

The d and f block elements & coordination compounds

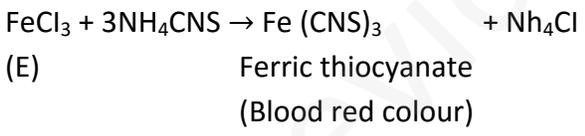
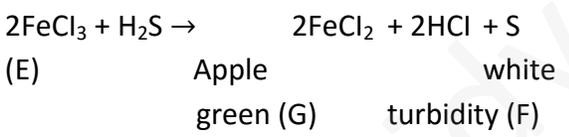
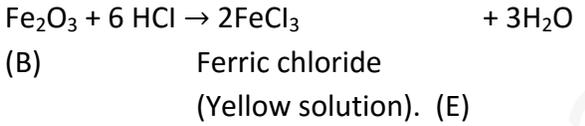
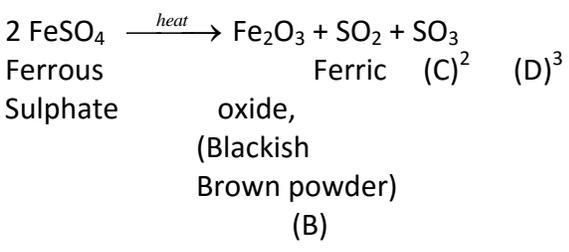
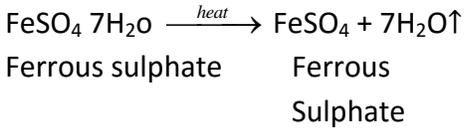
SUBJECTIVE PROBLEMS:

Sol 1.

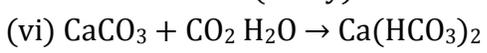
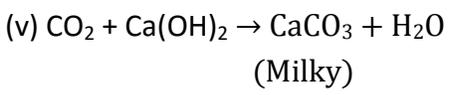
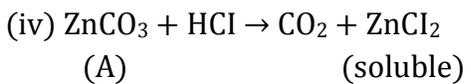
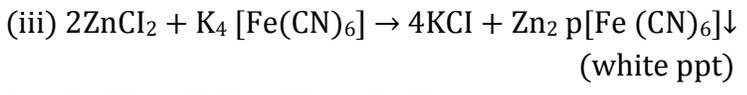
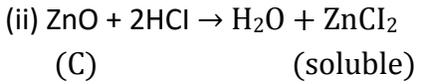
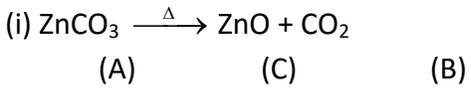
(i) Since the compound (A) on strong heating gives two oxides of sulphur (C and D) which might be SO_2 and SO_3 , it must be a **sulphate**.

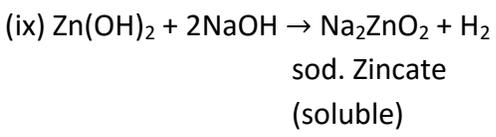
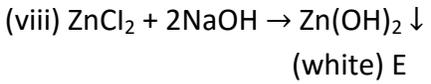
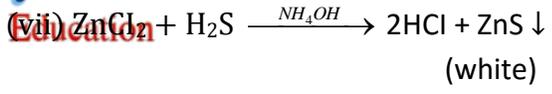
(ii) The reaction of compound (E) with thiocyanate to give blood red coloured compound (H) indicates that (E) must have **Fe^{3+} ion**.

Thus the compound (A) must be ferrous sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which explain all given reactions as below (Fe^{2+} ion of FeSO_4 is changed to Fe^{3+} during heating).

