eVidyarthi FREE Thetidnand f block elements & co ordination compounds

SUBJECTIVE PROBLEMS:

<u>Sol 1.</u>

(i) Since the compound (A) on strong heating gives two oxides of sulphur (C and D) which might be SO₂ and SO₃, 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 explain all given reactions as below (Fe^{2+} ion of $FeSO_4$ is changed to Fe^{3+} during heating).

 $FeSO_4 7H_2O \xrightarrow{heat} FeSO_4 + 7H_2O^{\uparrow}$ Ferrous sulphate Ferrous Sulphate \xrightarrow{heat} Fe₂O₃ + SO₂ + SO₃ 2 FeSO₄ $(D)^{3}$ Ferric $(C)^2$ Ferrous Sulphate oxide, (Blackish Brown powder) (B) $Fe_2O_3 + 6 HCI \rightarrow 2FeCI_3$ + 3H₂O Ferric chloride (B) (Yellow solution). (E) $2\text{FeCl}_3 + \text{H}_2\text{S} \rightarrow$ $2FeCl_2 + 2HCl + S$ (E) Apple white green (G) turbidity (F) $FeCl_3 + 3NH_4CNS \rightarrow Fe (CNS)_3$ + Nh₄Cl Ferric thiocyanate (E) (Blood red colour) Sol 2. (i) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$ (A) (C) (B) (ii) $ZnO + 2HCI \rightarrow H_2O + ZnCI_2$ (C) (soluble) (iii) $2ZnCI_2 + K_4 [Fe(CN)_6] \rightarrow 4KCI + Zn_2 p[Fe(CN)_6] \downarrow$ (white ppt) (iv) $ZnCO_3 + HCI \rightarrow CO_2 + ZnCI_2$ (soluble) (A) (v) $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ (Milky) (vi) $CaCO_3 + CO_2 H_2O \rightarrow Ca(HCO_3)_2$

EVidyarthi FREE (Bil) ZanGda+ H₂S —^{NH₄OH}→ 2HCI + ZnS↓

> (white) (viii) $ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 \downarrow$ (white) E (ix) $Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + H_2$ sod. Zincate (soluble)

<u>Sol 3.</u>

(i)
$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + H_2O$$

(white)
(ii) $(NH_4)_2 Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$
(green)
(iii) $2KMnO_4 + 3H_2SO_4 + 5H_2S \xrightarrow{\Delta} K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$
(turbidity)

<u>Sol 4.</u>

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

FeCl₃ + 3H₂O \rightleftharpoons Fe(OH)₃ ↓ + 3HCl Brown ppt

<u>Sol 5.</u>

$$SO_2 + MnO_4^- + H^+ \rightarrow SO_4^{2-} + Mn^{2+} + H_2O_4^-$$

<u>Sol 6.</u>

(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. HCI, which dissolves in excess of dil. HCI, it must contain zinc salt.

Thus the mixture consists of ZnSO₄ and NaOH which explains all the given reactions.

Reactions :

(i)
$$\operatorname{ZnSO}_4 + 4\operatorname{NaOH} \rightarrow \underbrace{\operatorname{Na}_2 ZnO_2 + \operatorname{Na}_2 SO_4}_{soluble} + 2\operatorname{H}_2O$$

(ii) $\operatorname{Zn}_2\operatorname{SO}_4 2\operatorname{HCI} \rightarrow 2\operatorname{NaCI} + \operatorname{Zn}(\operatorname{OH})_2 \downarrow$
 $\operatorname{Zn}(\operatorname{OH})_2 + 2\operatorname{HCI} \rightarrow \operatorname{ZnCI}_2 + 2\operatorname{H}_2O$
Sol 7.
(i) $2\operatorname{CuSO}_4 + \operatorname{SO}_2 + 2\operatorname{H}_2O + 2\operatorname{KCNS} \rightarrow 2\operatorname{CuCNS} \downarrow + \operatorname{K}_2\operatorname{SO}_4 + 2\operatorname{H}_2\operatorname{SO}_4$
Cuprous thiocyanate
(white)
(ii) $\operatorname{Fe}_2(\operatorname{SO}_4)_3 + 2\operatorname{KI} \rightarrow 2\operatorname{FeSO}_4 + \operatorname{K}_2\operatorname{SO}_4 \operatorname{I}_2$

