

The d and f block elements & co ordination compounds

SUBJECTIVE PROBLEMS:

Q 1.

A certain inorganic compound (A) on heating loses its water of crystallization. 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).

<u>Q 2.</u>

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 HCI with the evolution of gas which is identical in all respects with 'B'. The gas 'B' turns lime water milky, but the milk Inness 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 further addition of the base. Identify the compounds A, B, D, and E. (IIT JEE 1979 – 4 Marks)

<u>Q 3.</u>

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 paramagnetic acidified with dilute sulphuric acid. (IIT JEE 1979 2 Marks)

Q 4.

A solution of $FeCl_3$ in water gives a brown precipitate on standing. (IIT JEE 1980 – 1 Marks)

Q 5.

Complete the following equation (no balancing is needed):

$$SO_2 + MnO_4^- + \dots \rightarrow SO_4^{2-} + Mn^{2+} + \dots$$
 (IIT JEE 1981 – 1 Marks)

Q 6.

An unknown solid mixture contains one or two of the following: $CaCO_3$, $BaCI_2$, $AgNO_3$, Na_2SO_4 , $ZnSO_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is produced which dissolves with further addition of the acid. What is/are present in the solid? Give equations to explain the appearance of the precipitate and its dissolution.

(IIT JEE 1981 – 2 Marks)



<u>Q 7.</u>

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. (IIT JEE 1982 1 Marks)
- (ii) aqueous solution of ferric sulphate and potassium iodide are mixed. (IIT JEE 1984 2 Marks)
- (iii) aqueous solution of potassium magnate and acid are mixed. (IIT JEE 1984 2 Marks)
- (iv) aqueous solution of potassium chromate and acid are mixed. (IIT JEE 1981 2 Marks)
- (v) potassium permanganate interacts with manganese dioxide in presence of potassium

hydroxide; (IIT JEE 1985 – 1 Marks)

- (vi) potassium Ferro cyanide is heated with concentrated sulphuric acid; (IIT JEE 1985 1 Marks)
- (vii) Gold is dissolved in aqua retia. (IIT JEE 1987 1 Marks)
- (viii) Write balanced equations for the extraction of silver from silver glance by cyanide process.

(IIT JEE 1988 – 1 Marks)

- (ix) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. (IIT JEE 1989 1 Marks)
- (x) Cobalt(II) solution reacts with KNO₂ in acetic acid medium. (IIT JEE 1989 1 Marks)
- (xi) Write balanced equations for the extraction of copper from copper pyrites by self-reduction. (IIT JEE 1990 2 Marks)
- (xii) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4 . (IIT JEE 1990 1 Marks)
- (xiii) Iron reacts with cold dilute nitric acid. (IIT JEE 1990 1 Marks)
- (xiv) Potassium permanganate is added to a hot solution of manga nous sulphate.

(IIT JEE 1990 – 1 Marks)

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

(IIT JEE 1992 – 1 Marks)

 $Cu + NHO_3 \rightarrow \dots + NO + NO_2 + \dots$

(xvi) Na₂CO₃ is added to a solution of copper sulphate.

(IIT JEE 1992 – 1 Marks)

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

(xvii) Potassium dichromate and concentrated hydrochloric acid are heated together.

(IIT JEE 1992 – 1 Marks)

(xviii) AgBr + $Na_2S_2O_3 \rightarrow +$ (IIT JEE 1993 – 1 Marks)

(xix) $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \rightarrow + +$ (IIT JEE 1993 – 1 Marks)

(xx) $[MnO_4]^{2^-} + H^+ \rightarrow \dots + [MnO_4]^- + H_2O$ (IIT JEE 1993 – 1 Marks)

(xxi) SO_2 (aq) + $Cr_2O_7^{2-}$ + $2H^+ \rightarrow \dots + \dots + \dots + \dots$ (IIT JEE 1994 – 1 Marks)

(xxii) Write a balanced equation for the reaction of argentite with KCN and name the products in solution. (IIT JEE 1996 – 1 Marks)

(xxiii) Write balanced equations for the oxidation of cuprous oxide to cupric hydroxide by alkaline KMnO₄. (IIT JEE 1997C – 1 Marks)



(xxiv) Write balanced equations for the reaction of alkaline per bromate with zinc giving tetrahydroxyzincate anion. (IIT JEE 1997C – 1 Marks) (xxv) Write balanced equations for the reaction of zinc with dilute nitric acid. (IIT JEE 1997 – 1 Marks) Q 8. Give balanced equations for extraction of silver from its sulphide ore (IIT JEE 1982 – 2 Marks) Q 9. Give reasons for the following: (i) Silver bromide is used in photography. (IIT JEE 1983 – 1 Marks) (ii) Most transition metal compounds are coloured. (IIT JEE 1986 – 1 Marks) (iii) Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^T$. Explain. (IIT JEE 1987 – 1 Marks) (iv) The colour of mercurous chloride, Hg₂Cl₂, changes from white to black when treated with (IIT JEE 1988 – 1 Marks) ammonia. (v) The species [CuCl₄]²⁻ exists while [Cul₄]²⁻ does not (IIT JEE 1992 – 1 Marks) (vi) CrO₃ is an acid anhydride. (IIT JEE 1999 – 2 Marks) Q 10. State the conditions under which the following preparation is carried out. Potassium permanganate form manganese hydroxide. Give the necessary equations which need not be balanced. (IIT JEE 1983 – 1 Marks) Q 11. What happen when: (i) aqueous ammonia is added drop wise to a solution of copper sulphate till it is in excess. (IIT JEE 1985 – 1 Marks) (ii) CrCl₃ solution is treated with sodium hydroxide and then with hydrogen peroxide. (IIT JEE 1985 – 1 Marks) Q 12.

