CHAPTER 17

The d- and f-Block Elements and Co-ordination Compounds

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. AgCN dissolves in excess KCN solution to give the complex compound .... *(1980)*
2. Mn^{2+} can be oxidised to MnO_4^- by .... (SnO_2, PbO_2, BaO_2) *(1981 - 1 Mark)*
3. Galvanization of iron denotes coating with .... *(1983 - 1 Mark)*
4. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy. *(1987 - 1 Mark)*
5. The salts .... and .... are isostructural. ($FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnSO_4.4H_2O$, $ZnSO_4.7H_2O$) *(1988 - 1 Mark)*
6. The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is .... *(1994 - 1 Mark)*
7. The IUPAC name of $[Co(NH_3)_6]Cl_3$ is .... *(1994 - 1 Mark)*
8. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... *(1997 - 1 Mark)*.
9. Silver jewellery items tarnish slowly in the air due to their reaction with .... *(1997 - 1 Mark)*

B True / False

1. Copper metal reduces Fe^{2+} in an acid medium. *(1982 - 1 Mark)*
2. Silver fluoride is fairly soluble in water. *(1982 - 1 Mark)*
3. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. *(1984 - 1 Mark)*
4. Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3*d*-orbital of neutral atom. *(1987 - 1 Mark)*
5. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. *(1989 - 1 Mark)*
6. Cu^+ disproportionates to Cu^{2+} and elemental copper in solution. *(1991 - 1 Mark)*

C MCQs with One Correct Answer

1. When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is *(1979)*
   (a) 1 : 1 (b) 1 : 2
   (c) 2 : 1 (d) 9 : 4
2. Which of the following is the weakest base *(1980)*
   (a) NaOH (b) $Ca(OH)_2$
   (c) KOH (d) $Zn(OH)_2$
3. One of the constituent of German silver is *(1980)*
   (a) Ag (b) Cu
   (c) Mg (d) Al
4. Which of the following dissolve in hot conc. NaOH solution *(1980)*
   (a) Fe (b) Zn
   (c) Cu (d) Ag
5. How many unpaired electrons are present in Ni^{2+}? *(1981 - 1 Mark)*
   (a) 0 (b) 2
   (c) 4 (d) 8
6. Sodium thiosulphate is used in photography because of its *(1981 - 1 Mark)*
   (a) reducing behaviour
   (b) oxidising behaviour
   (c) complex forming behaviour
   (d) reaction with light
7. Iron is rendered passive by treatment with concentrated *(1982 - 1 Mark)*
   (a) H_2SO_4 (b) H_3PO_4
   (c) HCl (d) HNO_3
8. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in *(1982 - 1 Mark)*
   (a) slag (b) gangue
   (c) metallic calcium (d) calcium carbonate
9. Zinc-copper couple that can be used as a reducing agent is obtained by : *(1984 - 1 Mark)*
   (a) mixing zinc dust and copper gauze
   (b) zinc coated with copper
   (c) copper coated with zinc
   (d) zinc and copper wires welded together
10. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by *(1988 - 1 Mark)*
    (a) $MnSO_4.4H_2O$ (b) $CuSO_4.5H_2O$
    (c) $FeSO_4.6H_2O$ (d) $NiSO_4.6H_2O$

11. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$ *(1991 - 1 Mark)*

(a) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

(b) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic

(d) $Ni(CO)_4$ is diamagnetic and $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

12. Which one is solder ? *(1995S)*

(a) Cu & Pb (b) Zn & Cu

(c) Pb & Sn (d) Fe & Zn

13. Which pair gives Cl_2 at room temperature? *(1995S)*

(a) $HCl_{(conc)} + KMnO_4$ (b) $NaCl + H_2SO_{4(conc)}$

(c) $NaCl + MnO_2$ (d) $NaCl + HNO_{3(conc)}$

14. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate? *(1996 - 1 Mark)*

(a) $Cu(CN)_2$ (b) $K_2[Cu(CN)_4]$

(c) $K[Cu(CN)_2]$ (d) $K_3[Cu(CN)_4]$

15. Which compound does not dissolve in hot, dilute HNO_3?

(a) HgS (b) PbS *(1996 - 1 Mark)*

(c) CuS (d) CdS

16. An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are : *(1996 - 1 Mark)*

(a) a colourless filtrate and a green residue

(b) a yellow filtrate and a green residue

(c) a yellow filtrate and a brown residue

(d) a green filtrate and a brown residue

17. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is *(1997 - 1 Mark)*

(a) CrO_3 (b) Cr_2O_3

(c) Cr (d) $CrO(O_2)$

18. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ *(1997 - 1 Mark)*

(c) $\frac{4}{5}$ (d) 1

19. Which of the following is an organometallic compound? *(1997 - 1 Mark)*

(a) Lithium methoxide (b) Lithium acetate

(c) Lithium dimethylamide (d) Methyl lithium.

20. Which of the following compounds is expected to be coloured? *(1997 - 1 Mark)*

(a) Ag_2SO_4 (b) CuF_2

(c) MgF_2 (d) CuCl.

21. In the dichromate anion, *(1999 - 2 Marks)*

(a) 4 Cr – O bonds are equivalent

(b) 6 Cr – O bonds are equivalent

(c) all Cr – O bonds are equivalent

(d) all Cr – O bonds are nonequivalent

22. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are

(a) both square planar *(1999 - 2 Marks)*

(b) tetrahedral and square planar, respectively

(c) both tetrahedral

(d) square planar and tetrahedral, respectively

23. The chemical processes in the production of steel from haematite ore involve *(2000S)*

(a) reduction

(b) oxidation

(c) reduction followed by oxidation

(d) oxidation followed by reduction

24. The complex ion which has no '*d*' electron in the central metal atom is *(2001S)*

(a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$

(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

25. Anhydrous ferric chloride is prepared by *(2002S)*

(a) heating hydrated ferric chloride at a high temperature in a stream of air

(b) heating metallic iron in a stream of dry chlorine gas

(c) reaction of metallic iron with hydrochloric acid

(d) reaction of metallic iron with nitric acid

26. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is: *(2003S)*

(a) K_2MnO_4, purple green (b) $KMnO_4$, purple

(c) Mn_2O_3, brown (d) Mn_3O_4, black

27. In the process of extraction of gold, *(2003S)*

$$\text{Roasted gold ore } + CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$$

$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y]

(a) $X = [Au(CN)_2]^-, Y = [Zn(CN)_4]^{2-}$

(b) $X = [Au(CN)_4]^{3-}, Y = [Zn(CN)_4]^{2-}$

(c) $X = [Au(CN)_2]^-, Y = [Zn(CN)_6]^{4-}$

(d) $X = [Au(CN)_4]^-, Y = [Zn(CN)_4]^{2-}$

28. The species having tetrahedral shape is *(2004S)*

(a) $[PdCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$

(c) $[Pd(CN)_4]^{2-}$ (d) $[NiCl_4]^{2-}$

29. The spin magnetic moment of cobalt in the compound $Hg[Co(SCN)_4]$ is *(2004S)*

(a) $\sqrt{3}$ (b) $\sqrt{8}$

(c) $\sqrt{15}$ (d) $\sqrt{24}$

30. The product of oxidation of I^- with MnO_4^- in alkaline medium is *(2004S)*
(a) IO_3^- (b) I_2
(c) IO^- (d) IO_4^-

31. $(NH_4)_2Cr_2O_7$ on heating liberates a gas. The same gas will be obtained by *(2004S)*
(a) heating NH_4NO_2
(b) heating NH_4NO_3
(c) treating H_2O_2 with $NaNO_2$
(d) treating Mg_3N_2 with H_2O

32. Which pair of compounds is expected to show similar colour in aqueous medium? *(2005S)*
(a) $FeCl_2$ and $CuCl_2$ (b) $VOCl_2$ and $CuCl_2$
(c) $VOCl_2$ and $FeCl_2$ (d) $FeCl_2$ and $MnCl_2$

33. Which kind of isomerism is exhibited by octahedral $Co(NH_3)_4Br_2Cl$? *(2005S)*
(a) Geometrical and Ionization
(b) Geometrical and Optical
(c) Optical and Ionization
(d) Geometrical only

34. $CuSO_4$ decolourises on addition of KCN, the product formed is *(2006 - 3M, –1)*
(a) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$
(b) $[Cu(CN)_4]^{2-}$
(c) CuCN (d) $Cu(CN)_2$

35. Among the following metal carbonyls, the C–O bond order is lowest in *(2007)*
(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

36. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
(a) nitrogen (b) oxygen *(2008)*
(c) carbon dioxide (d) argon

37. Among the following, the coloured compound is
(a) CuCl *(2008)*
(b) $K_3[Cu(CN)_4]$
(c) CuF_2
(d) $[Cu(CH_3CN)_4]BF_4$

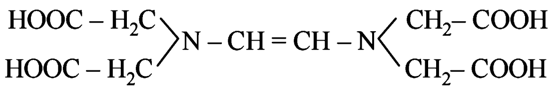
38. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is *(2008)*
(a) Tetrachloronickel (II) - tetraamminenickel (II)
(b) Tetraamminenickel (II) - tetrachloronickel (II)
(c) Tetraamminenickel (II) - tetrachloronickelate (II)
(d) Tetrachloronickel (II) - tetrachloronickelate (0) Ans. (C)

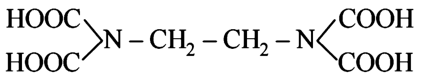
39. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are *(2008)*
(a) sp^3, sp^3 (b) sp^3, dsp^2
(c) dsp^2, sp^3 (d) dsp^2, sp^2

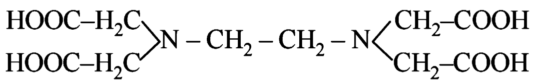
40. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is *(2009)*
(a) 0 (b) 2.84
(c) 4.90 (d) 5.92

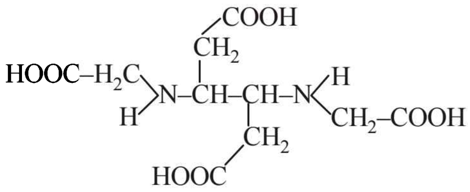
41. The ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is *(2010)*
(a) $[Cr(H_2O)_4(O_2N)]Cl_2$ (b) $[Cr(H_2O)_4Cl_2](NO_2)$
(c) $[Cr(H_2O)_4Cl(ONO)]Cl$ (d) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

42. The correct structure of ethylenediaminetetraacetic acid (EDTA) is *(2010)*

(a) 
$(HOOC-H_2C)_2N-CH=CH-N(CH_2-COOH)_2$

(b) 
$(HOOC)_2N-CH_2-CH_2-N(COOH)_2$

(c) 
$(HOOC-H_2C)_2N-CH_2-CH_2-N(CH_2-COOH)_2$

(d) 
$HOOC-H_2C(H)N-CH(CH_2COOH)-CH(CH_2COOH)-N(H)CH_2-COOH$

43. The complex showing a spin-only magnetic moment of 2.82 B.M. is : *(2010)*
(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2-}$
(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)_4]^{2-}$

44. Among the following complexes (**K–P**)
$K_3[Fe(CN)_6]$ (**K**), $[Co(NH_3)_6]Cl_3$ (**L**), $Na_3[Co(oxalate)_3]$ (**M**), the $[Ni(H_2O)_6]Cl_2$ (**N**), $K_2[Pt(CN)_4]$ (**O**) and $[Zn(H_2O)_6](NO_3)_2$ (**P**) the diamagnetic complexes are *(2011)*
(a) K, L, M, N (b) K, M, O, P
(c) L, M, O, P (d) L, M, N, O

45. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : *(2012)*
(a) Tetraaquadiaminecobalt (III) chloride
(b) Tetraaquadiamminecobalt (III) chloride
(c) Diaminetetraaquacoblat (II) chloride
(d) Diamminetetraaquacobalt (III) chloride

46. The colour of light absorbed by an aqueous solution of $CuSO_4$ is: *(2012)*
(a) orange-red (b) blue-green
(c) yellow (d) violet

47. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature depend-ent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively *(2012)*
(a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral

48. Consider the following complex ions, P, Q and R.
$P = [FeF_6]^{3-}$, $Q = [V(H_2O)_6]^{2+}$ and $R = [Fe(H_2O)_6]^{2+}$
The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is *(JEE Adv. 2013)*

(a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$

49. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is *(JEE Adv. 2016)*

(a) 2 (b) 3
(c) 4 (d) 5

D MCQs with One or More Than One Correct

1. Potassium manganate (K_2MnO_4) is formed when *(1988 - 1 Mark)*
(a) chlorine is passed into aqueous $KMnO_4$ solution
(b) manganese dioxide is fused with potassium hydroxide in air
(c) formaldehyde reacts with potassium permanganate in presence of a strong alkali
(d) potassium permanganate reacts with conc. sulphuric acid

2. The aqueous solutions of the following salts will be coloured in the case of *(1990 - 1 Mark)*
(a) $Zn(NO_3)_2$ (b) $LiNO_3$
(c) $Co(NO_3)_2$ (d) $CrCl_3$
(e) Potash alum

3. Among the following ions which one has the highest paramagnetism? *(1993 - 1 Mark)*
(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$

4. Which of the following alloys contains(s) Cu and Zn? *(1993 - 1 Mark)*
(a) Bronze (b) Brass
(c) Gun metal (d) Type metal

5. In nitroprusside ion the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by *(1998 - 2 Marks)*
(a) estimating the concentration of iron
(b) measuring the concentration of CN^-
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound.

6. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese *(1998 - 2 Marks)*
(a) gives hardness to steel
(b) helps the formation of oxides of iron
(c) can remove oxygen and sulphur
(d) can show highest oxidation state of +7.

7. If the bond length of CO bond in carbon monoxide is 1.128Å, then what is the value of CO bond length in $Fe(CO)_5$? *(2006 - 5M, –1)*
(a) 1.15Å (b) 1.128Å
(c) 1.13Å (d) 1.118Å

8. The compound(s) that exhibit(s) geometrical isomerism is (are) *(2009)*
(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$
(c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2Cl_2]$

9. Reduction of the metal centre in aqueous permanganate ion involves *(2011)*
(a) 3 electrons in neutral medium
(b) 5 electrons in neutral medium
(c) 3 electrons in alkaline medium
(d) 5 electrons in acidic medium

10. The equilibrium *(2011)*

$$2Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$$

in aqueous medium at 25°C shifts towards the left in the presence of
(a) NO_3^- (b) Cl^-
(c) SCN^- (d) CN^-

11. For the given aqueous reactions, which of the statement (s) is (are) true?

$$\text{excess KI} + K_3[Fe(CN)_6] \xrightarrow{\text{dilute } H_2SO_4} \text{brownish-yellow solution}$$

$$\downarrow ZnSO_4$$

$$\text{white precipitate} + \underbrace{\text{brownish-yellow filtrate}}$$

$$\downarrow Na_2S_2O_3$$

$$\text{colourless solution}$$

(a) The first reaction is a redox reaction. *(2012)*
(b) White precipitate is $Zn_3[Fe(CN)_6]_2$.
(c) Addition of filtrate to starch solution gives blue colour.
(d) White precipitate is soluble in NaOH solution.

12. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) *(JEE Adv. 2013)*
(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$
(b) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
(c) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$
(d) $[Pt(NH_3)_3](NO_3)Cl$ and $[Pt(NH_3)_3Cl]Br$

13. The pair(s) of reagents that yield paramagnetic species is/are *(JEE Adv. 2014)*
(a) Na and excess of NH_3
(b) K and excess of O_2
(c) Cu and dilute HNO_3
(d) O_2 and 2-ethylanthraquinol

14. The correct statement(s) about Cr^{2+} and Mn^{3+} is(are) [Atomic numbers of Cr = 24 and Mn = 25] ***(JEE Adv. 2015)***

(a) Cr^{2+} is a reducing agent

(b) Mn^{3+} is an oxidizing agent

(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration

(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

15. Fe^{3+} is reduced to Fe^{2+} by using ***(JEE Adv. 2015)***

(a) H_2O_2 in presence of NaOH

(b) Na_2O_2 in water

(c) H_2O_2 in presence of H_2SO_4

(d) Na_2O_2 in presence of H_2SO_4

E Subjective Problems

1. A certain inorganic compound (A) on heating loses its water of crystallisation. On further heating, a blackish brown powder (B) and two oxides of sulphur (C and D) are obtained. The powder (B) on boiling with hydrochloric acid gives a yellow solution (E). When H_2S is passed in (E) a white turbidity (F) and an apple green solution (G) are obtained. The solution (E) on treatment with thiocyanate ions gives a blood red coloured compound (H). Identify compounds from (A) to (H). ***(1978)***

2. A white amorphous powder (A) on heating yields a colourless, non-combustible gas (B) and a solid (C). The latter compound assumes a yellow colour on heating and changes to white on cooling. 'C' dissolves in dilute acid and the resulting solution gives a white precipitate on adding $K_4Fe(CN)_6$ solution.

'A' dissolves in dilute HCl with the evolution of gas, which is identical in all respects with 'B'. The gas 'B' turns lime water milky, but the milkiness disappears with the continuous passage of gas. The solution of 'A', as obtained above, gives a white precipitate (D) on the addition of excess of NH_4OH and passing H_2S. Another portion of the solution gives initially a white precipitate (E) on the addition of sodium hydroxide solution, which dissolves on futher addition of the base. Identify the compounds A, B, D, and E. ***(1979)***

3. State with balanced equations, what happens when

(i) Silver is treated with hot concentrated sulphuric acid.

(ii) Ammonium dichromate is heated.