(iii) $2MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + MnO_4^- + 2H_2O$ (iv) $2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$ eVidvarthi FREE Edilyshow) (orange red) (v) $2KMnO_4 + 4KOH + MnO_2 \rightarrow 3K_2MnO_4 + 2H_2O$ or $2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH +$ 3[0] (vi) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \xrightarrow{heat} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO_4 + 3(NH_4)_2SO_4 + 3(NH_4)_2SO_4 + 6CO_4 + 3(NH_4)_2SO_4 + 3(NH_4)_2S$ (vii) $3HCI + HNO_3 \rightarrow NOCI + 2H_2O + 2(CI)$ (agua regia) $Au + 2[CI] \xrightarrow{HCI} AuCI_3 \xrightarrow{HCI} HAuCI_4$ Aurochloric acid (viii) Ag₂S $+ 4 \text{NaCN} \rightleftharpoons 2 \text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$ (silver glance) $4Na_2S + SO_2 + 2H_2O \rightarrow 2Na_2SO_4 + NaOH + 2S$ **[NOTE :** Na₂S is converted into Na₂SO₄ to avoid reversibility of first reaction] $2NaAg(CN)_2 + Zn \rightarrow Na_2 [Zn (CN)_4] + 2Ag$ Sod. Zinc cvanide (ix) $AgCI + 2NaCN \rightleftharpoons NaCI + Na [Ag(CN)_2]$ $2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$ Soluble (x) $CoCI_2 + 2KNO_2 \rightarrow Co(NO_2)_2 + 2KCI$ $KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$ $Co(NO_2)_2 + 3KNO_2 + 2HNO_2 \rightarrow K_3[Co(NO_2)_6]\downarrow + NO + H_2O_2$ Pot cobaltinitrite (yellow ppt.) $2CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$ (xi)(copper pyrites) Roasting $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$ $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$ $Cu_2O + FeS \longrightarrow Cu_2S + FeO$ $FeO + SiO_2 \longrightarrow FeSiO_3 (slag)$ Smelting with coke and sand $\begin{array}{rll} 2\mathrm{Cu}_2\mathrm{S} \ + \ 3\mathrm{O}_2 & \longrightarrow 2\mathrm{Cu}_2\mathrm{O} \ + \ 2\mathrm{SO}_2\\ \mathrm{Cu}_2\mathrm{S} \ + \ 2\mathrm{Cu}_2\mathrm{O} & \longrightarrow 6\mathrm{Cu} \ + \ \mathrm{SO}_2 \ \uparrow \end{array}$ Bessemerization (xii) $K_2Cr_2O_7 + 4naCI + 6H_2SO_4 \rightarrow 2CrO_2 CI_2 \uparrow$ $+ 4NaHSO_4 + 2KHSO_4 + 3H_2O$ chromyl chloride (orange) (xiii) $4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O_3$

(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

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

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

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

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

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FREE (Xi) $2GuSO_4 + 2Na_2CO_3 + H_2O \rightarrow CuCO_3$. $Cu(OH)_2 + 2Na_2SO_4 + CO_2$ (xvii) $K_2Cr_2O_7 + 14HCI \xrightarrow{heat} 2KCI + 2CrCI_3 + 7H_2O + 3CI_2$ (xviii) $AgBr + 2Na_2S_2O_3 \rightarrow Na_3 [Ag(S_2O_3)_2] + NaBr$ (xix) $(NH_4)_2S_2O_8 + 2H_2O + MnSO_4 \rightarrow MnO_2 + 2H_2SO_4 + (NH_4)_2SO_4$ (xx) $3[MnO_4]^{2\cdot} + 4H^+ \rightarrow MnO_2 + 2[MnO_4]^{-} + 2H_2O$ (xxi) $3SO_2 + Cr_7O_7^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ (xxii) $Ag_2S + 2KCN \rightarrow K[Ag(CN)_2] + K_2S$ (Argentite) potassium Argent cyanide (xxiii) KMnO_4 + Cu_2O + KOH $\rightarrow 2$ Cu(OH)_2 + K_2MnO_4 (xxiv) Zn + 2OH⁻ + $BrO_4^- + H_2O \rightarrow [Zn(OH)_4]^{2\cdot} + BrO_3^-$ (xxv) [Zn + 2HNO_3 (dil) $\rightarrow Zn(NO_3)_2 + 2[H]] * 4$ $\frac{2HNO_3 + 8[H] \rightarrow N_2O + 5H_2O}{4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O}$

