt}(\text{NH}_3)_2(\text{en})_2(\text{SCN})_2]$  CN = 8

28. (A)

Sol. Correct name is dichlorodimethylglyoximatecobalt (II)

29. (D)

Sol. (A)  $[\text{Cu}(\text{NH}_3)_4]^{2+} = 29 - 2 + 8 = 35$

$[\text{Fe}(\text{CN})_6]^{3-} = 26 - 3 + 12 = 35$

(B)  $[\text{Fe}(\text{CN})_6]^{4-} = 26 - 2 + 12 = 36$

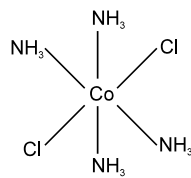
$[\text{Co}(\text{NH}_3)_6]^{3+} = 27 - 3 + 12 = 36$

(C)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-} = 27 - 3 + 12 = 36$

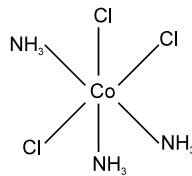
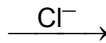
$[\text{Ni}(\text{CO})_4] = 28 + 8 = 36$

30. (B)

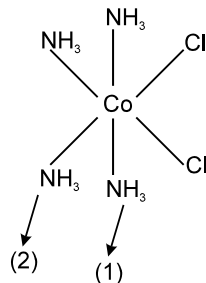
Sol. Moderate



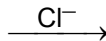
symmetrical



only single product



replacable positions



two isomers product

31. (C)

Sol.  $[\text{Ni}(\text{CN})_4]^{2-}$  –  $\text{dsp}^2$  – square planar

$[\text{Ag}(\text{NH}_3)_2]^+$  –  $\text{sp}$  – linear

$[\text{Fe}(\text{CO})_5]$  –  $\text{dsp}^3$  – trigonal bipyramidal

$[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  –  $\text{d}^2\text{sp}^3$  – octahedral

$[\text{NiCl}_4]^{2-}$  –  $\text{sp}^3$  – tetrahedral

32. (C)

Sol.  $[\text{Mn}(\text{CN})_6]^{3-}$ :  $\text{Mn}^{3+} = 3\text{d}^4 4\text{s}^0 = t_{2g}^{2,1,1} e_g^{0,0} = \text{d}^2\text{sp}^3$  hybridised no. of unpaired electrons = 2  
magnetic moment =  $\mu_B = \sqrt{2 \times 4}$  BM  $\approx 2.8$  BM

$[\text{MnBr}_4]^{2-}$ :  $\text{Mn}^{2+} = 3\text{d}^5 4\text{s}^0 = e_g^{1,1} t_{2g}^{1,1,1} = \text{sp}^3$  hybridised no. of unpaired electrons = 5  
magnetic moment =  $\mu_B = \sqrt{5 \times 7}$  BM  $\approx 5.9$  BM

33. (A,B,D)

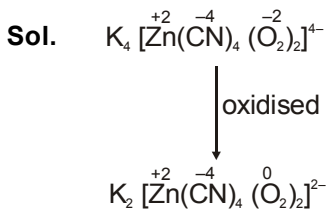
Sol. In 'A' both are  $sp^3d$   
 In 'B' both are  $sp^3d$   
 In 'C'  $[ClF_2O]^+$  is  $sp^3$  but  $[ClF_4O]^-$  is  $sp^3d^2$   
 In 'D' both are  $sp^3d^2$

34. (A,B)

Sol. The complex must be  
 $[Rh ClH_2 (PPh_3)_3]$

for gives electronic configuration of  $t_{2g}^{2,2,2}, e_g^{0,0}$  and it will be  $d^2sp^3$  hybridised, diamagnetic complex

35. (C,D)



so there is oxidation of  $O_2^-$  to  $O_2$   
 so O-O bond length decreases and paramagnetic moment increases.