(iii) Hydrogen sulphide is passed through a solution of potassium peramagnate acidified with dilute sulphuric acid. ***(1979)***

4. A solution of $FeCl_3$ in water gives a brown precipitate on standing. ***(1980)***

5. Complete the following equation (no balancing is needed) :

$$SO_2 + MnO_4^- + ... \longrightarrow SO_4^{2-} + Mn^{2+} + ...$$

(1981 - 1 Mark)

6. State with balanced equations what happens when :

(*i*) sulphur dioxide gas is bubbled through an aqueous solution of copper sulphate in presence of potassium thiocyanate. ***(1982 - 1 Mark)***

(*ii*) aqueous solution of ferric sulphate and potassium iodide are mixed. ***(1984 - 2 Marks)***

(*iii*) aqueous solution of potassium manganate and acid are mixed. ***(1984 - 2 Marks)***

(*iv*) aqueous solution of potassium chromate and acid are mixed. ***(1984 - 2 Marks)***

(*v*) potassium permanganate interacts with manganese dioxide in presence of potassium hydroxide; ***(1985 - 1 Mark)***

(*vi*) potassium ferrocyanide is heated with concentrated sulphuric acid; ***(1985 - 1 Mark)***

(*vii*) Gold is dissolved in *aqua regia*. ***(1987 - 1 Mark)***

(*viii*) Write balanced equations for the extraction of silver from silver glance by cyanide process. ***(1988 - 1 Mark)***

(*ix*) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. ***(1989 - 1 Mark)***

(*x*) Cobalt(II) solution reacts with KNO_2 in acetic acid medium. ***(1989 - 1 Mark)***

(*xi*) Write balanced equations for the extraction of copper from copper pyrites by self-reduction. ***(1990 - 2 Marks)***

(*xii*) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4. ***(1990 - 1 Mark)***

(*xiii*) Iron reacts with cold dilute nitric acid. ***(1990 - 1 Mark)***

(*xiv*) Potassium permanganate is added to a hot solution of manganous sulphate. ***(1990 - 1 Mark)***

(*xv*) Copper reacts with HNO_3 to give NO and NO_2 in molar ratio of 2 : 1. ***(1992 - 1 Marks)***

$Cu + HNO_3 \rightarrow .... + NO + NO_2 + ...$

(*xvi*) Na_2CO_3 is added to a solution of copper sulphate. ***(1992 - 1 Marks)***

$CuSO_4 + Na_2CO_3 + H_2O \rightarrow .... + Na_2SO_4 + ...$

(*xvii*) Potassium dichromate and concentrated hydrochloric acid are heated together. ***(1992 - 1 Mark)***

(*xviii*) $AgBr + Na_2S_2O_3 \rightarrow .... + ...$ ***(1993 - 1 Mark)***

(*xix*) $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \rightarrow .... + ... + ...$ ***(1993 - 1 Mark)***

(*xx*) $[MnO_4]^{2-} + H^+ \longrightarrow .... + [MnO_4]^- + H_2O$ ***(1994 - 1 Mark)*** (*xxi*) $SO_2(aq) + Cr_2O_7^{2-} + 2H^+ \longrightarrow .... + ... + ...$

(1994 - 1 Mark)

(*xxii*) Write a balanced equation for the reaction of argentite with KCN and name the products in solution.

(1996 - 1 Mark)

(*xxiii*) Write balanced equations for the reaction of zinc with dilute nitric acid. ***(1997 - 1 Mark)***

7. Give balanced equations for extraction of silver from its sulphide ore ***(1982 - 2 Marks)***

8. Give reasons for the following :

(*i*) Silver bromide is used in photography.

(1983 - 1 Mark)

(*ii*) Most transition metal compounds are coloured.

(1986 - 1 Mark)

(*iii*) Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$. Explain.

(1987 - 1 Mark)

(*iv*) The colour of mercurous chloride, Hg_2Cl_2, changes from white to black when treated with ammonia.

(1988 - 1 Mark)

(*v*) The species $[CuCl_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not.

(1992 - 1 Mark)

(*vi*) CrO_3 is an acid anhydride. ***(1999 - 2 Marks)***

9. State the conditions under which the following preparation is carried out.

Potassium permanganate from manganese hydroxide.

Give the necessary equations which need not be balanced.

(1983 - 1 Mark)

10. What happens when :

(*i*) aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess. ***(1985 - 1 Mark)***

(*ii*) $CrCl_3$ solution is treated with sodium hydroxide and then with hydrogen peroxide. ***(1985 - 1 Mark)***

11. Mention the products formed when zinc oxide is treated with excess of sodium hydroxide solution. ***(1986 - 1 Mark)***

12. What is the actual reducing agent of haematite in blast furnace? ***(1987 - 1 Mark)***

13. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^- ,by the following two steps. Complete and balance the equations : ***(1993 - 2 Marks)***

$$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \rightarrow ......+[Fe(H_2O_6)]^{3+} + H_2O$$

$$[Fe(H_2O)_6]^{2+} + ... \rightarrow ......+ H_2O$$

14. Identify the complexes which are expected to be coloured. Explain ***(1994 - 2 Marks)***

(i) $[Ti(NO_3)_4]$ (ii) $[Cu(NCCH_3)_4]^+ BF_4^-$

(iii) $[Cr(NH_3)_6]^{3+}3Cl^-$ (iv) $K_3[VF_6]$

15. Write down the IUPAC names of the following compounds:

(*i*) $[Co(NH_3)_5ONO]Cl_2$ ***(1995 - 1 Mark)***

(*ii*) $K_3[Cr(CN)_6]$ ***(1995 - 1 Mark)***

(*iii*) $[Cr(NH_3)_5CO_3]Cl$ ***(1996 - 1 Mark)***

16. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.

(1996 - 2 Marks)

17. Write the formulae of the following complexes :

(*i*) Pentamminechlorocobalt(III) ***(1997 - 1 Mark)***

(*ii*) Lithium tetrahydroaluminate(III). ***(1997 - 1 Mark)***

18. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations.

(1998 - 4 Marks)

19. Work out the following using chemical equations

(1998 - 2 Marks)

In moist air copper corrodes to produce a green layer on the surface.

20. A, B, and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4, whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify A, B and C.

(1999 - 6 Marks)

21. Write the chemical reaction associated with the 'brown ring test'. ***(2000 - 2 Marks)***

22. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. ***(2000 - 4 Marks)***

23. (*i*) Write the chemical reactions involved in the extraction of metallic silver from argentite.

(*ii*) Write the balanced chemical equation for developing photographic films. ***(2000 - 4 Marks)***

24. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spin–only value). ***(2001 - 5 Marks)***

25. Deduce the structure of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species. ***(2002 - 5 Marks)***

26. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.

$K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ BM ***(2003 - 4 Marks)***

27. Nickel chloride, when treated with dimethylglyoxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following. ***(2004 - 4 Marks)***

(a) Draw the structure of the complex showing H-bonds

(b) Give oxidation state of nickel and its hybridisation

(c) Predict the magnetic behaviour of the complex

28. Some reactions of two ores, A_1 and A_2 of the metal M are given below. ***(2004 - 4 Marks)***

$$\begin{tikzcd}[A_1] \arrow[r, "\text{calcination}"] \arrow[d, "\text{KI/HCl}"'] & \underset{\text{Black}}{[C]}\downarrow + CO_2 + H_2O \\ {[D]}\downarrow + I_2 & \end{tikzcd}$$

$$[A_2] \xrightarrow{\text{roasting}} [G]\uparrow + M; \quad [G] + K_2Cr_2O_7 \xrightarrow{H^+} \text{Green solution}$$

Identify A_1, A_2, M, C, D, and G, and explain using the required chemical reactions.

29. $$Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} \underset{\substack{\text{Blood red}\\ \text{colouration}}}{(A)} \xrightarrow[\text{excess}]{F^-} \underset{\text{colourless}}{(B)}$$

What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic moment of (B). ***(2005 - 4 Marks)***

30. Write the chemical reaction involved in developing of a black and white photographic film. An aqueous $Na_2S_2O_3$ solution is acidified to give a milky white turbidity. Identify the product and write the balanced half chemical reaction for it. ***(2005 - 4 Marks)***

31. $$\underset{\substack{\text{(Colourless}\\ \text{liquid)}}}{MCl_4} \xrightarrow{Zn} \underset{(A)}{\text{Purple colour compound}}; \ M = \text{Transition metal}$$

$$MCl_4 \xrightarrow{\text{moist air}} \underset{\text{white fumes}}{(B)}$$

Identify (A), (B) and MCl_4. Also explain colour difference between MCl_4 and (A). ***(2005 - 4 Marks)***

F Match the Following

DIRECTIONS (Q. No. 1 and 2) : *Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :*

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

1. Match the complexes in Column I with their properties listed in Column II. ***(2007)***

Column I	***Column II***
(A) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(p) geometrical isomers
(B) $[Pt(NH_3)_2Cl_2]$	(q) paramagnetic
(C) $[Co(H_2O)_5Cl]Cl$	(r) diamagnetic
(D) $[Ni(H_2O)_6]Cl_2$	(s) metal ion with +2 oxidation state

2. Match each of the reactions given in **Column I** with the corresponding product(s) given in **Column II**. ***(2009)***

Column I	***Column II***
(A) $Cu + \text{dil } HNO_3$	(p) NO
(B) $Cu + \text{conc } HNO_3$	(q) NO_2
(C) $Zn + \text{dil } HNO_3$	(r) N_2O
(D) $Zn + \text{conc } HNO_3$	(s) $Cu(NO_3)_2$
	(t) $Zn(NO_3)_2$

DIRECTIONS (Q. No. 3) : Following question has matching lists. The codes for the list have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

3. Match each coordination compound in List-I with an appropriate pair of characteristics from List- II and select the correct answer using the code given below the lists.
{en = $H_2NCH_2CH_2NH_2$; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78} *(JEE Adv. 2014)*

	List-I		**List-II**
P.	$[Cr(NH_3)_4Cl_2]Cl$	1.	Paramagnetic and exhibits ionisation isomerism
Q.	$[Ti(H_2O)_5Cl](NO_3)_2$	2.	Diamagnetic and exhibits *cis-trans* isomerism
R.	$[Pt(en)(NH_3)Cl]NO_3$	3.	Paramagnetic and exhibits *cis-trans* isomerism
S.	$[Co(NH_3)_4(NO_3)_2]NO_3$	4.	Diamagnetic and exhibits ionisation isomerism

Code:

	P	**Q**	**R**	**S**
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

G Comprehension Based Questions

PASSAGE 1

The coordination number of Ni^{2+} is 4.

$$NiCl_2 + KCN(\text{excess}) \longrightarrow A \text{ (cyano complex)}$$

$$NiCl_2 + \text{Conc. } HCl(\text{excess}) \longrightarrow B \text{ (chloro complex)}$$

1. The IUPAC name of A and B are *(2006 - 5M, –2)*
(a) Potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)
(b) Tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)
(c) Tetracyanonickel (II), tetrachloronickel (II)
(d) Potassium tetracyanonickel (II), potassium tetrachloronickel (II)

2. Predict the magnetic nature of A and B *(2006 - 5M, –2)*
(a) Both are diamagnetic
(b) A is diamagnetic and B is paramagnetic with one unpaired electron
(c) A is diamagnetic and B is paramagnetic with two unpaired electrons
(d) Both are paramagnetic

3. The hybridization of A and B are *(2006 - 5M, –2)*
(a) dsp^2, sp^3 (b) sp^3, sp^3
(c) dsp^2, dsp^2 (d) sp^3d^2, d^2sp^3

PASSAGE 2

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4.5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. *(2010)*

4. Partial roasting of chalcopyrite produces
(a) Cu_2S and FeO (b) Cu_2O and FeO
(c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3

5. Iron is removed from chalcopyrite as
(a) FeO (b) FeS
(c) Fe_2O_3 (d) $FeSiO_3$

6. In self-reduction, the reducing species is
(a) S (b) O^{2-}
(c) S^{2-} (d) SO_2

PASSAGE 3

When a metal rod **M** is dipped into an aqueous colourless concentrated solution of compound **N**, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate **O**. Addition of aqueous NH_3 dissolves **O** and gives an intense blue solution. *(2011)*

7. The metal rod **M** is
(a) Fe (b) Cu
(c) Ni (d) Co

8. The compound **N** is
(a) $AgNO_3$ (b) $Zn(NO_3)_2$
(c) $Al(NO_3)_3$ (d) $Pb(NO_3)_2$

9. The final solution contains
(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$
(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$
(c) $[Ag(NH_3)_2]^{+}$ and $[Cu(NH_3)_4]^{2+}$
(d) $[Ag(NH_3)_2]^{+}$ and $[Ni(NH_3)_6]^{2+}$

H Assertion & Reason Type Questions

Read the following statement-1(Asseration/Statement) and Statement -2 (Reason/Explanation) and answer as per the options given below :

(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

1. **Statement-1 :** To a solution of potassium chromate if a strong acid is added it changes its colour from yellow to orange.
Statement-2 : The colour change is due to the oxidation of potassium chromate. *(1988 - 2 Marks)*

2. **Statement-1 :** Zn^{2+} is diamagnetic.
Statement-2 : Two electrons are lost from 4s orbital to form Zn^{2+}. *(1998 - 2 Marks)*

3. **Statement-1 :** The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.
and
Statement-2 : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. *(2008 - 2 Marks)*

4. **Statement-1 :** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
and
Statement-2 : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. *(2008)*

I Integer Value Correct Type

1. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4.5H_2O$ is *(2009 - 4 Marks)*

2. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is *(2009 - 4 Marks)*

3. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is *(2010)*

4. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to *(2011)*

5. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in $[Co(EDTA)]^{1-}$complex ion is *(JEE Adv. 2013)*

6. Consider the following list of reagents: *(JEE Adv. 2014)*
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$.
The total number of reagents that can oxidise aqueous iodide to iodine is

7. In the complex acetylbromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe–C bond(s) is *(JEE Adv. 2015)*

8. Among the complex ions, $[Co(NH_2–CH_2–CH_2–NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is *(JEE Adv. 2015)*

9. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is
[Atomic number of Fe = 26] *(JEE Adv. 2015)*

10. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is *(JEE Adv. 2016)*

11. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is *(JEE Adv. 2016)*

Section-B JEE Main / AIEEE

1. A square planar complex is formed by hybridisation of which atomic orbitals? **[2002]**
(a) s, p_x, p_y, d_{yz}
(b) $s, p_x, p_y, d_{x^2-y^2}$
(c) s, p_x, p_y, d_{z^2}
(d) s, p_y, p_z, d_{xy}

2. The type of isomerism present in nitropentammine chromium (III) chloride is **[2002]**
(a) optical
(b) linkage
(c) ionization
(d) polymerisation.

3. $CH_3 – Mg – Br$ is an organo metallic compound due to **[2002]**
(a) Mg – Br bond
(b) C – Mg bond
(c) C – Br bond
(d) C – H bond.

4. Most common oxidation states of Ce (cerium) are **[2002]**
(a) +2, +3
(b) +2, +4
(c) +3, +4
(d) +3, +5.

5. Arrange Ce^{+3}, La^{+3}, Pm^{+3} and Yb^{+3} in increasing order of their ionic radii. **[2002]**
(a) $Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$
(b) $Ce^{+3} < Yb^{+3} < Pm^{+3} < La^{+3}$
(c) $Yb^{+3} < Pm^{+3} < La^{+3} < Ce^{+3}$
(d) $Pm^{+3} < La^{+3} < Ce^{+3} < Yb^{+3}$.

6. Which of the following ions has the maximum magnetic moment? **[2002]**
(a) Mn^{+2}
(b) Fe^{+2}
(c) Ti^{+2}
(d) Cr^{+2}.

7. The most stable ion is **[2002]**
(a) $[Fe(OH)_3]^{3-}$
(b) $[Fe(Cl)_6]^{3-}$
(c) $[Fe(CN)_6]^{3-}$
(d) $[Fe(H_2O)_6]^{3+}$.

8. When $KMnO_4$ acts as an oxidising agent and ultimately forms $[MnO_4]^{-2}$, MnO_2, Mn_2O_3, Mn^{+2} then the number of electrons transferred in each case respectively is

(a) 4, 3, 1, 5 (b) 1, 5, 3, 7 **[2002]**
(c) 1, 3, 4, 5 (d) 3, 5, 7, 1.

9. The radius of La^{3+} (Atomic number of La = 57) is 1.06Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ?

(a) 1.40 Å (b) 1.06 Å **[2003]**
(c) 0.85 Å (d) 1.60 Å

10. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solutions. What is the reason for it ? **[2003]**

(a) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
(b) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(c) Copper hydroxide is an amphoteric substance
(d) In acidic solutions hydration protects copper ions

11. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is

(a) $[Co(NH_3)_3Cl_3]. 2\,NH_3$ **[2003]**
(b) $[Co(NH_3)_4Cl_2]\,Cl\,.\,NH_3$
(c) $[Co(NH_3)_4Cl]\,Cl_2.\,NH_3$
(d) $[Co(NH_3)_5Cl]\,Cl_2$

12. In the coordination compound, $K_4[Ni(CN)_4]$, the oxidation state of nickel is **[2003]**

(a) 0 (b) +1
(c) +2 (d) –1

13. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is **[2003]**

(a) HgI_2 (b) HgO
(c) Pb_3O_4 (d) $(NH_4)_2Cr_2O_7$

14. A reduction in atomic size with increase in atomic number is a characteristic of elements of **[2003]**

(a) d-block (b) f-block
(c) radioactive series (d) high atomic masses

15. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid? **[2003]**

(a) $Cr_2O_7^{2-}$ and H_2O are formed
(b) CrO_4^{2-} is reduced to +3 state of Cr
(c) CrO_4^{2-} is oxidized to +7 state of Cr
(d) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

16. Which one of the following nitrates will leave behind a metal on strong heating ? **[2003]**

(a) Copper nitrate (b) Manganese nitrate
(c) Silver nitrate (d) Ferric nitrate

17. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ? **[2004]**

(a) $(n-1)d^3\,ns^2$ (b) $(n-1)d^5\,ns^1$
(c) $(n-1)d^8\,ns^2$ (d) $(n-1)d^5\,ns^2$

18. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey power. This transformation is related to **[2004]**

(a) a change in the partial pressure of oxygen in the air
(b) a change in the crystalline structure of tin
(c) an interaction with nitrogen of the air at very low temperature
(d) an interaction with water vapour contained in the humid air

19. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is **[2004]**

(a) c, a (b) b, c
(c) a, b (d) a, b, c

20. The coordination number of a central metal atom in a complex is determined by **[2004]**

(a) the number of ligands around a metal ion bonded by sigma and pi-bonds both
(b) the number of ligands around a metal ion bonded by pi-bonds
(c) the number of ligands around a metal ion bonded by sigma bonds
(d) the number of only anionic ligands bonded to the metal ion.