<u>Sol 8.</u>

Equations for extraction of silver from its sulphide ore.

Cyanide Process :

Ag₂S +2NaCN → Na₂S + 2AgCN (sulphide ore) AgCN + NaCN → Na[Ag(CN)₂] Sod. Argent cyanide (sulphide) 2Na[Ag(CN)₂] + Zn → Na₂[Zn(CN)₄] + 2Ag \downarrow

[NOTE : Zn is more electropositive than Ag.]

<u>Sol 9.</u>

(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, CI⁻ cannot effect this change and thus $[CuCI_4]^{2-}$ exists.

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

 $H_2CrO_4 \xrightarrow{Dehydration} CrO_3 + H_2O$

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

<u>Sol 10.</u>

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



(i) $CuSO_4 + 4NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O \text{ or } CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2-SO_4$ $Cu(OH)_2 + 2(NH_4)_2SO_4$

$$\rightarrow [Cu(NH_3)_4]SO_4 + 2H_2O + H_2SO_4$$

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

 $CrCI_3 + 3NaOH \rightarrow Cr(OH)_3 \downarrow + 3NaCI$

Green

 $\frac{2Cr(OH)_3 + NaOH + 3[O] \rightarrow 2Na_2CrO_4 + 5H_2O}{2CrCI_3 + 10NaOH + 3H_2O_2 \rightarrow 2Na_2CrO_4 + 6NaCI + 8H_2O}$

Yellow

ALTERNATIVE SOLUTION : Precipitates, having green colouration of $Cr(OH)_3$ are formed. The green precipitate then dissolves to produce a yellow solution of chromate. Reaction are $CrCI_3 + 3NaOH \rightarrow Cr(OH)_3 \downarrow + 3NaCI$

(green)

 $\mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + [0]$

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

<u>Sol 12.</u>

 $ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$ Sod. Zincate

Sol 13.

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

<u>Sol 14.</u>

 $3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \rightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$ $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

<u>Sol 15.</u>

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) $[Cu(NC CH_3)_4]^+ BF_4^-$; 29Cu⁺: [Ar] 3d¹⁰ 4s⁰

(iii) [Cr(NH₃)₆]⁺³ 3CI⁻; ₂₄Cr³⁺ : [Ar] 3d³ 4s⁰

(iv) K₃ [VF₆]; ₂₃V⁺³ : [Ar] 3d² 4s⁰

<u>Sol 16.</u>

(i) Pent5amminenitridctocobalt (III) chloride

(ii) Potassium hexacyanochromate (III)

(iii) Pentamminecarbonatochromium (III) chloride.

<u>Sol 17.</u>

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

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FREE 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 4s² configuration while in copper it is removed from 4s¹ configuration. So more amount of energy is required for the removal of electron of 4s² (completely filled orbital) than that of 4s¹ while the second ionization potential of Cu is higher than that of zinc because Cu⁺ has 3d¹⁰ (stable configuration) in comparison to Zn⁺ (4s¹ configuration).

<u>Sol 18.</u>

Pentammine isothiocyanato chromium (III) tetra chlorozincate.

Yes, this compound is coloured because Cr³⁺. Has 3d³ configuration (has unpaired electron in d-orbitals) which show colour, through d-d transition.

