HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

2. General electronic configuration of transition elements is [Noble gas] $(n-1)\,d^{1-10}\,ns^{1-2}$.

3. **(A)** The order of penetration of the electrons present in different sub-shells of same energy level is s > p > d > f.

(B) The decrease in size is small after mid way. In the beginning, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), where as the shielding effect of d-electrons is small. After mid way as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

(C) The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

(D) In transition elements, the atomic volumes are large because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high. The densities of the second row are high and third row values are even higher because of lanthanoid contraction.

4. The lesser number of oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a fewer orbitals are available in which the electron can share with other for higher valence.

5. The order of shielding effect of various orbital electrons is s > p > d > f. Due to the poor shielding effect of 4f-electrons in 5d-series elements, there is enhanced increase in effective nuclear charge. As a result of this the valence electrons are tightly bound with the nucleus and thus their removal require higher energy.

10. $\sqrt{15} = \sqrt{n(n+2)}$; n = 3, and three unpaired electrons are found when Mn is in Mn^{4+} i.e., $3d^3\,4s^0$ configuration as its metal electron configuration is $[Ar]^{18}\,3d^5\,4s^2$.

11. **(A)** $Cu^+[Ar]^{18}\,3d^{10}$, so n = 0 ; $Zn^{2+}\,[Ar]^{18}\,3d^{10}$, so n = 0; $Sc^{3+}\,[Ar]^{18}\,3d^0$, so n = 0

(B) $Mn^{2+}\,[Ar]^{18}\,3d^5$, so n = 5 ; $Fe^{3+}\,[Ar]^{18}\,3d^5$, so n = 5 ; $Ni^{2+}\,[Ar]^{18}\,3d^8$, so n = 2

(C) $Cr^{2+}\,[Ar]^{18}\,3d^4$, so n = 4 ; $Mn^{3+}\,[Ar]^{18}\,3d^4$, so n = 4 ; $Sc^{3+}\,[Ar]^{18}\,3d^0$, so n = 0

(D) $Cu^{2+}\,[Ar]^{18}\,3d^9$, so n = 1 ; $Ni^{2+}\,[Ar]^{18}\,3d^8$, so n = 2; $Ti^{4+}\,[Ar]^{18}\,3d^0$, so n = 0

12. $_{30}Zn\,[Ar]^{18}\,3d^{10}$, so n = 0, $Fe^{2+}\,[Ar]^{18}\,3d^6$, so n = 4 ; $Ni^{2+}\,[Ar]^{18}\,3d^8$, so n = 2 ; $Cu^{2+}\,[Ar]^{18}\,3d^9$, so n = 1.

14. $3.87 = \sqrt{n(n+2)}$; n = number of unpaired electrons. So n = 3.

15. The colour of the compounds of transition metals may be attributed to the presence of incomplete (n – 1) d-sub-shell. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called **crystal field splitting**. In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called **d-d transitions**. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals to higher energy set of orbitals.

16. In Ti^{4+}, Cu^+ and Zn^{2+}, all have electrons paired so all are diamagnetic. Cr^{3+} with electron configuration $[Ar]^{18}\,3d^3$ has three unpaired electrons. So it undergoes d-d transition of electrons in presence of ligands according to CFT and thus it is coloured.

18. Cu^{2+} ion ($3d^9$) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

21. The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.

These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

22. Transition metals like Fe, Co, Ni, Cu etc. form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.

23. It is a white powder which becomes yellow on heating due to change in the structure of lattice (due to cation excess defect) but again turns white on cooling.

25. $Cu + H_2O + CO_2 \longrightarrow CuCO_3.Cu(OH)_2$.

Green crust of basic copper carbonate is formed.

26. Mn_2O_7 is an acid anhydride of $HMnO_4$ and thus MnO_4^- is oxo-salt of Mn_2O_7.

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4\,;$$

$$2HMnO_4 + 2KOH \longrightarrow 2KMnO_4 + 2H_2O.$$

30. $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ (weak alkaline medium).

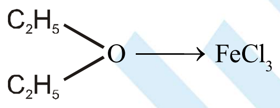
31. **(A)** $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$

(B) Chromyl chloride test ; $Cr_2O_7^{2-} + 4Cl^- + 6H^+ \longrightarrow 2CrO_2Cl_2\uparrow$ (deep red) $+ 3H_2O$

(C) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(D) $2Cl^- + F_2 \longrightarrow Cl_2 + 2F^-$

32. Dissolves in both ether and water forming solvated/hydrated monomeric species,



$[Fe(H_2O)_4Cl_2]Cl\,.\,2H_2O$

solvated $FeCl_3$ hydrated $FeCl_3$

33. $4FeO.\ Cr_2O_3$ (chromite ore) $+ 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Roasting in air}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

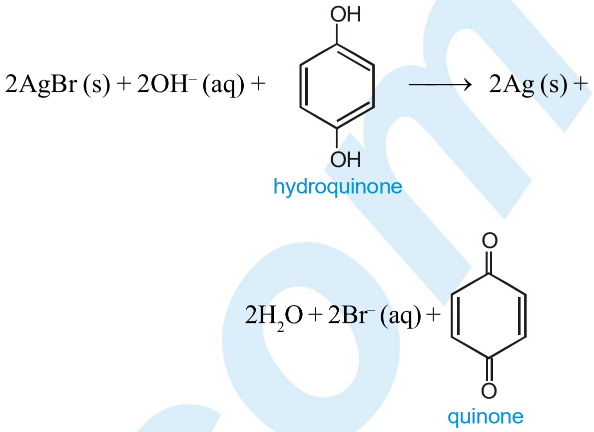
$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O\,;$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$

34. CrO_3 is an acidic oxide and reacts with NaOH forming salt.

$$CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O.$$

36.



38. $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$

$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$

41. $4FeSO_4 + 2H_2O + O_2 \longrightarrow 4Fe(OH).SO_4$ (basic ferric sulphate)

42. Electronic configuration of f-block element $(n-2)\ f^{1-14}$, $(n-1)d^{10}$, ns^2 f-block starts with 6th period (n = 6).

44. Lanthanum = d-block element.

Cerium = lanthanoide element & samarium, plutonium = actinoide element.

45. Due to poor shielding of (n – 2)f-electrons, size of Zr and Hf remain same.

46. Electronic configuration lanthanoid $4f^{1-14}\ 5d^1\ 6s^2$ and electronic configuration of actinoide $5f^{1-14}\ 6d^1, 7s^2$.

48. Across lanthanoide series basicity of lanthanoide hydroxide decreases.

51. The atomic radii of the transition metals lie in-between those of s- and p-block elements. In the beginning, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), whereas the shielding effect of d-electrons is small and orbital electrons are added to the penultimate d–subshell rather than to the outer shell of the atom.

52. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction.** This is because of poor shielding of one of the 4 f-electrons by another in the sub-shell.

53. (A) = 8.95 **(B)** = 8.91 **(C)** = 3.0 **(D)** = 7.14.

Across the period atomic volumes decreases upto copper due poor shielding of d-orbital electrons and addition of extra electrons in inner orbitals and then increases in zinc due to interelectronic repulsions in completely filled d- and s-orbitals. Consequently densities increase from Sc to Cu and then decreases in Zn.

55. **(A)** According to the definition of transition metals, they have partially filled (n – 1)d orbitals except copper and zinc thus mostly show paramagnetism.

(B) It is the property of heavier p-block elements.

(C) Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed.

(D) Show variable oxidation states as (n – 1)d and is orbitals have nearly the same energy and, thus ns as well as (n – 1)d orbital electrons can be lost giving variable oxidation state.

56. After mid way i.e. after Cr as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

57. Valence shell electron configuration of ${}_{30}Zn^{2+}$ is $3d^{10}\,4s^{o}$. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.

Valence shell electron configuration of ${}_{28}Ni^{2+}$ is $3d^{8}\,4s^{o}$. As there are 2 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

Valence shell electron configuration of ${}_{24}Cr^{3+}$ is $3d^{3}\,4s^{o}$. As there are 3 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

60. $Cr^{3+} + e^{-} \xrightarrow{\quad} Cr^{2+}$, $E^{\ominus} = -0.41$ volts and

$Mn^{3+} + e^{-} \xrightarrow{\quad} Mn^{2+}$, $E^{\ominus} = +1.51$ volts

This shows that Cr^{2+} is unstable and has a tendency to acquire more stable Cr^{3+} state by acting as a reducing agent. On the other hand Mn^{3+} is unstable and is reduced to more stable Mn^{2+} state.

61. **(A)** Valence shell electron configuration of V^{3+} is $[Ar]^{18}\,3d^{2}$; so n = 2

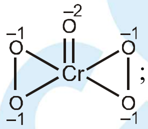
(B) Valence shell electron configuration of Cr^{3+} is $[Ar]^{18}\,3d^{3}$; so n = 3

(C) Valence shell electron configuration of Fe^{3+} is $[Ar]^{18}\,3d^{5}$; so n = 5

(D) Valence shell electron configuration of Co^{3+} is $[Ar]^{18}\,3d^{6}$; so n = 4

63. **(I)** $[Cr(H_2O)_6]Cl_3$, x + 6(0) = +3 ; so x = +3

(II) CrO_5 ,



; so x = +6

(III) $K_3[CrO_8]^{3-}$ or $[Cr(O_2)_4]^{3-}$, here ligand is peroxo i.e. O_2^{2-} ; x + 4 (–2) = –3 ; so x = +5.

(IV) $(NH_3)_3CrO_4$ or $[Cr(O_2)_2]$, here ligand is peroxo i.e. O_2^{2-} ; x + 2 (–2) = 0 ; so x = +4.

64. Electron configuration of Mn is $[Ar]^{18}\,3d^{5}\,4s^{2}$ and thus it contains five unpaired electrons. Hence it can show the highest oxidation state equal to + 7.

66. **(A)** Valence shell electron configuration of Cu^{+} is $[Ar]^{18}\,3d^{10}$; so n = 0

(B) Valence shell electron configuration of Zn^{2+} is $[Ar]^{18}\,3d^{10}$; so n = 0

(C) Valence shell electron configuration of Sc^{3+} is $[Ar]^{18}\,3d^{0}$; so n = 0

(D) Valence shell electron configuration of V^{4+} is $[Ar]^{18}\,3d^{1}$; so n = 1

As V^{4+} has one unpaired electron and so in presence of water as ligand it will undergo d-d transition of electron. Hence V^{4+} ions will produce colour in the solution.

67. **(A)** In $Cr_2O_7^{2-}$, the valence shell electron configuration of Cr(VI) is $3d^{0}$. Thus Cr(VI) is diamagnetic but coloured due to the charge transfer spectrum.