21. Which one of the following complexes is an outer orbital complex ? **[2004]**

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{4-}$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$

(Atomic nos. : Mn = 25; Fe = 26; Co = 27, Ni = 28)

22. Coordination compounds have great importance in biological systems. In this context which of the following statements is **incorrect** ? **[2004]**

(a) Cyanocobalamin is B_{12} and contains cobalt
(b) Haemoglobin is the red pigment of blood and contains irons
(c) Chlorophylls are green pigments in plants and contain calcium
(d) Carboxypeptidase - A is an exzyme and contains zinc.

23. Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statements about cerium is **incorrect**? **[2004]**

(a) The +4 oxidation state of cerium is not known in solutions

(b) The +3 oxidation state of cerium is more stable than the +4 oxidation state

(c) The common oxidation states of cerium are +3 and +4

(d) Cerium (IV) acts as an oxidizing agent

24. Which one of the following has largest number of isomers ? **[2004]**

(a) $[Ir(PR_3)_2H(CO)]^{2+}$

(b) $[Co(NH_3)_5Cl]^{2+}$

(c) $[Ru(NH_3)_4Cl_2]^+$

(d) $[Co(en)_2Cl_2]^+$ (R = alkyl group, en = ethylenediamine)

25. The correct order of magnetic moments (spin only values in B.M.) anong is **[2004]**

(a) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$

(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$

(c) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$

(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(Atomic nos. : Mn = 25, Fe = 26, Co = 27)

26. The oxidation state Cr in $[Cr(NH_3)_4Cl_2]^+$ is **[2005[**

(a) 0 (b) +1

(c) +2 (d) +3

27. Heating mixture of Cu_2O and Cu_2S will give **[2005[**

(a) Cu_2SO_3 (b) $CuO + CuS$

(c) $Cu + SO_3$ (d) $Cu + SO_2$

28. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is: **[2005[**

(a) +3 (b) +2

(c) +6 (d) +4

29. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives **[2005[**

(a) HgO (b) Hg_2O

(c) $NH_2-Hg-Hg-Cl$ (d) $HgNH_2Cl$

30. The lanthanide contraction is responsible for the fact that **[2005[**

(a) Zr and Zn have the same oxidation state

(b) Zr and Hf have about the same radius

(c) Zr and Nb have similar oxidation state

(d) Zr and Y have about the same radius

31. The IUPAC name of the coordination compound $K_3[Fe(CN)_6]$ is **[2005[**

(a) Tripotassium hexacyanoiron (II)

(b) Potassium hexacyanoiron (II)

(c) Potassium hexacyanoferrate (III)

(d) Potassium hexacyanoferrate (II)

32. Which of the following compounds shows optical isomerism? **[2005[**

(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3-}$

(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

33. Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ? **[2005[**

(a) $[Co(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Mn(CN)_6]^{3-}$ (d) $[Cr(CN)_6]^{3-}$

(At. Nos : Cr = 24, Mn = 25, Fe = 26, Co = 27)

34. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is **[2005[**

(a) d^5 (in strong ligand field)

(b) d^3 (in weak as well as in strong fields)

(c) d^4 (in weak ligand fields)

(d) d^4 (in strong ligand fields)

35. Which of the following factors may be regarded as the main cause of lanthanide contraction? **[2005[**

(a) Greater shielding of 5d electrons by 4f electrons

(b) Poorer shielding of 5d electrons by 4f electrons

(c) Effective shielding of one of 4f electrons by another in the subshell

(d) Poor shielding of one of 4f electron by another in the subshell

36. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is : **[2006[**

(a) pentaammine nitrito-N-cobalt(II) chloride

(b) pentaammine nitrito-N-cobalt(III) chloride

(c) nitrito-N-pentaamminecobalt(III) chloride

(d) nitrito-N-pentaamminecobalt(II) chloride

37. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[2006[**

(a) MCl_2 is more ionic than MCl_4

(b) MCl_2 is more easily hydrolysed than MCl_4

(c) MCl_2 is more volatile than MCl_4

(d) MCl_2 is more soluble in anhydrous ethanol than MCl_4

38. Nickel (Z = 28) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively : **[2006]**

(a) one, square planar (b) two, square planar
(c) one, tetrahedral (d) two, tetrahedral

39. In $Fe(CO)_5$, the Fe – C bond possesses **[2006]**

(a) ionic character (b) σ-character only
(c) π-character (d) both σ and π characters

40. Lanthanoid contraction is caused due to **[2006]**

(a) the same effective nuclear charge from Ce to Lu
(b) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
(c) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(d) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

41. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion? **[2006]**

(a) One (b) Two
(c) Six (d) Three

42. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28) **[2006]**

(a) 6 (b) 1.73
(c) 2.84 (d) 4.90

43. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence **[2007]**

(a) $PbX_2 << SnX_2 << GeX_2 << SiX_2$
(b) $GeX_2 << SiX_2 << SnX_2 << PbX_2$
(c) $SiX_2 << GeX_2 << PbX_2 << SnX_2$
(d) $SiX_2 << GeX_2 << SnX_2 << PbX_2$.

44. Identify the incorrect statement among the following:

(a) 4f and 5f orbitals are equally shielded. **[2007]**
(b) d-Block elements show irregular and erratic chemical properties among themselves.
(c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
(d) The chemistry of various lanthanoids is very similar.

45. Which of the following has a square planar geometry?

(a) $[PtCl_4]^{2-}$ (b) $[CoCl_4]^{2-}$ **[2007]**
(c) $[FeCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$
(At. nos.: Fe = 26, Co = 27, Ni = 28, Pt = 78)

46. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because **[2007]**

(a) the 5f orbitals extend further from the nucleus than the 4f orbitals
(b) the 5f orbitals are more buried than the 4f orbitals
(c) there is a similarity between 4f and 5f orbitals in their angular part of the wave function
(d) the actinoids are more reactive than the lanthanoids.

47. The coordination number and the oxidation state of the element 'E' in the complex $[E\,(en)_2\,(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively, **[2008]**

(a) 6 and 2 (b) 4 and 2
(c) 4 and 3 (d) 6 and 3

48. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being **[2008]**

(a) 4f orbitals more diffused than the 5f orbitals
(b) leasser energy difference between 5f and 6d than between 4f and 5d orbitals
(c) more energy difference between 5f and 6d than between 4f and 5d orbitals
(d) more reactive nature of the actionids than the lanthanoids

49. In which of the following complexes of the Co (at. no. 27), will the magnitude of Δ_o be the hightest? **[2008]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

50. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl

(a) gets oxidised by oxalic acid to chlorine **[2008]**
(b) furnishes H^+ ions in addition to those from oxalic acd
(c) reduces permanganate to Mn^{2+}
(d) Oxidises oxalic acid to carbon doxide and water

51. Which of the following has an optical isomer **[2009]**

(a) $[Co(en)\,(NH_3)_2]^{2+}$ (b) $[Co(H_2O)_4(en)]^{3+}$
(c) $[Co(en)_2\,(NH_3)_2]^{3+}$ (d) $[Co(NH_3)_3Cl]^+$

52. In context with the transition elements, which of the following statements is incorrect? **[2009]**

(a) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
(b) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.

53. Which of the following pairs represent linkage isomers? **[2009]**

(a) $[Pd(P\,Ph_3)_2(NCS)_2]$ and $[Pd\,(\,P\,Ph_3)_2\,(SCN)_2]$
(b) $[Co(NH_3)_5NO_3]\,SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(c) $[PtCl_2(NH_3)_4]\,Br_2$ and $[Pt\,Br_2\,(NH_3)_4]\,Cl_2$
(d) $[Cu(NH_3)_4][Pt\,Cl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

54. Knowing that the chemistry of lanthanoids(Ln) is dominated by its + 3 oxidation state, which of the following statements is incorrect? **[2009]**

(a) The ionic size of Ln (III) decrease in general with increasing atomic number

(b) Ln (III) compounds are generally colourless.

(c) Ln (III) hydroxide are mainly basic in character.

(d) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.

55. A solution containing 2.675 g of $CoCl_3 . 6 NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is

(At. mass of Ag = 108 u) **[2010]**

(a) $[Co(NH_3)_6]Cl_3$ (b) $[CoCl_2(NH_3)_4]Cl$

(c) $[CoCl_3(NH_3)_3]$ (d) $[CoCl(NH_3)_5]Cl_2$

56. Which one of the following has an optical isomer? **[2010]**

(a) $[Zn(en)(NH_3)_2]^{2+}$ (b) $[Co(en)_3]^{3+}$

(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Zn(en)_2]^{2+}$

(en = ethylenediamine)

57. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? **[2011]**

(a) The complex involves d^2sp^3 hybridisation and is octahedral in shape.

(b) The complex is paramagnetic.

(c) The complex is an outer orbital complex

(d) The complex gives white precipitate with silver nitrate solution.

58. In context of the lanthanoids, which of the following statements is not correct? **[2011]**

(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.

(b) All the members exhibit +3 oxidation state.

(c) Because of similar properties the separation of lanthanoids is not easy.

(d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

59. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is : **[2011]**

(a) 1.82 BM (b) 5.46 BM

(c) 2.82 BM (d) 1.41 BM

60. The outer electron configuration of Gd (Atomic No. : 64) is : **[2011]**

(a) $4f^3 5d^5 6s^2$ (b) $4f^8 5d^0 6s^2$

(c) $4f^4 5d^4 6s^2$ (d) $4f^7 5d^1 6s^2$

61. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? **[2012]**

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$

(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

62. Iron exhibits +2 and + 3 oxidation states. Which of the following statements about iron is incorrect ? **[2012]**

(a) Ferrous oxide is more basic in nature than the ferric oxide.

(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.

(c) Ferrous compounds are less volatile than the corresponding ferric compounds.

(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

63. Which of the following complex species is not expected to exhibit optical isomerism ? **[JEE M 2013]**

(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2 Cl_2]^+$

(c) $[Co(NH_3)_3 Cl_3]$ (d) $[Co(en)(NH_3)_2 Cl_2]^+$

64. Which of the following arrangements does not represent the correct order of the property stated against it ? **[JEE M 2013]**

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour

(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution

(d) Sc < Ti < Cr < Mn : number of oxidation states

65. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^0_{M^{3+}/M^{2+}}$ value ? **[JEE M 2013]**

(a) Cr(Z = 24) (b) Mn(Z = 25)

(c) Fe(Z = 26) (d) Co(Z = 27)

66. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: **[JEE M 2014]**

(a) $L_4 < L_3 < L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$

(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

67. Which series of reactions correctly represents chemical reactions related to iron and its compound? **[JEE M 2014]**

(a) $Fe \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$

(b) $Fe \xrightarrow{O_2,\, \text{heat}} FeO \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$

(c) $Fe \xrightarrow{Cl_2,\, \text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2,\, \text{heat}} Fe_3O_4 \xrightarrow{CO,\, 600°C} FeO \xrightarrow{CO,\, 700°C} Fe$

68. Which of the following compounds is not colored yellow ? **[JEE M 2015]**

(a) $(NH_4)_3[As(Mo_3O_{10})_4]$ (b) $BaCrO_4$

(c) $Zn_2[Fe(CN)_6]$ (d) $K_3[Co(NO_2)_6]$

69. Match the catalysts to the correct processes : **[JEE M 2015]**

Catalyst		**Process**
(A) $TiCl_4$	(i)	Wacker process
(B) $PdCl_2$	(ii)	Ziegler - Natta polymerization
(C) $CuCl_2$	(iii)	Contact process
(D) V_2O_5	(iv)	Deacon's process

(a) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i)

(b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)

(c) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i)

(d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

70. The number of geometric isomers that can exist for square planar complex $[Pt\ (Cl)\ (py)\ (NH_3)\ (NH_2OH)]^+$ is (py = pyridine) : **[JEE M 2015]**

(a) 4 (b) 6

(c) 2 (d) 3

71. The color of $KMnO_4$ is due to : **[JEE M 2015]**

(a) L → M charge transfer transition

(b) σ - σ^* transition

(c) M → L charge transfer transition

(d) d – d transition

72. Which of the following compounds is metallic and ferromagnetic? **[JEE M 2016]**

(a) VO_2 (b) MnO_2

(c) TiO_2 (d) CrO_2

73. Which one of the following complexes shows optical isomerism? **[JEE M 2016]**

(a) *trans* $[Co(en)_2Cl_2]Cl$

(b) $[Co(NH_3)_4Cl_2]Cl$

(c) $[Co(NH_3)_3Cl_3]$

(d) *cis*$[Co(en)_2Cl_2]Cl$

(en = ethylenediamine)

74. The pair having the same magnetic moment is:
[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27] **[JEE M 2016]**

(a) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$

(b) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$

(c) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

(d) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$

17

The d- and f-Block Elements and Co-ordination Compounds

Section-A : JEE Advanced/ IIT-JEE

A 1. $K[Ag(CN)_2]$ 2. PbO_2 3. zinc 4. hydration/solvation
5. $FeSO_4.7H_2O, ZnSO_4.7H_2O$ 6. paramagnetism 7. hexaminecobalt (III) chloride
8. zero 9. H_2S

B 1. F 2. T 3. T 4. F 5. F 6. T

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

D 1. (b,c) 2. (c, d) 3. (b) 4. (b, c) 5. (c) 6. (a, c) 7. (d)
8. (c, d) 9. (a, d) 10. (b, c, d) 11. (a, c, d) 12. (b, d) 13. (a, b, c) 14. (a, b, c) 15. (a,b)

E 11. sodium zincate, water 12. CO 14. (iii), (iv)
15. (i) pentamminenitritocobalt (III) chloride, (ii) potassium hexacyanochromate (III)
(iii) pentamminecarbonatochromium (III) chloride
17. (i) $[CoCl(NH_3)_5]^{+2}$, (ii) $LiAlH_4$
20. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl](H_2O)Cl_2$, $[Cr(H_2O)_4Cl_2](H_2O)_2Cl$
24. $[Cr(NH_3)_4BrCl]Cl : (d^2sp^3)$; $[Cr(NH_3)_4Cl_2]Br : (d^2sp^3)$; 3.87 BM, 3.87 BM
26. Potassium amminotetracyanonitrosoniumchromate (I), (d^2sp^3), octahedral shape.
27. (b) +2, dsp^2; (c) diamagnetic
28. $\underset{A_1}{CuCO_3.Cu(OH)_2}, \underset{A_2}{Cu_2S}, \underset{M}{Cu}, \underset{C}{CuO}, \underset{D}{Cu_2I_2}, \underset{Y}{SO_2}$
29. $\underset{A}{Fe(SCN)_3}; \underset{B}{[FeF_6]^{3-}}$; trithiocyanoiron (III); 5.92 BM
31. $\underset{A}{[Ti(H_2O)_6]Cl_3}, HCl, \underset{B}{TiCl_4}, MCl_4$

F 1. (A - p, q, s); (B - p, r, s); (C - q, s); (D - q, s) 2. (A - p, s); (B - q, s); (C - r, t); (D - q, t) 3. (b)

G 1. (a) 2. (c) 3. (a) 4. (b) 5. (d) 6. (b) 7. (b) 8. (a) 9. (c)

H 1. (c) 2. (b) 3. (b) 4. (a)

I 1. 4 2. 6 3. 3 4. 6 5. 8 6. 7 7. 3 8. 6 9. 4
10. 6 11. 5

Section-B : JEE Main/ AIEEE

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

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **$K[Ag(CN)_2]$**
2. **PbO_2;**
3. **Zinc;**
4. **Hydration/solvation;** [A substance dissolves when its $\Delta H_{hydration}$ > lattice energy].
5. **$FeSO_4.7H_2O$, $ZnSO_4.7H_2O$;**
6. **Paramagnetism;** $[Mn(H_2O)_6]^{2+}$ shows paramagnetism because of presence of 5 unpaired electrons in the outer most orbital ($3d^5$) of Mn^{2+}.
7. **Hexammine cobalt (III) chloride**
8. **zero**
9. **H_2S;** It is due to formation of sulphide of silver (Ag_2S) which is black.

