Fill Ups of The d- and f-Block Elements & Co-ordination Compounds

Q.1. AgCN dissolves in excess KCN solution to give the complex compound .... (1980)

Ans. $K[Ag(CN)_2]$

Solution. $K[Ag(CN)_2]$

Q.2. Mn^{2+} can be oxidised to MnO^-_4 by................. (1981 - 1 Mark)
(SnO_2, PbO_2, BaO_2)

Ans. PbO_2

Solution. PbO_2;

Q.3. Galvanization of iron denotes coating with .... (1983 - 1 Mark)

Ans. zinc

Solution. Zinc;

Q.4. Silver chloride is sparingly soluble in water because its lattice energy is greater than.............. energy. (1987 - 1 Mark)

Ans. hydration/solvation

Solution. Hydration/solvation; [A substance dissolves when its $\Delta_{\text{Hhydration}}$ > lattice energy]

Q.5. The salts .... and .... are isostructural. (1988 - 1 Mark)

($FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnSO_4.4H_2O$, $ZnSO_4.7H_2O$)

Ans. $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$

Solution. $FeSO_4.7H_2O$, $ZnSO_4.7H_2O$;

Q.6. The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is.............

Ans. Para magnetism; $[Mn(H_2O)_6]^{2+}$ shows paramagnetic because of presence of 5 unpaired electrons in the outer most orbital ($3d^5$) of Mn^{2+}.

Q.7. The IUPAC name of $[Co(NH_3)_6]Cl_3$ is .... (1994 - 1 Mark)

Ans. paramagnetism

Solution. Hexammine cobalt (III) chloride

Q.8. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... (1997 - 1 Mark).

Ans. zero

Solution. zero

Q.9. Silver jewellery items tarnish slowly in the air due to their reaction with................

Ans. H_2S

Solution. H_2S; It is due to formation of sulphide of silver (Ag,S) which is black.

True / False of The d- and f-Block Elements & Co-ordination Compounds

Q.1. Copper metal reduces Fe^{2+} in an acid medium. (1982 - 1 Mark)

Ans. F

Solution. False : Copper metal does not reduces Fe^{2+} in an acidic medium

Q.2. Silver fluoride is fairly soluble in water. (1982 - 1 Mark)

Ans. T

Solution. 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.

Q.3. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. (1984 - 1 Mark)

Ans. T

Solution. 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.

Q.4. Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3d-orbital of neutral atom. (1987 - 1 Mark)

Ans. F

Solution. False : Dipositive zinc exhibits diamagnetism (and not paramagnetism) because it has no unpaired electron.

Q.5. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. (1989 - 1 Mark)

Ans. F

Solution. 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.

Q.6. Cu^+ disproportionates to Cu^{2+} and elemental copper in solution. (1991 - 1 Mark)

Ans. True

Solution. 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.

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

Subjective Ques of The D- & F-Block Elements & Co-ordination Compounds, (Part - 1)

Q.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)

Solution. (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).

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

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

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

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

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

Q.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)

Ans. True

Solution.

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

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

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

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

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

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

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

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

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

Q.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 permaganate acidified with dilute sulphuric acid. (1979)

Solution.

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

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

(iii) $2KMnO_4 + 3H_2SO_4 + 5H_2S \xrightarrow{\Delta}$
$K_2SO_4 + 2MnSO_4 + \underset{(turbidity)}{5S} + 8H_2O$

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

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

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

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

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

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

Q.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 Ferro cyanide 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 H2SO4. (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) $(NH_4)_2 S_2O_8 + H_2O + MnSO_4 \rightarrow$ .... + ... +........ (1993 - 1 Mark)

(xx) $[MnO_4]^{2-} + H^+ \rightarrow$......... + $[MnO_4]^- + H_2O$ (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)

Solution.