(B) In $(NH_4)_2[TiCl_6]$, the valence shell electron configuration of Ti(IV) is $3d^{0}$. Thus Ti(IV) is diamagnetic and colourless.

(C) In $VOSO_4$, the valence shell electron configuration of V(IV) is $3d^{1}$. Thus V(IV) is paramagnetic and blue coloured due to d-d transition.

(D) In $K_3[Cu(CN)_4]$, the valence shell electron configuration of Cu(I) is $3d^{10}$. Thus Cu(I) is diamagnetic and colourless.

71. (A), **(B)** and **(D)** given hydrated $FeCl_3$ and **(C)** yields anhydrous $FeCl_3$ according to the reaction,

$$2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3 \text{ (anhydrous)}.$$

72. (I) Show variable oxidation states as $(n - 1)d$ and ns orbitals have nearly the same energy and, thus ns as well as $(n - 1)d$ orbital electrons can be lost giving variable oxidation state.

(II) Colour of the compounds may be attributed to the incomplete $(n - 1)d$ subshell which may involved in d-d transition of electrons in presence of ligands.

(III) They have low volatility because of high enthalpies of atomization on account of strong metallic bonding.

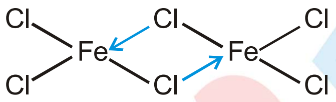
74. (A) Associated with d-d transition of electron.

(B) The transition metals form the reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

(C) Associated with the number of unpaired electrons participating in metallic bonding.

(D) As $\mu = \sqrt{n(n+2)}$, so it is associated with number of unpaired electron.

75. $2FeCl_3 \longrightarrow$



(gas)

76. HNO_3 being strong oxidising agent oxidises iron to its oxides (Fe_3O_4) which forms a thin protective layer over the metal. This makes the iron passive.

77. Mixture of anhydrous zinc chloride and concentrated HCl is called Lucas reagent. It is used for the distinction between primary, secondary and tertiary alcohols.

78. $Ag^+ + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$; soluble complex is formed.

80. $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO(O_2)_2$ (blue coloured) $+ 5H_2O$.

82. Cu(I) thiocyanate is used for the gravimetric estimation of Cu(II).

84. $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3\,H_2O$.

$\therefore \frac{2}{5}$ mole of MnO_4^- for one mole SO_3^{2-}.

85. $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4\,H_2O$.

Green coloured powder blown in air is Cr_2O_3.

87. $6KMnO_4 + 10FeC_2O_4 + 24H_2SO_4 \longrightarrow 3K_2SO_4 + 6MnSO_4 + 5Fe_2(SO_4)_3 + 20CO_2 + 24H_2O$.

$\therefore \frac{3}{5}$ mole of $KMnO_4$ for one mole ferrous oxalate.

88. (A) Have higher enthalpy of atomization because of the involvement of greater number of valence electrons in the bonding. So their melting points are higher.

(B) They show catalytic activity due to their variable oxidation states.

(C) Energy of ns and $(n -1)$ d orbitals are nearly same and thus electrons of ns and $(n-1)d$ orbitals can take part in bonding.

(D) Only heavier p-block elements show inert pair effect, not d-block elements.

89. According to crystal field theory the colour of the complex is due to the d-d transition of the electron in presence of ligands. For example, in $[Ti(H_2O)_6]^{3+}$ by absorbing green yellow component of white light, d-d transition of electron takes place and the aqueous solution appears purple as the purple is the complimentary colour of greenish-yellow.

90. (i) Valence shell electron configuration of Ti^{4+} is $3d^o\,4s^o$. As there is no unpaired electrons for d–d transition, the solution of ions will be colourless.

(ii) Valence shell electron configuration of Cu^+ is $3d^{10}\,4s^o$. As all electrons are paired, there is no d–d transition, so the solution of ions will be colourless.

(iii) Valence shell electron configuration of Co^{3+} is $3d^6\,4s^o$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

(iv) Valence shell electron configuration of Fe^{2+} is $3d^6\,4s^o$. As there are 4 unpaired electrons, there is d–d transition of electron, so the solution of ions will be coloured.

91. Valence shell electronic configuration of palladium is $4d^{10}\,5s^0$. As last electron enters in the 4d sub-shell, it belongs to 4d-series not 3d-series.

92. Electrons are always removed from outer most shell (4s-electron is farther from nucleus than 3d electron). Electron configuration of $_{29}Cu$ is $[Ar]^{18}\ 3d^{10}\ 4s^1$. As 4s–electron is farther from 3d-electron, it is less attracted by the nucleus than that of the 3d. Hence it is loosely bound with the nucleus and is easily removed.

93. **(C)** Along the period, the number of unpaired electrons increases and then decreases due to pairing of electrons so inter–atomic forces (i.e., metallic bond) increases upto middle of the series and then decreases. Boiling and melting points are directly proportionate to strength of metallic bond.

94. All transition elements are more metallic than the representative elements because of the greater availability of d-orbitals for bonding than that of s- (two orbitals) and p- (three orbitals) blocks elements.

95. Transition metal oxide with highest oxidation states is most acidic in character because of the very less difference in the values of electronegativity between Mn^{7+} and O^{2-} , and the decreasing order of acidic character is

$$\overset{+7}{Mn_2O_7} > \overset{+4}{MnO_2} > \overset{+3}{Mn_2O_3} >> \overset{+2}{MnO}.$$

96. **(A)** Valence shell electron configuration of Co^{3+} is $3d^6\ 4s^0$. So has 4 unpaired electrons.

(B) Valence shell electron configuration of Fe^{3+} is $3d^5\ 4s^0$. So has 5 unpaired electrons.

(C) Valence shell electron configuration of Cr^{2+} is $3d^4\ 4s^0$. So has 4 unpaired electrons.

(D) Valence shell electron configuration of V^{3+} is $3d^2\ 4s^0$. So has 2 unpaired electrons.

It has least number of unpaired electrons, so it has least magnetic moment.

97. The elements which show the greater number of oxidation states occur in or near the middle of the series. For example, in the first transition series, manganese exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of d electrons so that only a fewer orbitals are available in which the electron can share with other for higher valence.

98. **(A)** Electron configuration of V is $[Ar]\ 3d^3\ 4s^2$ and thus maximum 5 electrons participate in bonding.

(B) Electron configuration of Cr is $[Ar]\ 3d^5\ 4s^1$ and thus maximum 6 electrons participate in bonding.

(C) Electron configuration of Co is $[Ar]\ 3d^7\ 4s^2$. In octahedral splitting in presence of ligands, half filled t_{2g}^6 has higher CFSE and thus +3 oxidation state is most stable.

(D) Electron configuration of Sc is $[Ar]\ 3d^1\ 4s^2$ and thus maximum 3 electrons participate in bonding.

99. As stability of compounds in aqueous solution depends on the electrode potential which in turns depends on all these enthalpies.

100. **(A)** Valence shell electron configuration of Zn(II) is $3d^{10}\ 4s^0$. So has no unpaired electrons.

(B) Valence shell electron configuration of Mn(IV) is $3d^3\ 4s^0$. So has 3 unpaired electrons.

(C) Valence shell electron configuration of Fe(II) is $3d^6\ 4s^0$. So has 4 unpaired electrons.

(D) Valence shell electron configuration of Ti(III) is $3d^1\ 4s^0$. So has one unpaired electrons.

So, Fe(II) has highest value of magnetic moment as given by $\sqrt{n(n+2)}$ B.M or $\sqrt{4\times 6}$ B.M.

101. **(C)** it show maximum oxidation state equal to + 7 because the energy of (n – 1) d and ns orbitals are nearly same and thus seven electrons can participate in bonding.

102. It is because the unpairing of electrons in d-orbitals require a very high ionisation energy which is not available under bond forming condition. Therefore, transition metal form covalent compounds by simple sharing of electrons with more electronegative O and F.

103. Because of unpaired d-electrons, transition metals have variable valency which enables them to form unstable intermediate compounds. These intermediates give reaction paths of lower activation energy and, therefore increase the rate of the reaction.

104. First ionisation energies of 3d-series (first transition series) increase with increase in atomic number due to **(A)** increase in nuclear charge **(B)** decrease in atomic size.

EXERCISE - 2

Part # I : Multiple Choice

1. **(A)** The colour of the transition metal ions / compounds is attributed to d-d transition of electrons e.g. in $[Cu(NH_3)_4]^{2+}$.

(B) Charge transfer spectrum e.g. in MnO_4^- (no d electrons present).

(C) The colour change is not because of change in the geometry of the molecules.

(D) Yellow colour of the AgI is due to the polarisation of I^- by Ag^+.

3. **(A)** Coloured due to charge transfer from ligand to metal ion.

(B) Valence shell electron configuration of Cu(I) is $3d^{10}$ and, therefore, all electrons are paired ; Valence shell electron configuration of Cu(II) is $3d^9$ and, therefore, one electron is unpaired.

(C) CrO_3 is an acid anhydride of chromic acid.

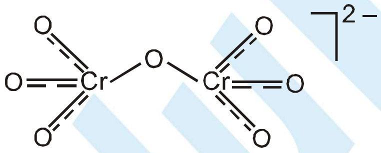
(D) Valence shell electron configuration of Ti^{3+} is $3d^1$ and, therefore, has one unpaired electron; so it is coloured. But valence shell electron configuration of Sc^{3+} is $3d^0$ and, therefore, it has no unpaired electron; so it is colourless.

5. **(A)** $2Ag^+ + S_2O_8^{2-} \longrightarrow 2Ag^{2+} + 2SO_4^{2-}$;

$Ag^{2+} + 4py \longrightarrow [Ag(py)_4]^{2+}$ (red).

(B) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$.

(C)



(D) Ti^{3+} has one unpaired electrons; So d-d transition is possible while Ti^{4+} has no electrons in d-orbitals.

7. **(A)** The great tendency of transition metal ions to form complexes is due to : (i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.

(B) The existence of the transition elements in different oxidation states is due to the participation of inner (n – 1) d-electrons in addition to outer ns-electrons because, the energies of the ns and (n – 1) d-sub-shells are nearly same.

(C) The transition metals show magnetic properties due to presence of number of unpaired electrons in d-orbitals.

(D) Most the transition metal ions are coloured, because they have unpaired electrons which can undergo d-d- transition in presence of ligands.