36. (A,C,D)

Sol. (A)  $H^+ BF_4^-$  (C)  $H^+ ClO_4^-$  (D)  $H^+ PF_6^-$

37. (A,B,C)

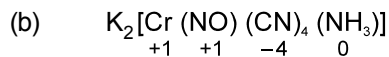
Sol. (A)  $Co(H_2O)_6]^{3+} = t_{2g}^{2,2,1} e_g^{1,1}$  CFSE =  $-0.8 \Delta_0$

38. (C)

Sol. Assertion is correct but reason is incorrect because  $OH^-$  ions combines with  $NH_4^+$  to form a weak base  $NH_4OH$

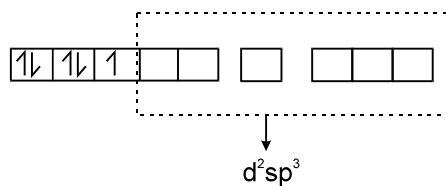
39.

Sol. (a) (i) linear,  $sp$  (ii) trigonal planar,  $sp^2$  (iii) octahedral,  $sp^3d^2$



Cr =  $3d^5, 4s^1$

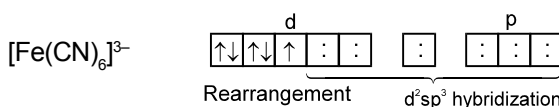
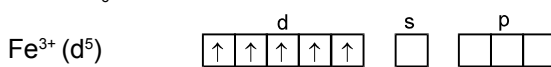
Cr<sup>+</sup> =  $3d^5$  ∴ NO must be in +1 state



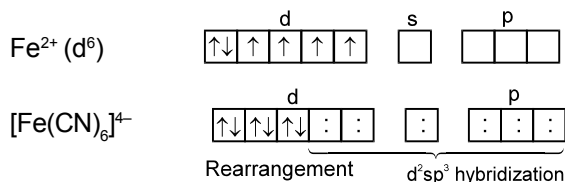
Name : potassium amminetetracyanonitrosoniumchromate (I)  
 or potassium amminetetracyanonitrosyliumchromate (I)

40.

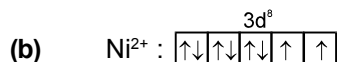
Sol. (a)  $[Fe(CN)_6]^{3-}$  involved  $d^2sp^3$  hybridization.



One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.  
 $[Fe(CN)_6]^{4-}$  involves also  $d^2sp^3$  hybridization but it has  $Fe^{2+}$  ion as central ion.

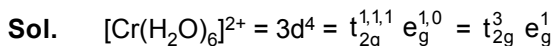


All orbitals are doubly occupied, hence it is diamagnetic in nature.



Thus only one 3d-orbital is available if all pairing occurs due to strong field ligand. Therefore,  $d^2sp^3$  hybridisation is not possible. Only  $sp^3d^2$  is possible which represent outer complex.

41. Ans. 3197



$$\begin{aligned} \text{CFSE} &= |-0.6 D_0| = 0.6 \times 6 \times 10^{-34} \times 3 \times 10^8 \times 15 \times 10^5 \times 6 \times 10^{23} \times 10^{-3} \text{ kJ/mole} \\ &= 972 \times 10^{-1} \text{ kJ/mole} \\ &= 97.2 \text{ kJ/mole} \\ &\approx 97 \text{ kJ/mole} \end{aligned}$$

Ans. 3197

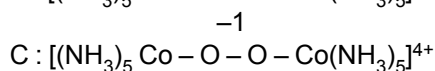
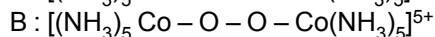
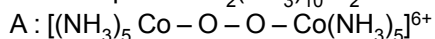
42.

Sol.  $\text{Co} = \frac{36.875}{59} = 0.625$

$$\text{NH}_3 = \frac{53.125}{17} = 3.125$$

$$\text{O} = \frac{10}{16} = 0.625$$

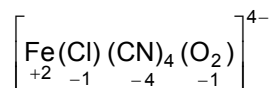
∴ The complex is  $\text{Co}_2(\text{NH}_3)_{10}\text{O}_2$  and the cations are



∴ Answer is 654

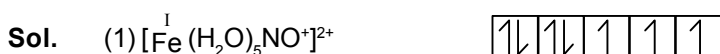
43. (C)

Sol. The given complex is actually



hence Fe(II) is  $t_{2g}^6, e_g^0$  due to effect of strong ligands but it is paramagnetic due to  $\text{O}_2^{-1}$  ligand.