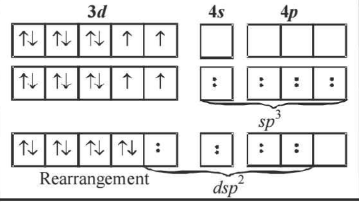
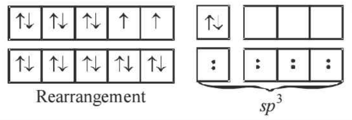
B. True/False

1. **False :** Copper metal does not reduces Fe^{2+} in an acidic medium.
2. **True :** Hydration energy of AgF is appreciably higher than its lattice energy because of smaller F^- ion and thus AgF is soluble in water. In rest of the halides, lattice energy is more than hydration energy to make them insoluble.
3. **True :** Insolubility of AgCl in H_2O is due to its high lattice energy on account of strong van der Waals attraction between silver and chloride ions in addition to electrostatic attraction between them. Further AgCl forms a complex with conc. NaCl solution and is therefore soluble.
4. **False :** Dipositive zinc exhibits diamagnetism (and not paramagnetism) because it has no unpaired electron.
5. **False :** Octahedral complexes of Fe(III) like $[Fe(CN)_6]^{3-}$ are low spin (d^2sp^3 hybridization) with one unpaired electron and have magnetic moment of about 1.9 BM. On the other hand, complexes of Fe(II) like $[Fe(CN)_6]^{2-}$ are low spin complex (d^2sp^3) has no unpaired electron and thus diamagnetic.
6. **True :** Cu^+ is the intermediate oxidation state between Cu^{++} and Cu. If the reduction potential from the intermediate oxidation state to the lower one is more positive than from the higher to the intermediate, then the intermediate state will undergo disproportional.

$$Cu^{++} \xrightarrow{+0.15\,V} Cu^+ \xrightarrow{+0.52\,V} Cu$$

C. MCQs with One Correct Answer

1. (a) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
   $Zn + 2NaOH \longrightarrow Na_2[ZnO_2] + H_2$
   ∴ Ratio of H_2 evolved is 1 : 1.
2. **(d)** ∵ Basicity of hydroxides decreases on moving left to right in a period.
3. **(b)** German silver is alloy of Cu + Zn + Ni
4. **(b)** $Zn + 2NaOH \longrightarrow \underset{\text{Sod.meta zincate(soluble)}}{Na_2[ZnO_2]} + H_2$
5. **(b)** $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$. It has 2 unpaired electrons.
   $3d$ orbital of Ni^{2+} ion. At No. of Ni = 28.
6. **(c)** Hypo solution ($Na_2S_2O_3$) is used in photography to remove the unaffected AgBr in the form of soluble complex.
   $$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Sod. argentothiosulphate}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$
7. **(d)** Conc. HNO_3 renders iron passive by forming a thin protective film of Fe_3O_4 on its surface.
8. **(a)** $CaCO_3 \xrightarrow{Heat} CaO + CO_2$;
   $$\underset{\text{Flux}}{CaO} + \underset{\text{impurity}}{SiO_2} \longrightarrow CaSiO_3\ (\text{slag}).$$
9. **(a)** Zinc-copper couple is obtained by mixing zinc dust with copper guaze.
10. **(b)** Mn^{2+} in $MnSO_4.4H_2O$ has d^5 configuration (five unpaired electrons); Cu^{2+} in $CuSO_4.5H_2O$ has d^9 configuration (one unpaired electron); Fe^{2+} in $FeSO_4.6H_2O$ has d^6 configuration (four unpaired electron); and Ni^{2+} in $NiSO_4.6H_2O$ has d^8 configuration (two unpaired electron). Thus $CuSO_4.5H_2O$ has lowest degree of paramagnetism.
11. **(c)**

Atom/Ion Complex	Configuration	No. of unpaired electrons	Magnetic nature
Ni^{2+} (d^8)		2	Paramagnetic
$[NiCl_4]^{2-}$		2	Paramagnetic
$[Ni(CN)_4]^{2-}$		0	Diamagnetic
Ni (d^8s^2)		2	Paramagnetic
$[Ni(CO)_4]$		0	Diamagnetic

12. **(c)** Solder is an alloy containing Sn – 67% and Pb – 33%.
13. **(a)** $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 3Cl_2$
14. **(d)** $CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$
    $2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$ (Cyanogen)
    $Cu_2(CN)_2 + 6KCN \longrightarrow 2K_3[Cu(CN)_4]$
15. **(a)** HgS does not dissolved in hot dil. HNO_3
16. **(c)** **TIPS/FORMULAE :**
    Chrome alum is $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
    The filtrate is yellow due to CrO_4^{2-} ion and residue is brown due to $Fe(OH)_3$.
17. **(b)** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{(green)}}{Cr_2O_3} + N_2 + 4H_2O$
    Hence green coloured powder blown in the air is Cr_2O_3.

18. **(a)** The reaction of MnO_4^- and SO_3^{2-} in acidic medium is derived as follows:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

$$\underline{SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5}$$

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Hence, 2 mole $2MnO_4^- \equiv 5$ mol SO_3^{2-}

i.e., $\frac{2}{5}$ mol $MnO_4^- \equiv 1$ mol SO_3^{2-}

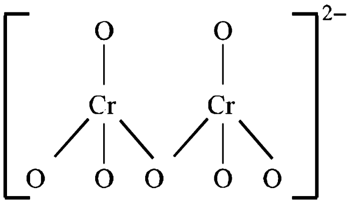
19. **(d)** Organometallic compounds are those compounds in which metal atom is directly bonded with C-atom. H_3C-Li.

20. **(b)** The electronic configurations of cations in the given salts are

$Ag^+(4d^{10}), Cu^{2+}(3d^9), Mg^{2+}(2s^2, 2p^6), Cu^+(3d^{10})$

Only Cu^{2+} ion has one unpaired electron in 3d orbital and so, its salt is expected to be coloured.

21. **(b)** The structure of $Cr_2O_7^{2-}$



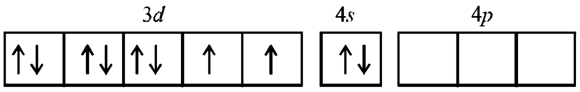
There are six normal Cr – O bonds and two bridged Cr – O bonds.

The six normal Cr – O bonds are expected to be equivalent and different from those of the bridged Cr – O bonds.

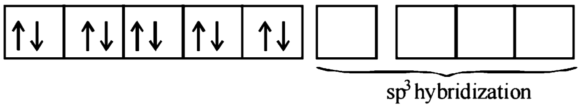
22. **(c)** **NOTE :** In metal carbonyl the metal is in **zero** oxidation state.

In $Ni(CO)_4$, O.N. of Ni = 0

For Ni (Z = 28)

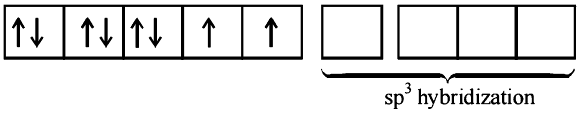


In presence of CO two 4*s* electrons pair up, thus



In $Ni(PPh_3)_2Cl_2$, O.N. of Ni = +2

For Ni^{2+}



PPh_3 and Cl^- can't pair up *d*-electrons, leading to sp^3 hybridization leading to tetrahedral geometry.

23. **(c)** Haematite ore (Fe_2O_3) is first reduced to cast iron which is then oxidised for removing carbon (impurity) as CO_2.

24. **(a)** In $[MnO_4]^-$, Mn is in +7 oxidation state.

Electronic configuration of Mn (Z = 25) : [Ar] $3d^5 4s^2$

Electronic configuration of Mn^{7+} : [Ar] $3d^0 4s^0$

Central atom in other ions have definite number of *d* electrons

No. of electrons

$$\underset{\text{in } Co^{3+} = \text{Six}}{[Co(NH_3)_6]^{3+}} \quad \underset{\text{in } Fe^{3+} = \text{Five}}{[Fe(CN)6]^{3-}} \quad \underset{\text{in } Cr^{3+} = \text{three}}{[Cr(H_2O)_6]^{3+}}$$

25. **(b)** $2Fe + 3Cl_2 \text{ (dry)} \rightarrow 2FeCl_3 \text{(anhydrous)}$

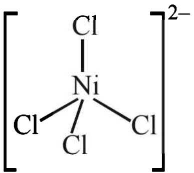
26. **(a)** Stable oxidation state of Mn in alkaline medium is +6. So, MnO_2 is oxidised to K_2MnO_4 (purple green) by atmospheric oxygen in KOH medium.

$$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{(Purple)}}{2K_2MnO_4} + 2H_2O$$

27. **(a)** $2Au + 4CN^- + H_2O + \frac{1}{2}O_2 \longrightarrow \underset{'X'}{2[Au(CN)_2]^-} + 2OH^-$

$$2[Au(CN)_2]^- + Zn \longrightarrow \underset{'Y'}{[Zn(CN)_4]^{2-}} + 2Au$$

28. **(b)** The configuration of Ni^{2+} is $3d^8$. For the elements of the first transition series, Cl^- behaves as a weak field/ high spin ligand. Hence Ni in $[NiCl_4]^{2-}$ is sp^3 hybridised leading to tetrahedral shape.



sp^3, Tetrahedral

29. **(c)** **TIPS/FORMULAE :**

$\mu = \sqrt{n(n+2)}$ BM (μ = spin magnetic moment)

Here Co is present as Co^{2+} ion which has 3 unpaired electrons. So the spin magnetic moment will be $\sqrt{3(3+2)}$, i.e. $\sqrt{15}$ BM.

30. **(a)** $6MnO_4^- + I^- + 6OH^- \longrightarrow 6MnO_4^{2-} + IO_3^- + 3H_2O$

31. **(a)** $(NH_4)_2Cr_2O_7 \xrightarrow{\text{heat}} N_2 + Cr_2O_3 + 4H_2O$

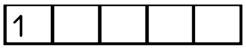
$NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Same gas i.e., N_2)

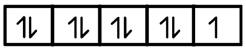
$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

$Mg_3N_2 + 3H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

$2NaNO_2 + H_2O_2 \longrightarrow Na_2O_2 + 2HNO_2$

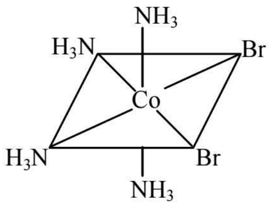
32. **(b)** Colour of transition metal ion salt is due to *d-d* transition of unpaired electrons of *d*-orbital. Metal ion salt having similar number of unpaired electrons in *d*-orbitals shows similar colour in aqueous medium.

V^{4+}: $[Ar]3d^1$


Cu^{2+}: $[Ar]3d^9$


Number of unpaired electrons = 1

33. **(a)** $Co(NH_3)_4Br_2Cl$ will show both geometrical and ionization isomerism.
$[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4BrCl]Br$ are ionization isomers and geometrical isomers are



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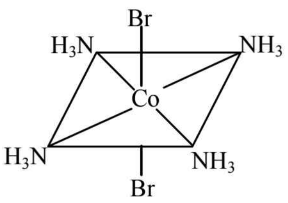

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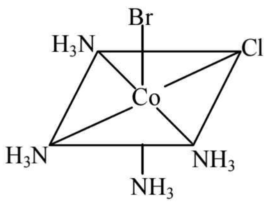

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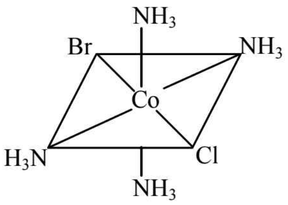

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34. **(a)** $CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$

$$\underset{\text{unstable}}{Cu(CN)_2} \rightleftharpoons CuCN + \frac{1}{2}(CN)_2$$

$$CuCN + 3\,KCN \rightleftharpoons \underset{\text{colourless}}{K_3[Cu(CN)_4]^{3-}}$$

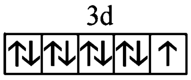
35. **(d)** An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

36. **(b)** In the presence of oxygen, Ag metal forms a water soluble complex $Na[Ag(CN)_2]$ with dilute solution of NaCN

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow \underset{\text{(Soluble)}}{4Na[Ag(CN)_2]} + 4NaOH$$

37. **(c)** **NOTE :** Colour is due to d – d transitions. Coloured compounds contain partly filled d-orbital.
The oxidation state of copper in various compounds is + 1 and + 2. In CuF_2 it is in + 2 oxidation state. In + 2 state its configuration is

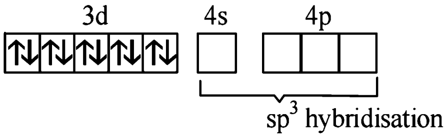
$Cu^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

i.e.


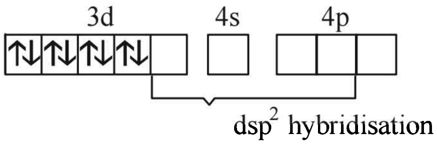
It has one unpaired electron due to this it is coloured. The colour is due to d-d transitions.
(**NOTE :** CuF_2 possesses blue colour in crystalline form)

38. **(c)** The correct IUPAC name of the given compound is tetramminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.

39. **(b)** **NOTE : :** In carbonyls O.S. of metal is zero
In $[Ni(CO)_4]$, the oxidation state of nickel is zero. Its configuration in $Ni(CO)_4$ is

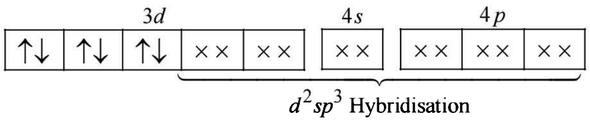
$[Ni(CO)_4]$;


In $[Ni(CN)_4]^{2-}$ the oxidation state of Ni is 2+ and its configuration is

$[Ni(CN)_4]^2$


Thus the hybridisations of nickel in these compounds are sp^3 and dsp^2 respectively.
Hence (b) is the correct answer.

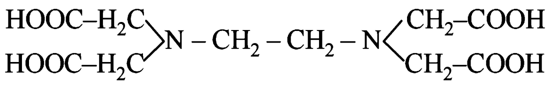
40. **(a)** Chromium in $Cr(CO)_6$ is in zero oxidation state and has $[Ar]^{18}\,3d^5 4s^1$ as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in $Cr(CO)_6$.



Since the complex has no unpaired electron, its magnetic moment is zero.

41. **(b)** Ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is $[Cr(H_2O)_4Cl_2]NO_2$.

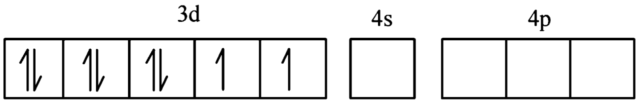
42. **(c)** The correct structure of EDTA is



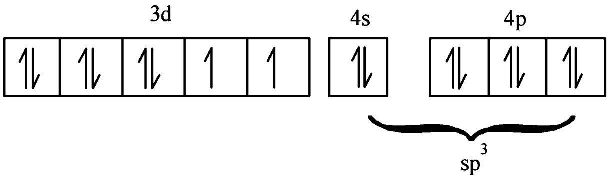
$$\begin{matrix} HOOC{-}H_2C \\ HOOC{-}H_2C \end{matrix}\!\!>N - CH_2 - CH_2 - N<\!\!\begin{matrix} CH_2{-}COOH \\ CH_2{-}COOH \end{matrix}$$

43. **(b)** $[NiCl_4]^{2-}$, O.S. of Ni = +2

$Ni(28) = 3d^8\,4s^2$



Cl^- being weak ligand it cannot pair up the two electrons present in 3d orbital



No. of unpaired electrons = 2

Magnetic moment, $\mu = 2.82$ BM.

44. **(c)**

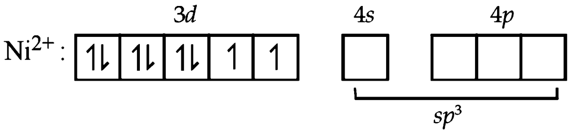
Complex	No. of electrons in outer *d* orbital	No. of unpaired electron (s)
$[Fe(CN)_6]^{3-}$	$3d^5$	1 (CN^- causes pairing of electrons)
$[Co(NH_3)_6]^{3+}$	$3d^6$	–
$[Co(oxal.)_3]^{3-}$	$3d^6$	–
$[Ni(H_2O)_6]^{2+}$	$3d^8$	2
$[Pt(CN)_4]^{2-}$	$5d^8$	D (CN^- causes pairing of electrons)
$[Zn(H_2O)_6]^{2+}$	$3d^{10}$	–

Thus L, M, O and P are diamagnetic.

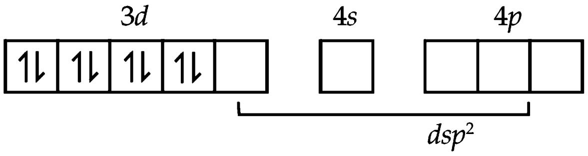
45. **(d)** $[Co(H_2O)_4(NH_3)_2]Cl_3$
= Diamminetetraaquacobalt (III) chloride.

46. **(a)** $CuSO_4$ will be absorbing orange-red colour and hence will be of blue colour.

47. **(c)** In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni^{2+} whose electronic configuration is [Ar] $3d^8 4s^0$.



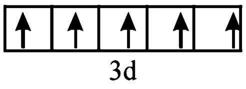
In the above paramagnetic state the geometry of the complex is sp^3 giving tetrahedral geometry.
The diamagnetic state is achieved by pairing of electrons in 3*d* orbital.



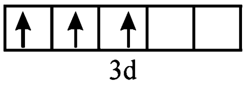
Thus the geometry of the complex will be dsp^2 giving square planar geometry.

48. **(b)** The electronic configuration of central metal ion in complex ions P, Q and R are

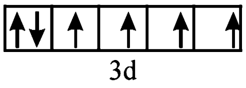
P = $[FeF_6]^{3-}$; Fe^{3+} :



Q = $[V(H_2O)_6]^{2+}$; V^{2+}



R = $[Fe(H_2O)_6]^{2+}$; Fe^{2+}



Higher the no. of unpaired electron(s), higher will be magnetic moment.
Thus the correct order of spin only magnetic moment is Q < R < P

49. **(b)**

	Compound/Ion	Magnetic nature of compound
1.	$[Ni(CO)_4]$	Diamagnetic
2.	$[NiCl_4]^{2-}$	Paramagnetic
3.	$[Co(NH_3)_4Cl_2]Cl$	Diamagnetic
4.	$Na_3[CoF_6]$	Paramagnetic
5.	Na_2O_2	Diamagnetic
6.	CsO_2	Paramagnetic

So total number of paramagnetic compounds is 3.