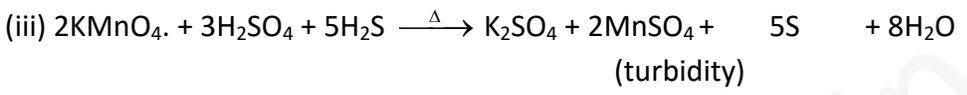
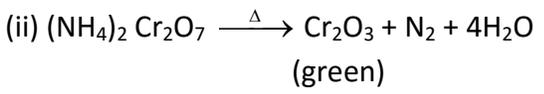
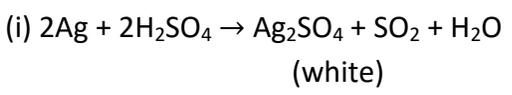


Sol 2.



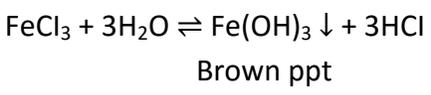


Sol 3.

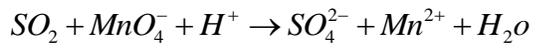


Sol 4.

On standing FeCl_3 is hydrolyses and produces colloidal solution of Fe(OH)_3 which is in form of brown precipitate



Sol 5.



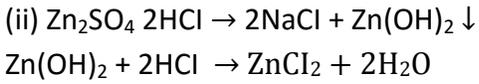
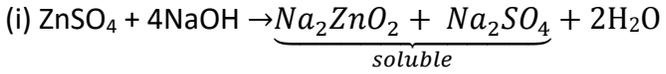
Sol 6.

(i) Since the mixture is soluble in water to give strong alkaline solution, it must contain NaOH as one of the constituents.

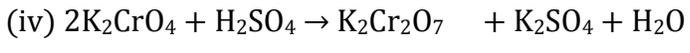
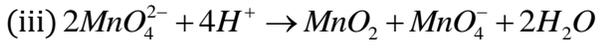
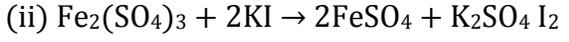
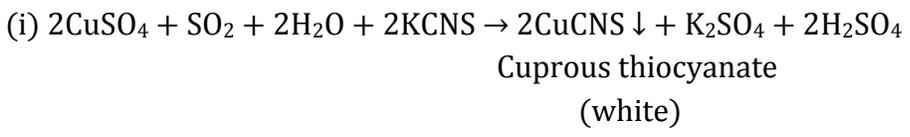
(ii) Since the aqueous solution gives precipitate with dil. HCl, which dissolves in excess of dil. HCl, it must contain zinc salt.

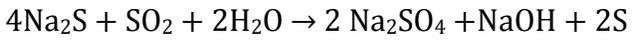
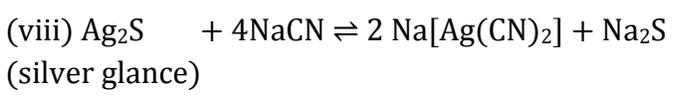
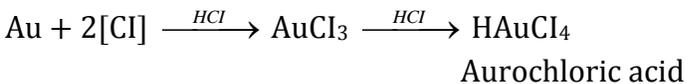
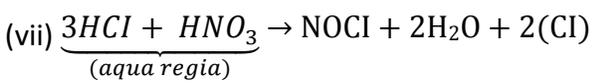
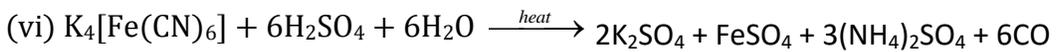
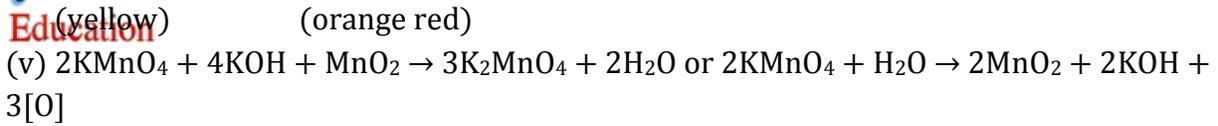
Thus the mixture consists of ZnSO_4 and NaOH which explains all the given reactions.