44. (C)



(2)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ , will not exhibit stereo isomerism

(3)  $[\text{RhCl}(\text{PPh}_3)_3]$  →  $4d^8$  configuration so  $dsp^2$

$[\text{Zn}(\text{CN})_4]^{2-}$   $3d^{10}$  configuration. No empty d-orbital available for  $dsp^2$  hybridisation. So it undergoes  $sp^3$  hybridisation, although,  $\text{CN}^-$  is stronger ligand.

(4) Cr(I) as NO is  $\text{NO}^+ \rightarrow 3d^5 - d^2sp^3$  as  $\text{CN}^-$  stronger ligand ;  $\mu = 1.73 \text{ B.M}$



- 45. Ans.** (A – p,q,s) ; (B – q,r,s) ; (C – p,q,s) ; (D – q,r,s)  
**Hint.** (A) Ni  $\longrightarrow$  zero oxidation state and CO stronger ligands – pairing takes place  $\longrightarrow$   $sp^3$ .  
 (B) Ag  $\longrightarrow$  + 3 oxidation state  $\longrightarrow$   $4d^8$  configuration  $\longrightarrow$   $dsp^2$ .  
 (C) Zn  $\longrightarrow$  + 2 oxidation state  $\longrightarrow$   $d^{10}$  configuration, all electrons are paired  $\longrightarrow$   $sp^3$ .  
 (D) Rh  $\longrightarrow$  + 1 oxidation state  $\longrightarrow$   $4d^8$  configuration  $\longrightarrow$   $dsp^2$ .  
 In all these species, all electrons are paired and thus diamagnetic.

- 46. Ans.** (A – p, q, s) ; (B – q, r, s) ; (C – p, q, s) ; (D – q, r)  
**Sol.** (A) Ni  $\longrightarrow$  zero oxidation state and CO stronger ligands – pairing takes place hybridisation  $sp^3$ .  
 (B) Ag  $\longrightarrow$  + 3 oxidation state  $\longrightarrow$   $4d^8$  configuration  $\longrightarrow$   $dsp^2$ .  
 (C) Zn  $\longrightarrow$  + 2 oxidation state  $\longrightarrow$   $3d^{10}$  configuration, all electrons are paired  $\longrightarrow$   $sp^3$ .  
 (D) Rh  $\longrightarrow$  + 1 oxidation state  $\longrightarrow$   $4d^8$  configuration  $\longrightarrow$   $dsp^2$ .  
 $[\text{RhCl}(\text{PPh}_3)_3]$  is red violet because of charge transfer from ligand to metal.

**47. Ans.** 311

**Sol.** Net stabilization energy of  $\text{Fe}^{2+}$  will  $\text{CN}^-$

$$\text{ligands } t_{2g}^{2,2,2} e_g^{0,0} = -2.4 \Delta_0 + 2P = (-2.4 \times 25000 + 2 \times 15000) \text{ cm}^{-1}$$

$$= -30000 \text{ cm}^{-1}$$

$$\text{net stabilisation energy of } \text{Fe}^{2+} \text{ ions with } \text{H}_2\text{O} \text{ ligands } t_{2g}^{2,1,1} e_g^{1,1} = -1.6 \Delta_0 + 1.2\Delta_0 = -0.4\Delta_0$$

$$= -4000 \text{ cm}^{-1}$$

$$\text{so required difference} = 26000 \text{ cm}^{-1}$$

$$= 26000 / 83.7 \text{ kJ/mol}$$

$$= \mathbf{310.6 \text{ kJ/mole}}$$

$$= \mathbf{311 \text{ kJ/mole}}$$

**48.**

**Sol.** Net stabilization energy of  $\text{Fe}^{2+}$  will  $\text{CN}^-$

$$\text{ligands } t_{2g}^{2,2,2} e_g^{0,0} = -2.4 \Delta_0 + 3P = (-2.4 \times 25000 + 3 \times 15000) \text{ cm}^{-1}$$

