Chapter
The d-and f-Block Elements

Topic-1: *d*-Block Elements

1 MCQs with One Correct Answer

1. In the scheme given below, X and Y, respectively, are

$$\text{Metal halide} \xrightarrow{\text{aq. NaOH}} \text{White precipitate (P)} + \text{Filtrate (Q)}$$

$$\text{P} \xrightarrow[\text{heat}]{\text{aq. } H_2SO_4,\ PbO_2\text{ (excess)}} \text{X (a coloured species in solution)}$$

$$\text{Q} \xrightarrow[\text{warm}]{MnO(OH)_2,\ \text{conc. } H_2SO_4} \text{Y (gives blue–coloration with KI–starch paper)}$$

[Adv. 2023]

(a) CrO_4^{2-} and Br_2 (b) MnO_4^{2-} and Cl_2
(c) MnO_4^- and Cl_2 (d) $MnSO_4$ and HOCl

2. Which of the following combination will produce H_2 gas? **[Adv. 2017]**
(a) Fe metal and conc. HNO_3
(b) Cu metal and conc. HNO_3
(c) Zn metal and NaOH(aq)
(d) Au metal and NaCN(aq) in the presence of air

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

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

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

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

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

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

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

10. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is: **[2003S]**
(a) K_2MnO_4, purple green
(b) $KMnO_4$, purple
(c) Mn_2O_3, brown
(d) Mn_3O_4, black

11. Anhydrous ferric chloride is prepared by **[2002S]**
(a) heating hydrated ferric chloride at a high temperature in a stream of air
(b) heating metallic iron in a stream of dry chlorine gas
(c) reaction of metallic iron with hydrochloric acid
(d) reaction of metallic iron with nitric acid

12. In the dichromate anion, **[1999 - 2 Marks]**
(a) 4 Cr – O bonds are equivalent
(b) 6 Cr – O bonds are equivalent
(c) all Cr – O bonds are equivalent
(d) all Cr – O bonds are nonequivalent

13. Which of the following compounds is expected to be coloured? **[1997 - 1 Mark]**
(a) Ag_2SO_4 (b) CuF_2
(c) MgF_2 (d) CuCl.

14. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is **[1997 - 1 Mark]**
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

15. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is **[1997 - 1 Mark]**
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) $CrO(O_2)$

16. An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are : **[1996 - 1 Mark]**
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and a brown residue

17. Which compound does not dissolve in hot, dilute HNO_3? **[1996 - 1 Mark]**
(a) HgS (b) PbS (c) CuS (d) CdS

18. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate? **[1996 - 1 Mark]**
(a) $Cu(CN)_2$ (b) $K_2[Cu(CN)_4]$
(c) $K[Cu(CN)_2]$ (d) $K_3[Cu(CN)_4]$

19. Which pair gives Cl_2 at room temperature? **[1995S]**
(a) $HCl_{(conc)} + KMnO_4$ (b) $NaCl + H_2SO_{4(conc)}$
(c) $NaCl + MnO_2$ (d) $NaCl + HNO_{3(conc)}$

20. Which one is solder ? **[1995S]**
(a) Cu & Pb (b) Zn & Cu
(c) Pb & Sn (d) Fe & Zn

21. Zinc-copper couple that can be used as a reducing agent is obtained by : **[1984 - 1 Mark]**
(a) mixing zinc dust and copper gauze
(b) zinc coated with copper
(c) copper coated with zinc
(d) zinc and copper wires welded together

22. Iron is rendered passive by treatment with concentrated **[1982 - 1 Mark]**
(a) H_2SO_4 (b) H_3PO_4 (c) HCl (d) HNO_3

23. Sodium thiosulphate is used in photography because of its **[1981 - 1 Mark]**
(a) reducing behaviour
(b) oxidising behaviour
(c) complex forming behaviour
(d) reaction with light