Reactions :

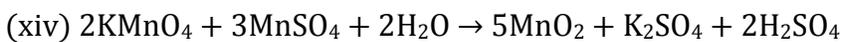
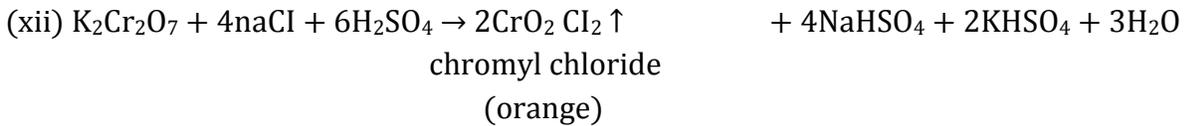
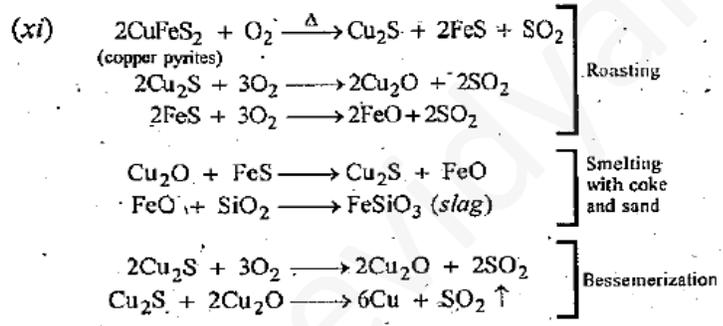
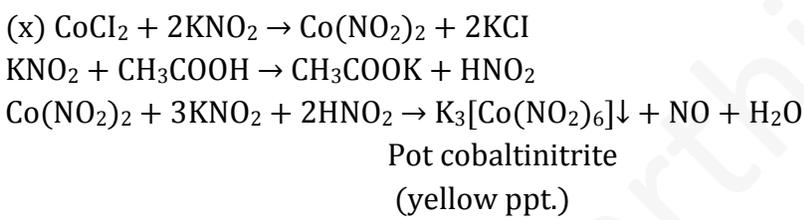
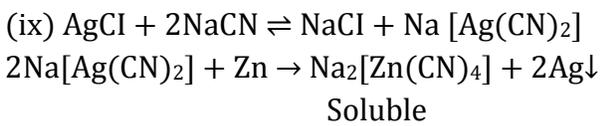
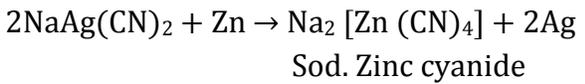


Sol 7.

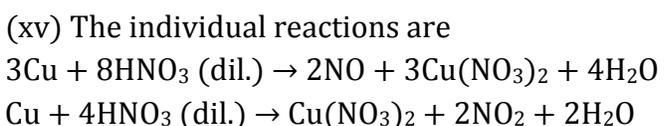




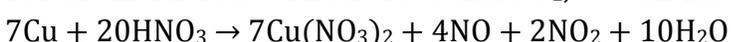
[NOTE : Na_2S is converted into Na_2SO_4 to avoid reversibility of first reaction]

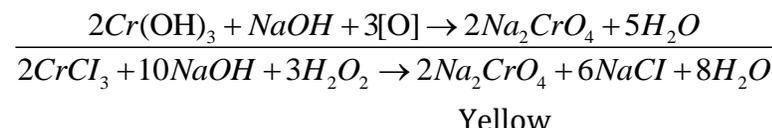
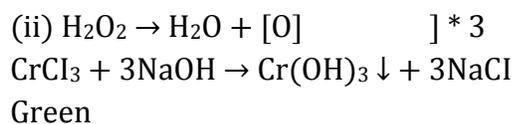
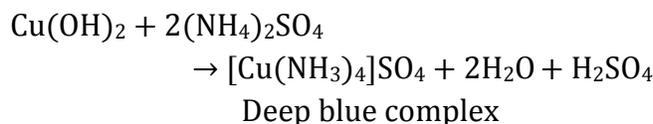
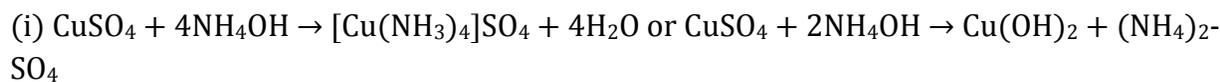


This is known as **Volhard method** for estimation of manganese.