$$= -15000 \text{ cm}^{-1}$$

$$\text{net stabilisation energy of } \text{Fe}^{2+} \text{ ions with } \text{H}_2\text{O} \text{ ligands } t_{2g}^{2,1,1} e_g^{1,1} = -0.0 \Delta_0 + P$$

$$= 11000 \text{ cm}^{-1}$$

$$\text{so required difference} = 26000 \text{ cm}^{-1} = 26 \times 10^5 \text{ m}^{-1}$$

$$= 6 \times 10^{-34} \times 3 \times 10^8 \times 26 \times 10^5 \times 6 \times 10^{23} \times 10^{-3} \text{ kJ/mole}$$

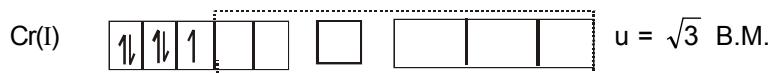
$$= 2808 \times 10^{-1} \text{ kJ/mole}$$

$$= 281 \text{ kJ/mole}$$

**Ans.** 280.8 kJ/mol = **281**

**49. (A)**

**Hint :**



$d^2sp^3$

**50. Ans.** (A – q,r), (B – p,s), (C – p,r), (D – q,r)

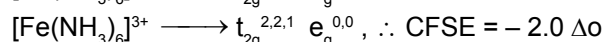
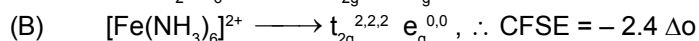
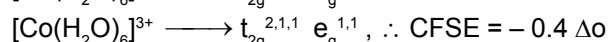
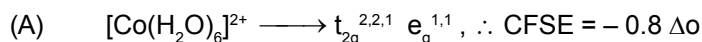
| Complex                                  | Oxidation state | Type                            | Magnetic property |
|--|-----------------|---------------------------------|-------------------|
| $[\text{Fe}(\text{CN})_6]^{4-}$          | +2              | $d^2sp^3$ inner orbital complex | Diamagnetic       |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | +2              | $sd^3d^2$ outer orbital complex | Paramagnetic      |
| $[\text{Cu}(\text{NH}_3)_4]^{2+}$        | +2              | $d sp^2$ inner orbital complex  | Paramagnetic      |
| $[\text{Ni}(\text{CN})_4]^{2+}$          | +2              | $d sp^2$ inner orbital complex  | Diamagnetic       |

**Sol.**



60. (A,B,C)

Sol. Moderate



(C) For co-ordination no six, two empty d-orbitals are not available for  $d^2sp^3$  as Ni(II) has  $3d^8 4s^0$  configuration.

(D) d-orbital involved is  $dx^2 - y^2$  not  $dz^2$

61. Ans. 2485

Sol. Moderate

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  mol. wt. = 266.5

$$\text{moles given} = \frac{2.665}{266.5} = 0.01$$

$$\text{moles of AgNO}_3 \text{ consumed} = \frac{3.4}{170} = 0.02$$

(m = 108 + 14 + 48 = 170)

$\therefore \text{Cl}^-$  (free) = 0.02 mole

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

when subjected to dehydration it will lose 0.01 mole  $\text{H}_2\text{O}$  i.e. 0.18 gm = 180 mg

$\therefore$  remaining wt. = 2665 – 180 = 2485

62. (B)

Sol. Similar to no. of replaceable  $\text{H}^+$  from acid,

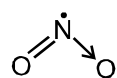
For salt  $2\text{K}_4[\text{Fe}(\text{CN})_6]$  replaces  $6\text{K}^+$

$\text{K}_4[\text{Fe}(\text{CN})_6]$  replaces  $3\text{K}^+$  in the reaction

So n factor is 3

63. (A,C,D)

Sol. Which have unpaired  $e^-$



$\text{NO} \equiv \text{O}_2^+$  have one unpaired electron.