24. How many unpaired electrons are present in Ni^{2+}? **[1981 - 1 Mark]**
(a) 0 (b) 2 (c) 4 (d) 8

25. Which of the following dissolve in hot conc. NaOH solution **[1980]**
(a) Fe (b) Zn (c) Cu (d) Ag

26. One of the constituent of German silver is **[1980]**
(a) Ag (b) Cu (c) Mg (d) Al

27. Which of the following is the weakest base **[1980]**
(a) NaOH (b) $Ca(OH)_2$
(c) KOH (d) $Zn(OH)_2$

28. When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is **[1979]**
(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4

2 Integer Value Answer

29. 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 **[Adv. 2016]**

30. Consider the following list of reagents: **[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

31. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is **[2009 - 4 Marks]**

4 Fill in the Blanks

32. Silver jewellery items tarnish slowly in the air due to their reaction with ..... . **[1997 - 1 Mark]**

33. The salts ..... and ..... are isostructural. ($FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnSO_4.4H_2O$, $ZnSO_4.7H_2O$) **[1988 - 1 Mark]**

34. Silver chloride is sparingly soluble in water because its lattice energy is greater than ..... energy. **[1987 - 1 Mark]**

35. Galvanization of iron denotes coating with ..... . **[1983 - 1 Mark]**

36. Mn^{2+} can be oxidised to MnO_4^- by ..... . (SnO_2, PbO_2, BaO_2) **[1981 - 1 Mark]**

37. AgCN dissolves in excess KCN solution to give the complex compound ..... **[1980]**

5 True / False

38. Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3*d*-orbital of neutral atom. **[1987 - 1 Mark]**

39. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. **[1984 - 1 Mark]**

40. Silver fluoride is fairly soluble in water. **[1982 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

41. Fusion of MnO_2 with KOH in presence of O_2 produces a salt W. Alkaline solution of W upon electrolytic oxidation yields another salt X. The manganese containing ions present in W and X, respectively are Y and Z. Correct statement(s) is (are) **[Adv. 2019]**
(a) In both Y and Z, p-bonding occurs between p-orbitals of oxygen and d-orbitals of manganese
(b) In aqueous acidic solution, Y undergoes disproportionation reaction to give Z and MnO_2
(c) Both Y and Z are coloured and have tetrahedral shape
(d) Y is diamagnetic in nature while Z is paramagnetic

42. Consider the following reactions (unbalanced) **[Adv. 2019]**
Zn + hot conc. $H_2SO_4 \rightarrow G + R + X$
Zn + conc. $NaOH \rightarrow T + Q$
$G + H_2S + NH_4OH \rightarrow Z$ (a precipitate) $+ X + Y$
Choose the correct option(s)
(a) The oxidation state of Zn in T is + 1
(b) Bond order of Q is 1 in its ground state
(c) Z is dirty white in colour
(d) R is a V-shaped molecule

43. Fe^{3+} is reduced to Fe^{2+} by using **[Adv. 2015]**
(a) H_2O_2 in presence of NaOH
(b) Na_2O_2 in water
(c) H_2O_2 in presence of H_2SO_4
(d) Na_2O_2 in presence of H_2SO_4

44. The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) [Atomic numbers of Cr = 24 and Mn = 25] **[Adv. 2015]**
(a) Cr^{2+} is a reducing agent
(b) Mn^{3+} is an oxidizing agent
(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

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

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

$$\text{excess KI} + K_3[Fe(CN)_6] \xrightarrow{\text{dilute } H_2SO_4} \text{brownish-yellow solution} \xrightarrow{ZnSO_4} \text{white precipitate} + \underbrace{\text{brownish - yellow filtrate}} \xrightarrow{Na_2S_2O_3} \text{colourless solution}$$

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

47. The equilibrium **[2011]**

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

in aqueous medium at 25°C shifts towards the left in the presence of

(a) NO_3^- (b) Cl^- (c) SCN^- (d) CN^-

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

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

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

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

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

7 Match the Following

53. Match each of the reactions given in **Column-I** with the corresponding product(s) given in **Column-II**. **[2009]**