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

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

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

[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

$3Cu + 8HNO_3$ (dil.) → $2NO + 3Cu(NO_3)_2 + 4H_2O$

$Cu + 4HNO_3$ (dil.) → $Cu(NO_3)_2 + 2NO_2 + 2H_2O$

For the molar ratio of 2 : 1 of NO and NO2, 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*) $\underset{\text{(Argentite)}}{Ag_2S} + 2KCN \longrightarrow \underset{\text{potassium Argentocyanide}}{K[Ag(CN)_2]} + K_2S$

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

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

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

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

Cyanide Process:

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

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

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

[NOTE : Zn is more electropositive than Ag.]

Q.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 [CuI4]2– does not. (1992 - 1 Mark)

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

Solution. (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.

Q.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)

Solution. $2Mn(OH)_2 + 5NaBiO_3 + 18H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 5N_a^+ + 11H_2O$

Q.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)

Solution.

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

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

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

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

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

Ans. sodium zincate, water

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

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

Ans. CO

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

Q.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)

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

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

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

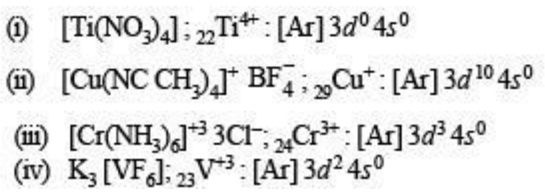
$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

Q.14. Identify the complexes which are expected to be coloured. Explain

(i) $[Ti(NO_3)_4]$
(ii) $[Cu(NCCH_3)_4]+ BF_4^-$
(iii) $[Cr(NH_3)_6]^{3+}3Cl^-$
(iv) $K_3 [VF_6]$

Ans. (iii), (iv)

Solution. 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

Q.15. Write down the IUPAC names of the following compounds:
(i) $[Co(NH_3)_5\,ONO]Cl_2$ (1995 - 1 Mark)
(ii) $K_3[Cr\,(CN)_6]$ (1995 - 1 Mark)
(iii) $[Cr(NH_3)_5CO_3]Cl$ (1996 - 1 Mark)

Ans. (i) pentamminenitritocobalt (III) chloride,

(ii) potassium hexacyanochromate (III)

(iii) pentamminecarbonatochromium (III) chloride

Solution. (i) Pentamminenitritocobalt (III) chloride

(ii) Potassium hexacyanochromate (III)

(iii) Pentamminecarbonatochromium (III) chloride.

Subjective Ques of The D- & F-Block Elements & Co-ordination Compounds, (Part - 2)

Q.16. Compare qualitatively the first and second ion isation potentials of copper and zinc. Explain the observation. (1996 - 2 Marks)

Solution.

$$_{29}\mathrm{Cu} = 1s^2, 2s^2\, 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$$
$$_{30}\mathrm{Zn} = 1s^2, 2s^2\, 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$$

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 4s2 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 4s1 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).

Q.17. Write the formulae of the following complexes :
(i) Pentamminechlorocobalt(III) (1997 - 1 Mark)
(ii) Lithium tetrahydroaluminate(III). (1997 - 1 Mark)

Ans. (i) $[CoCl(NH_3)_5]^{+2}$, (ii) $LiAlH_4$

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

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

Q.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)

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

$$C + O_2 \rightarrow CO_2$$
$$CO_2 + O \rightarrow 2CO$$

$$3CO + Fe_2O_3 \rightarrow \underset{\text{(Steel)}}{2Fe} + 3CO_2 \quad \text{(Reduction of } Fe_2O_3 \text{ to form steel)}$$
$$SiO_2 + \underset{\text{(Lime)}}{CaO} \rightarrow \underset{\text{(Slag)}}{CaSiO_3} \quad \text{(Slag, } CaSiO_3 \text{ is used as building material)}$$

Q.19. Work out the following using chemical equations (1998 - 2 Marks)

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

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

Q. 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)

Ans. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl](H_2O)Cl_2$, $[Cr(H_2O)_4Cl_2](H_2O)_2Cl$

Solution. The complex A does not react with concentrated H_2SO_4 implying that all water molecules are coordinated with Cr3+ 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

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

= 17.98 g This corresponds to one mole of water. Hence, the structure of the compound B will be $[Cr(H_2O)_5Cl](H_2O)Cl_2$

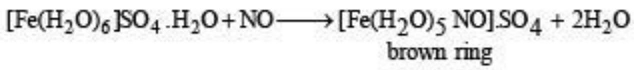
NOTE : The compound C loses 13.5% of its mass when treated with concentrated H2SO4 which is twice of the mass lost by the compound B. Hence, the structure of the compound C will be $[Cr(H_2O)_4Cl_2](H_2O)_2Cl$.