B.O. = 2.5

$\text{Ag}^+$  is diamagnetic

$\text{Cu}^{+2}$  is paramagnetic complex

64. (C)

Sol. Wilinon's catalyst

- $[\text{RhCl}(\text{pph}_3)_3]$
- square planar
- $dsp^2$  hybridised
- diamagnetic
- Hydrogenation catalyst

65. (D)

Sol. (A)  $[\text{Mn}(\text{CO})_6]^+$   
 $\text{Mn}^+ = 3d^5 4s^1 \approx 3d^6 = d^2sp^3$  hybridised

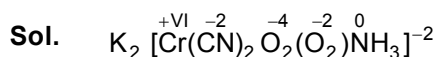
(B)  $[\text{Fe}(\text{CO})_5]$   
 $\text{Fe} = 3d^6 4s^2 \approx 3d^8 = dsp^3$  hybridised

(C)  $[\text{Cr}(\text{CO})_6]$   
 $\text{Cr} = 3d^5 4s^1 \approx 3d^6 = d^2sp^3$  hybridised

(D)  $[\text{V}(\text{CO})_6]^-$   
 $\text{V} = 3d^3 4s^2$   
 $\text{V}^- = 3d^6 = d^2sp^3$  hybridised

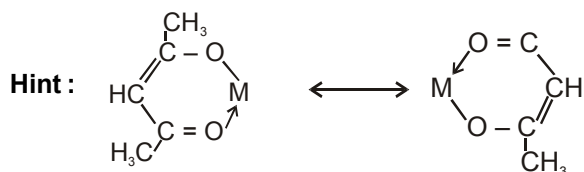
$\text{V}^-$  - having greater -ve charge density can easily back donate & hence C – O bond order is lowest

66. (A)

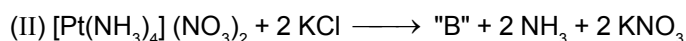
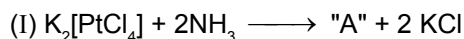


So IUPAC name is potassium amminedicyanodioxoperoxochromate (VI)

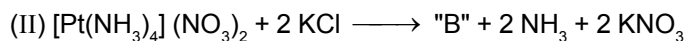
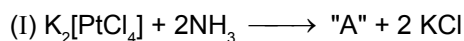
67. (A)



A chemist performs the following reactions :



He finds that both A and B are white, crystalline compounds that give elemental analysis for empirical formula  $PtCl_2(NH_3)_2$ . However, A is most soluble in polar solvents, such as ethanol, while B is soluble in petroleum ether and carbon tetrachloride. The compound which has non-zero dipole moment is also used as anti-cancer agent.



68. (A)

Sol.  $Ma_5b$  or  $Ma_6$  do not show

69. (B)

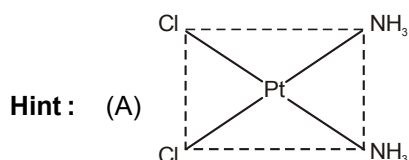
Hint : Compound 'A' is soluble in polar solvent.

$\therefore$  It should have some dipole moment. So the compound is  $cis-[PtCl_2(NH_3)_2]$ .

70. (A)

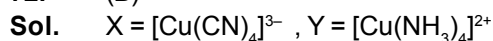
Hint :  $5d^8$  configuration.

71. (C)



dipole moment is nonzero, so is polar in nature and is used as anti-cancer

72. (B)



73. (D)

Sol.  $X = [Cu(CN)_4]^{3-}$  -  $3d^{10}$  configuration, hybridisation is  $sp^3$  and it is diamagnetic in nature.

$Y = [Cu(NH_3)_4]^{2+}$  -  $3d^9$  configuration one unpaired d-electron jumps to higher energy orbital (4p) making one d-orbital empty for  $dsp^2$  hybridisation.

74. (D)

Sol.  $[Cu(CN)_4]^{3-}$ ,  $d^{10}$  configuration, all electrons are paired so diamagnetic with strong  $CN^-$  ligands and no d-d transition is possible.

$[Cu(NH_3)_4]^{2+}$ ,  $d^9$  configuration containing one electron unpaired so paramagnetic, therefore, deep blue coloured (fact)

So answer is none.

75. (B)

76. (A)

Hint : Experimental value – calculated value of CFSE (– 24 k cal/mole).

77. (B)

Hint : Order of  $\Delta_0$  will be  $\text{Br}^- < \text{H}_2\text{O} < \text{en}$ .