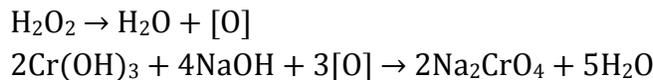


For the molar ratio of 2 : 1 of NO and NO₂, we will have

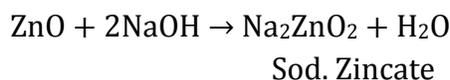




ALTERNATIVE SOLUTION : Precipitates, having green colouration of $\text{Cr}(\text{OH})_3$ are formed. The green precipitate then dissolves to produce a yellow solution of chromate. Reaction are



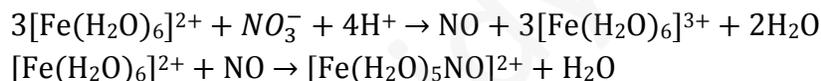
Sol 12.



Sol 13.

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

Sol 14.



Sol 15.

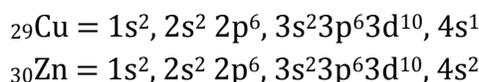
For the explanation of colouration of complexes, first of all find out the number of unpaired electrons present in outer available d-orbitals

- (i) $[\text{Ti}(\text{NO}_3)_4]$; ${}_{22}\text{Ti}^{4+}$: $[\text{Ar}] 3d^0 4s^0$
- (ii) $[\text{Cu}(\text{NC CH}_3)_4]^+$ BF_4^- ; ${}_{29}\text{Cu}^+$: $[\text{Ar}] 3d^{10} 4s^0$
- (iii) $[\text{Cr}(\text{NH}_3)_6]^{+3}$ 3Cl^- ; ${}_{24}\text{Cr}^{3+}$: $[\text{Ar}] 3d^3 4s^0$
- (iv) $\text{K}_3[\text{VF}_6]$; ${}_{23}\text{V}^{+3}$: $[\text{Ar}] 3d^2 4s^0$

Sol 16.

- (i) Pentamminenitridocobalt (III) chloride
- (ii) Potassium hexacyanochromate (III)
- (iii) Pentamminecarbonatochromium (III) chloride.

Sol 17.



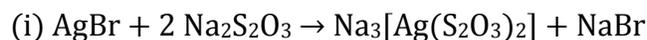
On the basis of configuration of Cu and Zn, first ionization potential of Zn is greater than that of copper because in zinc the electron is removed from $4s^2$ configuration while in copper it is removed from $4s^1$ configuration. So more amount of energy is required for the removal of electron of $4s^2$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

Sol 18.

Pentammine isothiocyanato chromium (III) tetra chlorozincate.

Yes, this compound is coloured because Cr^{3+} . Has $3d^3$ configuration (has unpaired electron in d-orbitals) which show colour, through d-d transition.

Sol 19.



(Hypo) soluble complex



Yellow ppt.

(potassium hex nitro Cobalt ate III)

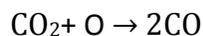
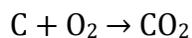
Sol 20.

(i) $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ Formula of pentamminechlorocobalt (III)

(ii) LiAlH_4 Formula of lithium tetrahydroaluminate (III)

Sol 21.

Hematite (Fe_2O_3) on burning with coke and lime at 2000°C result in the following reactions.

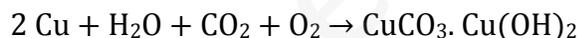


(steel)



(Lime) (Slag)

Sol 22.