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

Marks)

Solution. $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

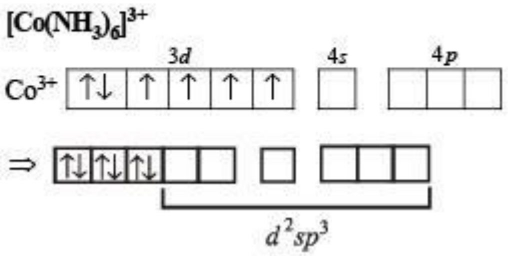
$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

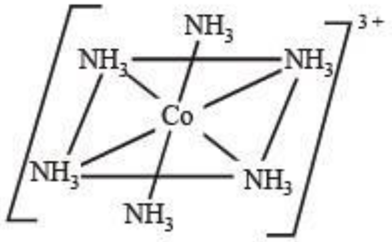


$$[Fe(H_2O)_6]SO_4.H_2O + NO \longrightarrow \underset{\text{brown ring}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$$

Q.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)

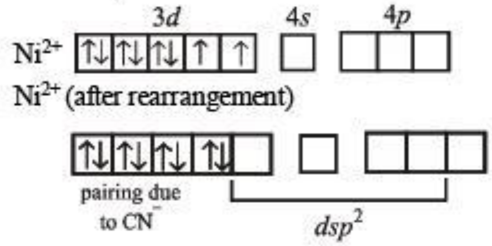
Solution.

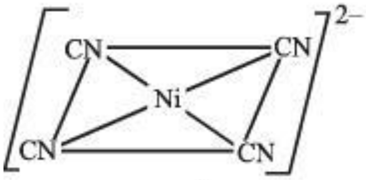




Octahedral complex, d^2sp^3 hybridisation

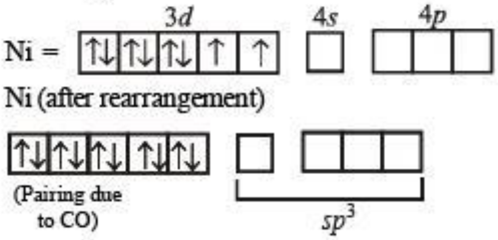
$[Ni(CN)_4]^{2-}$

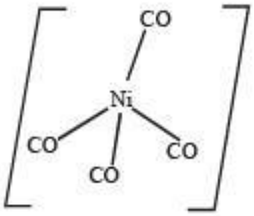




Square planar dsp^2 hybridisation

$[Ni(CO)_4]$





Tetrahedral (sp^3 hybridisation)

Q.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)

Solution. (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.

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

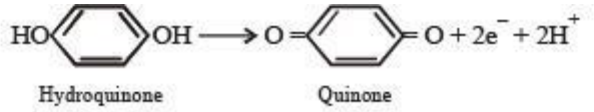
Oxygen of air converts Na_2S to Na_2SO_4 thereby preventing reaction to take place in the reversible direction.

(3) Recovery of silver.

Silver is precipitated out by adding electropositive metal, Zn.

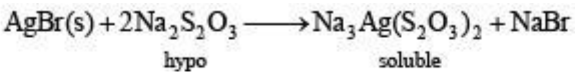
$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$

(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.