<u>Sol 19.</u>

(i) $AgBr + 2 Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$ (Hypo) soluble complex (ii) $CoCI_2 + 7KNO_2 + 2CH_3COOH \rightarrow K_3[Co(NO_2)_6] + 2CH_3COOK + 2KCI + NO + H_2O$ Yellow ppt. (potassium hex nitro Cobalt ate III)

<u>Sol 20.</u>

(i) [CoCI(NH₃)₅]²⁺ Formula of pentamminechlorocobalt (III)

(ii) LiAIH₄ Formula of lithium tetrahydroaluminate (III)

<u>Sol 21.</u>

Hematite (Fe $_2O_3$) on burning with coke and lime at 2000°C result in the following reactions.

 $C + O_2 \rightarrow CO_2$

 $CO_2 + O \rightarrow 2CO$

 $3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$ (Reduction of Fe₂O₃ to form steel) (steel)

 $SiO_2 + CaO \rightarrow CaSiO_3$ (Slag, CaSiO₃ is used as building material)

(Lime) (Slag)

<u>Sol 22.</u>

 $2 \operatorname{Cu} + \operatorname{H}_2 \operatorname{O} + \operatorname{CO}_2 + \operatorname{O}_2 \rightarrow \operatorname{CuCO}_3. \operatorname{Cu}(\operatorname{OH})_2$

Green basic copper carbonate

<u>Sol 23.</u>

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 $[Cr(H_2O)_6]CI_3$.

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 * molar mass f the complex = 6.75/100 * 266.5 g = 17.98 g

This corresponds to one mole of water. Hence, the structure of the compound B will be $[Cr(H_2O)_5CI](H_2O)CI_2$



FREE NOTE: The compound C loses 13.5% of its mass when treated with concentrated H₂SO₄ which is twice fo the mass lost by the compound B. Hence, the structure of the compound C will be [Cr(H₂O)₄ Cl₂](H₂O)₂ Cl.

<u>Sol 24.</u>

$$\begin{split} &NaNO_{3} + H_{2}SO_{4} \rightarrow NaHSO_{4} + HNO_{3} \\ & 6FeSO_{4} + 2HNO_{3} + 3H_{2}SO_{4} \rightarrow 3Fe_{2}(SO_{4})_{3} + 4H_{2}O + 2NO \\ & [Fe(H_{2}O)_{6}]SO_{4} . H_{2}O + NO \rightarrow [Fe(H_{2}O)_{5} NO] SO_{4} + 2H_{2}O \end{split}$$

<u>Sol 25.</u>



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Sol 26.

(i) Argentite is Ag_2S . Silver is extracted form 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.

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

Oxygen of air converts Na₂S to Na₂SO₄ 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

HO OH
$$\rightarrow O = O + 2e^{-} + 2H^{+}$$

Hydroguinone Quinone

Hydroquinone 🦳 🕗

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

(Reducing of activated AgBr to elemental silver.)

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

 $AgBr(s) + 2Na_2S_2O_3 \rightarrow Na_3Ag(S_2O_3)_2 + NaBr$ soluble hypo

Sol 27.

Compound (A) on treatment with $AgNO_3$ gives white precipitate of AgCI, which is readily soluble in dil. Aq. NH₃. 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(NH₃)₄BrCI]CI. Compound (B) on treatment with AgNO₃ 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** BM

<u>Sol 28.</u>

Cl⁻ is a weak ligand which is unable to pair the electrons of Ni²⁺. Therefore, here hybridization is sp³ and shape will be **tetrahedral.**

Electronic configuration of Ni^{+2} (No. of electrons = 26) in presence of Cl^{-1} 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 hybridization is dsp² and shape will be square planar.

Electronic configuration of Ni²⁺ in presence of CN⁻ ion, a strong ligand.



 dsp^{2} Hybridisation For structure of $[Ni(CN)_{4}]^{2^{-}} = \sqrt{0(0 + 2)} = 0.01$ BM

<u>Sol 29.</u>

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.

UIPAC name :

Potassium amminetetracyanonitrosochromate (I).