9. $4\,Cl^- + Cr_2O_7^{2-} + 6H^+ \longrightarrow 2CrO_2\,Cl_2\uparrow$ (deep red) $+ 3H_2O$

$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-}$ (yellow) $+ 2H_2O + 2Cl^-$

$CrO_2Cl_2 + H_2O \longrightarrow H_2CrO_4 + HCl$

10. **(A)** Used in developing of photography plate. i.e. to reduce Ag^+ to Ag↓.

(B) Fixing of photography plate i.e. to remove unreduced AgBr.

(C) & **(D)** reactions are not involved in photography.

11. $2\,MnO_2 + 4KOH + O_2(KNO_3) \longrightarrow 2K_2MnO_4 + 2H_2O$.

$MnO_4^{2-} \xrightarrow[\text{oxidation}]{\text{electrolytic}} MnO_4^- + e^-$.

12. **(A)** Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of CrO_5.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$$

(B) In alkaline medium with 30% H_2O_2, a red-brown K_3CrO_8 (diperoxo) is formed. It is tetra peroxo species $[Cr(O_2)_4]^{3-}$ and thus the Cr is in +V oxidation state.

(C) In ammoniacal solution a dark red-brown compound, $(NH_3)_3CrO_4$ - diperoxo compound with Cr(IV) is formed.

(D) In CrO_4^{2-} the Cr is in its highest +6 oxidation state. So it can not be further oxidised.

13. **(A)** $6AgNO_3 + 3I_2$ (excess) $+ 3H_2O \longrightarrow$

$HIO_3 + 5AgI + 5HNO_3$

(B) $AgNO_3$ (excess) $+ KCN \longrightarrow AgCN$(white) $+ KNO_3$.

15. **(A)** $Na_2Cr_2O_7$ is not used as primary standard because it is hygroscopic in nature.

(B) $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$

$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$

(C) $PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$

$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3AsO_3$

(D) $3FeS_2 + 2H_2O + 11O_2 \longrightarrow 2FeSO_4 + Fe_2(SO_4)_3 + 2H_2SO_4$

16. **(A)** $CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}$; $CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(B) $3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$.

(C) No colour change.

(D) No colour change.

17. **(A)** As metal ions generally contain one or more unpaired electrons in them & hence their complexes are generally paramagnetic

(B) Because of having larger number of unpaired electrons in their atoms, they have stronger inter atomic interaction and hence stronger bonding between the atoms.

(C) It is attributed to the presence of unpaired electrons, and thus d-d transition of electrons may occur in most of the compounds producing coloured solutions.

(D) This activity is ascribed to their ability to adopt multiple oxidation state and to form complexes.

18. **(A)** $5HCHO + MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5HCOOH + 3H_2O$.

(B) $4KOH + 2MnO_2$ (manganese dioxide) $+ O_2 \rightarrow 2K_2MnO_4$ (potassium mangnate) $+ 2H_2O$.

(C) $Mn(OH)_2 + O_2^{2-} \rightarrow MnO_4^{2-}$ (mangnate) $+ 2OH^-$.

(D) $2KMnO_4 \xrightarrow{750K} K_2MnO_4$ (potassium mangnate) $+ MnO_2 + O_2$.

19. **(A)** In both compounds central metals have + 6 oxidation states.

MnO_4^{2-} ; $x + 4(-2) = -2$, So, $x = 6$. ;

CrO_2Cl_2 ; $x + 2(-2) + 2(-1) = 0$, So, $x = 6$.

(B) Sodium dichromate is $Na_2Cr_2O_7.2H_2O$, so it can not be weighed correctly for the preparation of standard solution.

(C) $2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3$ (green) $+ 3/2\ O_2$.

(D) $4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4$ (green) $+ 2H_2O + O_2$

20. **(A)** and **(B)** statements are correct. These statements are factual.

(C) Along the period, the electronegativity of metals decreases and therefore the difference of electronegativities between metal and oxygen decreases. Hence, the acidic character increases, so the correct order is $TiO < VO < CrO < MnO$.

(D) V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_2^+ respectively.

21. **(A)** In MnO_4^-, the valence shell electron configuration of Mn(VII) is $3d^0\ 4s^0$ and thus the colour of the compound is not due to d-d transition but is due to charge transfer spectrum.

(B) In CrO_3, the valence shell electron configuration of Cr(VI) is $3d^0\ 4s^0$ and thus the colour of the compound is not due to d-d transition but is due to charge transfer spectrum.

(C) In $CuCl_2$, the valence shell electron configuration of Cu(II) is $3d^9\ 4s^0$ and thus the colour of the compound is due to d-d transition of electron.

(D) In Cu_2O, the valence shell electron configuration of Cu(I) is $3d^{10}\ 4s^0$ and thus the colour of the compound is not due to d-d transition of electron but is because of charge transfer spectrum.

22. Cr_2O_3, V_2O_5 and ZnO react with alkalies and acids forming corresponding salts. But $\overset{+VII}{Mn_2}O_7$ is acidic. It dissolves in water forming $HMnO_4$, permanganic acid. $Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$.

23. $3CuCl_2.2H_2O \xrightarrow{\Delta} CuO + Cu_2Cl_2 + 2HCl + Cl_2 + H_2O$; only Cl_2 is liberated is wrong as evident from chemical equation.

24. **(A)** $2CuSO_4 + 2NaCl + 2H_2O + SO_2 \rightarrow Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$

(B) $Cu + HCl + [O] \rightarrow CuCl_2 + H_2O$; $CuCl_2 + Cu \rightarrow Cu_2Cl_2$

(C) $CuSO_4 + 2HCl \rightarrow CuCl_2 + H_2SO_4$; $CuCl_2 + Cu \rightarrow Cu_2Cl_2$

(D) $CuO + 2HCl \rightarrow CuCl_2 + H_2O$; Cu_2Cl_2 is not formed.

25. $S_1 : HCrO_4^- + 2H_2O_2 + H^+ \rightarrow CrO(O_2)_2$ (deep blue) $+ 3H_2O$.

$S_2 : CrO_3 + 2HCl \xrightarrow{\text{conc. } H_2SO_4} CrO_2Cl_2$(deep red) $+ H_2O$.

$S_3 : (NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$ (green).

$S_4 : K_2Cr_2O_7 + 2C \xrightarrow{\Delta} Cr_2O_3 + K_2CO_3 + CO\uparrow$.

26. **S_1 :** Both are oxidising agents.

$$5\,PbO_2 + 2\,Mn^{2+} + 4H^+ \longrightarrow 2\,MnO_4^- + 5Pb^{2+} + 2\,H_2O.$$

$$2\,Mn^{2+} + 5\,NaBiO_3 + 14\,H^+ \longrightarrow 2MnO_4^- + 5\,Bi^{3+} + 5\,Na^+ + 7\,H_2O.$$

S_2 : $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2(s) + 2H_2O.$

S_3 : $2KMnO_4 + 5H_2 \xrightarrow{\Delta} 2KOH + 2MnO + 4H_2O.$

27. **S_1 :** Due to strong interatomic forces, they have high melting points.

S_2 : Some of the hydrochloric acid is oxidised to chlorine.

S_3 : $MnO_4^- + e^- \xrightarrow{OH^-} MnO_4^{2-}$

S_4 : $2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + H_2O$

28. **S_1 :** It is because Mn^{2+} has $3d^5$ configuration which has extra stability.

S_2 : Not titanium but Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

S_3 : It is not stable as it undergoes disproportionation ; $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$. The E^o value for this is favourable.

S_4 : Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

29. **S_1 :** T – Because of Lanthanide contraction

S_2 : F – Along the period the ionization energies generally increase because (i) nuclear charge increases and (ii) size of atoms decreases.

S_3 : T - It is factual

S_4 : F – In CrO_4^{2-}, the valence shell electron configuration is $3d^0\,4s^0$ an thus the yellow colour of the compound is not due to d-d transition but due to charge transfer to metal atom from O-atom, thereby, changing O^{2-} ion to O^- ion (momentary).

30. If a non-metal occupies interstitial sites of a metal, the metal becomes less malleable. This is because the non-metal atom forms covalent bonds with metal atoms and covalent bond is rigid and directional.

31. **(A)** $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ (strong alkaline medium)

(B) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (acidic medium)

(C) $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ (neutral medium)

32. $MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$ (neutral / weak alkaline medium)

33. $2KMnO_4 \xrightarrow{750K} K_2MnO_4 + MnO_2 + O_2$.

34. ${}_{22}Ti = 3d^2\,4s^2$, $Ti^{2+} = 3d^2$; ${}_{23}V = 3d^3\,4s^2$, $V^{3+} = 3d^2$.

${}_{24}Cr = 3d^5\,4s^1$, $Cr^{4+} = 3d^2$; ${}_{25}Mn = 3d^5\,4s^2$, $Mn^{5+} = 3d^2$

35. **(A)** Oxidation state of iron is +3 but it can exceed to a maximum of +6. Oxidation state of cobalt is +3 but it can exceed to a maximum of +4.

(B) Highest oxidation state of Cr in CrO_2Cl_2 is + 6 and highest oxidation state of Mn in MnO_4^- is + 7.

(C) Oxidation state of titanium is +2 but it can exceed to a maximum of +4. Oxidation state of Mn is +4 but it can exceed to a maximum of +7.

(D) Oxidation state of cobalt is +3 but it can exceed to a maximum of +4. Oxidation state of Mn is +7 which is its highest oxidation state.

36. $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$; $2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$.

$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$.

37. $2KMnO_4 + 6HCl \rightarrow 2KCl + 2MnCl_2 + 3H_2O + 5O.$

$2HCl + O \rightarrow H_2O + Cl_2\,] \times 5.$

$16HCl + 2KMnO_4 \rightarrow 8H_2O + 5Cl_2 + 2KCl + 2MnCl_2$.

Cl_2 is greenish yellow gas.

38. Fe(II)SO_4, S (IV) O_2 and H_2O_2 (–1) can acts as reducing agent and as such reduce MnO_4^- (pink) to Mn^{2+} (almost colourless).

Fe(III) is in highest oxidation state in $FeCl_3$ and, therefore, it cannot act as reducing agent. Hence it does not decolourise an acidified aqueous solution of $KMnO_4$.

39. $2HCl + MnO_2 \rightarrow MnCl_2 + H_2O + O.$

$2HCl + O \rightarrow H_2O + Cl_2$.

$4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2$.

$6HCl + 2KMnO_4 \rightarrow 2KCl + 2MnCl_2 + 3H_2O + 5O$

$2HCl + O \rightarrow H_2O + Cl_2\,] \times 5.$

$16HCl + 2KMnO_4 \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$.