The green complex absorbs red (low energy) light ; the red complex absorbs green (high energy) light ; the blue complex absorbs orange (medium-energy) light.

78. (A)

Sol. From the passage it is clear

79. (A)

Sol.  $\text{S}^{2-}$  is anion of a weak acid so is  $\text{CO}_3^{2-}$  ion, which is also anion of a weak acid, should be the most appropriate answer

80. (A)

Sol.  $\text{Al}^{3+}$  ion and  $\text{Ga}^{3+}$  ions behave similarly.

81.

Sol.  $\text{Al}(\text{OH})_3$  is amphoteric in nature

82. (A)

Sol.  $\text{NH}_3$  will be a basic ligand while others are neutral, so reacts readily with  $\text{Al}^{3+}$ .

83. (C)

Sol. 
$$240000 \text{ (J)} = \frac{hc}{\lambda} = \frac{6 \times 10^{-34} \times 3 \times 10^8 \times 6 \times 10^{23}}{\lambda_{(\text{nm})} \times 10^{-9}}$$

$$\therefore \lambda_{(\text{nm})} = 450$$
  
$$\therefore \text{yellow colour}$$

84. (A)

Sol.  $\text{CFSE} = -25 \text{ kcal /mole} = 0.6 \Delta_0$

so 
$$\Delta_0 = \frac{2.5 \times 10^3 \times 4.2}{0.6} = \frac{6 \times 10^{-34} \times 3 \times 10^8}{\lambda} \times 6 \times 10^{23}$$

85. (D)

86. (C)

87. (B)

Sol.  $\text{NCS}^-$  will be a strong field ligand

88. (A)

Sol. Only one  $\text{Cl}^-$  ion is of free ion from complex so 1 mole of complex will generate precipitate of half mole of  $\text{PbCl}_2$ .

89. (A)

Sol. **Moderate**

Why two geometrical isomers are possible of  $\text{M}[(\text{AA})_2\text{ab}]$ .

90. (B)

Sol.  $\text{Ti}^{+3}$  is  $3d^1$  system, 
$$\Delta_0 = 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2 \frac{\text{J}}{\text{ion}}$$
  
$$= 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2 \times 10^{-3} \times 6.02 \times 10^{23} \frac{\text{kJ}}{\text{mol}} = 243 \frac{\text{kJ}}{\text{mol}}$$

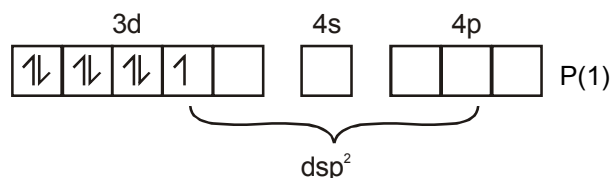
Now, 
$$\text{CFSE} = 0.4 \times \Delta_0 = 0.4 \times 243 = 97.2 \frac{\text{kJ}}{\text{mol}}$$

91. (C)

Sol. Since this is a  $d^1$  system.

92.

Sol. (1)  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$   $D(0)$ ,  $\uparrow\downarrow$   $\uparrow$   $\uparrow$   $P(4)$ ,  $\uparrow\downarrow$   $\uparrow\downarrow$   $P(3)$ ,



93. (A)

94. (B)

95. (D)

Sol. 93 to 95

$$\Delta T_f = i \times K_f \times m ; \text{ here, } \Delta T_f = 273 - 269.28 = 3.72 \text{ K}$$

$$\Rightarrow 3.72 = i \times 1.86 \times 1$$

$$\therefore i = \frac{3.72}{1.86 \times 1} = 2$$

i.e. given complex will give two ions when dissolved in water. So probable formula of the complex is  $[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ .

In this complex, let O.S. of Pd be x, then

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

$$\therefore x = +4$$

$\text{Pd}^{4+} {}_{36}[\text{Kr}] sp^3d^2$  hybridization

$[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  has four unpaired electrons (N).