Green basic copper carbonate

Sol 23.

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 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

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 coordinate to Cr^{3+} ion.

The mass of water molecules removed per mole of the complex

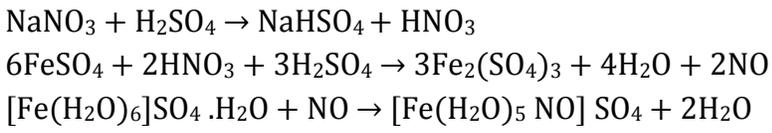
$= 6.75/100 * \text{molar mass of the complex} = 6.75/100 * 266.5 \text{ g} = 17.98 \text{ g}$

This corresponds to one mole of water. Hence, the structure of the compound B will be



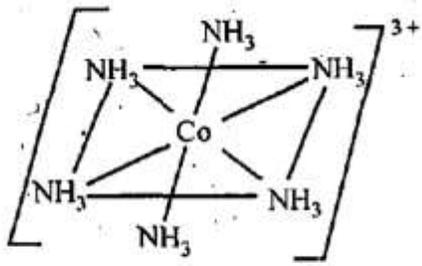
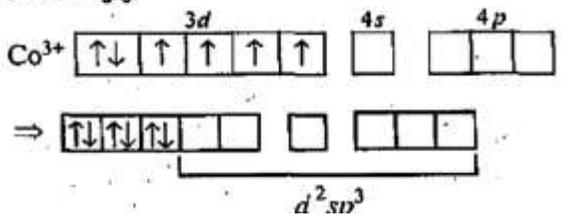
NOTE: The compound C loses 13.5% of its mass when treated with concentrated H_2SO_4 which is twice to the mass lost by the compound B. Hence, the structure of the compound C will be $[Cr(H_2O)_4 Cl_2](H_2O)_2 Cl$.

Sol 24.

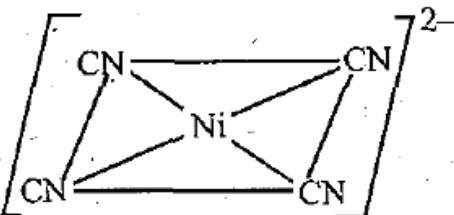
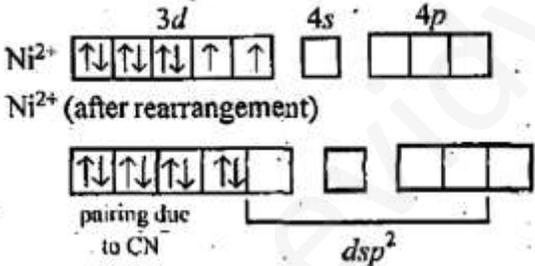


Sol 25.

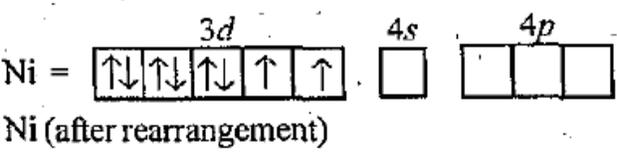
25. $[Co(NH_3)_6]^{3+}$

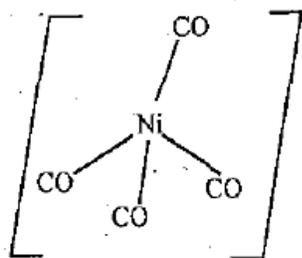
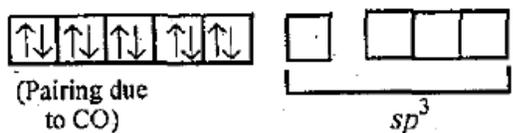


$[Ni(CN)_4]^{2-}$



$[Ni(CO)_4]$





Tetrahedral (sp^3 hybridisation)

Sol 26.