D. MCQs with One or More Than One Correct

1. **(b, c)** $2MnO_2 + 4KOH + O_2 \xrightarrow{heat} 2K_2MnO_4 + 2H_2O$;
$2KOH + HCHO + 2\,KMnO_4$
$\longrightarrow K_2MnO_4 + H_2O + HCOOH$

2. **(c, d)** Aqueous solution of $Co(NO_3)_2$ and $CrCl_3$ in which Co^{2+} (d^7) and Cr^{3+} (d^3) contains incompletely filled *d*-orbitals are coloured.

3. **(b)** Highest parmagnetic character will be shown by the ion having maximum number of unpaired electrons in their *d*-subshells.
$_{25}Cr^{3+}$ has 3 unpaired electrons ;
$_{26}Fe^{2+}$ has 4 unpaired electrons
$_{29}Cu^{2+}$ has 1 unpaired electrons ;
$_{30}Zn^{2+}$ has no unpaired electrons
So (a), (b) & (c) show paramagnetism. Out of which (b) has the highest paramagnetism.

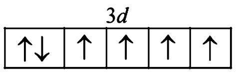
4. **(b, c)** Brass : Cu (60-80%), Zn (40-20%); Gun Metal : Cu (87%), Sn (10%), Zn (3%).

5. **(c)** The magnetic moment (μ) of a species is related to its number of unpaired electrons (*n*) in form of following expressions.

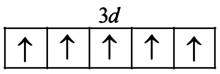
$$\mu = \sqrt{n(n+2)}\ \text{B.M}$$

The number of unpaired electrons in the given pairs are as follows:

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

or  Thus here $n = 4$.

$Fe^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$

or  Thus here $n = 5$

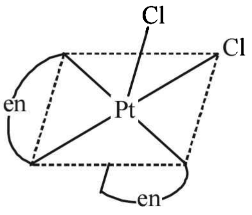
$\overset{+}{N}O$ or $\underset{xx}{\overset{+}{N}} = \ddot{O}:$ $n = 0$; NO or $\overset{\times}{\times}N \overset{\times\bullet\bullet}{\equiv} O\!:$ $n = 1$

The given combinations differ in the number of unpaired electrons. Hence these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion.

6. **(a, c)** Mn makes steel harder and increases its elasticity and tensile strength. Further Mn acts as deoxidiser. MnO reacts with S present in cast iron, gets oxidised and then combine to form slag.

7. **(d)** The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fe) leading to contraction of bond between C and O of CO.

8. **(c,d)**



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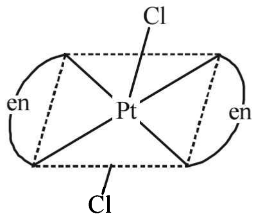

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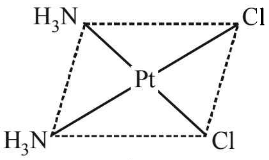

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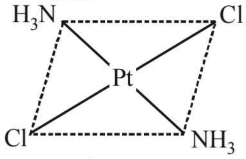

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9. **(a,d)** In acidic medium

$$MnO_4^- \longrightarrow Mn^{2+}$$

Change in oxidation state of Mn = 7 – 2 = 5
Thus electrons lost = 5
In neutral medium

$$MnO_4^- \longrightarrow MnO_2$$

Change in oxidation state of Mn = 7 – 4 = 3
∴ Electrons lost = 3

10. **(b,c,d)** Cu^{2+} ions will react with CN^- and SCN^- forming $[Cu(CN)_4]^{3-}$ and $[Cu(SCN)_4]^{3-}$ leading the reaction in the backward direction.

$$Cu^{2+} + 2CN^- \rightarrow Cu(CN)_2$$

$$2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2$$

$$CuCN + 3CN^- \rightarrow [Cu(CN)_4]^{3-}$$

$$Cu^{2+} + 4SCN^- \rightarrow [Cu(SCN)_4]^{3-}$$

Cu^{2+} also combines with $CuCl_2$ which reacts with Cu to produce CuCl pushing the reaction in the backward direction.

$$CuCl_2 + Cu \rightarrow 2CuCl\downarrow$$

11. **(a, c, d)**

$$KI(aq) + K_3[Fe(CN)_6](aq) \longrightarrow \underset{\text{Brownish-yellow}}{KI_3(aq) + K_4[Fe(CN)_6](aq)}$$

$$\Big\downarrow {\scriptstyle ZnSO_4(aq)}$$

$$\underset{\text{white ppt}}{K_2Zn_3[Fe(CN)_6]_2} \text{ or } \underset{\text{white ppt}}{\{K_2Zn[Fe(CN)_6]\}}\downarrow + KI_3(aq)$$

$$\Big\downarrow {\scriptstyle Na_2S_2O_3}$$

$$\underset{\text{Colourless}}{I^-(aq) + S_4O_6^{2-}(aq)}$$

$$\underset{\text{white ppt.}}{K_2Zn[Fe(CN)_6]} + NaOH \longrightarrow [Zn(OH)_4]^{2-}(aq) + [Fe(CN)_6]^{4-}(aq)$$

12. **(b,d)** The pair of complex ions $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$ show geometrical isomerism. The pair of complexes $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$ show ionisation isomerism. The other pairs given do not have same type of isomerism.

13. **(a, b, c)** $Na + NH_3$ (excess) → Dilute solution of Na in liq. NH_3 → Paramagnetic

$K + O_2$ (excess) → KO_2 (O_2^- is paramagnetic)

$Cu + HNO_3$ (dil.) → $Cu(NO_3)_2 + NO$
(NO is paramagnetic)

2-Ethylanthraquinol + O_2 →
2-Ethylanthraquinone + H_2O_2
(H_2O_2 is diamagnetic)

14. **(a, b, c)**

Cr^{2+} is a reducing agent and Mn^{3+} is an oxidizing agent and both have electronic configuration d^4.

$$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41V \qquad E^\circ_{Mn^{3+}/Mn^{2+}} = 1.51V$$

Above E° values explains reducing nature of Cr^{2+} and oxidizing behaviour of Mn^{3+}.

15. **(a, b)**

E. Subjective Problems

1. (i) Since the compound (A) on strong heating gives two oxides of sulphur (C and D) which might be SO_2 and SO_3, it must be a **sulphate.**

(ii) The reaction of compound (E) with thiocyanate to give blood red coloured compound (H) indicates that (E) must have **Fe^{3+} ion.**

Thus the compound (A) must be ferrous sulphate, $FeSO_4.7H_2O$, which explains all given reactions as below (Fe^{2+} ion of $FeSO_4$ is changed to Fe^{3+} during heating).

$$\underset{\substack{\text{Ferrous sulphate}\\ (A)}}{FeSO_4 . 7H_2O} \xrightarrow{\text{heat}} \underset{\substack{\text{Ferrous}\\ \text{sulphate}}}{FeSO_4} + 7H_2O\uparrow$$

$$\underset{\substack{\text{Ferrous}\\ \text{sulphate}}}{2\,FeSO_4} \xrightarrow{\text{heat}} \underset{\substack{\text{Ferric}\\ \text{oxide,}\\ \text{(Blackish}\\ \text{brown powder)}\\ (B)}}{Fe_2O_3} + \underset{(C)}{SO_2} + \underset{(D)}{SO_3}$$

$$\underset{(B)}{Fe_2O_3} + 6\,HCl \longrightarrow \underset{\substack{\text{Ferric chloride}\\ \text{(Yellow solution), (E)}}}{2FeCl_3} + 3H_2O$$

$$\underset{(E)}{2FeCl_3} + H_2S \longrightarrow \underset{\substack{\text{Apple}\\ \text{green (G)}}}{2FeCl_2} + 2HCl + \underset{\substack{\text{White}\\ \text{turbidity (F)}}}{S}$$

$$\underset{(E)}{FeCl_3} + 3NH_4CNS \longrightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \text{(blood red colour)}}}{Fe(CNS)_3} + 3NH_4Cl$$

2. (i) $\underset{(A)}{ZnCO_3} \xrightarrow{\Delta} \underset{(C)}{ZnO} + \underset{(B)}{CO_2}$

(ii) $\underset{(C)}{ZnO} + 2HCl \longrightarrow H_2O + \underset{\text{(soluble)}}{ZnCl_2}$

(iii) $2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow 4KCl + \underset{\text{(white ppt)}}{Zn_2[Fe(CN)_6]}\downarrow$

(iv) $\underset{(A)}{ZnCO_3} + HCl \longrightarrow CO_2 + \underset{\text{(soluble)}}{ZnCl_2}$

(v) $\underset{(B)}{CO_2} + Ca(OH)_2 \longrightarrow \underset{\text{(Milky)}}{CaCO_3} + H_2O$

(vi) $CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{(soluble)}}{Ca(HCO_3)_2}$

(vii) $ZnCl_2 + H_2S \xrightarrow{NH_4OH} 2HCl + \underset{\text{(white)}}{ZnS\downarrow}$

(viii) $ZnCl_2 + 2NaOH \longrightarrow 2NaCl + \underset{\text{(white) E}}{Zn(OH)_2\downarrow}$

(ix) $Zn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{sod. zincate}\\ \text{(soluble)}}}{Na_2ZnO_2} + H_2$

3. (i) $2Ag + 2H_2SO_4 \longrightarrow \underset{\text{(white)}}{Ag_2SO_4} + SO_2 + H_2O$

(ii) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{(green)}}{Cr_2O_3} + N_2 + 4H_2O$

(iii) $2KMnO_4 + 3H_2SO_4 + 5H_2S \xrightarrow{\Delta}$

$K_2SO_4 + 2MnSO_4 + \underset{\text{(turbidity)}}{5S} + 8H_2O$

4. On standing $FeCl_3$ is hydrolysed and produces colloidal solution of $Fe(OH)_3$ which is in form of brown precipitate.

$$FeCl_3 + 3H_2O \rightleftharpoons \underset{\text{Brown ppt}}{Fe(OH)_3\downarrow} + 3HCl$$

5. $SO_2 + MnO_4^- + H^+ \rightarrow SO_4^{2-} + Mn^{2+} + H_2O$

6. (*i*) $2CuSO_4 + SO_2 + 2H_2O + 2KCNS$

$\rightarrow \underset{\substack{\text{Cuprous thiocyanate}\\ \text{(white)}}}{2CuCNS\downarrow} + K_2SO_4 + 2H_2SO_4$

(*ii*) $Fe_2(SO_4)_3 + 2KI \rightarrow 2FeSO_4 + K_2SO_4 + I_2$

(*iii*) $2\,MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + MnO_4^- + 2H_2O$

(*iv*) $\underset{\text{(yellow)}}{2K_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{(orange red)}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$

(*v*) $2KMnO_4 + 4KOH + MnO_2 \rightarrow 3K_2MnO_4 + 2H_2O$

or $2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O]$

(*vi*) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O$

$\xrightarrow{\text{heat}} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(*vii*) $\underbrace{3HCl + HNO_3}_{\text{(aqua regia)}} \rightarrow NOCl + 2H_2O + 2(Cl)$

$Au + 2[Cl] \xrightarrow{HCl} AuCl_3 \xrightarrow{HCl} \underset{\text{Aurochloric acid}}{HAuCl_4}$

(*viii*) $\underset{\text{(silver glance)}}{Ag_2S} + 4NaCN \rightleftharpoons 2\,Na[Ag(CN)_2] + Na_2S$

$4Na_2S + SO_2 + 2H_2O \rightarrow 2\,Na_2SO_4 + 4\,NaOH + 2S$

[**NOTE :** Na_2S is converted into Na_2SO_4 to avoid reversibility of first reaction]

$2NaAg(CN)_2 + Zn \rightarrow \underset{\text{Sod. Zincocyanide}}{Na_2\,[Zn(CN)_4]} + 2Ag$

(*ix*) $AgCl + 2NaCN \rightleftharpoons NaCl + Na\,[Ag(CN)_2]$

$2Na[Ag(CN)_2] + Zn \rightarrow \underset{\text{soluble}}{Na_2[Zn(CN)_4]} + 2Ag\downarrow$

(*x*) $CoCl_2 + 2KNO_2 \rightarrow Co(NO_2)_2 + 2KCl$

$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$

$Co(NO_2)_2 + 3KNO_2 + 2HNO_2$

$\rightarrow \underset{\substack{\text{Pot. cobaltinitrite}\\ \text{(yellow ppt.)}}}{K_3[Co(NO_2)_6]\downarrow} + NO + H_2O$

(*xi*)

$$\left.\begin{array}{l} \underset{\text{(copper pyrites)}}{2CuFeS_2} + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2 \\ 2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \\ 2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \end{array}\right]\text{Roasting}$$

$$\left.\begin{array}{l} Cu_2O + FeS \longrightarrow Cu_2S + FeO \\ FeO + SiO_2 \longrightarrow FeSiO_3\ (\textit{slag}) \end{array}\right]\begin{array}{l}\text{Smelting}\\ \text{with coke}\\ \text{and sand}\end{array}$$

$$\left.\begin{array}{l} 2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \\ Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow \end{array}\right]\text{Bessemerization}$$

(*xii*) $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4$

$\rightarrow \underset{\substack{\text{chromyl chloride}\\ \text{(orange)}}}{2CrO_2Cl_2\uparrow} + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

(*xiii*) $4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

(*xiv*) $2KMnO_4 + 3MnSO_4 + 2H_2O$

$\rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

This is known as **Volhard method** for estimation of manganese.

(*xv*) The individual reactions are

$3Cu + 8HNO_3\,(\text{dil.}) \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$

$Cu + 4HNO_3\,(\text{dil.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

For the molar ratio of 2 : 1 of NO and NO_2, we will have

$7Cu + 20HNO_3 \rightarrow 7Cu(NO_3)_2 + 4NO + 2NO_2 + 10H_2O$

(*xvi*) $2CuSO_4 + 2Na_2CO_3 + H_2O$

$\rightarrow CuCO_3.Cu(OH)_2 + 2Na_2SO_4 + CO_2$

(*xvii*) $K_2Cr_2O_7 + 14HCl \xrightarrow{\text{heat}}$

$2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(*xviii*) $AgBr + 2Na_2S_2O_3 \rightarrow \underset{\text{Sod. argento thiosulphate}}{Na_3\,[Ag(S_2O_3)_2]} + NaBr$

(*xix*) $(NH_4)_2S_2O_8 + 2H_2O + MnSO_4$

$\rightarrow MnO_2 + 2H_2SO_4 + (NH_4)_2SO_4$

(*xx*) $3[MnO_4]^{2-} + 4H^+ \rightarrow MnO_2 + 2[MnO_4]^- + 2H_2O$

(*xxi*) $3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

(*xxii*) $\underset{\text{(Argentite)}}{Ag_2S} + 2KCN \longrightarrow \underset{\substack{\text{potassium}\\ \text{Argentocyanide}}}{K[Ag(CN)_2]} + K_2S$

(*xxiii*) $[Zn + 2HNO_3(\text{dil}) \rightarrow Zn(NO_3)_2 + 2[H]] \times 4$

$$\begin{array}{l} 2HNO_3 + 8[H] \rightarrow N_2O + 5H_2O \\ \hline 4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O \end{array}$$

7. Equations for extraction of silver from its sulphide ore.

Cyanide Process :

$\underset{\text{(sulphide ore)}}{Ag_2S} + 2NaCN \rightarrow Na_2S + 2AgCN$

$$\underset{\text{Sod. argentocyanide (soluble)}}{AgCN + NaCN \rightarrow Na[Ag(CN)_2]}$$

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

[**NOTE :** Zn is more electropositive than Ag.]

8. (*i*) It is because silver bromide, being sensitive to light, reduces into metallic silver grains when light fall on it.

(*ii*) The transition metals form **coloured compounds** and **coloured complexes**. They have vacant *d*-orbitals. Electrons take up energy from the visible region and move to higher energy levels. The visible colour of the substance is the complementary colour of the absorbed light.

[**NOTE :** The colour is due to *d-d* transitions]

(*iii*) Zinc is cheaper and stronger reducing agent than copper and zinc is volatile

(*iv*) Mercurous chloride changes from white to black when treated with ammonia due to the formation of finely divided mercury.

(*v*) Cu^{2+} is reduced to Cu^+ by I^-, hence cupric iodide is converted into cuprous iodide so $[CuI_4]^{2-}$ does not exist, Cl^- cannot effect this change and thus $[CuCl_4]^{2-}$ exists.

(*vi*) CrO_3 is acid anhydride of H_2CrO_4 (Chromic acid) [Anhydride are formed by loss of water from acid]

$$H_2CrO_4 \xrightarrow{\text{Dehydration}} CrO_3 + H_2O$$

In $H_2Cr_2O_4$, Cr is present in + 6 oxidation state.