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

54. Match the following, choosing one item from column **X** and one from column **Y**. **[Multiple Concepts, 1982 - 3 Marks]**

X		Y	
(*i*)	Hg_2Cl_2	(a)	cassiterite
(*ii*)	$(NaPO_3)_n$	(b)	lunar caustic
(*iii*)	NO_3^-	(c)	producer gas
(*iv*)	SnO_2	(d)	water softener
(*v*)	$KCl.MgCl_2.6H_2O$	(e)	brown ring test
(*vi*)	$AgNO_3$	(f)	carnallite
(*vii*)	$CO + N_2$	(g)	calomel

8 Comprehension/Passage Based Questions

Paragraph - II

When potassium iodide is added to an aqueous solution of potassium ferricyanide, a reversible reaction is observed in which a complex P is formed. In a strong acidic medium, the equilibrium shifts completely towards P. Addition of zinc chloride to P in a slightly acidic medium results in a sparingly soluble complex Q.

55. The number of moles of potassium iodide required to produce two moles of P is _____. **[Adv. 2024]**

56. The number of zinc ions present in the molecular formula of Q is _____. **[Adv. 2024]**

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

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

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

59. The final solution contains

(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$

(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$

(c) $[Ag(NH_3)_2]^{+}$ and $[Cu(NH_3)_4]^{2+}$

(d) $[Ag(NH_3)_2]^{+}$ and $[Ni(NH_3)_6]^{2+}$

9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.

(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.

(c) If Statement -1 is correct but Statement -2 is incorrect.

(d) If Statement -1 is incorrect but Statement -2 is correct.

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

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

10 Subjective Problems

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

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). **[2005 - 4 Marks]**

63. 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 turbitity. Identify the product and write the balanced half chemical reaction for it. **[2005 - 4 Marks]**

64. (*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]**

65. Write the chemical reaction associated with the 'brown ring test'. **[2000 - 2 Marks]**

66. Work out the following using chemical equations **[1998 - 2 Marks]**
In moist air copper corrodes to produce a green layer on the surface.

67. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation. **[1996 - 2 Marks]**

68. 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]**

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

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

69. Mention the products formed when zinc oxide is treated with excess of sodium hydroxide solution. **[1986 - 1 Mark]**

70. 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]**

71. 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]**

72. Give reasons for the following :
(*i*) CrO_3 is an acid anhydride. **[1999 - 2 Marks]**
(*ii*) The species $[CuCl_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not. **[1992 - 1 Mark]**
(*iii*) The colour of mercurous chloride, Hg_2Cl_2, changes from white to black when treated with ammonia. **[1988 - 1 Mark]**
(*iv*) Zinc and not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$. Explain. **[1987 - 1 Mark]**
(*v*) Most transition metal compounds are coloured. **[1986 - 1 Mark]**
(*vi*) Silver bromide is used in photography. **[1983 - 1 Mark]**

73. State with balanced equations what happens when :
(*i*) Write balanced equations for the reaction of zinc with dilute nitric acid. **[1997 - 1 Mark]**
(*ii*) Write a balanced equation for the reaction of argentite with KCN and name the products in solution. **[1996 - 1 Mark]**
(*iii*) $[MnO_4]^{2-} + H^+ \longrightarrow \ldots\ldots + [MnO_4]^- + H_2O$ **[1994 - 1 Mark]**
(*iv*) $SO_2(aq) + Cr_2O_7^{2-} + 2H^+ \longrightarrow \ldots\ldots + \ldots\ldots + \ldots\ldots$ **[1994 - 1 Mark]**
(*v*) $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \rightarrow \ldots + \ldots\ldots + \ldots\ldots$ **[1993 - 1 Mark]**
(*vi*) $AgBr + Na_2S_2O_3 \rightarrow \ldots + \ldots\ldots$ **[1993 - 1 Mark]**
(*vii*) Potassium dichromate and concentrated hydrochloric acid are heated together. **[1992 - 1 Mark]**
(*viii*) Na_2CO_3 is added to a solution of copper sulphate. **[1992 - 1 Marks]**
$CuSO_4 + Na_2CO_3 + H_2O \rightarrow \ldots\ldots + Na_2SO_4 + \ldots\ldots$
(*ix*) Copper reacts with HNO_3 to give NO and NO_2 in molar ratio of 2 : 1. **[1992 - 1 Marks]**
$Cu + HNO_3 \rightarrow \ldots\ldots + NO + NO_2 + \ldots\ldots$