40. $CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$;

$CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-}$ (orange red) $+ H_2O$

41. Aqueous solution of $CuSO_4$ is acidic in nature, it converts some $CuCrO_4$ to $CuCr_2O_7$.

42. $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Fusion}} Na_2\overset{+VI}{Cr}O_4 \xrightarrow[H_2O]{H^+}$

$Na_2\overset{+VI}{Cr_2}O_7 \xrightarrow{H^+/H_2O_2} \overset{+VI}{Cr}O(O_2)_2$ (deep blue violet)

$\xrightarrow{H_2O} \underset{(Y)}{O_2} + \underset{(Z)}{H_2O} + Cr^{3+}$. (X)

$Na_2Cr_2O_7 + H_2SO_4 \rightarrow 2CrO_3$ (bright orange/red- chromic anhydride) $+ Na_2SO_4 + H_2O$.

43. $2KMnO_4 + 3H_2SO_4 \rightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$

$(MnO_3)_2SO_4 + H_2O \rightarrow Mn_2O_7 + H_2SO_4$

$$Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \frac{3}{2}O_2$$

44. **(A)** $K_2Cr_2O_7 \xrightarrow[OH^-]{H_2O_2} K_3CrO_8$.

(B) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO(O_2)_2 + 5H_2O$.

(C) $K_2Cr_2O_7 + 2H_2SO_4$ (concentrated & cold) $\longrightarrow$
$2CrO_3 + 2KHSO_4 + H_2O$.

(D) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$.

45. **(A)** $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$.

(B) In acidic solution, actually chromate is converted to dichromate.

$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$.

(C) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$.

(D) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$.

46. The phenomenon is called spitting of Ag.

47. Quinol developer (a reducing agent) reduces AgBr to Ag.

$2AgBr^*(s) + 2OH^-(aq) + C_6H_5(OH)_2(aq) \longrightarrow 2Ag(s)$
$+ 2H_2O + C_6H_4O_2(aq) + 2Br^-(aq)$

Where AgBr* represents a molecules of AgBr exposed to light.

48. **(A)** $AgCl + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaCl$.

(B) $AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$.

(C) $NaNO_3$ does not react with AgCl.

(D) $3AgCl + Na_3AsO_3 \rightarrow Ag_3AsO_3 + 3NaCl$.

49. Iron lies below copper in electrochemical series and, therefore, displaces the copper from copper sulphate solution according to the following reaction.

$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$.

The redox reaction involves oxidation of Fe to Fe^{2+} and reduction of Cu^{2+} to Cu.

50. **(A)** $CuSO_4$ reacts with KI to give Cu_2I_2 (white precipitate) but not with KCl.

(B) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2\uparrow$.

(C) Fehling's solution mainly contains $CuSO_4$ and NaOH. When warmed with glucose (with – CHO group) gives red precipitate of Cu_2O. Glucose reduces the Cu^{2+} to Cu_2O (red).

(D) $CuSO_4$ on heating gives CuO).

$$CuSO_4 \xrightarrow{1000K} CuO + SO_2 + \frac{1}{2}O_2.$$

51. Cu_2Cl_2 absorbs CO.

$Cu_2Cl_2 + 2CO \longrightarrow 2CuCl.CO$.

52. Developing involves the decomposition of AgBr to Ag. This decomposition has to be proportional to the extent of light exposure. This is carried out with a weak reducing agent.

$2AgBr^*(s) + 2OH^-(aq) + C_6H_5(OH)_2(aq) \longrightarrow 2Ag(s)$
$+ 2H_2O + C_6H_4O_2(aq) + 2Br^-(aq)$

Where AgBr* represents a molecules of AgBr exposed to light.

53. Transition metal ions in lower oxidation states form cations. These cations act as Lewis acids, e.g.

$Fe \longrightarrow Fe^{2+}$ (Lewis acid) $+ 2e^-$.

54. $CuCl_2 + Cu \xrightarrow[\text{boil}]{\text{conc. HCl}} Cu_2Cl_2$.

55. $CuFeS_2 + 4O_2 \xrightarrow{\Delta} CuSO_4(s) + FeSO_4(s)$

(A) $CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 + 2K_2SO_4$

(B) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

(C) $CuSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cu(OH)_2\downarrow$ (insoluble in excess NaOH)

(D) $Fe^{2+} + 2K_3[Fe(CN)_6] \rightarrow Fe_3[Fe(CN)_6]_2$ (deep blue)

56. $Cu(hot) + H_2O(g) \rightarrow CuO + H_2$.

57. **(C)** $FeCl_3$ exists as Fe_2Cl_6 (a dimer) in vapour state.The solution is acidic due to the formation of HCl and brown due to the formation of $Fe(OH)_3$.

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3$ (Brown) $+ 3HCl$.

58. $_{21}La(OH)_3$ is more basic than $Lu(OH)_3$.

59. After uranium all elements are transuranic element.

61. In electron configuration of d-block element last electron filled in (n – 1) d subshell & these element placed between s-block & p-block element in periodic table. In f-block element, last electron filled in (n – 2) f-subshell and these elements are placed in IIIrd B group in transition element. These element knwon as inner transition metal elements.

62. All f and d-block element contains only metal.

63. Np and Pu shows maximum oxidation number + 7.

64. Curium, Californium, uranium are actionide elements

65. Lanthanide contraction is due to increase in effective nuclear charge.

66. Strong metallic bonds between the atoms of transition elements attribute to their high melting and boiling points. Zinc has all electrons paired ([Ar] $3d^{10}$ $4s^2$) and thus do not participate in metallic bonding. So accordingly its melting point is least.

67. Cr^{3+} is most stable because in aqueous solution it has higher CFSE on account of half filled t^3_{2g} energy level of 3d orbitals in octahedral spliting.

68. **(A)** Greater the number of valence electrons, stronger is the resultant bonding and thus greater is the enthalpies of atomization.

(B) Cr^+ has half-filled valence shell electron configuration $3d^5$, so it has higher second ionisation energy. Similarly Cu^+ has completely filled stable valence shell electron configuration, $3d^{10}$, so it has higher second ionisation energy.

(C) Sum of first two ionisation energies (IE_1 + IE_2) of Ni(II) is less than that of Pt(II). Similarly sum of first four ionisation energies of Pt(IV) is less than that of Ni(IV).

(D) Element occurs in the middle of the period, eg., manganese has +7 oxidation state as it contains five unpaired electrons.

69. Ni^{2+}, Fe^{2+} and Cu^{2+} has 2, 4 and 1 unpaired electrons respectively. So in presence of ligands d-d transition takes place and these hydrated ions produce colour in aqueous solutions. Cu^+ is diamagnetic with $3d^{10}$ configuration; so no d-d transition is possible and thus colourless.

70. **(A)** This activity is ascribed to their ability to adopt multiple oxidation state and to form complexes.

(B) Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between the atoms.

(C) Transition metals like Fe, Co, Ni, Cu etc. form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.

71. **(A)** $PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$

(B) It possesses powerful corrosive action on organic tissues, which it turns black especially in presence of light. The blackening is due to finely divided metallic silver, reduced by organic tissue.

(C) $AgCN\ (s) + CN^-\ (aq) \longrightarrow [Ag(CN)_2]^-$ (soluble complex).

(D) Zr is the element of the 4d series 4th group while Ta is a element of 5d series 5th group so have differ atomic sizes.

Part # II : Assertion & Reason

2. Statement-1 : $CuSO_4 . 5H_2O$ (blue) $\xrightarrow{250°C}$ $CuSO_4$ (white) + $5H_2O\uparrow$. Anhydrous copper sulphate becomes white because there is no d-d transition of electron in absence of ligands according to crystal field theory.

Statement-2 : Four water molecules are coordinated to Cu^{2+} and fifth one is hydrogen bonded to two water molecules and anion, SO_4^{2-}.

4. The atomic radii, in general, increase down the group. The atomic radii of second series are larger than those of first transition series. In the atoms of the second transition series, the number of shells are more than those of the Ist transition series. As a result, the atoms of IInd transition series are larger than those of the elements of the first transition series. But the atomic radii of the second and third transition series are almost the same. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number.

5. The atomic radii of the second (4d series) and third, (5d series) transition series are almost the same.

This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

6. Statement-1 : The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favourable of strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomization. So tungsten has very high melting point.

Statement-2 : It is not a covalent compound but is a metal i.e an element.

7. Statement-1 : Correct statement as it gives oxy acid $H_2Cr_2O_7$; $2CrO_3 + H_2O \longrightarrow H_2Cr_2O_7$.

Statement-2 : Correct statement ;

$K_2Cr_2O_7 + 2H_2SO_4$ (concentrated and cold) $\longrightarrow CrO_3\downarrow$ (bright orange) $+ 2KHSO_4 + H_2O$.

9. Permanganate titrations is not carried out in presence of HCl because it may oxidise some of the HCl to Cl_2 gas according to the following chemical reaction ; $2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$. Hence we do not get the correct end point for the given titration.

12. The atomic radii of the second (4d series) and third, (5d series) transition series are almost the same.

This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called

Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

13. Statement-1 : Electron configuration of Cr(g) is $[Ar]^{18}\,3d^5\,4s^1$ and, therefore, it has six unpaired electrons.

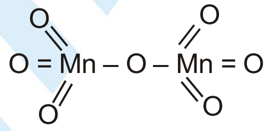
Statement-2 : Fully filled orbital is more stable than half filled orbital on account of more number of exchange of electrons resulting into the greater release of exchange energy.

15. Statement-1 : Correct statement and Statement-2 is correct explanation of Statement-1 .

Green $\rightarrow \overset{+6}{\text{Mn}}\text{O}_4^{2-} - [Ar]^{18}\,3d^1\,4S^o$; there is one unpaired electron, so paramagnetic.

Purple $\rightarrow \overset{+6}{\text{Mn}}\text{O}_4^{2-} - [Ar]^{18}\,3d^o\,4s^o$; here all electrons are paired, so diamagnetic.

16. Both Statement-1 and Statement-2 are correct and Statement-2 is not the correct explanation of Statement-1. Manganese with fluorine forms MnF_4 in highest oxidation state because of high electronegativity of fluorine.



Oxygen forms multiple bonds to metals which explain its superioty over fluorine.

17. S_1 and S_2 are correct statements but S_2 is not correct explanation of S_1. As the oxidation states of metals increase, the electronegativity values also increase. As a result the difference of electronegativities between metal and oxygen decreases and, therefore, acidic character of oxides increase.

18. S_1 and S_2 are correct but S_2 is not correct explanation of S_1.

S_1 : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$; $E^o = +1.51V$.

S_2 : $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2\,(s) + 4H^+$; $E^o = +0.46V$.