9. $2Mn(OH)_2 + 5NaBiO_3 + 18H^+$

$$\rightarrow 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 11H_2O$$

10. (*i*) $CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

or $CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$

$Cu(OH)_2 + 2(NH_4)_2SO_4$

$$\rightarrow \underset{\text{deep blue complex}}{[Cu(NH_3)_4]SO_4} + 2H_2O + H_2SO_4$$

(*ii*) $H_2O_2 \rightarrow H_2O + [O] \quad] \times 3$

$$\underset{\text{green}}{CrCl_3} + 3NaOH \rightarrow Cr(OH)_3\downarrow + 3NaCl$$

$$2Cr(OH)_3 + 4NaOH + 3[O] \rightarrow 2Na_2CrO_4 + 5H_2O$$

$$2CrCl_3 + 10NaOH + 3H_2O_2 \rightarrow \underset{\text{yellow}}{2Na_2CrO_4} + 6NaCl + 8H_2O$$

11. $ZnO + 2NaOH \rightarrow \underset{\text{Sod. Zincate}}{Na_2ZnO_2} + H_2O$

12. Carbon monoxide is the actual reducing agent of haematite in blast furnace.

13. $3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \rightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

14. For the explanation of colouration of complexes, first of all find out the number of unpaired electrons present in outer available *d*-orbitals

(i) $[Ti(NO_3)_4]$; ${}_{22}Ti^{4+}$: $[Ar]\,3d^0\,4s^0$

(ii) $[Cu(NC\,CH_3)_4]^+\ BF_4^-$; ${}_{29}Cu^+$: $[Ar]\,3d^{10}\,4s^0$

(iii) $[Cr(NH_3)_6]^{+3}\,3Cl^-$; ${}_{24}Cr^{3+}$: $[Ar]\,3d^3\,4s^0$

(iv) $K_3\,[VF_6]$; ${}_{23}V^{+3}$: $[Ar]\,3d^2\,4s^0$

Due to the presence of unpaired electrons in *d*-orbitals, two complexes *i.e.*, $[Cr(NH_3)_6]^{3+}\,3Cl^-$ and $K_3\,[VF_6]$ are coloured. Others having all paired electrons are colourless

15. (*i*) Pentamminenitritocobalt (III) chloride

(*ii*) Potassium hexacyanochromate (III)

(*iii*) Pentamminecarbonatochromium (III) chloride.

16. ${}_{29}Cu = 1s^2, 2s^2\,2p^6, 3s^2 3p^6 3d^{10}, 4s^1$

${}_{30}Zn = 1s^2, 2s^2\,2p^6, 3s^2 3p^6 3d^{10}, 4s^2$

On the basis of configuration of Cu and Zn, first ionisation potential of Zn is greater than that of copper because in zinc the electron is removed from $4s^2$ configuration while in copper it is removed from $4s^1$ configuration. So more amount of energy is required for the removal of electron of $4s^2$ (completely filled orbital) than that of $4s^1$ while the second ionisation potential of Cu is higher than that of zinc because Cu^+ has $3d^{10}$ (stable configuration) in comparison to Zn^+ ($4s^1$ configuration).

17. (*i*) $[CoCl(NH_3)_5]^{2+}$ Formula of pentamminechlorocobalt (III)

(*ii*) $LiAlH_4$ Formula of lithium tetrahydroaluminate (III)

18. Haematite(Fe_2O_3) on burning with coke and lime at 2000 °C results in the following reactions.

$C + O_2 \rightarrow CO_2$

$CO_2 + O \rightarrow 2CO$

$3CO + Fe_2O_3 \rightarrow \underset{\text{(Steel)}}{2Fe} + 3CO_2$ (Reduction of Fe_2O_3 to form steel)

$\underset{\text{(Lime)}}{SiO_2 + CaO} \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$ (Slag, $CaSiO_3$ is used as building material)

19. $2\,Cu + H_2O + CO_2 + O_2 \rightarrow \underset{\text{Green basic copper carbonate}}{CuCO_3.\,Cu(OH)_2}$

20. The complex A does not react with concentrated H_2SO_4 implying that all water molecules are coordinated with Cr^{3+} ion. Hence, its structure would be $[Cr(H_2O)_6]Cl_3$.

The compound B loses 6.75% of its original mass when treated with concentrated H_2SO_4. This loss is due to the removal of water molecules which is/are not directly coordinated to Cr^{3+} ion.

The mass of water molecules removed per mole of the complex

$$= \frac{6.75}{100} \times \text{molar mass of the complex} = \frac{6.75}{100} \times 266.5\text{ g}$$

$= 17.98$ g

This corresponds to one mole of water. Hence, the structure of the compound B will be $[Cr(H_2O)_5Cl](H_2O)Cl_2$

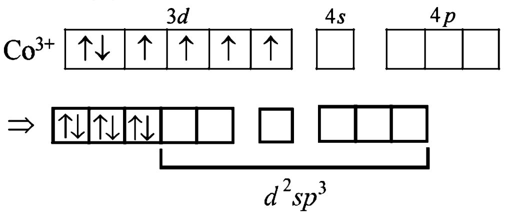
NOTE : The compound C loses 13.5% of its mass when treated with concentrated H_2SO_4 which is twice of the mass lost by the compound B. Hence, the structure of the compound C will be $[Cr(H_2O)_4Cl_2](H_2O)_2\,Cl$.

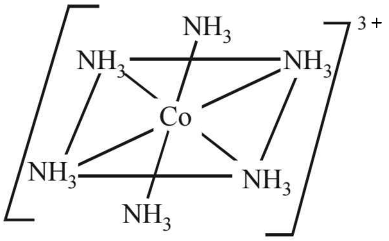
21. $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$[Fe(H_2O)_6]SO_4.H_2O + NO \longrightarrow \underset{\text{brown ring}}{[Fe(H_2O)_5\,NO].SO_4} + 2H_2O$$

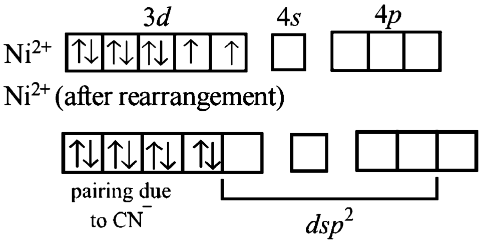
22. **$[Co(NH_3)_6]^{3+}$**

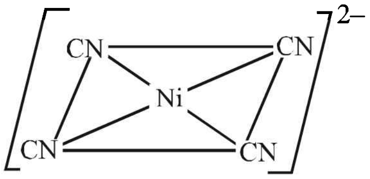




Octahedral complex, d^2sp^3 hybridisation

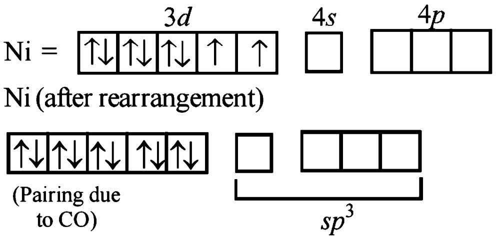
$[Ni(CN)_4]^{2-}$

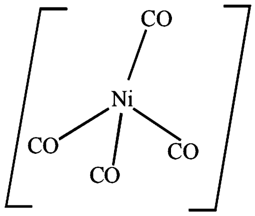




Square planar dsp^2 hybridisation

$[Ni(CO)_4]$





Tetrahedral (sp^3 hybridisation)

23. (*i*) Argentite is Ag_2S. Silver is extracted from its ore argentite (silver glance, Ag_2S) as follows :

(1) Silver glance is concentrated by froth flotation.

(2) Leaching : The concentrated ore is ground to fine powder and dissolved in dilute solution of sodium cyanide.

$$Ag_2S + 4NaCN \longrightarrow 2NaAg(CN)_2 + Na_2S$$

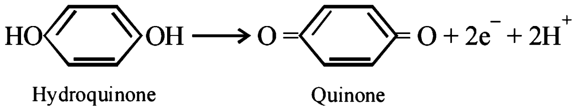
Oxygen of air converts Na_2S to Na_2SO_4 thereby preventing reaction to take place in the reversible direction.

(3) Recovery of silver.

Silver is precipitated out by adding electropositive metal, Zn.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

(*ii*) For development, activated grains are preferentially reduced by mild reducing agents like hydroquinone



$$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-$$

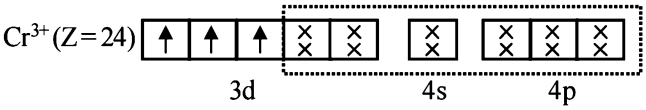
(Reduction of activated AgBr to elemental silver.)

The photographic film is permanently fixed by immediately washing out any non activated AgBr grains in hypo emulsion.

$$AgBr(s) + \underset{\text{hypo}}{2Na_2S_2O_3} \longrightarrow \underset{\text{soluble}}{Na_3Ag(S_2O_3)_2} + NaBr$$

24. Compound (A) on treatment with $AgNO_3$ gives white precipitate of AgCl, which is readily soluble in dil.aq. NH_3. Therefore it has at least one Cl^- ion in the ionization sphere furthermore chromium has coordination number equal to 6. So its formula is **$[Cr(NH_3)_4BrCl]Cl$**.

Compound (B) on treatment with $AgNO_3$ gives pale yellow precipitate of AgBr soluble in conc. NH_3. Therefore it has Br^- in the ionization sphere. So its formula is **$[Cr(NH_3)_4Cl_2]Br$**.



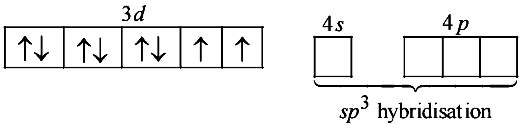
State of hybridization of chromium in both (A) and (B) is ***d^2sp^3***.

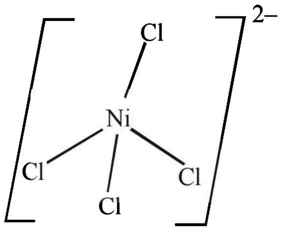
Spin magnetic moment of (A) or (B),

$$\mu_{spin} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = \mathbf{3.87\ BM}$$

25. Cl^- is a weak ligand which is unable to pair the electrons of Ni^{2+}. Therefore, here hybridisation is sp^3 and shape will be **tetrahedral.**

Electronic configuration of Ni^{+2} (No. of electrons = 26) in presence of Cl^- ion, a weak ligand.

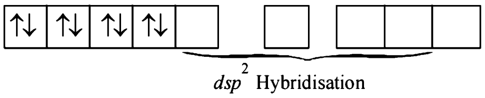




Magnetic moment of $[NiCl_4]^{2-} = \sqrt{2(2+2)} = 2.82$ BM

On the other hand, CN^- is a stong ligand which pairs up the

electrons of Ni^{2+}. Therefore, here hybridisation is dsp^2 and shape will be square planar.
Electronic configuration of Ni^{2+} in presence of CN^- ion, a strong ligand.



For structure of $[Ni(CN)_4]^{2-}$, refer question 24 in Section (E).

Magnetic moment of $[Ni(CN)_4]^{2-} = \sqrt{0(0+2)} = 0.0\,BM$

26. The spin magnetic moment, μ of the complex is 1.73 BM.

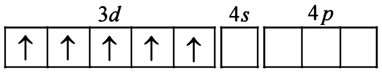
$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$

It means that nucleus of the complex, chromium ion **has one unpaired electron**. So the ligand NO is **unit positively** charged.

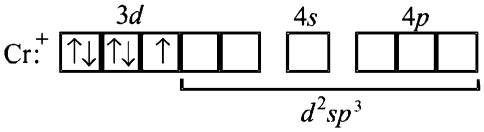
IUPAC name :

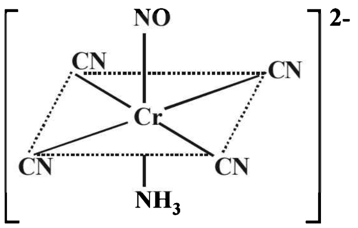
Potassium amminetetracyanonitrosochromate (I).

(a) Electronic configuration of Cr^+ :



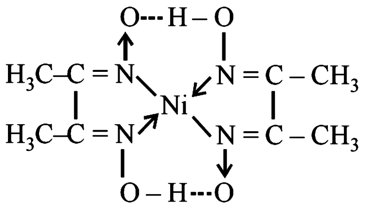
(b) Electronic configuration of Cr^+ under the influence of strong field ligand CN^-





So, Hybridization : d^2sp^3; Shape : Octahedral

27. (a)



Bis(dimethylglyoximato) nickel (II)

(b) Charge on Ni in the complex is +2 and it is dsp^2 hybridised

(c) Since number of unpaired electrons in Ni^{2+} is zero, the complex is diamagnetic.

28. Calcination of the ore A_1 to form CO_2 indicates that A_1 should be a carbonate. Further, reaction of A_1 with HCl and KI to evolve I_2 indicates that A_1 would also be hydroxide. So the possible formula for the ore, should be $CuCO_3.Cu(OH)_2$ which explains all the given reactions

$$\underset{(A_1)}{CuCO_3.Cu(OH)_2} \xrightarrow{\text{calcination}} \underset{\text{(C) black}}{2CuO\downarrow} + CO_2 + H_2O$$

$$\underset{(A_1)}{CuCO_3.Cu(OH)_2} + 4HCl \longrightarrow 2CuCl_2 + CO_2 + 3H_2O$$

$$2CuCl_2 + 4KI \longrightarrow \underset{(D)}{Cu_2I_2\downarrow} + 4KCl + I_2$$

Roasting of A_2 gives gas G whose nature is identified as SO_2 as it gives green colour with acidified $K_2Cr_2O_7$. So A_2 should be sulphide of copper.

$$\underset{(A_2)}{2Cu_2S} + 3O_2 \xrightarrow{\text{roasting}} 2Cu_2O + \underset{(G)}{2SO_2}$$

$$Cu_2S + 2Cu_2O \xrightarrow{\text{self reduction}} \underset{(M)}{6Cu} + SO_2$$

$$\underset{(G)}{3SO_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{(Green colour)}}{Cr_2(SO_4)_3} + 4H_2O$$

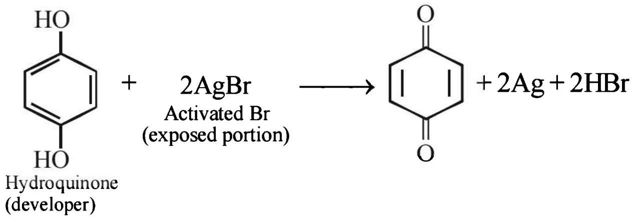
29. $$Fe^{3+} + \underset{\text{(excess)}}{SCN^-} \longrightarrow \underset{\substack{\text{(blood red)}\\ (A)}}{[Fe(SCN)(H_2O)_5]^{2+}}$$

$$[FeSCN(H_2O)_5]^{2+} + 6F^- \longrightarrow \underset{(B)}{[FeF_6]^{3-}} + SCN^-$$

IUPAC name of A is pentaaquathiocyanatoferrate (III) ion
IUPAC name of B is hexafluoroferrate (III)
In $[FeF_6]^{3-}$ coordination no. of Fe = 6
In $[FeF_6]^{3-}$ oxidation state of Fe = + 3
∴ It has 5 unpaired electrons, $n = 5$, Fe^{3+} is $3d^5$
Magnetic moment $(\mu) = \sqrt{n(n+2)}$ (B.M.)

$\sqrt{5(5+2)} = \sqrt{35} = 5.92$ B.M.

30. Reaction involved in developing of a black and white photographic film.



$$\underset{\text{unexposed portion}}{AgBr} + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

$$Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2SO_3 + \underset{\text{colloidal sulphur}}{S\downarrow}$$

31. $[A] = [Ti(H_2O)_6]Cl_3$ $[B] = HCl$

$$TiCl_4 \xrightarrow[\text{heat}]{Zn} TiCl_3 \xrightarrow{H_2O} \underset{\text{purple [A]}}{[Ti(H_2O)_6]Cl_3}$$

$$TiCl_4 + \underset{\text{(moist air)}}{(n+2)H_2O} \longrightarrow TiO_2(H_2O)_n + \underset{\substack{\text{white}\\ \text{fumes [B]}}}{4HCl\uparrow}$$

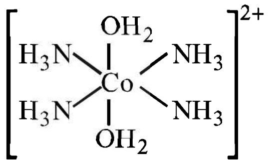
$Ti^{4+} = [Ar]\,3d^0;\ Ti^{3+} = [Ar]\,3d^1$

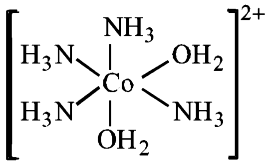
$TiCl_4$ is colourless since Ti^{4+} has no d electrons, hence *d-d* transition is impossible. On the other hand, Ti^{3+} is coloured due to *d-d* transition. Ti^{3+} absorbs greenish yellow compound of white light, hence its aqueous solution is purple which is complementary colour of greenish yellow in white light.

F. Match the Following

1. **(A) : (p), (q) and (s)**

In $[Co(NH_3)_4(H_2O)_2]^{2+}$, Co is in + 2 state having $3d^7$ configuration, which makes it paramagentic due to odd electrons. Moreover, it is an octahedral complex showing *cis-trans* isomerism w.r.t., H_2O.

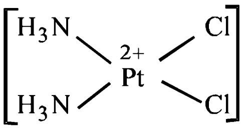

trans

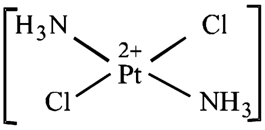

(*cis*)

$Co^{2+} = 3d^7$ (Paramagnetic)

(B) : (p), (r) and (s)

In $[Pt(NH_3)Cl_2]$, Pt is in + 2 state with configuration $5d^8$. Since NH_3 is a strong field ligand, it will pair all the electrons making the complex diamagnetic. Moreover, it is a square planar complex showing cis-trans isomerism.


(*cis*)


(*trans*)

$Pt^{2+} = 5d^8 4s^0$ (diamagnetic)

(C) : (q) and (s) In $[Co(H_2O)_5Cl]Cl$, Co is in + 2 state with $3d^7$ configuration making it paramagnetic.

(D) : (q) and (s) In $[Ni(H_2O)_6]Cl_2$, Ni is in + 2 state with $3d^8$ configuration. It is attached with weak field ligands, therefore it is paramagnetic.