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

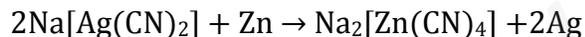
- (1) Silver glance is concentrated by froth flotation.
- (2) Leaching : The concentrated ore is ground to fine powder and dissolved in dilute solution of sodium cyanide.



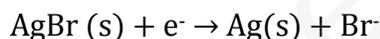
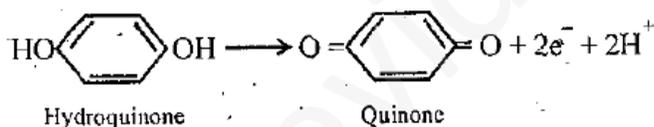
Oxygen of air converts Na_2S to Na_2SO_4 thereby preventing reaction to take place in the reversible direction

- (3) Recovery of silver.

Silver is precipitated out by adding electropositive metal, Zn.

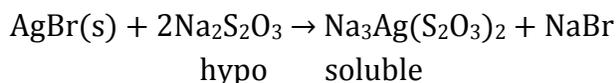


(ii) For development, activated grains are preferentially reduced by mild reducing agents like hydroquinone



(Reducing of activated $AgBr$ to elemental silver.)

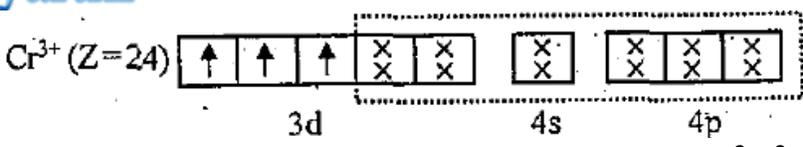
The photographic film is permanently fixed by immediately washing out any non activated $AgBr$



Sol 27.

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),

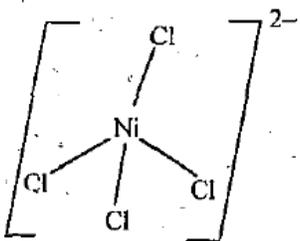
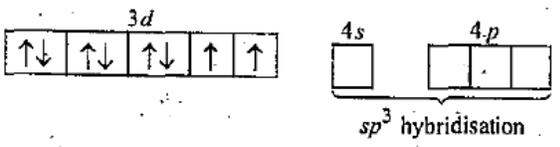
$$M_{spin} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$$

$$= 3.87 \text{ BM}$$

Sol 28.

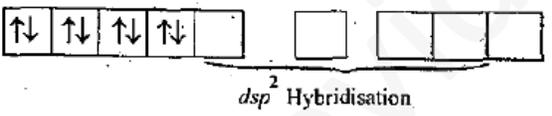
Cl^- is a weak ligand which is unable to pair the electrons of Ni^{2+} . Therefore, here hybridization is sp^3 and shape will be **tetrahedral**.

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



Magnetic moment of $[NiCl_4]^{2-} = \sqrt{2(2+2)} = 2.82 \text{ BM}$ On the other hand, CN^- is a strong ligand which pairs up the electrons of Ni^{2+} . Therefore, here hybridization 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 $[Ni(CN)_4]^{2-} = \sqrt{0(0+2)} = 0.01 \text{ BM}$

Sol 29.

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

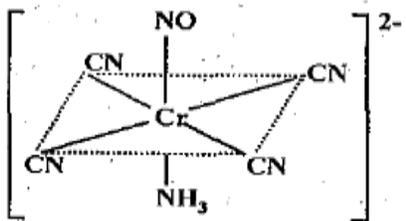
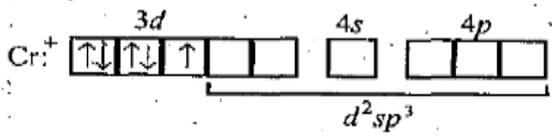
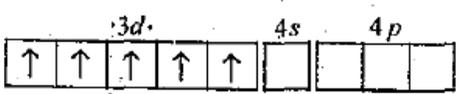
$$M = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$$

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).