19. **S_1 :** $Mn^{3+} = [Ar]^{18}\,3d^4$, so n = 4 ; $Cr^{3+} = [Ar]^{18}\,3d^3$, so n = 3 ; $V^{3+} = [Ar]^{18}\,3d^2$, so n = 2 ; $Ti^{+3} = [Ar]^{18}\,3d^1$, so n = 1.

S_2 : Cr^{3+} is most stable according to CFSE (half filled t_2g) configuration gives higher CFSE value, $3\times0.4=1.2\Delta_0$ in octahedral spliting in presence of ligands.

20. Greater the number of valence electrons, stronger is the resultant bonding and higher the enthalpy of atomisation.

21. **S_1 :** False ; Sc^{3+} ion has no unpaired electron ($3d^o\ 4s^o$) and thus has zero magnetic moment.

S_2 : Magnetic moment is due to 'spin only' = $\sqrt{n(n+2)}$ B.M. value. n is number of unpaired electron(s).

22. Statement-1 and Statement-2 both are correct and Statement-2 is the correct explanation of Statement-1.

$2HCl + [O] \rightarrow H_2O + Cl_2\,(s)$.

23. $K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$

$[CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O] \times 2$

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

CrO_2Cl_2 (Chromyl chloride) is liberated as deep red vapours.

24. **S_1 :** Due to charge transfer spectrum (from ligand to metal) the colour developed is intense as compared to d–d transition.

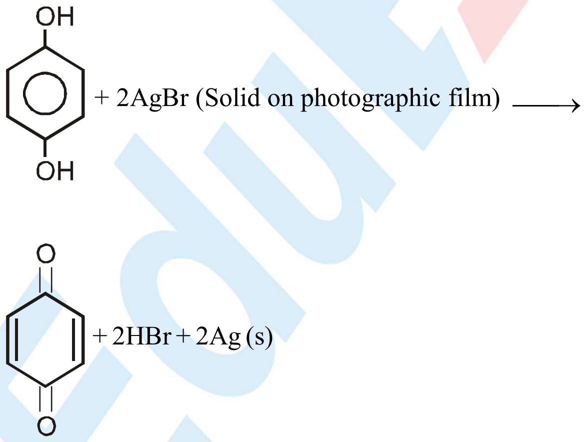
S_2 : True. $CrO_4^{2-} = x + 4(-2) = -2\ ;\ x = +6$.

25. $PH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3PO_3$.

26. Statement-2 is the correct explanation of Statement-1

27. $FeCl_3.6H_2O + 6SOCl_2 \rightarrow FeCl_3 + 12HCl\uparrow + 6SO_2\uparrow$.

28.



+ 2AgBr (Solid on photographic film) ⟶

+ 2HBr + 2Ag (s)

EXERCISE - 3

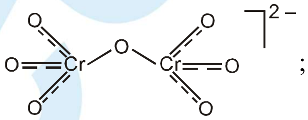
Part # I : Matrix Match Type

1. **(A)** $3\overset{+6}{Mn}O_4^{2-} + 2CO_2 \longrightarrow 2\overset{+7}{Mn}O_4^{-} + \overset{+4}{Mn}O_2 + 2CO_3^{2-}$

The nature of the reaction is thus disproportionation and in the product, MnO_4^-, Mn showed the highest oxidation state of +7.

(B) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

The nature of the reaction is redox only and in the product, CrO_4^{2-}, Cr showed the highest oxidation state of + 6.



;

hence, $Cr_2O_7^{2-}$ has dimeric bridged tetrahedral metal ion.

(C) $2FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$. SO_2 and SO_3 are pungent smelling colourless gases. In SO_3, the sulphur is present in its highest oxidation state of +6.

(D) $\overset{2+}{Cu}Cl_2 2H_2O \longrightarrow \overset{2+}{Cu}O + \overset{1+}{Cu_2}Cl_2 + 2HCl + Cl_2 + 5H_2O$. HCl and Cl_2 are pungent smelling gases. In CuO, Cu is present in its highest oxidation state of +2.

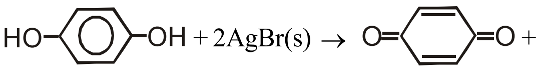
3. **(A)** Cu(I) and Zn (II) have valence shell electron configuration $3d^{10}$; all electrons are paired so the complexes are diamagnetic and colourless.

(B) Mn(+7) and Cr(+6) have valence shell electron configuration $3d^0$. There is no electron in d-orbitals but they are coloured due to charge transfer spectrum. Mn and Cr showed their highest oxidation state of +7 and +6 respectively.

(C) Cu(I) and Hg (II) have valence shell electron configuration $3d^{10}$; all electrons are paired so the compound are diamagnetic but they are coloured due to charge transfer spectrum.

(D) V (IV) and Cu(II) have valence shell electron configuration $3d^1$ and $3d^9$ respectively. Both have one unpaired electrons, so undergo d-d-transition of electron and have similar colour.

6. **(A)**



2HBr + 2Ag (black silver particles)

Hydroquinone acts as developer

(B) $BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2CrO_2Cl_2 + 2BaSO_4 + 3H_2O$

(C) $FeSO_4 + K_3[Fe(CN)_6] \longrightarrow KFe^{II}[Fe^{III}(CN)_6] + K_2SO_4$

(D) $Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

(E) $Co(NO_3)_2 + ZnO \xrightarrow{\Delta} CoZnO_2$ or $CoO.\ ZnO$

7. **(A)** $2\overset{+2}{Fe}SO_4 \xrightarrow{\Delta} \overset{+3}{Fe_2}O_3 + \overset{+4}{S}O_2 + \overset{+6}{S}O_3$

(B) $2Mn^{2+} + 5\overset{+5}{S_2}O_8^{2-} + 8H_2O \longrightarrow 2\overset{+7}{Mn}O_4^- + 10\overset{+6}{S}O_4^{2-} + 16H^+$; colour is due to charge transfer spectrum.

(C) $Na_2Cr_2O_7 + H_2SO_4 \longrightarrow 2CrO_3$ (bright orange) + $Na_2SO_4 + H_2O$; CrO_3 is strongly acidic and coloured due to charge transfer.

(D) $N_2H_4 + 2CuSO_4 \longrightarrow Cu + N_2 + 2H_2\overset{+6}{S}O_4$

8. **(A)** Oxidation state + 8 of osmium & ruthenium.

(B) Density of osmium 22.57 g cm^{-3}.

(C) Electron configuration of Cr ; $[Ar]^{18}\ 3d^5\ 4s^1$; maximum number of unpaired electrons = 6.

(D) Tc radioactive element.

9. **(A)** Cu^{2+} has valence shell electron configuration $3d^9$; so there is one unpaired electrons and thus d–d transition is possible and, therefore, it is coloured.

(B) Zn^{2+} has valence shell electron configuration $3d^{10}$; all electrons are paired so diamagnetic and colourless. ZnO dissolves in acid as well as alkali forming salts.

(C) Cr^{3+} has valence shell electron configuration $3d^3$; so there are three unpaired electrons and thus paramagnetic and coloured. Cr_2O_3 is amphoteric in nature.

(D) Ni^{2+} has valence shell electron configuration $3d^8$; so there are two unpaired electrons and thus paramagnetic and coloured.

Part # II : Comprehension

Comprehension # 1 :

1. **(A)** $2MnO_4^- + 2NH_3 \longrightarrow 2MnO_2 + N_2 + 2OH^- + 2H_2O$

(B) It is due to charge transfer from O^{2-} to empty d-orbital of Mn(VII).

(C) MnO_4^- is in highest oxidation state i.e. +VII and thus can not be oxidised further.

(D) $MnO_2 + OH \longrightarrow MnO_2^{2-} \xrightarrow{e^-} MnO_4^-$

3. (III) Electron configuration of Mn(VI) in MnO_4^{2-} is $[Ar]^{18}\ 3d^1$. So it is paramagnetic and tetrahedral. Electron configuration of Mn(VII) in MnO_4^- is $[Ar]^{18}\ 3d^0$. So it is diamagnetic and tetrahedral.

(IV) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$.

(Solution : 5 to 7)

$A = MnSO_4$, $B = K_2MnO_4$, $C = KMnO_4$, $D = MnO_2$, $E = HMnO_4$, $F = BaSO_4$.

$MnSO_4(A) + 2KNO_3 + K_2CO_3 \longrightarrow K_2MnO_4$**(B)** $+ 2KNO_2 + 2CO_2 + K_2SO_4$

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

$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2\downarrow$; $Mn(OH)_2 + Br_2 + 2NaOH \longrightarrow MnO_2$**(D)** $+ 2NaBr + 2H_2O$

$MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$

$Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4(E) + 5Pb(NO_3)_2 + 2H_2O$

$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$ (white) (F)

Comprehension # 2 :

2. μ = 1.73 indicates that the titanium ion has one unpaired electron. The valence shell electron configuration of titanium is $[Ar]^{18}\ 3d^2\ 4s^2$. So it will lose three electrons to have one unpaired electron and thus the oxidation state of titanium is +3.

3. **(A)** In VCl_3, the vanadium(III) has valence shell electron configuration $3d^2$. So its aqueous solution will be coloured due to d-d-transition of electron.

(B) In $VOSO_4$, the vanadium(IV) has valence shell electron configuration $3d^1$. So its aqueous solution will be coloured due to d-d-transition of electron.

(C) In Na_3VO_4, the vanadium(V) has valence shell electron configuration $3d^0$. So its aqueous solution will be colourless as there will be no d-d-transition.

(D) In $[V(H_2O)_5SO_4]2H_2O$, the vanadium(II) has valence shell electron configuration $3d^3$. So its aqueous solution will be coloured due to d-d-transition of electron.

Comprehension # 3 :

1. **(C)** Cu^+ also form some coloured complexes/compounds due to charge transfer e.g., Cu_2O is red and Cu_2S is black.
2. It is fact, charge transfer transition always produces intense colour as compared to d-d transition.
3. **(A)** In CTML the transfer of electron in the form of charge from metal to ligand is momentary. So it can not be taken as redox type of reaction.

   (B) Cu_2O is red in colour due to charge transfer from O^{2-} to Cu(I).

   (C) Vermilion (HgS) is a red coloured compound because of charge transfer spectrum.

Comprehension # 4 :

1. Due to stable half filled electronic configuration, the delocalisation of electrons is less and thus metallic bond is much weaker than preceding elements.
2. **(I)** The transition elements (with the exception of copper) are very much hard and have low volatility. They have high enthalpies of atomisation because of more number of unpaired electrons available for bonding. Cr, Mo and W have maximum number of unpaired electrons and therefore, these are very hard metals and have maximum enthalpies of atomization.