Now, magnetic moment ( $\mu$ ) =  $\sqrt{N(N+2)}$  B.M.

$$= \sqrt{4(4+2)} = \sqrt{24}$$

$$= 4.89 \text{ B.M.}$$

1. You are given the following two complexes X and Y which are isomers of each other X is  $\text{Hg}[\text{Co}(\text{SCN})_4]$ . It is further given that paramagnetic moment of X is found to be more than Y. Then which of the following is correct.

(A\*) Anion of X will be tetrahedral and that of Y will be square planar.  
 (B) Anion of X will be square planar but that of Y will be tetrahedral  
 (C) Both the anions will be tetrahedral  
 (D) Both the anions will be square planar

**Sol.** X :  $\text{Hg}[\text{Co}(\text{SCN})_4]$       Y :  $[\text{Co}(\text{NCS})_4]$   
 Co(II) is  $\text{sp}^3$                       Co(II) is  $\text{dsp}^2$   
 paramagnetic = (3e)      paramagnetic = (1e)

2. In the reaction :  $[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow$  the complex formed will be :  
 (A\*) Tetrahedral      (B) square planar      (C) octahedral      (D) triangular bipyramidal

**Sol.**  $2[\text{Ag}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag}$   
 Tetrahedral

3. It is given that a complex formed by one  $\text{Ni}^{2+}$  ion and some  $\text{Cl}^-$  ions and some  $\text{PPh}_3$  molecules does not show geometrical isomerism and its solution does not show electrical conductance. Then which is correct about the complex :

(A) It is square planar      (B\*) It is tetrahedral      (C) It is diamagnetic      (D) none of the above is correct

**Sol.**  $[\text{NiCl}_2(\text{PPh}_3)_2]$  is non-ionic and tetrahedral

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

(A)  $\text{Ni}(\text{Co})_4$       (B\*)  $\text{K}[\text{AgF}_4]$       (C)  $\text{Na}_2[\text{Zn}(\text{CN})_4]$       (D) None of these

**Sol.**  $\text{K}[\text{AgF}_4]$  is square planar because Ag(III) is  $4d^8$  and complex is diamagnetic.

5. It is an experiment fact that  $\text{Cs}_2[\text{CuCl}_4]$  is orange coloured but  $(\text{NH}_4)_2[\text{CuCl}_4]$  is yellow. It is further known that total paramagnetic moment of a unpaired electron is due to spin as well as due to nature of orbital, 'd' orbital contributing more than 's' or 'p'. Thus the total paramagnetic moment of orange compound is found to be more than that of yellow compound. Then which of the following is correct :

(A\*) Anion of orange compound is tetrahedral and that of yellow is square planar  
 (B) Anion of orange compound is square planar and that of yellow is tetrahedral  
 (C) Both the anions are tetrahedral  
 (D) Both the anions are square planar

**Sol.**  $\text{Cs}_2[\text{CuCl}_4]$  (orange) is tetrahedral because in Cu(II) the unpaired electron is in 3d. But  $(\text{NH}_4)_2[\text{CuCl}_4]$  yellow is square planar because the unpaired electron is not in 3d rather in some promoted state 's' or 'p'.

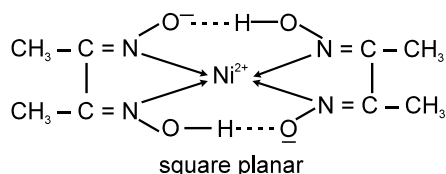
6. It is an experiment fact that :



Which of the following is wrong about this red ppt :

(A) It is a non-ionic complex      (B) It involves intra molecular H-bonding  
 (C\*) Ni(II) is  $\text{sp}^3$  hybridised      (D) It is a diamagnetic complex

**Sol.** The complex is



7. It is experimentally found that the compound  $\text{K}_3[\text{Ni}(\text{CN})_5]$  shows an increase in its weight when placed in a magnetic balance and four metal-ligand bond lengths are equal but the rest is different. Then which of the following set of informations is correct :

(i) The transition metal is  $\text{sp}^3\text{d}$  hybridised  
 (ii) The net dipole moment of complex is  $\neq$  zero  
 (iii) The transition metal is  $\text{dsp}^3$  hybridised