Mention the products formed when zinc oxide is treated with excess of sodium hydroxide solution. (IIT JEE 1986 – 1 Marks)

Q 13.

What is the actual reducing agent of hematite in blast furnace?

(IIT JEE 1987 – 1 Marks)

Q 14.

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: (IIT JEE 1993 – 2 Marks) $[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \rightarrow \dots + [Fe(H_2O_6)]^{3+} + H_2O [Fe(H_2O)_6]^{2+} + \dots + H_2O$



Q 15.

Identify the complexes which are expected to be coloured. Explain (IIT JEE 1994 – 2 Marks)

- (i) $[Ti(NO_3)_4]$
- (ii) [Cu(NCCH₃)₄]⁺ BF₄⁻
- (iii) $[Cr(NH_3)_6]^{3+}3CI^{-}$
- (iv) K₃ [VF₆]

Q 16.

Write down the IUPAC names of the following compounds:

(i) $[Co(NH_3)_5 ONO]Cl_2$ (IIT JEE 1995 – 1 Marks)(ii) $K_3[Cr(CN)_6]$ (IIT JEE 1995 – 1 Marks)(iii) $[Cr(NH_3)_5CO_3]Cl$ (IIT JEE 1996 – 1 Marks)

Q 17.

Compare qualitatively the first and second ionization potentials of copper and zinc. Explain the observation. (IIT JEE 1996 – 2 Marks)

Q 18.

Write the IUPAC name of the compound [Cr(NH₃)₅(NCS)] [ZnCl₄]. Is this compound coloured?

(IIT JEE 1997– 2 Marks)

Q 19.

Write equations for the reaction of:

(i) silver bromide with hypo in photographic process. (IIT JEE 1997C – 1 Marks)

(ii) cobaltous chloride with excess KNO₂ in aqueous acidic solution. (IIT JEE 1997C – 1 Marks)

Q 20.

Write the formulae of the following complexes:

(i) pentamminechlorocobalt(III) (IIT JEE 1997 – 1 Marks)

(ii) Lithium tetrahydroaluminate(III) (IIT JEE 1997 – 1 Marks)

Q 21.

When the ore hematite 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.

(IIT JEE 1998 – 4 Marks)

Q 22.

Work out the following using chemical equations (IIT JEE 1998 – 2 Marks)
In moist air copper corrodes to produce a green layer on the surface.

Q 23.

A, B, and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6CI_3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4 , whereas B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentration H_2SO_4 . Identify A, B and C. (IIT JEE 1999 – 6 Marks)



Q 24.

Write the chemical reaction associated with the brown ring test'. (IIT JEE 2000 – 2 Marks)

Q 25.

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

Q 26.

- (i) Write the chemical reactions involved in the extraction of metallic silver from argentite.
- (ii) Write the balanced chemical equation for developing photographic films.

(IIT JEE 2000 – 4 Marks)

Q 27.

A metal complex having composition $Cr(NH_3)_4$ Cl_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). (IIT JEE 2001 – 5 Marks)

Q 28.

Deduce the structure of $[NiCi_4]^{2^-}$ and $[Ni(CN)_4]^{2^-}$ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species. (IIT JEE 2002 – 5 Marks)

Q 29.

Write the IUPAC nomenclature of the given complex along with its hybridization and structure. K_2 [Cr(NO)(NH₃)(CN)₄], μ = 1.73 BM (IIT JEE 2003 – 4 Marks)

Q 30. Nickel chloride, when treated with dimethylgyloxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following. (IIT JEE 2004 – 4 Marks)

- (a) Draw the structure of the complex showing H-bonds
- (b) Give oxidation state of nickel and its hybridization
- (c) Predict the magnetic behavior of the complex

Q 31.

Some reactions of two ores, A_1 and A_2 of the metal M are given below.

(IIT JEE 2004 – 4 Marks)

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

$$\downarrow \text{Black}$$

$$\downarrow \text{KI/HCI} \rightarrow [D] \downarrow +I_2$$

$$[A_2]$$
 reasting G $\uparrow +M$; $[G]+K_2Cr_2O_7$ $\stackrel{H^+}{\longrightarrow}$ Green solution

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



Q 32.

$$Fe^{3+} \xrightarrow{SCN^{-}} (A) \xrightarrow{F^{-}} (B)$$
Blood red
colouration

What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic momentum of (B)

(IIT JEE 2005 – 4 Marks)

Q 33.

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 tubitity. Identify the product and write the balanced half chemical reaction for it. (IIT JEE 2005 – 4 Marks)

Q 34.

MCI₄
$$\xrightarrow{Zn}$$
 Purple colour compound; M = Transition metal
(colouless (A)
liquid)

MCI₄ $\xrightarrow{moist \ aire}$ (B)
While fumes

Identify (A), (B) and MCI₄. Also explain colour difference between MCI₄ and (A).

(IIT JEE 2005 – 4 Marks)