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

(xi) Iron reacts with cold dilute nitric acid. **[1990 - 1 Mark]**

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

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

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

(xv) 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]**

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

(xvii) Gold is dissolved in *aqua regia*. **[1987 - 1 Mark]**

(xviii) Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. **[1987 - 1 Mark]**

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

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

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

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

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

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

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

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

[1981 - 1 Mark]

75. A solution of $FeCl_3$ in water gives a brown precipitate on standing. **[1980]**

76. 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 permanganate acidified with dilute sulphuric acid. **[1979]**

77. 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 $K_4[Fe(CN)_6]$ 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]**

78. 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]**

Answer Key

Topic-1 : *d*-Block Elements

1. (c) **2.** (c) **3.** (a) **4.** (c) **5.** (b) **6.** (a) **7.** (b) **8.** (a) **9.** (a) **10.** (a)
11. (b) **12.** (b) **13.** (b) **14.** (a) **15.** (b) **16.** (c) **17.** (a) **18.** (d) **19.** (a) **20.** (c)
21. (b) **22.** (d) **23.** (c) **24.** (b) **25.** (b) **26.** (b) **27.** (d) **28.** (a) **29.** (6) **30.** (7)
31. (6) **32.** H_2S **33.** ($FeSO_4.7H_2O$, $ZnSO_4.7H_2O$) **34.** (Hydration/solvation) **35.** (Zinc) **36.** (PbO_2)
37. ($K[Ag(CN)_2]$) **38.** (False) **39.** (True) **40.** (True) **41.** (a, b, c) **42.** (b, c, d) **43.** (a, b)
44. (a, b, c) **45.** (a, b, c) **46.** (a, c, d) **47.** (b, c, d) **48.** (a, d) **49.** (a, c) **50.** (b, c)
51. (c, d) **52.** (b, c) **53.** (A) –p, s ; (B) –q, s ; (C) –r, t ; (D) –q, t
54. i – (g); ii – (d); iii – (e); iv – (a); v – (f); vi – (b); vii – (c) **55.** (2) **56.** (3 or 2) **57.** (b) **58.** (a) **59.** (c)
60. (b) **61.** (c)

Hints & Solutions

Topic-1: *d*-Block Elements

1. **(c)** $MnCl_2 + NaOH \rightarrow \underset{(P)}{Mn(OH)_2}\downarrow + \underset{(Q)}{NaCl}$

(white ppt.) (Filterate)

$$Mn(OH)_2 \xrightarrow[\text{heat}]{PbO_2 + H^+(H_2SO_4)} \underset{(X)}{MnO_4^-} + Pb^{2+}$$

$$Cl^- \xrightarrow{MnO(OH)_2 / \text{conc.}\, H_2SO_4 / \text{warm}} MnCl_2 + H_2O + NaHSO_4 + Cl_2$$

$$Cl_2 + KI \rightarrow I_2 \xrightarrow{\text{Starch}} \underset{\text{colouration}}{\text{blue}}$$

2. **(c)** (Fe becomes passive on reaction with concentrated HNO_3). However, cold relatively conc. HNO_3 reacts with Fe as below.

$Fe + 6HNO_3 \rightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$

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

$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Au(CN)_2] + 4NaOH$

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

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

4. **(c)** Colour is due to $d - d$ transitions. Coloured compounds contain partly filled *d*-orbital.