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

Q.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)

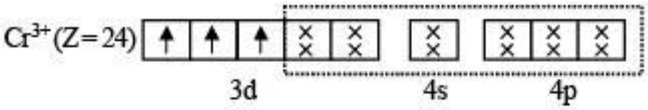
Ans. $[Cr(NH_3)_4BrCl]Cl$: (d^2sp^3); $[Cr(NH_3)_4Cl_2]Br$: (d^2sp^3); 3.87 BM, 3.87 BM

Solution. 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

$[Cr(NH_3)_4Cl_2]Br$



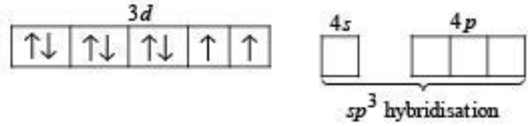
State of hybridization of chromium in both (A) and (B) is d^2sp^3.
Spin magnetic moment of (A) or (B),

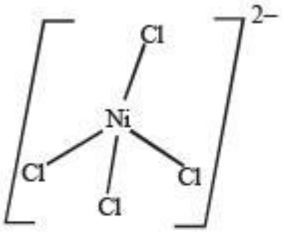
$$\mu_{spin} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87\ \text{BM}$$

Q.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)

Solution. 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.

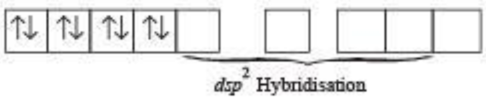




Magnetic moment of $[NiCl_4]^{2-} = \sqrt{2(2+2)} = 2.82$ BM

On the other hand, CN^- is a strong 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 $[Ni(CN)_4]^{2-} = \sqrt{0(0+2)} = 0.0 BM$

Q.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)

Ans. Potassium amminotetracyanonitrosoniumchromate (I), (d^2sp^3), octahedral shape.

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

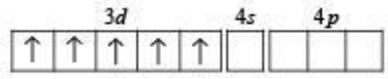
$$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$$

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

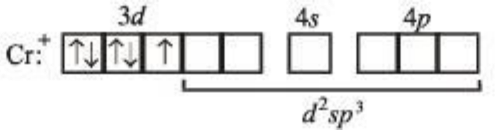
IUPAC name :

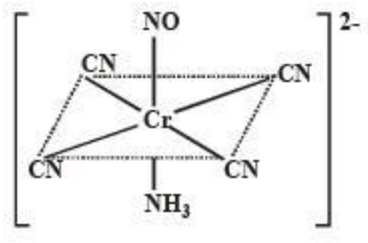
Potassium amminetetracyanonitrosochr (I)

(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

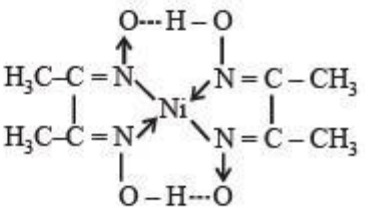
Q.27. Nickel chloride, when treated with dimethylgyloxime in presence of

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 behavior of the complex

Ans. (b)$^{+2}$, dsp^2; (c) diamagnetic

Solution.

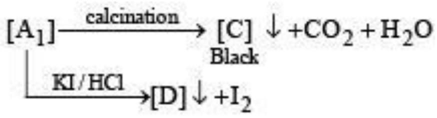
(a)



(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.

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



$$[A_1] \xrightarrow{\text{calcination}} \underset{\text{Black}}{[C]} \downarrow + CO_2 + H_2O$$

$$[A_1] \xrightarrow{KI/HCl} [D] \downarrow + I_2$$

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

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

Ans. $\underset{A_1}{CuCO_3.Cu(OH)_2}, \underset{A_2}{Cu_2S}, \underset{M}{Cu}, \underset{C}{CuO}, \underset{D}{Cu_2I_2}, \underset{Y}{SO_2}$

Solution. Calcination of the ore A_1 to form CO_2 in dicates 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.

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

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

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

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

Q.29.

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

Ans. $\underset{A}{Fe(SCN)_3}$; $\underset{B}{[FeF_6]^{3-}}$; trithiocyanoiron (III); 5.92 BM

Solution.