(a) Electronic configuration of Cr^+ :





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

So, Hybridization : d²sp³ ; Shape : Octahedral

<u>Sol 30.</u>

30. (a)
$$H_{3}C-C = N \qquad \downarrow \qquad N = C - CH_{3}$$
$$H_{3}C-C = N \qquad \downarrow \qquad N = C - CH_{3}$$
$$H_{3}C-C = N \qquad N = C - CH_{3}$$
$$\downarrow \qquad \downarrow \qquad 0 - H - O$$
Bis(dimethylglyoximato) nickel (II)

Bis(dimethylglyoximato) nickel (II)

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

(c) Since number of unpaired electrons in NI²⁺ is zero, the complex is diamagnetic.

<u>Sol 31.</u>

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 $CuCO_3.Cu(OH)_2$ which explains all the given reactions

$$CuCO_3.Cu(OH)_2 \xrightarrow{calcination} 2CuO \downarrow +CO_2 + H_2O$$

$$(A_1) (C) black$$

$$CuCO_3.Cu(OH)_2 + 4HCI \rightarrow 2CuCI_2 + CO_2 + 3H_2O$$

$$(A_1)$$

$$2CuCI_2 + 4KI \rightarrow Cu_2 \downarrow + 4KCI + I_2$$

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.

$$\begin{array}{cccc} 2\text{Cu}_2\text{S} + 3\text{O}_2 & \xrightarrow{\text{roasting}} & 2\text{Cu}_2\text{O} + 2\text{SO}_2\\ (\text{A}_2) & (\text{G})\\ \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} & \xrightarrow{\text{self} \quad \text{reduction}} & 6\text{Cu} + \text{SO}_2\\ & (\text{M})\\ 3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}\\ (\text{G}) & (\text{Green colour})\\ \hline \text{G} & (\text{Green colour})\\ \hline \text{Sol 32.}\\ \text{Fe}^{3+} + \text{SCN}^- \rightarrow [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}\\ & (\text{excess}) & (\text{blood red})\\ & (\text{A})\\ [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+} + 6\text{F}^- \rightarrow [\text{Fe}\text{F}_6]^{3-} + \text{SCN}^-\\ & (\text{B})\\ \end{array}$$
IUPAC name of A is pentaaquathiocyanatoferrate (I

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

In $[FeF_6]^{3-}$ oxidation state of Fe = 6

In $[FeF_6]^{3-}$ oxidation state of Fe = + 3



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

<u>Sol 33.</u>

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



unexposed portion

 $Na_2S_2O_3 \qquad + 2H^+ \rightarrow 2Na^+ + H_2SO_3 + S \downarrow$

colloidal sulphur

<u>Sol 34.</u>

 $\begin{array}{l} [A] \ [\text{Ti}(h_2O)_6]\text{CI}_3 \ [B] \ \text{HCI} \\ \hline \text{Ti}\text{CI}_4 & \xrightarrow{Zn} & \text{Ti}\text{CI}_3 & \xrightarrow{H_2O} & [\text{Ti}(H_2O)_6]\text{CI}_3 \\ \hline \text{Ti}\text{CI}_4 + (n+2) \ \text{H}_2O \rightarrow \text{Ti}O_2 \ (\text{H}_2O)_n + 4 \ \text{HCI} \uparrow \\ & (\text{moist air}) & \text{white} \\ & \text{fumes} \ [B] \end{array}$

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

TiCI₄ is colourless since Ti⁴⁺ has no d electrons, hence d-d transition is impossible. On the other hand, Ti³⁺ 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(H₂O)₅CI]CI, is in +2 state with 3d⁷ configuration making it paramagnetic.

(D) : **(q)** and **(s)** In $[Ni(H_2O)_6]CI_2$, NIi 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)
$$3Cu + 8 HNO_3$$
 (dil.) $\rightarrow 2NO + Cu(NO_3)_2 + 4H_2O$
P 5
(B) $Cu + 4HNO_3$ (conc.) $\rightarrow 2NO_2 + Cu(NO_3)_2 + 2H_2O$
Q 5
(C) $4Zn + 10HNO_3$ (dil.) $\rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
t r
(D) $Zn + 4HNO_3$ (conc.) $\rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
t q

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