   (II) The melting and boiling points of the transition series elements are generally very high. The melting points of the transition elements rise to a maximum and then fall as the atomic number increases. Strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points. In a particular series, the metallic strength increases upto the middle with increasing number of unpaired electrons i.e up to d^5. After chromium, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

   (III) In d-block elements the last but one (i.e. the penultimate) shell of electrons is expanding. Hence nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

Comprehension # 5 :

1. $Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$.
2. $3K_2\overset{+6}{Mn}O_4 + 2CO_2 \longrightarrow 2K\overset{+7}{Mn}O_4 + \overset{+4}{Mn}O_2 + 2K_2CO_3$.
3. $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$.

   $(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$.

   $Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \frac{3}{2}O_2$.
4. $MnO_2 + HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$.

   $Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$.
5. **(A)** $Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN_6)] \downarrow$ (brown).

   (B) The red coloured oxide is Cu_2O because Cu^+ has $[Ar]^{18}\,3d^{10}\,4s^0$ i.e., pseudo inert gas electronic configuration.

   (C) $KMnO_4$ (B compound) in acidic medium oxidises Cu_2O to CuO which is black in colour.

   Reactions involved in comprehension :

   $2MnO_2 + KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$.

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

   $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$.

   $(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$.

   $Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \frac{3}{2}O_2$.

Comprehension # 6 :

1. $NH_4Br + AgNO_3 \rightarrow AgBr + NH_4NO_3$.
2. $2AgBr + C_6H_4(OH)_2$ (Quinol–developer) $\rightarrow 2Ag + 2HBr + C_6H_4O_2$ (Quinone).
3. A developer is usually a weak reducing agent such as potassium ferrous oxalate or an alkaline solution of pyrogallol or an alkaline solutions of quinol, etc.
4. Silver halides except silver fluoride are photosensitive.
5. $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2]$ (Sodium argentothiosulphate–soluble complex) + NaBr.

EXERCISE - 4

Subjective Type

1. It is because Mn^{2+} has $3d^5$ configuration which has extra stability.

2. In transition elements the oxidation states vary from +1 to any highest oxidation state by one. For example, for manganese it may vary as +2, +3, +4, +5, +6, +7. In the non-transition elements the variation is selective, always differing by 2, e.g. +2, +4 or +3, +5 or +4, +6 etc.

3. Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

4. Ag^+ is a stronger Lewis acid as it has pseudo inert gas configuration (high polarising power due to less screening effect of inner d–electrons) whereas Na^+ is a weaker acid as it has inert gas configuration (less polarising power).

5. Because of small size and high electronegativity of oxygen and fluorine, they can oxidise the metal to its highest oxidation state.

6. Stable oxidation states :

Vanadium = $3d^3$: (+2), +3, +4 and +5

Chromium = $3d^5$: +2, +3, +6

Manganese = $3d^5$: +2, +4, +6, +7

Nickel = $3d^8$: +2, +3, + 4 (In complex)

In ground state for $3d^4$ configuration no one metal occur.

7. Consider its high $\Delta_a H^\theta$ and low $\Delta_{hyd} H^\theta$

8. Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

9. Cr^{2+} is stronger reducing agent than Fe^{2+}.

Change from d^4 to d^3 occurs in case of Cr^{2+} to Cr^{3+} but from d^6 to d^5 occurs in case of Fe^{2+} to Fe^{3+}. In a medium (like water) d^3 is more stable as compared to d^5 according to CFSE (CFSE for octahedral spliting in case of d^3 is –1.2 Δ_o while for d^5 is 0).

10. Copper has less standard oxidation potential (E°_{op}) than H and thus cannot liberate H_2 from acids. However, it dissolves in nitric acid because HNO_3 is strong oxidant.

$$3Cu + 8HNO_3\,\text{(dilute)} \longrightarrow 3Cu\,(NO_3)_2 + 4H_2O + 2NO$$

11. Iron has more E°_{op} than Cu and thus liberated Cu^{2+} ions from solution to discharge blue colour.

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$

12. Cu(I) salts undergo disproportionation in aqueous solution.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

13. $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

The E° value for this is favourable.

14. $FeCl_3$ hydrolyses in water to form acidic solution.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

or $$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

15. I^- ion is a stronger reducing agent in comparison to Cl^- ion. Fe^{3+} is easily reduced by iodide ion.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

16. The electron configuration of Mn^{3+} is $[Ar]^{18}\,3d^4$ so n = 4;
The electron configuration of Cr^{3+} is $[Ar]^{18}\,3d^3$ so n = 3;
The electron configuration of V^{3+} is $[Ar]^{18}\,3d^2$ so n = 2;
The electron configuration of Ti^{3+} is $[Ar]^{18}\,3d^1$ so n = 1.

Cr^{3+} is most stable in aqueous solution because it has half filled t^3_{2g} energy level of 3d orbitals in octahedral crystal field spliting and according to crystal field theory (CFT) it has highest value of CFSE i.e. –1.2 Δ_O.

17. Hg^+ has [Xe] 4 f^{14} $5d^{10}$ $6s^1$ configuration and thus Hg^+ ion should be paramagnetic due to one unpaired electron but Hg^+ ions show diamagnetic nature and for this it exists as Hg_2^{2+} by sharing of one electron each. Cuprous ions are diamagnetic with [Ar] $3d^{10}$ configuration and so written as Cu^+.

18. Copper sulphate dissolves in the ammonium hydroxide due to formation of a copper complex. Ferrous sulphate reacts with NH_4OH to form insoluble $Fe(OH)_2$. It does not form any complex with NH_4OH.

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Deep blue solution}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$$FeSO_4 + 2NH_4OH \longrightarrow \underset{\text{Insoluble}}{Fe(OH)_2} + (NH_4)_2\,SO_4$$

19. **(a)** $FeSO_4.7H_2O$ (green) $\longrightarrow FeSO_4 + 7H_2O$

(A) (B)

$$Fe^{2+}(aq) + [Fe(CN)_6]^{3-}(aq) \longrightarrow Fe^{3+}(aq) + [Fe(CN)_6]^{4-}(aq)$$

(B)

$$4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow \text{(Turnbull's blue-(C))}$$

$$2FeSO_4 \xrightarrow[\text{strong}]{\Delta} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

(B) (D) (E) (F)

$$3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow 2Cr^{3+}\text{(green solution)} + 3SO_4^{2-} + H_2O$$

(E)

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \downarrow \text{(white)}$$

(b) According to CFT there is no d-d transition of electrons in absence of ligands in anhydrous ferrous sulphate.

20. $ZnSO_3 + H_2SO_4 \longrightarrow ZnSO_4 + SO_2\downarrow + H_2O$

(A) **(C)** **(B)**

$$5SO_2 + 2IO_3^- + 4H_2O \longrightarrow I_2 + 5SO_4^{2-} + 8H^+$$

I_2 + starch solution $\longrightarrow$ blue colour solution.

$$SO_3^{2-} + Ba^{2+} \longrightarrow BaSO_3 \downarrow \text{(white)}$$

$$BaSO_3 + 2H^+ \longrightarrow Ba^{2+} + SO_2 + H_2O$$

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow \text{(white)}$$

$$Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$$

$$Zn^{2+} + 2NH_3 + 2H_2O \longrightarrow Zn(OH)_2\downarrow + 2NH_4^+$$

$$Zn(OH)_2\downarrow + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2OH^-$$

$$3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \longrightarrow K_2Zn_3[Fe(CN)_6]_2\downarrow$$

$$K_2Zn_3[Fe(CN)_6]_2 + 12OH^- \longrightarrow 2[Fe(CN)_6]^{4-} + 3[Zn(OH)_4]^{2-} + 2K^+.$$

21. $2KMnO_4 + 2NH_3 \longrightarrow 2MnO_2 + 2KOH + 2H_2O + N_2$

22. $X = CuSO_4$

23. H_2S is oxidised to colloidal sulphur (milky) by $K_2Cr_2O_7$.
$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O +$ 3S Colloidal (milky)

24. **(i)** $KMnO_4 + 3H_2SO_4 \longrightarrow K^+ + MnO_3^+$ (green) $+ 3HSO_4^- + H_3O^+$

$$2MnO_3^+ + Na_2CO_3 \longrightarrow 2MnO_3 + CO_2 + \frac{1}{2}O_2 + 2Na^+$$

(ii) $2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$

$$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$$

25. $Ag_2S + 2CuCl_2 + 2Hg \longrightarrow Hg_2Cl_2 + 2CuCl + S + 2Ag.$

26. $La(OH)_3$ is more basic than $Lu(OH)_3$, As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+} the ionization energy increases and therefore metallic character decreases. Hence, the basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.

27. Ce(III) having the configuration $4f^1 5d^0 6s^0$ can easily lose an electron to acquire the configuration $4f^0$ and form Ce(IV). In fact, this is the only (+IV) lanthanoide which exists in solution.

28. Small non-metallic atoms (e.g. H, B, C, N etc.) are able to fit in the interstitial sites of transition metal lattice to form interstitial compounds. These are non-stoichiometric compounds.

29. In a particular series, the metallic strength increases upto the middle with increasing number of unpaired electrons i.e up to d^5. After chromium, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons. Magnitude of metallic bond is greater for Cr($3d^5\,4s^1$) as compared to that of Zn($3d^{10}\,4s^o$).

30. In presence of Cl^- ion the disproportionation of Cu^+ i.e.

$$2Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

is reversed because precipitation of copper (I) chloride drives the disproportionation reaction to the left.

$$Cu_{(s)} + Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow 2CuCl_{(s)}$$

31. Due to usual contraction in size across a horizontal period and partly because the orbitals electrons are added to penultimate d-shell rather than to the outer shell of atom.

32. The number of unpaired electrons increases from Sc_{21} : [Ar] $3d^1$, $4s^2$ to $_{24}Cr$: [Ar]$3d^5\,4s^1$ and after chromium, the pairing of electrons takes place and thus number of unpaired electrons goes on decreasing continuously to ^{30}Zn : [Ar]$3d^{10}$, $4s^2$.

33. For first five elements, the effective nuclear charge predominates over shielding effect and thus ionisation energy increases. In next five elements, shielding effect increases more rapidly due to dense packing of electrons in d-orbitals (pairing takes place) and the effective nuclear charge and shielding effect counter balance each other to show a net result of constant or irregular but closer trend in ionisation energy values.

34. MnO_2 (pyrolusite) $+ KOH \xrightarrow{[O]} K_2MnO_4$ (dark green) (A) $+ H_2O$.

$3K_2MnO_4 + 2H_2O \xrightarrow{\text{dil. } H_2SO_4} 2KMnO_4$ (purple) (B) $+ MnO_2 + 4KOH$.