The oxidation state of copper in various compounds is + 1 and + 2. In CuF_2 it is in + 2 oxidation state. In + 2 state its configuration is

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

$3d$

i.e. ⇅ ⇅ ⇅ ⇅ ↑

It has one unpaired electron due to which it is coloured. (CuF_2 possesses blue colour in crystalline form)

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

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

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

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

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

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

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

Cu^{2+}: $[Ar]3d^9$ | ⇅ | ⇅ | ⇅ | ⇅ | 1 |

Number of unpaired electrons = 1

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

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

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

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

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

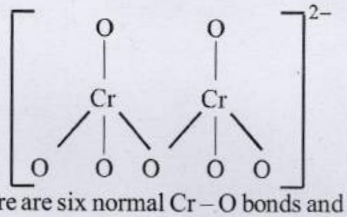
9. **(a)** $6MnO_4^- + I^- + 6OH^- \longrightarrow 6MnO_4^{2-} + IO_3^- + 3H_2O$

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

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

11. **(b)** $2Fe + 3Cl_2\,(dry) \rightarrow 2FeCl_3\,(anhydrous)$

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



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

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

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

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

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

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

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

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

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

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

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

15. **(b)** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{(green)}}{Cr_2O_3} + N_2 + 4H_2O$

Hence, green coloured powder blown in the air is Cr_2O_3.

16. **(c)** Chrome alum is $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

Sodium peroxide (Na_2O_2) will act as an oxidizing agent. It will oxidise Cr^{3+} to Cr^{6+} and Fe^{2+} to Fe^{3+}.

$$Cr^{3+} \longrightarrow \underset{\text{yellow}}{CrO_4^{2+}}$$

$$Fe^{2+} \longrightarrow \underset{\text{brown residue}}{Fe(OH)_3\downarrow}$$

Hence, the filtrate will be yellow in colour and the residue will be brown in colour.

17. **(a)** HgS does not dissolved in hot dil. HNO_3.

18. **(d)** $CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$

$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$ (Cyanogen)

$Cu_2(CN)_2 + 6\,KCN \longrightarrow 2K_3[Cu(CN)_4]$

19. **(a)** $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 3Cl_2$

20. **(c)** Solder is an alloy containing Sn – 67% and Pb – 33%.

21. **(b)** In Zn–Cu couple, Zn is activated by Cu. It is used as a reducing agent in organic synthesis.

The proportion of Zn is about 90% and it can be prepared by coating Zn with copper.

22. **(d)** Conc. HNO_3 renders iron passive by forming a thin protective film of Fe_3O_4 on its surface.

23. **(c)** Hypo solution ($Na_2S_2O_3$) is used in photography to remove the unaffected AgBr in the form of soluble complex.

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

24. **(b)** $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{1}\boxed{1}$. It has 2 unpaired electrons.

3*d* orbital of Ni^{2+} ion. At No. of Ni = 28.

25. **(b)** $Zn + 2NaOH \longrightarrow \underset{\substack{\text{Sod.meta}\\ \text{zincate(soluble)}}}{Na_2[ZnO_2]} + H_2$

26. **(b)** German silver is alloy of Cu + Zn + Ni

27. **(d)** $\because$ Basicity of hydroxides decreases on moving left to right in a period.

28. **(a)** $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Zn + 2NaOH \longrightarrow Na_2[ZnO_2] + H_2$

$\therefore$ Ratio of H_2 evolved is 1 : 1.

29. **(6)** $\overset{+7}{8MnO_4^-} + 3\overset{+2}{S_2O_3^{2-}} + H_2O \longrightarrow \overset{+4}{8MnO_2} + 6\overset{+6}{SO_4^{2-}} + 2OH^-$

$\therefore$ 8 moles of MnO_4^- form 6 moles of SO_4^{2-}.

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

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

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

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

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

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

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

31. **(6)** $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

Oxidation number of Mn in K_2MnO_4 is 6

K_2MnO_4; $2 + x - 8 = 0$

$x = 6$

32. **H_2S;** It is due to formation of sulphide of silver (Ag_2S) which is black.