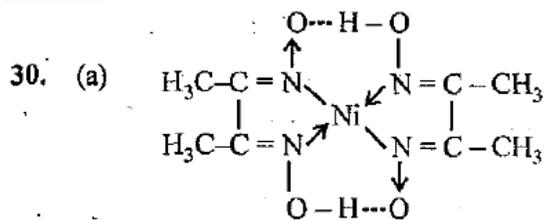
(a) Electronic configuration of Cr^+ :



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

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

Sol 30.



Bis(dimethylglyoximate) nickel (II)

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

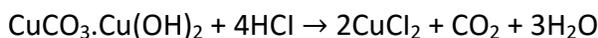
(c) Since number of unpaired electrons in Ni^{2+} is zero, the complex is diamagnetic.

Sol 31.

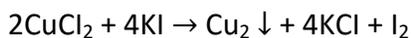
Calcinations of the ore A_1 to form CO_2 indicates that A_1 should be a carbonate. Further, reaction of A_1 with HCl and KI to evolve I_2 indicates that A_1 would also be hydroxide. So the possible formula for the ore, should be $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ which explains all the given reactions



(A₁) (C) black

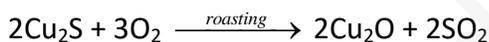


(A₁)

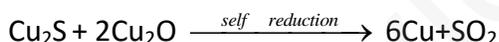


(D)

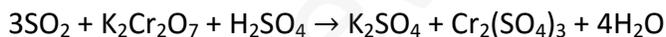
Roasting of A_2 gives gas G whose nature is identified as SO_2 as it gives green colour with acidified $\text{K}_2\text{Cr}_2\text{O}_7$. So A_2 should be sulphide of copper.



(A₂) (G)



(M)



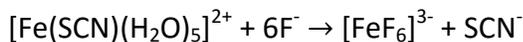
(G) (Green colour)

Sol 32.



(excess) (blood red)

(A)



(B)

IUPAC name of A is pentaquathiocyanatoferrate (III) ion IUPAC name of B is hexafluoroferrate (III)

In $[\text{FeF}_6]^{3-}$ oxidation state of Fe = 6

In $[\text{FeF}_6]^{3-}$ oxidation state of Fe = + 3

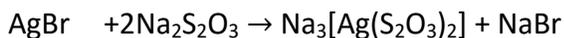
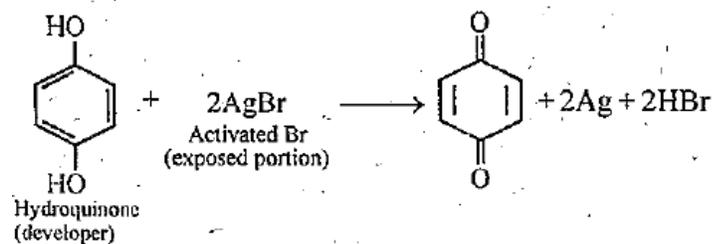
It has 5 unpaired electrons, $n = 5$, Fe^{3+} is $3d^5$

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

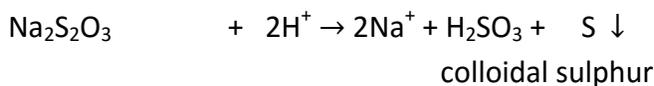
$$\sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

Sol 33.

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

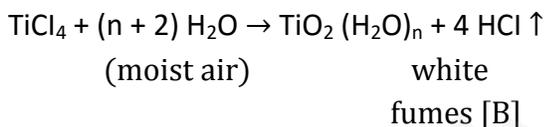
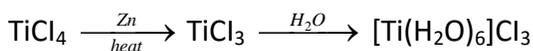


unexposed portion



Sol 34.

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



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

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

(C) : (q) and (s) In $[Co(H_2O)_5Cl]Cl$, 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