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

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

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

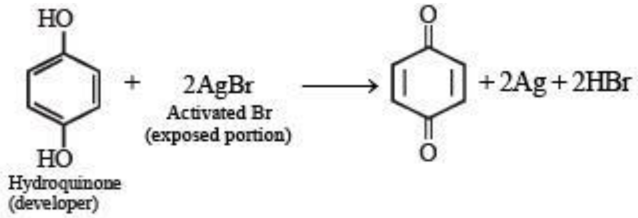
∴ It has 5 unpaired electrons, n = 5, Fe^{3+} is $3d^5$

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

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

Q.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)

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



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

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

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

Ans. $\underset{A}{[Ti(H_2O)_6]Cl_3}, \underset{B}{HCl}, TiCl_4, MCl_4$

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

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

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

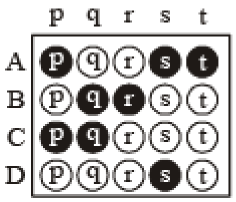
$$Ti^{4+} = [Ar]\,3d^0;\ Ti^{3+} = [Ar]\,3d^1$$

$TiCl^4$ 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.

Match the Following of The d- & f-Block Elements & Co-ordination Compounds

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.

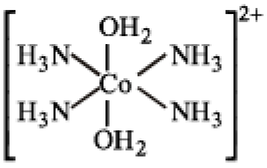


Q.1. Match the complexes in Column I with their properties listed in Column II.

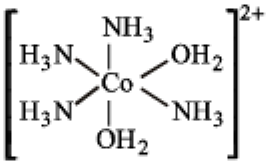
Column I	**Column II**
(A) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(p) geometrical isomers
(B) $[Pt(NH_3)_2Cl_2]$	(q) paramagnetic
(C) $[Co(H_2O)_5Cl]Cl$	(r) diamagnetic
(D) $[Ni(H_2O)_6]Cl_2$	(s) metal ion with +2 oxidation state

Ans. (A - p, q, s); (B - p, r, s); (C - q, s); (D - q, s)

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


trans

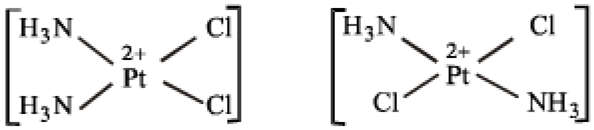
$Co^{2+} = 3d^7$ (Paramagnetic)


(*cis*)

(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.

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

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

Ans. (A - p, s); (B - q, s); (C - r, t); (D - q, t)

Solution.

(A) $3Cu + 8\ HNO_3$ (dil.)

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

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

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

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.

Q.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}

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

Ans. (b)

Solution.

Complex	**Magnetic character**	**Isomerism**

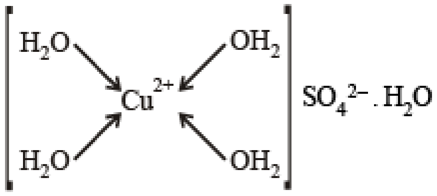
P, [Cr(NH_3)$_4$$Cl_2$]Cl	Cr^3+ is d^3, hence paramagnetic	cis-trans
Q, [Ti(H2O)$_5$Cl](NO3)2	Ti^3 + is d^1, hence paramagnetic.	ionization
R, [Pt(en)(NH_3)Cl]NO_3	Pt ^{2}+ is d^8, complex is square planar, all electrons are paired, hence diamagnetic	ionization
S, [Co(NH_3)$_4$(NO_3)$_2$]NO_3	Co^3+ is d^6, all electrons are paired due to strong ligands, hence diamagnetic	cis-trans

Integer Value of The d- & f-Block Elements & Co-ordination Compounds

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

Ans. 4

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



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

Ans. 6

Solution. $2MnO_2 + 4KOH + O_2 \rightarrow 2K\ 2MnO_4 + 2H_2O$

Oxidation number of Mn in K_2MnO_4 is 6

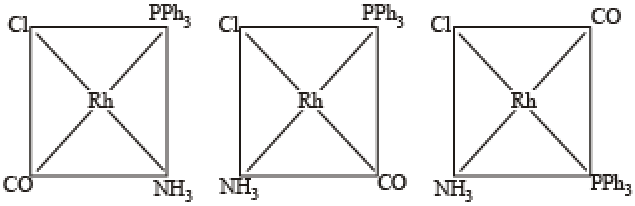
K_2MnO_4 ; $2 + x - 8 = 0$

$x = 6$

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

Ans. 3

Solution.