33. **$FeSO_4.7H_2O$, $ZnSO_4.7H_2O$;**

34. **Hydration/solvation;** [A substance dissolves when its $\Delta H_{\text{hydration}}$ > lattice energy].

35. **Zinc;**

36. **PbO_2;** Pb^{4+} can be easily reduced to Pb^{2+}.

37. **$K[Ag(CN)_2]$**

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

39. **True :** Insolubility of AgCl in H_2O is due to its high lattice energy. Further, AgCl forms a complex with conc. NaCl solution and is therefore soluble.

40. **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.

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

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} \underset{(W)}{2K_2MnO_4} + 2H_2O$$

$$\underset{(W)}{2K_2MnO_4} + 2H_2O \longrightarrow \underset{(X)}{2KMnO_4} + 2KOH\,(g) + H_2$$

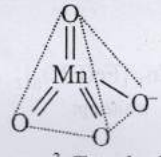
$$K_2MnO_4 \longrightarrow 2K^+ + \underset{(Y)}{MnO_4^{2-}}\ \text{(mangnate ion)}$$

$$KMnO_4 \longrightarrow K^+ + \underset{(Z)}{MnO_4^-}\ \text{(permangnate ion)}$$

MnO_4^{2-}

- sp^3, Tetrahedral
- Green colour
- Mn^{6+} : [Ar] $4s^0 3d^1$
- Paramagnatic

MnO_4^-



- sp^3, Tetrahedral
- Purple colour
- Mn^{7+} : [Ar] $4s^0 3d^0$
- Diamagnetic

Disproportionation of MnO_4^{2-} undergoes in acidic medium but not in base, concerned reaction is as under :

$$3\overset{+6}{MnO_4^{2-}} + 4H^+ \longrightarrow \overset{+4}{MnO_2} + 2\overset{+7}{MnO_4^-} + 2H_2O$$

42. **(b, c, d)**

$$Zn + \underset{\text{Hot \& Conc.}}{H_2SO_4} \rightarrow G + R + X$$

$$Zn + H_2SO_4 \rightarrow \underset{(G)}{ZnSO_4} + \underset{(R)}{SO_2} + \underset{(X)}{2H_2O}$$

$$Zn + \text{Conc. } NaOH \rightarrow \underset{(T)}{Na_2\,ZnO_2} + \underset{(Q)}{H_2}$$

$$\underset{(G)}{ZnSO_4} + H_2S + NH_4OH \rightarrow \underset{(Z)}{ZnS} + \underset{(Y)}{(NH_4)_2SO_4} + \underset{(X)}{H_2O}$$

(a) Oxidation state of Zn in Na_2ZnO_2 is +2
(b) Bond order of Q is one for H_2.
(c) ZnS is white in colour
(d) SO_2 is angular in shape

43. (a, b)

(a) $2Fe^{3+} + \overset{-1}{H_2O_2} + 2OH^- \xrightarrow{[R]} 2Fe^{2+} + 2H_2O + \overset{0}{O_2}$ ($[O]$: $\overset{-1}{H_2O_2} \rightarrow \overset{0}{O_2}$)

(b) $Na_2O_2 + 2H_2O \longrightarrow H_2O_2 + 2NaOH$

The formed H_2O_2 will reduce Fe^{3+} to Fe^{2+}.

44. (a, b, c) Cr^{2+} is a reducing agent and Mn^{3+} is an oxidizing agent and both have electronic configuration d^4.

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

$E^\circ_{Mn^{3+}/Mn^{2+}} = 1.51V$

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

45. (a, b, c) $Na + NH_3$ (excess) → Dilute solution of Na in liq. NH_3 → Paramagnetic due to ammonioted e^-.