(i) $KI + 2KMnO_4 + H_2O \longrightarrow KIO_3$ **(C)** $+ 2MnO_2 + 2KOH$.

(ii) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$.

(iii) $2KMnO_4 + 2H_2SO_4$ (conc.) $\longrightarrow 2K_2SO_4 + Mn_2O_7$ (D) $+ H_2O$.

$2Mn_2O_7$ (D) $\longrightarrow 4MnO_2$ (E) $+ 3O_2$.

35. $\underset{(A)}{3MnO_2} + 6KOH + KClO_3 \xrightarrow{\Delta} \underset{(B)}{3K_2MnO_4} + KCl + 3H_2O$

In presence of CO_2, the medium becomes acidic

$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$.

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$.

(C)

36. The reaction involved are :

(i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$.

(ii) $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$.

(iii) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$.

(iv) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$.

(v) $K_2Cr_2O_7 + 7H_2C_2O_4 \longrightarrow K_2C_2O_4 + Cr_2(C_2O_4)_3 + 6CO_2 + 7H_2O$.

(vi) $Cr_2(C_2O_4)_3 + 3K_2C_2O_4 \longrightarrow 2K_3[Cr(C_2O_4)_3]$.

37. (A), a light green substance on heating gives gas (B) and (C) which turns dichromate solution to green and the solution so obtained gives white precipitate with $Ba(NO_3)_2$ solution and thus, (B) and (C) should be SO_2 and SO_3 and (A) be $FeSO_4$.

Reactions :

(i) $\underset{(A)}{2FeSO_4} \longrightarrow \underset{(D)}{Fe_2O_3}$ (brown) $+ \underset{(B)}{SO_2} + \underset{(C)}{SO_3}$

(ii) $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(iii) $K_2Cr_2O_7 + \underset{(B)}{3SO_2} + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$ (green) $+ H_2O$

$2K_2Cr_2O_7 + 8SO_3$ **(C)** $\longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3O_2$

(iv) $Cr_2(SO_4)_3 + 3Ba(NO_3)_2 \longrightarrow \underset{(E)}{3BaSO_4} + 2Cr(NO_3)_3$

(v) $Fe_2O_3 + 3C \xrightarrow{\text{Reducing flame}} 2Fe$ (magnetic substance) $+ 3CO \uparrow$

38. CuCl dissolves in conc. HCl due to the formation of a copper complex.

$CuCl + 2HCl \longrightarrow 2H[CuCl_2]$

39. (i) $\underset{(A)}{CuCO_3} \longrightarrow \underset{(B)}{CuO} + \underset{(C)}{CO_2}$

(ii) $CuO + H_2 \longrightarrow \underset{(D)}{Cu} + H_2O$

(iii) $CuO + HCl \longrightarrow CuCl_2 + H_2O$

$2CuCl_2 + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6]$ (chocolate brown) (E) $\downarrow + 4KCl$

(iv) $Ca(OH)_2 + CO_2$ **(C)** $\longrightarrow CaCO_3$ (white) $\downarrow + H_2O$.

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$ (soluble) (F)

40. In acid medium, the reaction has positive E^o_{RP} and thus acts as oxidant

$Cr_2O_7^{2-} + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$; $E^o_{RP} = +1.33V$

In basic medium $Cr_2O_7^{2-}$ is readily interconverted to CrO_4^{2-} and E^o_{RP} of CrO_4^{2-}/Cr^{3+} is negative

$Cr_2O_7^{2-}(aq) + H_2O(l) \longrightarrow 2CrO_4^{2-} + 2H^+$; $K_C = 10^{-14}$ and thus weak oxidant

$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \longrightarrow Cr(OH)_3(s) + 5OH(aq)$; $E^o_{RP} = -0.13V$

41. On heating hydrated ferric chloride anhydrous $FeCl_3$ is not formed but it is changed to Fe_2O_3.

$2FeCl_3.6H_2O \xrightarrow{\text{heat}} Fe_2O_3 + 6HCl + 9H_2O$.

$FeCl_3$ gets hydrolysed by the water of crystallisation on heating.

42. Aqueous solution of $FeCl_3$ is acidic due to hydrolysis.

$$\underset{\text{acid}}{[Fe(H_2O)_6]^{3+}} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{[Fe(H_2O)_5(OH)]^{2+}} + \underset{\text{acid}}{H_3O^+}$$

$NaHCO_3 + H^+ \longrightarrow Na^+ + CO_2 \uparrow + H_2O$

43. It produces burning sensation like caustic and leaves black stain like the moon luna on skin and thus called lunar caustic.

44. On heating it forms zinc oxychloride.

$$2ZnCl_2.2H_2O \longrightarrow Zn_2OCl_2 + 2HCl + 3H_2O.$$

45. **(i)** $CuSO_4.5H_2O \xrightarrow{100°C} CuSO_4 . H_2O$ **(A)** $\xrightarrow{230°C}$ $CuSO_4$ **(B)** $\xrightarrow{800°C}$ CuO **(C)** + SO_3 **(D)**.

(ii) $2AgNO_3 \xrightarrow{\text{Red heat}} 2Ag$ (E) + $2NO_2$ (F) + O_2 .

46. $AgNO_3$ decomposes on exposure to light and is thus stored in brown bottles to prevent the action of light.

$$2AgNO_3 \xrightarrow{hv} 2Ag + 2NO_2 + O_2$$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. (3) Cerium can also show the oxidation state of +4 in solution as it leads to a noble gas configuration, from $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$ to $[Xe]^{54}$, after losing four electrons. It is only Ce^{4+} which exist in solution among the lanthanides.

2. The atomic radii of the second and third transition series are almost the same. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm).

3. Lanthanide contraction is due to poor shielding of one of 4*f* electron by another in the sub-shell.

4. Valence shell electron configuration of $_{28}Ni^{2+}$ is $3d^8\ 4s^0$.

or 

So, number of unpaired electrons (n) = 2

$$\therefore \quad \mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} \approx 2.84$$

5. Lanthanoid contraction is due to ineffective shielding produced by larger f-subshell.

6. The decrease in the force of attraction exerted by the nucleus on the valency electrons due to presence of electrons in the inner shells is called shielding effect. An 4*f* orbital is nearer to the nucleus than 5*f* orbitals. In addition, the 20 electrons of 3d and 4d orbitals contribute the shielding to 4f electron while 44 electrons of 3d, 4d, 5d and 4f contribute the shielding to 5f. Hence shielding of 5*f* is more than 4f.

7. The distance between the nucleus and 5*f* orbitals (actinides) is more than the distance between the nucleus and 4*f* orbitals (lanthanides). Hence the hold of nucleus on valence electron decreases in actinides. For this Statement-2 the actinoids exhibit more number of oxidation states in general.

8. There is very small energy difference between 5f and 6d orbitals in actinoids than those of between 4f and 5d orbitals. Hence, electrons present in 5f and 6d orbitals can take part in bonding.

9. The basic character of any element changes with the oxidation state, low oxidation states are more basic and high oxidation state are more acidic. For example, MnO and Mn_2O_3 are basic while Mn_2O_7 is acidic in nature.

10. Most of the trivalent lanthanoid compounds except that of La^{3+} and Lu^{3+} are coloured both in the solid state and in the aqueous solution. The colour of these ions can be attributed due to the presence of unpaired f-electrons.

11. Generally across the first transition series, the negative values for standard electrode potential decrease (exception Mn- due to stable d^5 configuration)

Standard electrode potential –

	Mn	Cr	Fe	Co	
M^{2+}/M	–1.18	–0.90	–0.44	–0.28	eV

So, correct order is Mn > Cr > Fe > Co.

12. Availability of 4f electrons do not results in the formation of compounds in +4 state for all the members of the series.

13. Lutetium $(_{71}Lu) = [Xe]^{54}\ 4f^{14}5d^16s^2$

14. Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.

15. **(1)** V^{2+} = 3 unpaired electrons

Cr^{2+} = 4 unpaired electrons

Mn^{2+} = 5 unpaired electrons

Fe^{2+} = 4 unpaired electrons

Hence the order of paramagnetic behaviour should be

$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(2) ionic size decrease from left to right in same period.

(3) As per data from NCERT.

$Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$; $Cr^{3+}/Cr^{2+} = -0.41$

Sc^{3+} is highly stable (It does not show +2)

(4) The oxidation states increases as we go from group 3 to group 7 in same period.

Ans is (1)

16. $E^{o}_{Cr^{3+}/Cr^{2+}} = -0.41\ V$; $E^{o}_{Mn^{3+}/Mn^{2+}} = +1.57\ V$; $E^{o}_{Fe^{3+}/Fe^{2+}} = +0.77\ V$; $E^{o}_{Co^{3+}/Co^{2+}} = +1.97\ V$

SRP value normally increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. For e.g. $E^{o}_{Mn^{3+}/Mn^{2+}} = +1.57\ V$; $E^{o}_{Co^{3+}/Co^{2+}} = +1.97\ V$.

Part # II : IIT-JEE ADVANCED

1. $2MnO_4^- + I^- + H_2O \longrightarrow 2MnO_2 + IO_3^- + 2OH^-$.

2. MnO_4^- ; $x + 4(-2) = -1$ or $x = +7$;

CrO_2Cl_2 ; $x + 2(-2) + 2(-1) = +6$ or $x = +6$.

3. The colour of the transition metal ions is mainly attributed to d-d transition. d-d transition takes place because of the presence of unpaired electrons.

The metal ions having same number of unpaired electrons may give same colour in their aqueous solution.

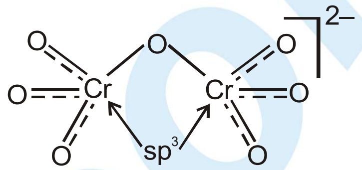
In $VOCl_2$, V^{IV} ion having $3d^1$ configuration has one unpaired electron. Similarly in $CuCl_2$, the Cu^{2+} ion having $3d^9$ configuration also has one unpaired electron. So $VOCl_2$ and $CuCl_2$ are expected to exhibit same colour i.e. blue colour.

Mn^{2+} has five unpaired and Fe^{2+} has four unpaired electrons.

6. **(A)** $O_2^- \rightarrow O_2 + O_2^{2-}$.

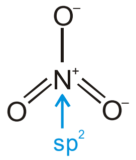
Nature of the reaction is redox as well as disproportionation as an ion is oxidised and reduced simultaneously.

(B) $2CrO_4^{2-} + H^+ \rightarrow Cr_2O_7^{2-} + H_2O$.