The number of geometrical isomers is 3.

Q.4. The volume (in mL) of 0.1 M AgNO, 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)

Ans. 6

Solution. m moles of $[Cr (H_2O)_5Cl]Cl_2$ = 0.01 × 30 = 0.3

m moles of Cl– = 0.3 × 2 = 0.6

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

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

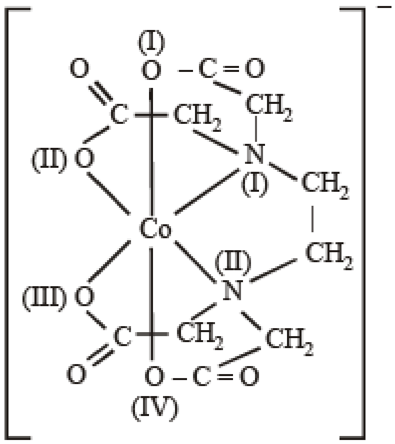
$0.1 \times V = 0.6$

$V = 6$ mL

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

Ans. 8

Solution.



Total no. of N – Co – O bonds are 8.

Q.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

Ans. 7

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

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

$H_2O2 + 2KI \rightarrow 2KOH + I_2$

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

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

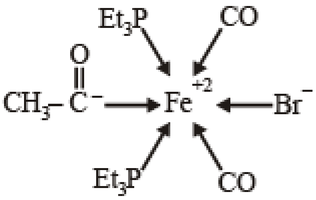
$FeCl_3 + 2KI \rightarrow 2KCl + FeCl_2 + I_2$

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

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

Ans. 3

Solution.

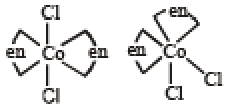


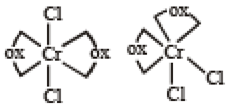
Q.8. Among the complex ions, $[Co(NH_2–CH_2–CH_2–NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3–}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^–$, $[Co(NH_2–CH_2–CH_2–NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) cis-trans isomerism is (JEE Adv. 2015)

Ans. 6

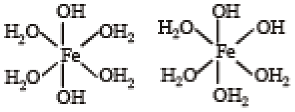
Solution. All the complexes given show cis-trans isomerism

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

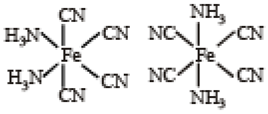




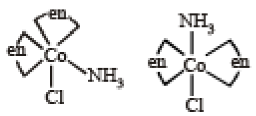
$[Fe(H_2O)_4(OH)_2]^+$



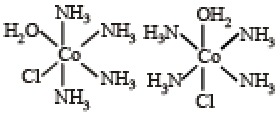
$[Fe(NH_3)_2(CN)_4]^–$



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



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



Q.9. For the octahedral complexes of Fe^{3+} in $SCN^–$ (thiocyanatoS) 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)

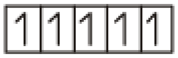
Ans. 4

Solution.

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

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

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

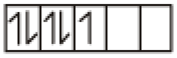
$\therefore \quad \mathrm{Fe^{3+}} \longrightarrow$ 

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.

$\therefore \mathrm{Fe^{3+}} \longrightarrow$ 

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).

Q.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)

Ans. 6

Solution. $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

$\therefore$ 8 moles of $MnO4^-$ form 6 moles of SO_4^{2-}

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

Ans. 5

Solution. $[CoL_2Cl_2]^-$ (L = $H_2NCH_2CH_2O^-$)

L is unsymmetrical didentate ligand.

So the complete is equivalent to $[M(AB)_2a_2]$ Possible G..I. are