2. **(A) –p, s ; (B) –q, s ; (C) –r, t ; (D) –q, t**

(A) $3Cu + 8\,HNO_3(\text{dil.})$

$$\longrightarrow \underset{p}{2NO} + \underset{s}{Cu(NO_3)_2} + 4H_2O$$

(B) $Cu + 4HNO_3(\text{conc.})$

$$\longrightarrow \underset{q}{2NO_2} + \underset{s}{Cu(NO_3)_2} + 2H_2O$$

(C) $4Zn + 10HNO_3(\text{dil.})$

$$\longrightarrow \underset{t}{4Zn(NO_3)_2} + \underset{r}{N_2O} + 5H_2O$$

(D) $Zn + 4HNO_3(\text{conc.})$

$$\longrightarrow \underset{t}{Zn(NO_3)_2} + \underset{q}{2NO_2} + 2H_2O$$

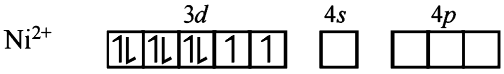
3. **(b)**

Complex	Magnetic character	Isomerism
P, $[Cr(NH_3)_4Cl_2]Cl$	Cr^{3+} is d^3, hence paramagnetic	cis-trans
Q, $[Ti(H_2O)_5Cl](NO_3)_2$	Ti^{3+} is d^1, hence paramagnetic.	ionization
R, $[Pt(en)(NH_3)Cl]NO_3$	Pt^{2+} is d^8, complex is square planar, all electrons are paired, hence diamagnetic	ionization
S, $[Co(NH_3)_4(NO_3)_2]NO_3$	Co^{3+} is d^6, all electrons are paired due to strong ligands, hence diamagnetic	cis-trans

G. Comprehension Based Questions

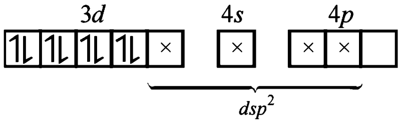
1. **(a)** $Ni^{2+} \xrightarrow[\text{excess}]{KCN} K_2[Ni(CN)_4];\ Ni^{2+} \xrightarrow[\text{(excess)}]{KCl} K_2[NiCl_4]$

2. **(c)** For $[Ni(CN)_4]^{2+}$; $Ni = [Ar]3d^8 4s^2$; $Ni^{2+} = [Ar]3d^8$



However, CN^- is a strong field ligand so it forces the 3*d* electrons to pair up and hence the effective configuration in this case will be

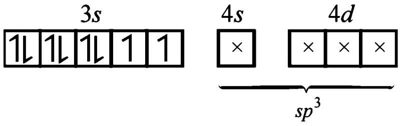
Ni^{2+} in presence of CN^-



Thus $[Ni(CN)_4]^{2-}$ exhibits dsp^2 hybridization and square planar shape. Since here number of unpaired electrons is zero the complex will be *diamagnetic*.

In case of $[NiCl_4]^{2-}$, Cl^- is a weak field ligand, so the effective configuration of Ni^{2+} in this complex will be as follows :

Ni^{2+} in presence of Cl^-



So here Ni^{2+} is sp^3 hybridised and thus tetrahedral in shape. Since the complex has two unpaired electrons, it will be *paramagnetic*.

3. **(a)** Discussed above.

4. **(b)** $2CuFeS_2 + O_2 \longrightarrow Cu_2S + SO_2\uparrow + 2FeS$

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$

5. **(d)** $FeO + SiO_2 \longrightarrow FeSiO_3$

6. **(b)** $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

The reducing species is the one which gets oxidised. So, it is S^{2-} ion getting oxidised to S^{4+}.

7. **(b)** 8. **(a)**

9. **(c)** $\underset{(M)}{Cu} + \underset{(N)}{2AgNO_3} \longrightarrow \underset{\text{Blue}}{Cu(NO_3)_2} + 2Ag$

$$\underset{\text{(remaining)}}{NaCl} + AgNO_3 \longrightarrow \underset{\text{(O)}}{AgCl\downarrow} + NaNO_3$$

$$2AgCl + 2NH_3(aq) \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]^+}$$

$$\underset{\text{(remaining)}}{Cu(NO_3)_2} + 4NH_3(aq) \longrightarrow \underset{\text{(Deep blue colour)}}{[Cu(NH_3)_4](NO_3)_2}$$

H. Assertion & Reason Type Questions

1. (c) The statement is correct

$$\underset{\text{(yellow)}}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{(orange)}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

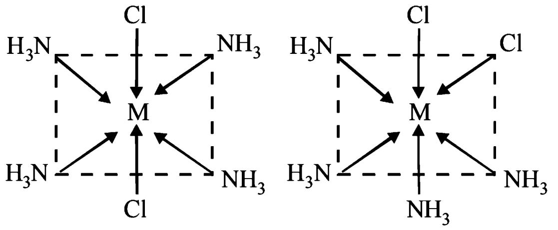
Oxidation state of Cr in Na_2CrO_4 and $Na_2Cr_2O_7$ is +6, i.e. no change in O.S. So explanation is wrong.

2. (b)

	3*d*					4*s*
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	

Zn^{2+} is diamagnetic because of absence of unpaired electrons.

3. (b) The geometrical isomers of $[M(NH_3)_4Cl_2]$ can be represented as follows:-



(trans-form) cis - form

These isomers are optically inactive and they posses axis of symmetry.

Both the statements are thus true. Out of two possible answers i.e. option (a) and (b) option (b) is correct as the statement 2 is not a correct explanation of statement 1.

For a molecule to be optically active it should not possess alternate axis of symmetry.

4. (a) In $[Fe(H_2O)_5NO]\,SO_4$, Let the oxidation state of Fe be x. Then for $[Fe(H_2O)_5NO]^{2-}$,

$x + 1 = +2$ or $x = +2 - 1 = +1$

Hence in this complex the oxidation state of Fe is + 1

Electronic configuration of Fe^+ can be represented as $Fe^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$. This unexpected configuration is due to presence of strong ligand field. Due to which 1 electron from $4s^1$ gets shifted to 3d– orbitals.

The $3d^7$ electrons in five 3d– orbitals can be shown as

	3d				
$3d^7$;	↑↓	↑↓	↑	↑	↑

In it we find 3 unpaired electrons.

Because of the presence of unpaired electrons the complex is paramagnetic i.e. statement 1 is true.

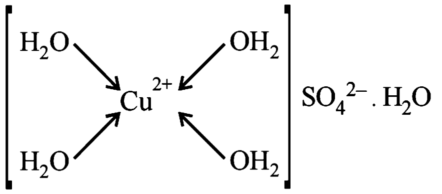
As is clear from above there are three unpaired electrons in this complex i.e. statement 2 is true.

Since paramagnetic behaviour is due to presence of unpaired electrons in it so statement 2 is correct explanation of statement 1.

In view of the above facts the correct answer is option (a)

I. Integer Value Correct Type

1. The number of water molecules directly bonded to the metal centre in $CuSO_4.5H_2O$ is 4.



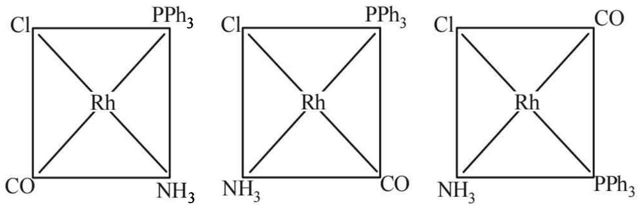
2. $$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Oxidation number of Mn in K_2MnO_4 is 6

K_2MnO_4; $2 + x - 8 = 0$

$x = 6$

3.



The number of geometrical isomers is 3.

4. 6

m moles of $[Cr(H_2O)_5Cl]Cl_2 = 0.01 \times 30 = 0.3$

m moles of $Cl^- = 0.3 \times 2 = 0.6$

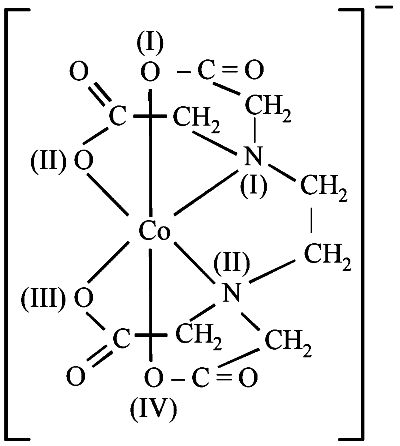
[1 mole of complex gives 2 Cl^- ions]

m moles of Ag^+ = m moles of Cl^-

$0.1 \times V = 0.6$

$V = 6\,mL$

5. (8)



Total no. of N – Co – O bonds are 8.

6. (7) $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

$2CuSO_4 + KI \rightarrow 2CuI + I_2 + 2K_2SO_4$

$H_2O_2 + 2KI \rightarrow 2KOH + I_2$

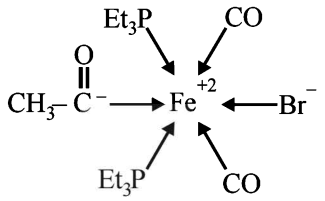
$Cl_2 + 2KI \rightarrow 2KCl + I_2$

$O_3 + H_2O + 2KI \rightarrow 2KOH + O_2 + I_2$

$FeCl_3 + 2KI \rightarrow 2KCl + FeCl_2 + I_2$

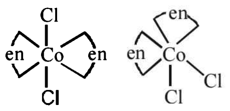
$HNO_3 + KI \rightarrow KNO_3 + I_2 + NO$

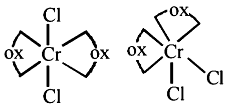
7. **(3)**



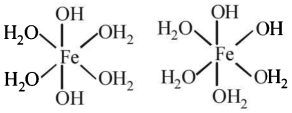
8. **(6)** All the complexes given show cis-trans isomerism

$[Co(NH_2—CH_2—CH_2—NH_2)_2Cl_2]^+$ $[CrCl_2(C_2O_4)_2]^{3-}$

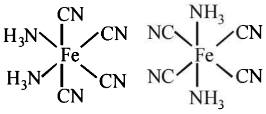




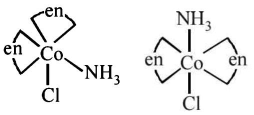
$[Fe(H_2O)_4(OH)_2]^+$



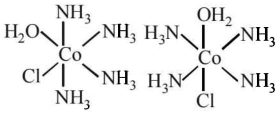
$[Fe(NH_3)_2(CN)_4]^-$



$[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$



$(Co(NH_3)_4(H_2O)Cl]^{2+}$



9. **(4)** $Fe(26) \longrightarrow [Ar]_{18}\, 3d^6 4s^2$

$Fe^{3+} \longrightarrow [Ar]_{18}\, 3d^5 4s^0$

SCN^- is weak field ligand hence pairing will not occur.

$\therefore \quad Fe^{3+} \longrightarrow \boxed{1}\boxed{1}\boxed{1}\boxed{1}\boxed{1}$

Unpaired electrons = 5

Magnetic moment = $\sqrt{5(5+2)}$ B.M.

$= \sqrt{35}$ B.M. = 5.92 B.M.

CN^- is strong field ligand hence pairing will take place.

$\therefore\ Fe^{3+} \longrightarrow \boxed{1\!\downarrow}\boxed{1\!\downarrow}\boxed{1}\boxed{\ }\boxed{\ }$

Unpaired electrons = 1

Magnetic moment = $\sqrt{1(1+2)}$B.M. = $\sqrt{3}$ B.M. = 1.732

Difference = 5.92 – 1.732 = 4.188

Hence answer is (4).

10. **(6)** $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$

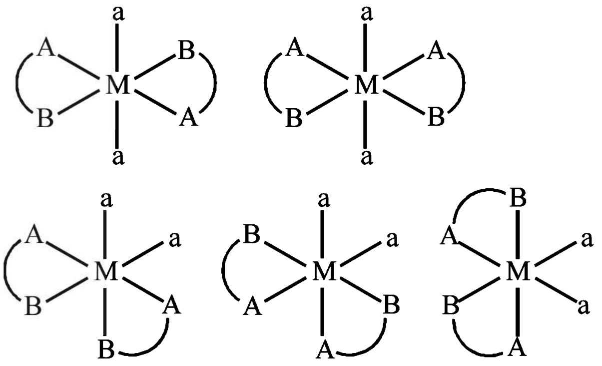
$8MnO_2 + 6SO_4^{2-} + 2OH^-$

$\therefore$ 8 moles of MnO_4^- form 6 moles of SO_4^{2-}

11. **(5)** $[CoL_2Cl_2]^-$ $(L = H_2NCH_2CH_2O^-)$

L is unsymmetrical didentate ligand.

So the complete is equivalent to $[M(AB)_2a_2]$ Possible G.I. are



Section-B JEE Main/ AIEEE

1. **(b)** A square planar complex is formed by hybridisation of s, p_x, p_y and $d_{x^2-y^2}$ atomic orbitals

2. **(b)** The chemical formula of nitropentammine chromium (III) chloride is

$\left[Cr(NH_3)_5 NO_2\right]Cl_2$

It can exist in following two structures

$\left[Cr(NH_3)_5 NO_2\right]Cl_2$ and

nitropentammine chromium (III) chloride

$\left[Cr(NH_3)_5 ONO\right]Cl_2$

Nitropentammine chromium (III) chloride

Therefore the type of isomerism found in this compound is linkage isomerism as nitro group is linked through N as $–NO_2$ or through O as –ONO.

3. **(b)** Compounds that contain at least one carbon metal bond are known as organometallic compounds. In CH_3-Mg-Br (Grignard's reagent) a bond is present between carbon and Mg (Metal) hence it is an organometallic compound.

4. **(c)** Common oxidation states of Ce(Cerium) are + 3 and + 4

5. **(a)** In lanthanides there is a regular decrease in the atomic radii as well as ionic radii of trivalent ions as the atomic number increases from Ce to Lu. This decrease in size of atoms and ions is known as **lanthanide contraction**. Although the atomic radii do show some irregualrities but ionic radii decreases from La to Lu. Thus the correct order is.

$Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$

86.8pm 97pm 102pm 103pm

6. **(a)** Mn^{++} –5 unpaired electrons

Fe^{++} – 4 unpaired electrons

Ti^{++} – 2 unpaired electrons

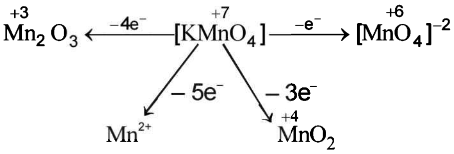
Cr^{++} – 4 unpaired electrons

hence maximum no. of unpaired electron is present in Mn^{++}.

NOTE : Magnetic moment $\propto$ number of unpaired electrons

7. **(c)** The cyano and hydroxo complexes are far more stable than those formed by halide ion. This is due to the fact that CN^- and OH^- are strong lewis bases (nucleophiles). Further $[Fe(OH)_5]^{3-}$ is not formed. hence most stable ion is $[Fe(CN)_6]^{3-}$

8. **(c)**



9. **(c)** Ionic radii $\propto \frac{1}{z}$

Thus, $\frac{z_2}{z_1} \Rightarrow \frac{1.06}{(\text{Ionic radii of } Lu^{3+})} = \frac{71}{57}$

$\Rightarrow$ Ionic radii of $Lu^{3+} = 0.85$ Å

10. **(a)** $\ddot{N}H_3 + H^+ \text{ (acid medium)} \rightleftharpoons \overset{+}{N}H_4$

11. **(d)** $Co(NH_3)_5Cl_3 \rightleftharpoons [Co(NH_3)_5Cl]^{+2} + 2Cl^-$

$\therefore$ Structure is $[Co(NH_3)_5Cl]Cl_2$.

Now $[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3$

$\rightarrow [Co(NH_3)_5Cl](NO_3)_2 + 2AgCl$

12. **(a)** Let the O. No of Ni in $K_4[Fe(CN)_6]$ be $= x$ then

$4(+1) + x + (-1) \times 4 = 0 \Rightarrow 4 + x - 4 = 0$

$x = 0$

13. **(a)** When KI is added to mercuric iodide it disssolve in it and form complex.

$$\underset{\substack{\text{red, solid} \\ \text{(insoluble)}}}{HgI_2} + KI \rightarrow \underset{\text{(soluble)}}{K_2[HgI_4]}$$

On heating HgI_2 decomposes as

$$HgI_2 \rightleftharpoons Hg + \underset{\text{(violet vapours)}}{I_2}$$

14. **(b)** *f*-block elements show a regular decrease in atomic size due to lanthanide/actinide contraction.

15. **(a)** When a solution of potassium chromate is treated with an excess of dilute nitric acid. Potassium dichromate and H_2O are formed.

$2K_2CrO_4 + 2HNO_3 \longrightarrow K_2Cr_2O_7 + 2KNO_3 + H_2O$

Hence $Cr_2O_7^-$ and H_2O are formed.

16. **(c)** $AgNO_3$ on heating till red **hot** decomposes as follows :

$$AgNO_3 \rightarrow Ag + NO_2 + \frac{1}{2}O_2$$

17. **(d)** $(n-1)d^5ns^2$ attains the maximum O.S. of + 7

18. **(b)** Grey tin $\rightleftharpoons$ white tin

Grey tin is brittle and crumbles down to powder in very cold climate

The conversion of grey tin to white tin is acompained by increase in volume., This is knwon as **tin plaque** or **tin disease**.

19. **(a)** CN^- ion acts good complexing as well as reducing agent.

20. **(c)** The coordination number of central metal atom in a complex is equal to number of monovalent ligands, twice the number of bidentate ligands and so on, around the metal ion bonded by coordinate bonds.

Hence coordination number = no. of σ bonds formed by metals with ligands

21. **(d)** Hybridisation

$$\underset{d^2sp^3}{[Fe(CN)_6]^{4-}}, \underset{d^2sp^3}{[Mn(CN)_6]^{4-}},$$

$$\underset{d^2sp^3}{[Co(NH_3]^{3+}}, \underset{sp^3d^2}{[Ni(NH_3)_6]^{2+}}$$

Hence $[Ni(NH_3)_6]^{2+}$ is outer orbital complex.

22. **(c)** The chlorophyll molecule plays an important role in photosynthesis, contain porphyrin ring and the metal Mg not Ca.