$Cr_2O_7^{2-}$ has dimeric bridged tetrahedral metal ion.

(C) NO_2^- is being oxidised and MnO_4^- being reduced according to the following reaction. So it is redox reaction, $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$.



(D) Fe^{2+} is being oxidised and NO_3^- being reduced according to the following reaction. So it is redox reaction,

$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow NO^+ + 3Fe^{3+} + 2H_2O$.

7. CuF_2 contains Cu^{+2}, having d^9 configuration, therefore, there is one unpaired electron which undergoes d–d transition in visible region. CuF_2 in crystalline form is blue in colour.

8. $2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Fusion}} 2K_2MnO_4 + 2H_2O$

Let the oxidation state of Mn in MnO_4^{2-} is x.

So $x + 4(-2) = -2$ or $x = 6$

9. In acidic medium, $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

(v.f.=5)

In neutral / faintly alkaline medium,

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$

(v.f.=3)

In strongly alkaline medium, $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

(v.f.=1)

10. $CuSO_4$ will be absorbing orange-red colour & hence will be of blue colour.

11. $AgNO_2 + HCl \longrightarrow AgCl\downarrow$

$AgNO_3 + HBr \longrightarrow AgBr\downarrow$

$AgNO_3 + HI \longrightarrow AgI\downarrow$

All these precipitates will get dissolved in hypo forming complex $Na_3[Ag(S_2O_3)_2]$

MOCK TEST

1. (D)

$VOSO_4 = VO^{2+} + SO_4^{2-} ; AX(-2) = +2 = +4.$

2. (D)

(A) $MNO_4^{-} = +7 ; [AR]^{18} 3d^5 4S^2 = 7.$

(B) $Cr_2O_7^{2-} = +6 ; [Ar]^{18} 3d^5\ 4s^1 = 6.$

(C) $VO_4^{3-} = +5 ; [Ar]^{18} 3d^3 4s^2 = 5.$

(D) $FeO_4^{2-} = +6 ; [Ar]^{18} 3d^8 4s^2 = 8.$

3. (D)

(A) In $MnSO_4.6H_2O$, Mn is in +2 oxidation state. The electronic configuration is , $[Ar]^{18} 3d^5 4s^0$ and thus it has five unpaired electrons.

(B) $CuSO_4.5H_2O$ one unpaired electrons.

(C) $FeSO_4.6H_2O$, four unpaired electrons.

(D) $NiSO_4.6H_2O$, two unpaired electrons.

Hence $MnSO_4.4H_2O$ has highest number of unpaired electrons and has highest degree of paramagnetism.

4. (D)

True statement, $2FeCl_3 \xrightarrow{300°C} (FeCl_3)_2(g)$

5. (D)

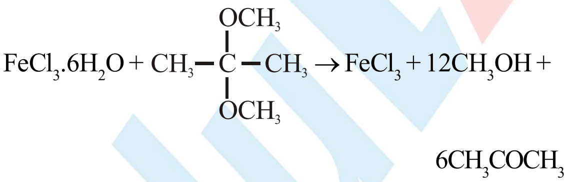
$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Fusion}}$

$Na_2\overset{+VI}{Cr}O_4 \xrightarrow[H_2O]{H^+} Na_2\overset{+VI}{Cr_2}O_7 \xrightarrow{H^+/H_2O_2} \overset{+VI}{Cr}O(O_2)_2$

(deep blue violet) $\xrightarrow{H_2O} O_2 + H_2O + Cr^{3+}$.

$Na_2Cr_2O_7 + H_2SO_4 \rightarrow 2CrO_3$ (chromic anhydride) + $Na_2SO_4 + H_2O$.

6. (A)



$$FeCl_3.6H_2O + CH_3-\underset{OCH_3}{\overset{OCH_3}{C}}-CH_3 \rightarrow FeCl_3 + 12CH_3OH + 6CH_3COCH_3$$

7. (A, B)

Fuse with KOH in presence of air or oxidising agents like KNO_3, $KClO_3$ etc.

$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

$MnO_4^{2-} \xrightarrow{\text{electrolyticoxidation}} MnO_4^{-} + e^{-}.$

8. (A, B)

(A) In making negative/postive of photographic film

(B) In fixing of photographic film by removing unreduced AgBr as soluble complex.

9. (A, B, D)

$3CuCl_2.2H_2O \xrightarrow{\Delta} CuO + Cu2Cl_2 + 2HCl + Cl_2 + H_2O ;$

(C) only Cl_2 is liberated is wrong as evident from chemical equation.

10. (A, B, C, D)

(A) $KMnO_4 + Cu_2O + KOH \longrightarrow 2Cu(OH)_2 + K_2MnO_4.$

(B) $2MnO_2 + 2K_2CO_3 + O_2$ (from KNO_3) $\longrightarrow 2K_2MnO_4 + 2CO_2.$

(C) $HCHO + 2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + HCOOH$

(D) $4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4 + 2H_2O + O_2.$

11. (A)

Greater the number of unpaired electrons, stronger is the resultant bonding and higher the enthalpy of atomisation.

12. (C)

$$\underset{\text{(yellow)}}{2\overset{+6}{Cr}O_4^{2-}} + 2H^+ \longrightarrow \underset{\text{(orange)}}{\overset{+6}{Cr_2}O_7^{2-}} + H_2O$$

There is no change in oxidation state. So the explanation is wrong.

13. (A)

S1 : Due to strong interatomic forces.

S2 : Hydrochloric acid is oxidised to chlorine.

S3 : $MnO_4^{-} + e^{-} \xrightarrow{OH^-} MnO_4^{2-}$

S4 : $2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + H_2O.$

14. (B)

S1 : It is because Mn^{2+} has $3d^5$ configuration which has extra stability.

S2 : Not Titanium but Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

S3 : Not stable as it undergoes disproportionation $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$. The E° value for this is favourable.

S4 : Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the + 3 state of Mn is of little importance.

15. (C)

As the oxidation state of metal associated with oxygen increases, the acidic character of oxide increase. So Mn_2O_7 is most acidic as it has higest, + 7, oxidation state.

16. (C)

(A), (B) and (D) all are correct statements.

(C) There is drope in enthalpy of atomization at manganese because of half filled stable electronic configuration leading to less mobilisation of electrons. This results in weaker metalic bonds.

17. (A)

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

18. (B)

Both V^{+4} ($[Ar]^{18}\ d^1\ 4s^0$) and Cu^{2+} ($[Ar]^{18}\ d^9\ 4s^0$) have one unpaired electron in the d-orbital and thus exhibit same colour.

19. (C)

$\mu = 1.73$ i.e. one unpaired electron, Ti (E.C.) = $[Ar]^{18}\ 3d^2, 4s^2$, so it will lose three electrons to have one unpaired electron and thus the oxidation state of titanium is +3.

20. (D)

(A) Has five unpaired electrons in 3d-sub shell. (B) is a obvious fact (C) number of unpaired electrons first increases to five and then pairing begins so number of unpaired electrons decreases.

21. (D)

(A) $2MnO_4^- + 2\,NH_3 \longrightarrow 2MnO_2 + N_2 + 2OH^- + 2H_2O$

(B) It is due to charge transfer.

(C) MnO_4^- is in highest oxidation state i.e. +VII and hence can not be oxidised.

(D) $MnO_2 + OH^- + O_2$ (air) $\xrightarrow{\text{Fusion}} MnO_4^{2-} \xrightarrow{e^-} MnO_4^-$.

22. (A)

(A) $MnSO_4$ = +II ; (B) MnO_4^{2-} = +VI ; (C) MnO_4^- = +VII

23. (D)

(III) $MnO_4^{2-} = [Ar]^{18}\ 3d^1$ paramagnetic and tetrahedral

(IV) $MnO_4^- = [Ar]^{18}\ 3d^0$ diamagnetic and tetrahedral

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

Solution of passage :

$MnSO_4(A) + 2KNO_3 + K_2CO_3 \longrightarrow K_2MnO_4\ (B) + 2KNO_2 + 2CO_2 + K_2SO_4$

$MnO_4^{2-} + e^- \xrightarrow{H^+} MnO_4^-\ (C)$

$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2\downarrow$; $Mn(OH)_2 + Br_2 + 2NaOH \longrightarrow MnO_2\ (D) + 2NaBr + 2H_2O$

$MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$

$Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4\ (E) + 5Pb(NO_3)_2 + 2H_2O$

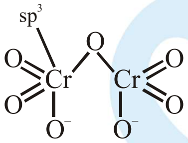
$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4\downarrow$ (white) (F).

Ans. A = $MnSO_4$, B = K_2MnO_4, C = $KMnO_4$, D = MnO_2, E = $HMnO_4$, F = $BaSO_4$.

24. (1 - p, s) : (2 - r) ; (3 - p, q) ; (4 - p)

(A) $O_2^- \rightarrow O_2 + O_2^{2-}$ (Redox and disproportionation)

(B) $CrO_4^{2-} + H^+ \rightarrow Cr_2O_7^{2-}$



(C) $MnO_4^- + NO_2^- + 6H^+ \rightarrow Mn^{2+} + NO_3^-\ (sp^2) + 3H_2O$

(D) $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \rightarrow 2NO + 6Fe^{3+} + 4H_2O + 4SO_4^{2-}$ (redox reaction)

25. (1 - q, r, s) ; (2 - p, q, r) ; (3 - p, q, s) ; (4 - q, r)

(A) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$.

(B) $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$;

MnO_4^- is coloulred due to charge transfer.

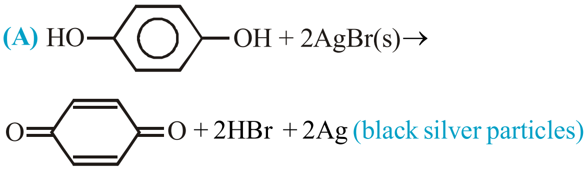
(C) $Na_2Cr_2O_7 + H_2SO_4 \longrightarrow 2CrO_3$ (bright orange) + $Na_2SO_4 + H_2O$;

CrO_3 is strongly acidic and coloured due to charge transfer

(D) $N_2H_4 + 2CuSO_4 \longrightarrow Cu + N_2 + 2H_2SO_4$

26. (1 - t), (2 - s), (3 - p), (4 - q), (5 - r)

(A)



Hydroquinone acts as developer

(B) $BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow K_2SO_4 + 2CrO_2Cl_2 + 2BaSO_4 + 3H_2O$

(C) $Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

(D) $Co(NO_3)_2 + ZnO \xrightarrow{\Delta} CoZnO_2$ or CoO. ZnO