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

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

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

46. (a, c, d)

(a) $\overset{-1}{KI}(aq) + \underset{}{K_3}\overset{+3}{[Fe(CN)_6]}(aq) \longrightarrow \underset{}{KI_3}(aq) + \underset{}{K_4}\overset{+2}{[Fe(CN)_6]}(aq)$

Brownish-yellow

$\xrightarrow{ZnSO_4(aq)}$

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

$\xrightarrow{Na_2S_2O_3}$

$I^-(aq) + S_4O_6^{2-}(aq)$

Colourless

(c) When the filterate containing KI_3 add to start solution, the dissolved I_2 will produce a blue colour solution.

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

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

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

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

$$\overset{+1}{CuCN} + 3CN^- \rightarrow [\overset{+1}{Cu}(CN)_4]^{3-}$$

$$Cu^{2+} + 4SCN^- \rightarrow [\overset{+1}{Cu}(SCN)_4]^{3-}$$

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

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

48. (a, d) Potassium permanganate will oxidize itself in this process.

In acidic medium

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

Change in oxidation state of Mn = 7 – 2 = 5

Thus electrons lost = 5

In neutral medium

$MnO_4^- \longrightarrow MnO_2$

Change in oxidation state of Mn = 7 – 4 = 3

∴ Electrons lost = 3

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

50. (b, c) Brass : Cu (60-80%), Zn (40-20%); Gun Metal : Cu (87%), Sn (10%), Zn (3%); Bronze : Cu, Sn; Type metal : Pb, Sb, Sn

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

$Zn(NO_3)_2$, $LiNO_3$, $KAl(SO_4)_2 \cdot 12H_2O$ (potash alum) do not have unpaired 'ℓ' in d-orbital.

52. (b, c) $2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} 2K_2MnO_4 + 2H_2O$;

$2KOH + HCHO + 2KMnO_4 \longrightarrow 2K_2MnO_4 + H_2O + HCOOH$

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

(A) $3Cu + 8HNO_3$ (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) $4Zn + 10HNO_3$ (dil.) $\longrightarrow \underset{t}{4Zn(NO_3)_2} + \underset{r}{N_2O} + 5H_2O$

(D) $Zn + 4HNO_3$ (conc.) $\longrightarrow \underset{t}{Zn(NO_3)_2} + \underset{q}{2NO_2} + 2H_2O$

54. (i) (g) (ii) (d) (iii) (e) (iv) (a) (v) (f) (vi) (b) (vii) (c)

55. (2) From this equation we need 2 mol of KI

$$2KI + 2K_3[Fe(CN)_6] \rightleftharpoons I_2 + \underset{(P)}{2K_4[Fe(CN)_6]}$$

56. (3 or 2)

$$\underset{(P)}{2K_4[Fe(CN)_6]} + 3ZnCl_2 \rightarrow \underset{(Q)}{K_2Zn_3[Fe(CN)_6]_2} + 6KCl$$

OR

$K_4[Fe(CN)_6] \rightarrow Zn_2[Fe(CN)_6]$

57. (b) **58.** (a)

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

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

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

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

60. (b)

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

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

61. (c) The statement-1 is correct

$\underset{\text{(yellow)}}{2K_2CrO_4} + H_2SO_4 \rightarrow \underset{\text{(orange)}}{K_2Cr_2O_7} + Na_2SO_4 + H_2O$

Oxidation state of Cr in K_2CrO_4 and $K_2Cr_2O_7$ is +6, *i.e.* no change in O.S. So explanation is wrong.

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

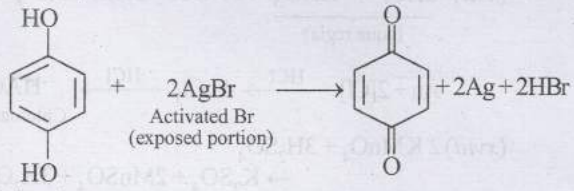
$TiCl_4 \xrightarrow[\text{heat}]{Zn} TiCl_3 \xrightarrow{H_2O} \underset{\text{purple [A]}}{[Ti(H_2O)_6]Cl_3}$

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

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

$TiCl_4$ 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.