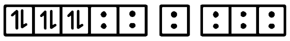
23. **(a)** The +4 oxidation state of cerium is also known in solution.

24. **(d)** Isomers

$$\underset{\text{cis and trans}}{[Ru(NH_3)_4Cl_2]^+}, \underset{\text{none}}{[Co(NH_3)_5Cl]^{2+}},$$

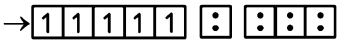
$$\underset{\text{cis and trans}}{[Ir(PR_3)_2H(CO)]^{2+}}, \underset{\substack{\text{cis and trans and} \\ \text{optical isomers}}}{[Co(en)_2Cl_2]^+}$$

25. **(c)** $[Fe(CN)_6]^{4-} \rightarrow$



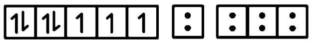
– no of unpaired electron = 0

$[MnCl_4]^{2-} \rightarrow$



– no of unpaired electron = 5

$[CoCl_4]^{2-} \rightarrow$



– no of unpaired electron = 3

NOTE : The greater the number of unpaired electrons, greater the magnitude of magnetic moment. Hence the correct order will be

$[MnCl_4]^{--} > [CoCl_4]^{--} > [Fe(CN)_6]^{4-}$

26. **(d)** Oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$.

Let it be x, $1 \times x + 4 \times 0 + 2 \times (-1) = 1$ Therefore $x = 3$.

27. **(d)** $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

self reduction.

28. **(a)** $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 3I_2 + 7H_2O + 2Cr^{3+}$

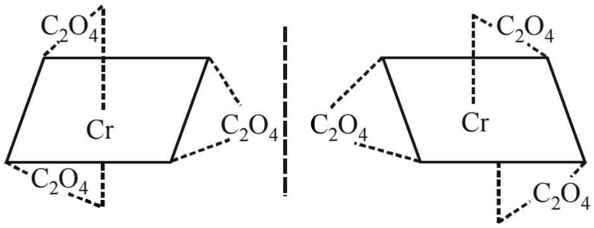
oxidation state of Cr is 3+.

29. **(d)** $Hg_2Cl_2 + 2NH_4OH \longrightarrow HgNH_2Cl + NH_4Cl + 2H_2O$

30. **(b)** **NOTE :** In vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small chang in size and some times sizes are same. This is due to lanthanide contraction this is the reason for Zr and Hf to have same radius.

31. **(c)** $K_3[Fe(CN)_6]$ is potassium hexacyano ferrate (III).

32. **(b)**



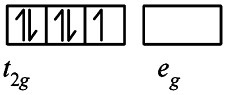
Non-superimposable mirror images, hence optical isomers.

33. **(a)**

		No. of unpaired electron
a)	Co^{3+}	4
b)	Fe^{3+}	1
c)	Mn^{3+}	4
d)	Cr^{3+}	3

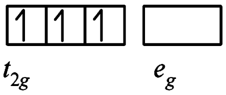
The effective magnetic moment is given by the number of unpaired electrons in a substance, the lesser the number of unpaired electrons lower is its magnetic moment in Bohr – Magneton and lower shall be its paramagnetism

34. **(d)** d^5 —— strong ligand field



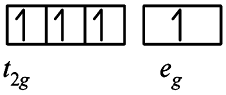
$\mu = n\sqrt{n+2} = \sqrt{3} = 1.73\text{BM}$

d^3— in weak as well as in strong field



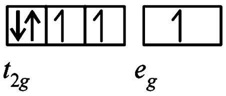
$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87\text{ B.M.}$

d^4– in weak ligand field



$\mu = \sqrt{4(8)} = \sqrt{24} = 4.89$

d^4– in strong ligand field



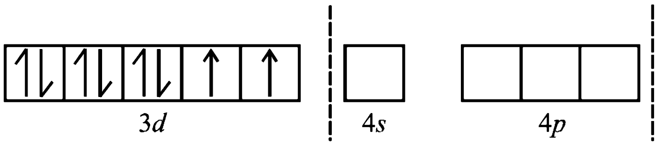
$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82.$

35. **(d)** In lanthanides, there is poorer shielding of 5*d* electrons by 4*f* electrons resulting in greater attraction of the nucleus over 5*d* electrons and contraction of the atomic radii.

36. **(b)** $[Co(NO)_2(NH_3)_5]Cl_2$
pentaammine nitrito-N-cobalt (III) chloride

37. **(a)** Metal atom in the lower oxidation state forms the ionic bond and in the higher oxidation state the covalent bond. because higher oxidation state means small size and great polarizing power and hence greater the covalent character. Hence MCl_2 is more ionic than MCl_4.

38. **(d)** $[NiX_4]^{2-}$, the electronic configuration of Ni^{2+} is



It contains two unpaired electrons and the hybridisation is sp^3 (tetrahedral).

39. **(d)** Due to some backbonding by sidewise overlapping of between d-orbitals of metal and p-orbital of carbon, the Fe–C bond in $Fe(CO)_5$ has both σ and π character.

40. **(b)** The configuration of Lanthanides show that the additional electron enters the 4f subshell. The shielding of one 4*f* electron by another is very little or imperfect. The imperfect shielding of *f* electrons is due to the shape of f orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity at each step. While no comparable increase in the mutual shielding effect of 4*f* occurs. This causes a contraction in the size of the 4*f* subshell. as a result atomic and ionic radii decreases gradually from La to Lu.

41. **(a)** EDTA has hexadentate four donor O atoms and 2 donor N atoms and for the formation of octahedral complex one molecule is required

42. **(c)** The number of unpaired electrons in $Ni^{2+}(aq) = 2$
Water is weak ligand hence no pairing will take place

$$\text{spin magnetic moment} = \sqrt{n(n+2)} = \sqrt{2(2+2)}$$
$$= \sqrt{8} = 2.82$$

43. **(d)** Reluctance of valence shell electrons to participate in bonding is called inert pair effect. The stability of lower oxidation state (+2 for group 14 element) increases on going down the group. So the correct order is $SiX_2 < GeX_2 < SnX_2 < PbX_2$

44. **(a)** 4f orbital is nearer to nucleus as compared to 5*f* orbital therefore, shielding of 4*f* is more than 5*f*.

45. **(a)** Complexes with dsp^2 hybridisation are square planar. So $[PtCl_4]^{2-}$ is square planar in shape.

46. **(a)** **NOTE :** More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance between nucleus and 5*f* orbitals is more as compared to distance between 4f orbital and nucleus. So actinoids exhibit more number of oxidation states in general than the lanthanoids.

47. **(d)** In the given complex we have two bidentate ligands (i.e en and C_2O_4), so coordination number of E is 6 $(2 \times 2 + 1 \times 2 = 6)$
Let the oxidation state of E in complex be x, then
$[x + (-2) = 1]$ or $x - 2 = 1$
or $x = +3$, so its oxidation state is + 3
Thus option (d) is correct.

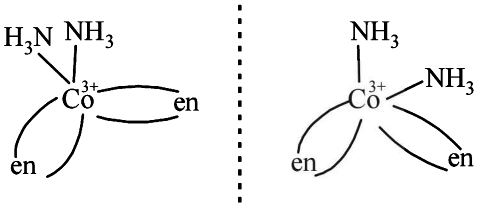
48. **(b)** **NOTE :** The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between 5*f* and 6*d* orbitals as compared to that between 4f and 5d orbitals.

In case of actinoids we can remove electrons from 5f as also from 6*d* and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b)

49. **(a)** In octahedral complex the magnitude of Δ_o will be highest in a complex having strongest ligand. Of the given ligands CN^- is strongest so Δ_o will be highest for $(Co(CN)_6)^{3-}$. Thus option (a) is correct.

50. **(c)** The titration of oxalic acid with $KMnO_4$ in presence of HCl gives unsatisfactory result because of the fact that $KMnO_4$ can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces $KMnO_4$ to Mn^{2+} thus the correct answer is (c).

51. **(c)**



Enantiomers of *cis*-$\left[Co(en)_2(NH_3)_2\right]^{3+}$

52. **(a)** Lower oxidation state of an element forms more basic oxide and hydroxide, while the higher oxidation state will form more acidic oxide/hydroxide. For example,

$$\underbrace{\overset{+2}{MnO} \quad \overset{+3}{Mn_2O_3}}_{\text{(basic)}} \quad \underset{\text{acidic}}{\overset{+7}{Mn_2O_7}}$$

53. **(a)** The SCN^- ion can coordinate through S or N atom giving rise to linkage isomerism

$M \leftarrow SCN$ thiocyanato

$M \leftarrow NCS$ isothiocyanato.

54. **(b)** Most of the Ln^{3+} compounds except La^{3+} and Lu^{3+} are coloured due to the presence of *f*-electrons.

55. **(a)** $$\underset{2.675\text{g}}{CoCl_3.6NH_3} \longrightarrow xCl^-$$

$$xCl^- + AgNO_3 \longrightarrow \underset{4.78\text{g}}{x\,AgCl\downarrow}$$

$$\text{Number of moles of the complex} = \frac{2.675}{267.5} = 0.01 \text{ moles}$$

$$\text{Number of moles of AgCl obtained} = \frac{4.78}{143.5} = 0.03$$

moles

$\therefore$ No. of moles of AgCl obtained = 3 × No. of moles of complex

$$\therefore n = \frac{0.03}{0.01} = 3$$

56. **(b)** For a substance to be optical isomer following conditions should be fulfiled

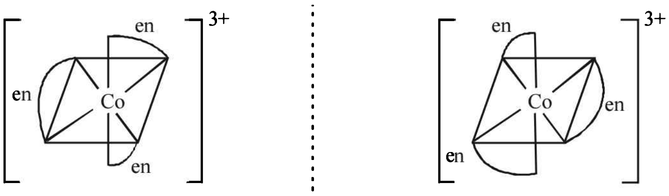
(a) A coordination compound which can rotate the plane of polarised light is said to be optically active.

(b) When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. The optical isomers are pair of molecules which are non-superimposable mirror images of each other.

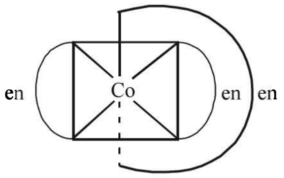
(c) This is due to the absence of elements of symmetry in the complex.

(d) Optical isomerism is expected in tetrahedral complexes of the type Mabcd.

Based on this only option (2) shows optical isomerism $[Co(en)_3]^{3+}$



d–form Mirror ℓ–form



'Meso' or optically inactive form

Complexes of Zn^{++} cannot show optical isomerism as they are tetrahedral complexes with plane of symmetry.

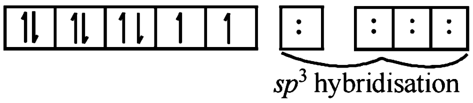
$\left[Co(H_2O)_4(en)\right]^{3+}$ have two planes of symmetry hence it is also optically inactive.

Hence the formula of the complex is $[Co(NH_3)_6]Cl_3$

57. **(c)** $[Cr(NH_3)_6]Cl_3$ is an inner orbital complex, because in this complex d-orbital used is of lower quantum number ie (n – 1). It results from $d^2\,sp^3$ (inner orbital) hybridization.

58. **(d)** The most stable oxidation states of lanthanides is + 3.

59. **(c)** $[NiCl_4]^{2-}(d^8)$



i.e the number of unpaired electrons in $[NiCl_4]^{2-}$ is 2.

$$n = \sqrt{n(n+2)} = \sqrt{2(4)} = 2\sqrt{2} = 2 \times 1.41$$
$$= 2.82 \text{ BM}$$

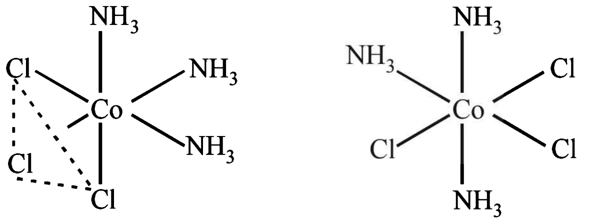
60. **(d)** The configuration of Gd is $4f^7\,5d^1\,6s^2$.

61. **(b)** $[Cr(en)_2Br_2]Br$

dibromidobis (ethylenediamine) chromium (III) Bromide.

62. **(d)** Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.

63. **(c)** Octahedral coordination entities of the type Ma_3b_3 exhibit Geometrical isomerism. The compound exists both as facial and meridional isomers.



Fac- Mer

64. **(a)**

(1) $V = 3d^3 4s^2$ $V^{2+} = 3d^3$ = 3 unpaired electron
$Cr = 3d^5 4s^1$ $Cr^{2+} = 3d^4$ = 4 unpaired electron
$Mn = 3d^5 4s^2$ $Mn^{2+} = 3d^5$ = 5 unpaired electron
$Fe = 3d^6 4s^2$ $Fe^{2+} = 3d^6$ = 4 unpaired electron

hence the correct order of paramagnetic behaviour
$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(2) For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series. hence the order is
$Mn^{++} > Fe^{++} > Co^{++} > Ni^{++}$

(3) In solution, the stability of the compounds depends upon electrode potentials, SEP of the transitions metal ions are given as
$Co^{3+} / Co = +1.97, Fe^{3+} / Fe = +0.77$;
$Cr^{3+} / Cr^{2+} = -0.41$, Sc^{3+} is highly stable as it does not show + 2 O. S.

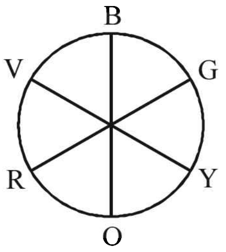
(4) Sc – (+ 2), (+ 3)
Ti – (+ 2), (+ 3), (+ 4)
Cr – (+ 1), (+ 2), (+ 3), (+ 4), (+ 5), (+ 6)
Mn – (+ 2), (+ 3), (+ 4), (+ 5), (+ 6), (+ 7)
i.e. Sc < Ti < Cr = Mn

$E_a = 53598.6$ J/mol $= 53.6$ kJ/mol.

65. **(d)** $E°_{Cr^{3+}/Cr^{2+}} = -0.41$ V $E°_{Fe^{3+}/Fe^{2+}} = +0.77$ V

$E°_{Mn^{3+}/Mn^{2+}} = +1.57$ V $E°_{Co^{3+}/Co^{2+}} = +1.97$ V

66. **(b)**



For a given metal ion, weak field ligands create a complex with smaller Δ, which will absorbs light of longer λ and thus lower frequency. Conservely, stronger field ligands create a larger Δ, absorb light of shorter λ and thus higher *v* i.e. higher energy.

Red	< Yellow	< Green	< Blue
λ = 650 nm	570 nm	490 nm	450 nm

So order of ligand strength is

$$L_1 < L_3 < L_2 < L_4$$

67. **(d)** In equation (i) $Fe_2(SO_4)_3$ and in equation (ii) $Fe_2(SO_4)_3$ on decomposing will form oxide instead of Fe.

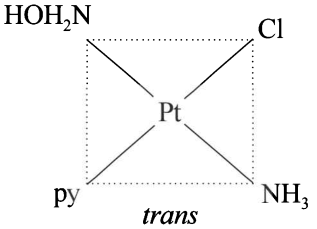
The correct sequence of reactions is

$$Fe \xrightarrow{O_2,\text{heat}} Fe_3O_4 \xrightarrow{Co, 600°C} Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe$$

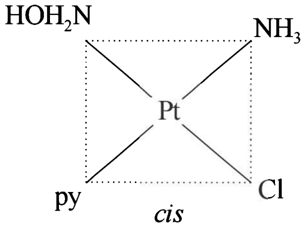
68. **(c)**

69. **(d)** (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

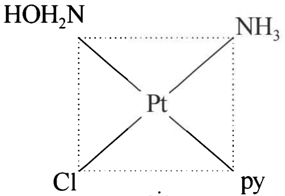
70. **(d)** Square planar complexes of type M[ABCD] form three isomers. Their position may be obtained by fixing the position of one ligand and placing at the *trans* position any one of the remaining three ligands one by one.



trans



cis

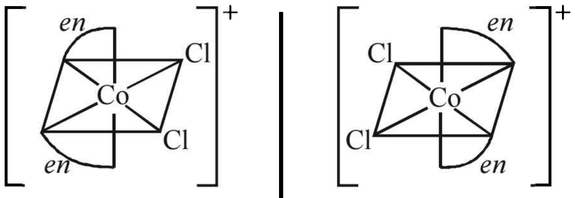


cis

71. **(a)** L → M charge transfer spectra. $KMnO_4$ is colored because it absorbs light in the visible range of electromagnetic radiation. The permanganate ion is the source of color, as a ligand to metal, (L → M) charge transfer takes place between oxygen's *p* orbitals and the empty *d*-orbitals on the metal. This charge transfer takes place when a photon of light is absorbed, which leads to the purple color of the compound.

72. **(d)** Out of all the four given metallic oxides CrO_2 is attracted by magnetic field very strongly. The effect persists even when the magnetic field is removed. Thus CrO_2 is metallic and ferromagnetic in nature.

73. **(c)** Optical isomerism occurs when a molecule is non-superimposable with its mirror image hence the complex *cis*-$[Co(en)_2Cl_2]Cl$ is optically active.



Cis-d-isomer Mirror *Cis-i-isomer*

74. **(d)**

	Complex	Metal ion	Configuration	Magnetic moment $\mu = \sqrt{n(n+2)}$
(a)	$[Cr(H_2O)_6]^{2+}$	Cr^{+2}	d^4	$\sqrt{24}$
(b)	$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	d^6	$\sqrt{24}$
(c)	$[CoCl_4]^{2-}$	Co^{2+}	d^7	$\sqrt{15}$
(d)	$[Mn(H_2O)_6]^{2+}$	Mn^{2+}	d^5	$\sqrt{35}$

Since (*a*) and (*b*), each has 4 unpaired electrons, they will have same magnetic moment.