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



Hydroquinone (developer)

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

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

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

(1) Silver glance is concentrated by froth flotation.

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

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

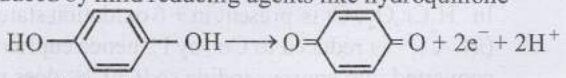
Oxygen of air converts Na_2S to Na_2SO_4 thereby preventing reaction to take place in the reversible direction.

(3) Recovery of silver.

Silver is precipitated out by adding electropositive metal, Zn.

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

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



Hydroquinone Quinone

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

(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.

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

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

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

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

66. $2Cu + H_2O + CO_2 + O_2 \rightarrow \underset{\text{Green basic copper carbonate}}{CuCO_3.Cu(OH)_2}$

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

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

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

68. $3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ \rightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$

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

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

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

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

$Cu(OH)_2 + 2(NH_4)_2SO_4 \rightarrow \underset{\substack{\text{deep blue}\\ \text{complex}}}{[Cu(NH_3)_4]SO_4} + 2H_2O + H_2SO_4$

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

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

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

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

71. $2Mn(OH)_2 + 5NaBiO_3 + 18H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 11H_2O$

72. (*i*) 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.

(*ii*) 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.

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

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

(*v*) 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.
[The colour is due to *d-d* transitions]

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

73. (*i*) $[Zn + 2HNO_3(dil) \rightarrow Zn(NO_3)_2 + 2[H]] \times 4$

$$\underline{2HNO_3 + 8[H] \rightarrow N_2O + 5H_2O}$$
$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(*ii*) $\underset{\text{(Argentite)}}{Ag_2S} + 4KCN \longrightarrow \underset{\substack{\text{potassium}\\ \text{Argentocyanide}}}{2K[Ag(CN)_2]} + K_2S$

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

(*iv*) $3SO_2 + \overset{+6}{Cr_2O_7^{2-}} + 2H^+ \rightarrow 2\overset{+3}{Cr^{3+}} + 3SO_4^{2-} + H_2O$

(*v*) $5(NH_4)_2S_2O_8 + 2MnSO_4 + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

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

(*vii*) $K_2Cr_2O_7 + 14HCl \xrightarrow{\text{heat}} 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$

(*viii*) $2CuSO_4 + 2Na_2CO_3 + H_2O \rightarrow CuCO_3.Cu(OH)_2 + 2Na_2SO_4 + CO_2$

(*ix*) The individual reactions are

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

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

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

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

(*x*) $2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

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

(*xi*) (a) $4Fe + 10HNO_3(6\%\ dilute) \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

(b) $4Fe + 10HNO_3(20\%\ dilute) \rightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$

(*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*)

$\underset{\text{(copper pyrites)}}{2CuFeS_2} + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$

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

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$ } Roasting

$Cu_2O + FeS \longrightarrow Cu_2S + FeO$

$FeO + SiO_2 \longrightarrow FeSiO_3\ (slag)$ } Smelting with coke and sand

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

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$ } Bessemerization

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

$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$

$Co(NO_2)_2 + 3KNO_2 + 2HNO_2 \rightarrow \underset{\substack{\text{Pot. cobaltinitrite}\\ \text{(yellow ppt.)}}}{K_3[Co(NO_2)_6]\downarrow} + NO + H_2O$

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

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

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

$4Na_2S + 5O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + 2S$

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

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

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

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

(*xviii*) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$5H_2C_2O_4 + 5[O] \rightarrow 10CO_2\uparrow + 5H_2O$

$$\underline{2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \rightarrow}$$
$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(*xix*) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \xrightarrow{\text{heat}} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

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

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

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

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

(*xxiv*) $2CuSO_4 + SO_2 + 2H_2O + 2KCNS \rightarrow \underset{\substack{\text{Cuprous thiocyanate}\\(\text{white})}}{2CuCNS\downarrow} + K_2SO_4 + 2H_2SO_4$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

78. (*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).

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

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

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

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

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